

Zintl Ions as Molecular Analogues of Liquid Alloys for C–H Activation



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Abstract

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This thesis describes the reactivity of the tris-hypersilyl substituted nonagermanide Zintl cluster $[\text{KGe}_9(\text{Hyp})_3]$ ($\text{Hyp} = \text{Si}(\text{SiMe}_3)_3$) towards group 9 and 10 transition metal organometallic complexes. The resulting Zintl clusters were then modified and tested in catalysis as molecular models for transition metal–main group element alloys (TMMGAs).

Firstly, nickel germanide clusters were synthesised, which were formed by vertex addition or substitution chemistry and further studied using cyclic voltammetry.

Next, the rhodium germanide cluster $[\text{Rh}(\text{COD})\{\text{Ge}_9(\text{Hyp})_3\}]$ ($\text{COD} = 1,5\text{-cyclooctadiene}$) was targeted in order to prepare a reactive metal alkene complex on the $[\text{Ge}_9(\text{Hyp})_3]$ support. This was then used as the first Zintl cluster based homogeneous catalyst in catalytic alkene hydrogenation.

This cluster was then modified by ligand substitution at the rhodium centre to produce highly fluxional clusters with the general formula $[\text{Rh}(\text{L})\{\text{Ge}_9(\text{Hyp})_3\}]$ ($\text{L} = \text{C}_2\text{Me}_2$, DPPE, PMe_3 , PPh_3 , IMe_4 , $(\text{Cp})_2\text{WH}_2$). These were studied in catalytic processes which involve H–H and C–H bond activation.

Finally, $[\text{Rh}(\text{COD})\{\text{Ge}_9(\text{Hyp})_3\}]$ was modified by the addition of group 9 and 10 metal alkene fragments to the germanium support, showing that the cluster can be controllably expanded towards homo- and hetero-multimetallic clusters.

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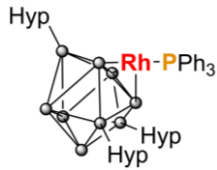
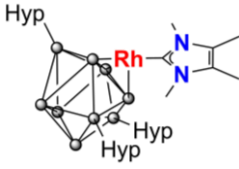
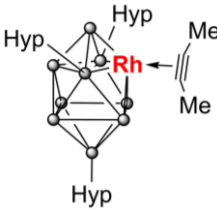
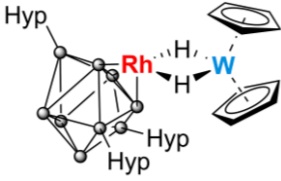
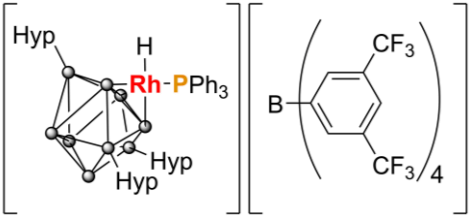
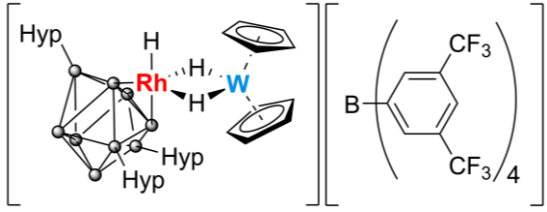
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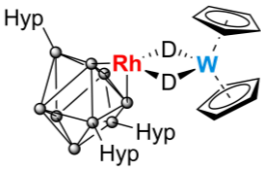
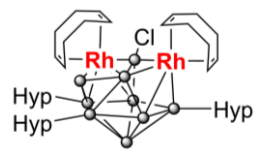
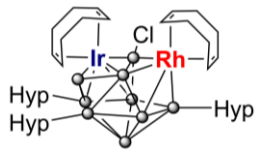
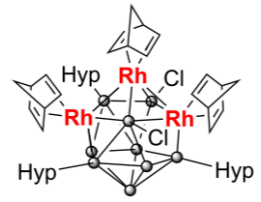
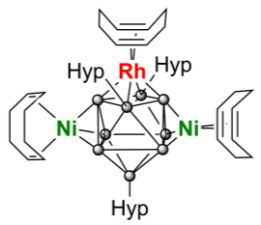
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2	Chemical structure of a nickel complex. The nickel atom (Ni) is shown in green, coordinated by three hydride ligands (Hyp) and a cyclopentadienyl ligand.
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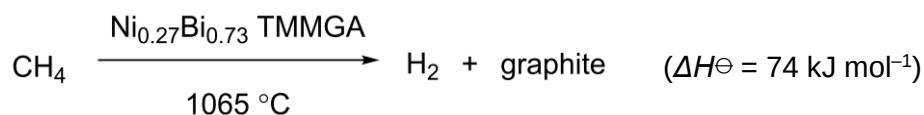
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1. Introduction

1.1. Transition Metal–Main Group Metal Alloys (TMMGAs)

Molten alloys of transition and main group metals (TMMGAs) combine the highly reactive properties of late transition metals and low melting points of main group metals. In principle, as well as lowering the melting point below 1000 °C, the main group metal effectively solvates the transition metal atoms, which are postulated to be the catalytically active species in such melts.¹ These alloys have recently been studied for their applications in industrially relevant processes such as light alkane dehydrogenation for the production of dihydrogen and alkenes or graphitic carbon.^{1–5} Methane, the primary component of natural gas, is currently extracted from highly abundant natural sources. However, due to its inertness and high transport costs, around 3.5% of this gas is typically “flared”, rather than used as a C₁ feedstock for the production of value-added chemicals.⁶ The amount of flaring is not well established but estimated to be in the region of 143 (±13.6) billion m³ per year, accounting for the production of 350 million tonnes of the greenhouse gas pollutant CO₂ which, for scale, is around 10% of the total annual CO₂ emissions by EU member states.⁷

In a landmark study by Upham et al., several TMMGAs were screened for their efficacies in methane dehydrogenation catalysis using a bubble column, allowing for the bubbling of methane through the melt and removal of the solid carbonaceous by-product by skimming. It was found that the 27% Ni–Bi system at a temperature of 1065 °C allowed for the most efficient production of hydrogen. In all cases (Scheme 1.1), nickel-containing alloys outperformed their platinum counterparts (Table 1.1). An example based on this work has also been considered for a direct industrial pilot.⁸



Scheme 1.1: Methane dehydrogenation using a nickel–bismuth molten alloy bubble column.¹

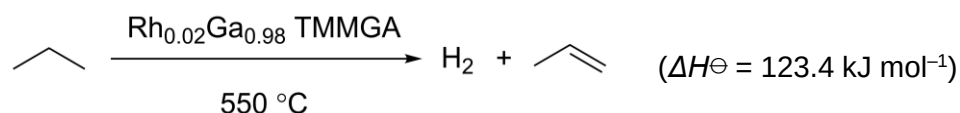
Table 1.1: Liquid alloy catalyst combinations screened by Upham et al.¹

Liquid catalyst	Rate of hydrogen production (mol H₂ produced × cm⁻² s⁻¹) (× 10⁻⁸)
27% Ni–Bi	1.7
27% Ni–Au	1.2
17% Ni–Pb	0.83
17% Ni–Ga	0.79
62% Pt–Bi	0.65
73% Ni–In	0.64
17% Ni–Sn	0.56
17% Ni–In	0.47
17% Pt–Bi	0.42
17% Cu–Sn	0.31
17% Pt–Sn	0.16

The 27% Ni–Bi system was found to be 95% efficient for methane to dihydrogen conversion at 1065 °C as measured by GC-MS; though this is highly temperature dependent, as efficiency was reduced to 86% when the temperature was lowered to 1040 °C. Increasing the pressure also appeared to increase side reactions in the headspace. It was found that although pure nickel deactivated within an hour, most likely due to carbon covering (coking) the active surfaces, the activity of the Ni_{0.27}Bi_{0.73} alloy did not change over 170 hours. This highlights one of the key advantages to use liquid-based methods for processes which produce carbon. The authors also reported that when these catalysts were exposed to propane, dihydrogen and carbon were also produced. Presumably the high working temperatures favour complete pyrolysis, rather than partial dehydrogenation to form propene.

Raman et al. reported the use of a Rh–Ga TMMGA in propane dehydrogenation (PDH) (Scheme 1.2).⁹ This is the first instance of a rhodium-based PDH catalyst. Using lower temperatures than those employed by Upham et al.¹ (550 °C) and 2% rhodium content, only

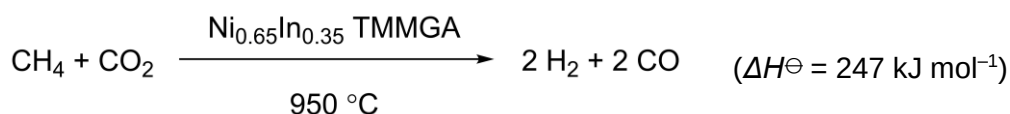
partial dehydrogenation was observed, producing propene and hydrogen with high selectivity. From an economic viewpoint, far less energy is required for hydrogen production and the products are of a higher value than hydrogen and carbon black or graphite.



Scheme 1.2: Propane dehydrogenation using a rhodium–gallium molten alloy.^{9,10}

TMMGA technology, which has the ability to resist deactivation by coking (*vide supra*), could fill a gap in the market on this point alone. The state-of-the-art catalyst for propane dehydrogenation, CATOFINTM, for example, requires similar operating temperatures (~600 °C). However, it needs to be regenerated every 12 minutes due to coking deactivating the catalyst.^{11,12}

TMMGAs have also been used in other industrially relevant reactions such as the dry reforming process. In a report by Palmer et al.,² methane and carbon dioxide were reacted with a Ni–In TMMGA in a bubble column at 950 °C to produce high quality syngas (CO + H₂) and carbon (Scheme 1.3).



Scheme 1.3: Dry reforming of methane using a nickel–indium TMMGA.^{2,13}

In this case, careful temperature control was required to prevent the formation of In₂O₃ and carbon. This catalyst overcame some of the problems faced in the use of solid metal catalysts in reforming processes such as coking and sintering. The authors claim it could specifically

apply to natural gas feedstocks which have a high CO₂ content and cannot be used in steam reforming.

1.2. Zintl Clusters as Molecular TMMGAs

Although the transformations available using TMMGAs are impressive, the harsh conditions required prevent *in situ* monitoring of reaction mechanisms and profiles. In addition, the molten alloy phase makes it highly challenging to observe and control the actual active site or species. Inspired by this, we were prompted to design and prepare molecular analogues of such alloys, in which a late transition metal fragment is supported on a main group metal cluster scaffold. In theory, this would allow us to study molecular analogues of TMMGAs using traditional solution-based techniques, whilst ensuring that the electronic environments of the active transition metals are similar to those present in a molten alloy. This thesis explores Zintl clusters comprised of transition metal and main group elements as possible molecular TMMGA candidates. Figure 1.1 presents known transition metal Zintl clusters that provide precedent that this is a valid synthetic target, though it must be noted that such clusters have not previously been used to mimic the reactivity of TMMGAs.

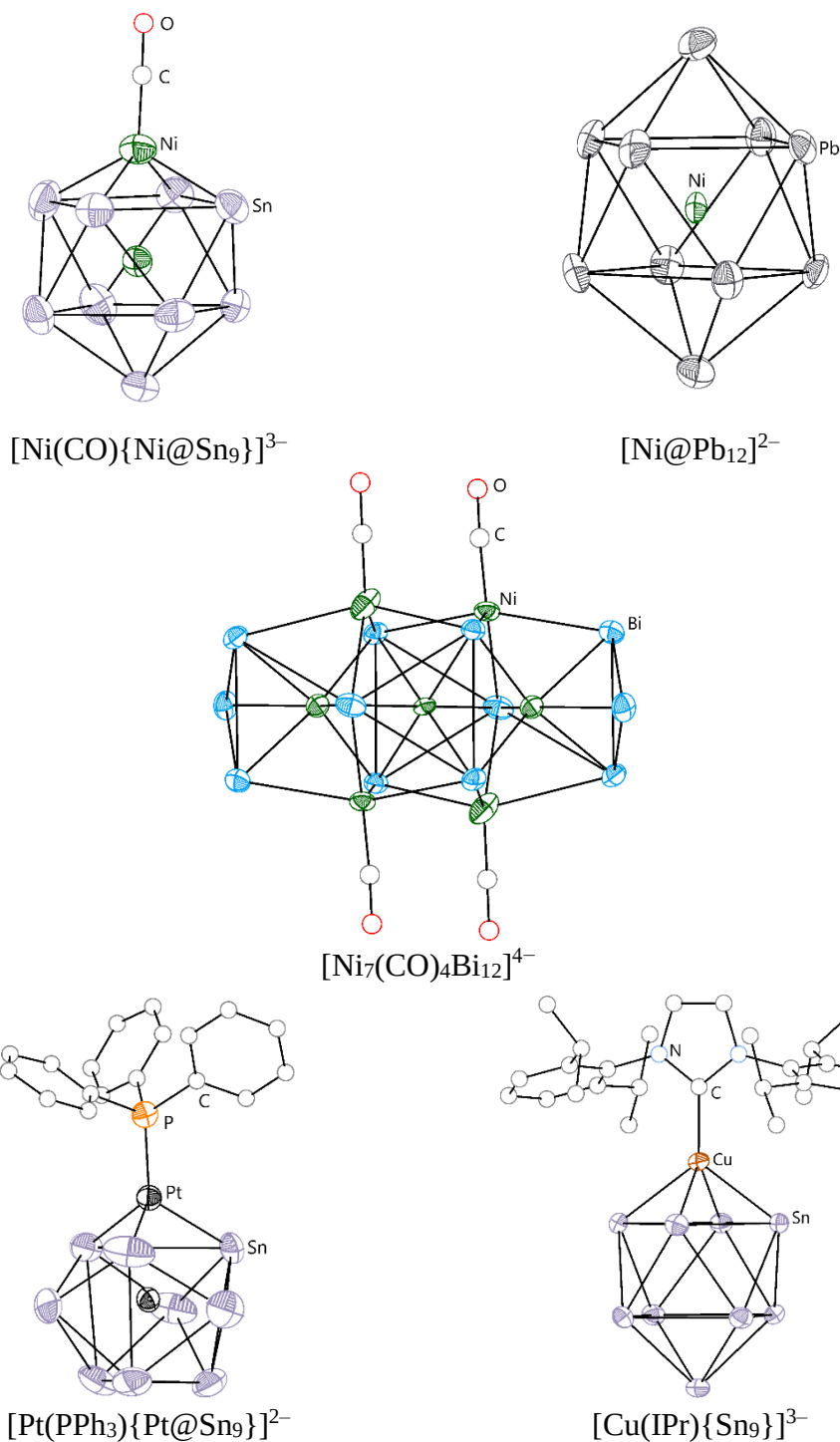
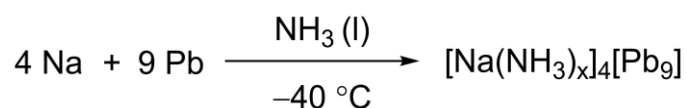


Figure 1.1: Single crystal X-ray structures of previously reported Zintl clusters with comparative compositions to TMMGAs active in methane dehydrogenation.^{14–17} Counter cations, solvents of crystallisation and hydrogen atoms have been omitted for clarity. Ellipsoid probability 50%. Carbon, nitrogen and oxygen atoms are pictured as spheres of an arbitrary radius.

Polyanionic Zintl clusters have fascinated inorganic chemists and theoreticians alike, and have been studied, primarily, in terms of their structure and bonding. Nevertheless, such systems can, in principle, be used as models for nanoparticles and alloys containing transition metals and main group atoms. Reports have shown Zintl clusters may be involved in the early stages of nanoparticle formation.^{18–26} However, prior to the start of this project, Zintl clusters had not yet been used in reactivity studies towards small molecules. Studying these clusters as molecular models of TMMGAs with methods commonly employed in organometallic chemistry (NMR spectroscopy, single crystal X-ray diffraction, cyclic voltammetry etc.) would, in theory, allow the detailed study of possible processes present in the bulk alloy melts.

1.2.1. History of Zintl Phases

Zintl phases are defined as intermetallic, typically diamagnetic alloys with a well-defined relationship between their chemical and electronic structure, e.g. $K_{12}Ge_{17}$.²⁷ Some of the first instances of these compounds were reported by Joannis, who at the end of the 19th century demonstrated that heavy p-block metals such as lead dissolve and react with sodium in liquid ammonia (Scheme 1.4).^{28–30}



Scheme 1.4: The reaction of Na and Pb in liquid ammonia.

It has been shown that upon evaporation of the solvent, the dissolved anionic species can undergo redox processes to produce other ions, e.g. $[\text{Na}(\text{NH}_3)_n]_3[\text{Sb}_7]$ decomposes to NaSb and NaSb₃ upon desolvation.²⁸ This made the preparation and isolation of these polyanionic species challenging. As such, the work laid dormant for approximately forty years, when it was next explored by Eduard Zintl in the 1930s. He performed potentiometric titrations to determine the alkali metal to main group metal ratio in liquid ammonia solutions of M_xE_y (M

= Na, K; E = Pb, Bi).³¹ His subsequent investigations aimed to bridge the gap between two very distinct compound classes: “metallic” and “non-metallic” by studying intermetallic species which did not fit into either category.²⁸ Unfortunately, given the analytical techniques available at the time, characterisation of the dissolved species could not be determined beyond their empirical compositions.

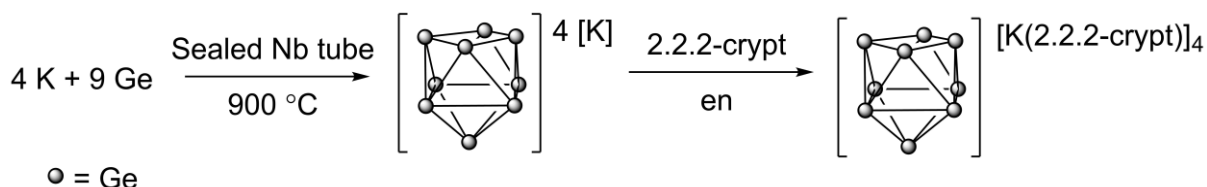
It was not until 40 years later, in the 1970s, when the research groups of Kummer and Corbett brought the chemistry of Zintl phases back into the limelight.^{32–38} This work, inspired by the findings of Klemm and Britton,^{39–42} was primarily focussed around the high-temperature synthesis of Zintl phases, isolation of Zintl ions using alkali metal sequestering agents, and characterisation of these salts using single crystal X-ray crystallography. This was the start of modern Zintl cluster chemistry, with the same analytical methods used today.

1.2.2. Synthesis of Zintl Clusters

Zintl clusters are defined as discrete molecules with three or more individual main group elements exhibiting significant element–element bonding, and are derived from Zintl phases. They can feature more than one main group element or non-main group element (e.g. transition metals, lanthanide elements etc.).⁴³ Zintl phases are most commonly prepared by high temperature syntheses involving the constituent elements sealed inside niobium or tantalum tubes. In essence, the niobium or tantalum tube has a high melting point (>2400 °C), is resistant to reduction, and is not typically incorporated into the reaction products. These are often encased in a quartz ampoule to avoid oxidation of the niobium or tantalum reaction vessels. In many cases, e.g. K_4Ge_9 , the resultant Zintl phases contain isolated clusters that can be extracted into solution.

Zintl phases can be extracted in polar, aprotic solvents such as ammonia, 1,2-ethylenediamine (en), *N,N*-dimethylformamide (DMF) or pyridine (py). This is often aided by addition of an

alkali metal cation sequestering agent (Scheme 1.5). Although these solvents allow access to dissolved Zintl ions, they also tend to degrade the Zintl phase precursor, being susceptible to reduction via deprotonation, decarbonylation or reductive coupling, respectively.



Scheme 1.5: Typical solid-state preparation of the Zintl phase K_4Ge_9 and solution extraction of Zintl ions. en = 1,2-ethylenediamine; 2.2.2-crypt = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane.

These effects vary in severity, but in all cases reduce the yields of ion formation. For example, in the case of bismuth, the Zintl phase K_5Bi_4 fragments into multiple species on dissolution, where only the Zintl ion Bi_4^{2-} can be isolated by crystallisation.³⁶ If a transition metal source is added to these mixtures, it can then lead to the synthesis of Zintl clusters, where different bismuth-containing fragments can be isolated. Such Zintl clusters typically contain coordinatively saturated transition metal fragments. For example, on adding $[\text{Ni}(\text{PPh}_3)_2(\text{CO})_2]$ to a solution of K_5Bi_4 and 2.2.2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane) or 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) in 1,2-ethylenediamine, five different anionic Zintl clusters were isolated containing various $\text{Ni}(\text{CO})$ and Bi ratios (Figure 1.2).^{15,44,45}

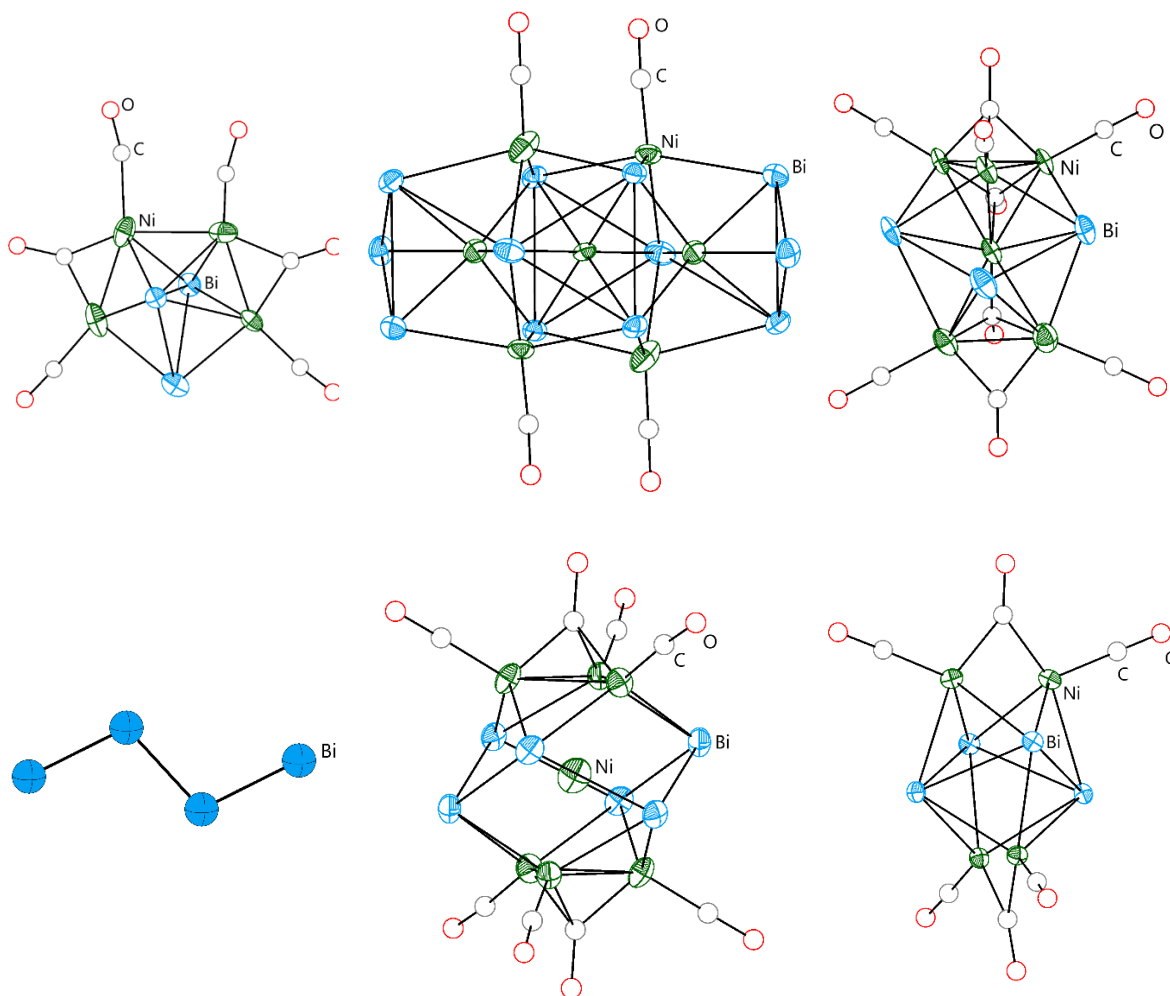


Figure 1.2: Single crystal X-ray structures of K_5Bi_4 ,⁴⁶ a Zintl phase; and five crystallographically characterised Zintl clusters produced on reaction with $[Ni(CO)_2(PPh_3)_2]$: $[K(2.2.2-crypt)]_3[Ni_4Bi_3(CO)_6]$, $[K(2.2.2-crypt)]_4[Ni@Ni_6Bi_{12}(CO)_4]$, $[K(18-crown-6)]_3[Ni_6Bi_3(CO)_9]$, $[K(18-crown-6)]_4[Ni@Ni_6Bi_6(CO)_8]$, and $[K(2.2.2-crypt)]_2[Ni_4Bi_4(CO)_6]$.^{15,46} Counter cations and solvents of crystallisation have been omitted for clarity. Ellipsoid probability 50%, except for K_5Bi_4 which does not have anisotropic displacement parameters. Connecting lines between atoms do not represent two centre, two electron bonds. Carbon and oxygen atoms are pictured as spheres of an arbitrary radius, hydrogen atoms have been omitted for clarity.

1.2.3. Electron Counting and Bonding in Group 14 Zintl ions and Clusters

Group 14 Zintl ions typically feature structures that are not electron precise, and are directly comparable to boranes and carboranes due to the isoelectronic and isolobal relationship between a group 14 element and a B–H fragment.⁴⁷ Therefore, the principles of the polyhedral skeletal electron pair theory can be adapted for use with Zintl ions. For example, a germanium vertex, with an *exo* facing lone pair of electrons, is isolobal and valence isoelectronic to a B–H vertex, both contributing three orbitals and two electrons to cluster bonding. Before electron counting such clusters, it would first be useful to revise these rules for electron counting in polyhedral boranes and carboranes.^{48–50}

For an *n*-vertex *closo* polyhedron, *n*+1 skeletal electron pairs are required for cluster stability, in order to fill all of the bonding orbitals and give rise to a large HOMO/LUMO gap. For a *nido* polyhedron, where one vertex is missing relative to its parent *closo* polyhedron, *n*+2 skeletal electron pairs are required. For an *arachno* polyhedron, where two vertices are missing relative to its parent *closo* polyhedron, *n*+3 skeletal electron pairs are required. This, along with the information in Table 1.2, allows the electron counting of most polyhedral boranes.

Table 1.2: Number of skeletal electrons contributed by main group moieties, reproduced from Albright et al.⁵¹ ^aX: one-electron ligand, for example, halogen; ^bL: two-electron ligand, for example, PPh₃, THF.

Group	A	A–H, A–X ^a	A–L ^b	AH ₂
1	–1	0	1	1
2	0	1	2	2
13	1	2	3	3
14	2	3	4	4
15	3	4	5	5
16	4	5	6	6
17	5	6		

An archetypal example for the application of this electron counting method is $\text{B}_{10}\text{H}_{10}^{2-}$,⁵² which has a skeletal electron count of 22 ($10 \times \text{B-H}$, $2 \times \text{charge}$), this equates to 11 valence electron pairs. As a 10-vertex structure, the cluster has a *closo* electron count, since it has $n+1$ valence electron pairs and thus adopts a bicapped square antiprismatic geometry.

The Zintl cluster Ge_9^{4-} (Figure 1.3, Left) also has 22 valence electrons ($9 \times \text{Ge}$, $4 \times \text{charge}$), but is a *nido* cluster due to its 9 vertices, equating to $n+2$ electron pairs. This gives rise to a mono-capped square antiprismatic geometry with C_{4v} symmetry. The germanium vertices of this Zintl ion have formal *exo* facing lone pairs of electrons, contributing the other two valence electrons to cluster bonding. It must be noted at this point that the heavier analogues of these clusters are regarded as highly fluxional, with low energy barriers between C_{4v} and D_{3h} symmetries, for example, the vibrational modes in Pb_9^{4-} have been calculated to be between $100\text{--}200\text{ cm}^{-1}$.^{53,54}

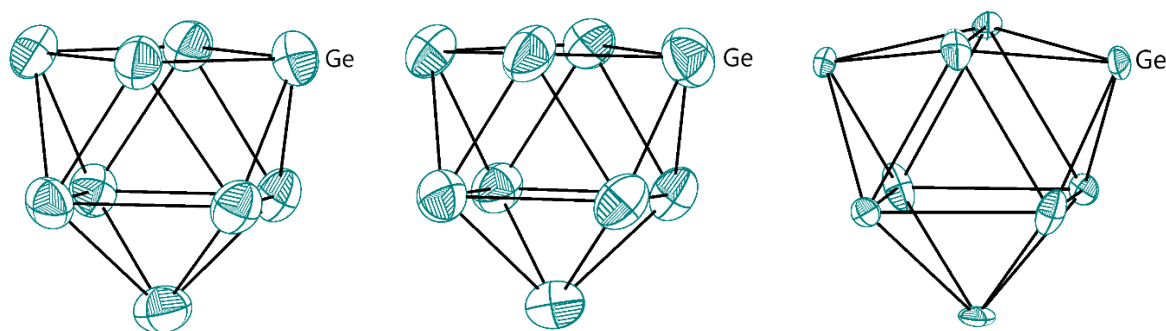


Figure 1.3: Single crystal X-ray structures of the Ge_9^{n-} ions; Left: $n = 4$, Middle: $n = 3$, Right: $n = 2$.^{55–57} Counter cations and solvents of crystallisation have been omitted for clarity. Ellipsoid probability 50%, connecting lines between atoms do not represent two centre, two electron bonds.

The oxidised Ge_9^{n-} ($n = 2, 3$) clusters are also known, showing geometries which are distorted away from the C_{4v} symmetric tetraanion. The paramagnetic Ge_9^{3-} cluster has C_{2v} symmetry

and the *closo* Ge_9^{2-} has a tricapped trigonal prismatic geometry with D_{3h} symmetry, as expected for a 9-vertex cluster with 20 valence electrons ($9 \times \text{Ge}, 2 \times \text{charge}$).^{51,58}

The isolobal analogy allows this method for electron counting to be extended to the transition metals. Two fragments are described as isolobal if their frontier orbitals have the same number and symmetry properties; as well as similar energy and radial extent.⁵¹ For example, a methyl radical $[\text{CH}_3]$ is isolobal with $[\text{Mn}(\text{CO})_5]$, $[(\text{Cp})\text{Fe}(\text{CO})_2]$ and $[(\text{PPh}_3)_3\text{Co}]$, all of which contribute one electron to cluster bonding. Interestingly, the reactions of alkyl halides or $[(\text{Cp})\text{Fe}(\text{CO})_2\text{Br}]$ and the tris-substituted Zintl cluster $[\text{KGe}_9(\text{Hyp})_3]$ ($\text{Hyp} = \text{Si}(\text{SiMe}_3)_3$) provide valence isoelectronic and structurally similar products (Figure 1.4), exemplifying the isolobal relationship of $[(\text{Cp})\text{Fe}(\text{CO})_2]$ and alkyl fragments.^{59,60}

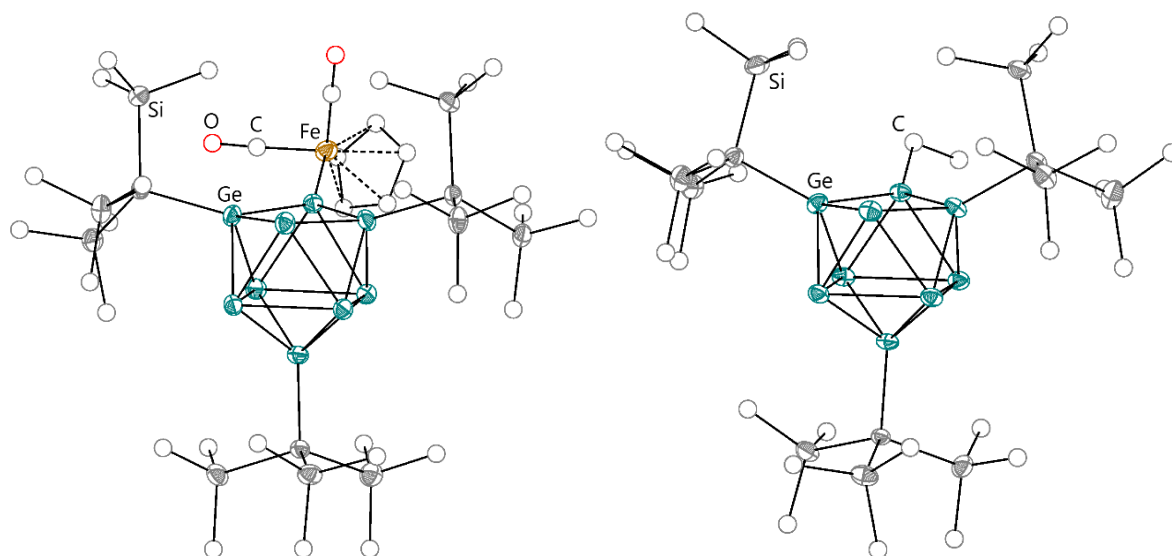
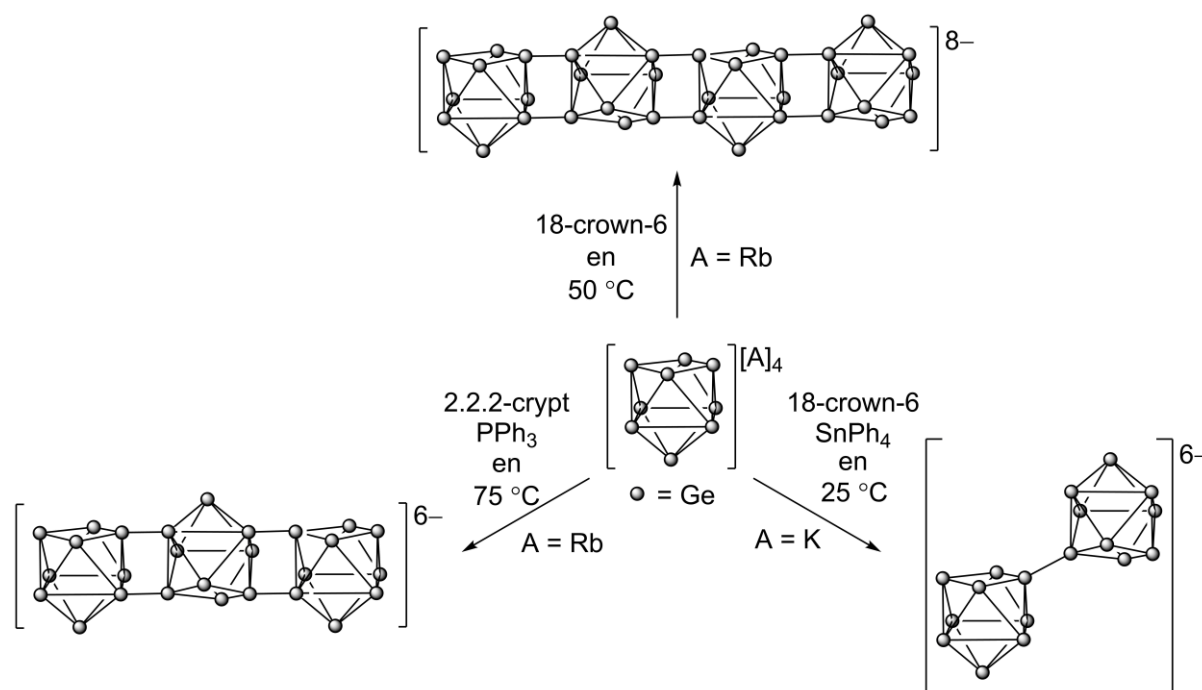


Figure 1.4: Single crystal X-ray structures of $[(\text{Cp})\text{Fe}(\text{CO})_2\{\text{Ge}_9(\text{Hyp})_3\}]$ and $[\text{Ge}_9(\text{Hyp})_3\text{Et}]$. Ellipsoid probability 50%, connecting lines between atoms do not represent two centre, two electron bonds. Carbon and oxygen atoms are pictured as spheres of an arbitrary radius, hydrogen atoms have been omitted for clarity.

1.2.4. The Ge_9^{4-} Zintl Ion

The Zintl ion Ge_9^{4-} was first prepared in the 1970s by Diehl and Kummer, by dissolving an alloy of nominal composition NaGe_2 in 1,2-ethylenediamine. The product was crystallised by slow diffusion of DME into the 1,2-ethylenediamine solution.^{39,61,62}

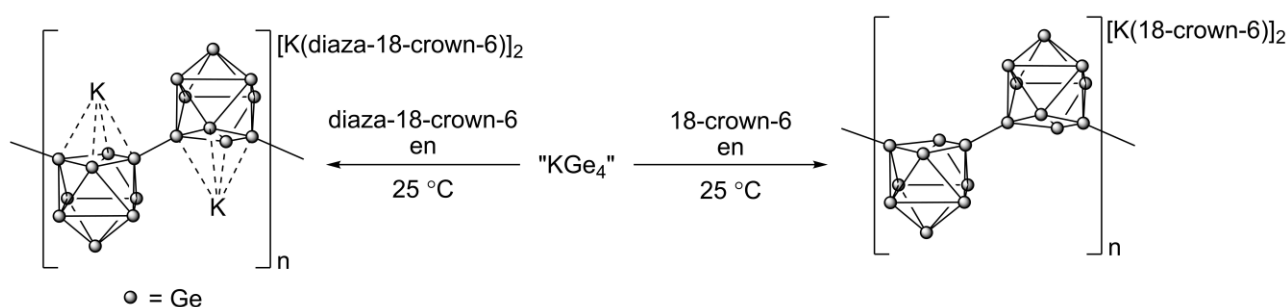
The Zintl phase, K_4Ge_9 , which contains Ge_9^{4-} clusters, exclusively yields Ge_9^{4-} Zintl ions upon dissolution, thus allowing for more controlled reactions. For this reason, it is one of the most widely studied Zintl ions.⁶³ This ion has been used as a building block in a bottom-up approach for the formation of germanium nanoparticles and nanostructured materials. Early publications from the Fässler and Sevov groups detail the controlled dimerization,^{64–67} oligomerisation,^{58,68,69} and polymerisation of these cluster anions (Scheme 1.6).^{70–73}



Scheme 1.6: Oligomerisation of Ge_9^{4-} under different reaction conditions.^{58,64,69}

As seen in Scheme 1.6, the conditions for oligomerisation are rather mild and comparable to the typical conditions required for the synthesis of new Zintl clusters (Scheme 1.5). This was extended further by Guloy et al., who used a mixture of potassium germanide alloys with a

nominal composition “KGe₄”, to polymerise such cages into chains of either (Ge₉[−])_n or (Ge₉^{2−})_n depending on the sequestering agent used (Scheme 1.7).^{70,74}



Scheme 1.7: Polymerisation of Ge₉^{4−} clusters.^{70,74}

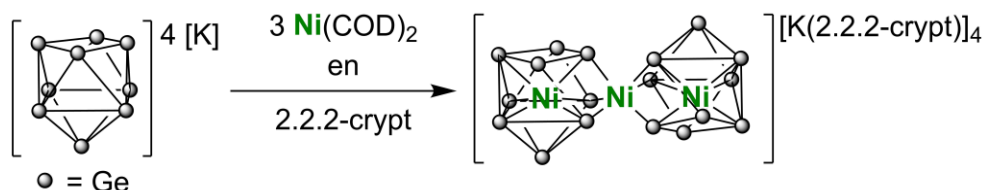
Ugrinov and Sevov were also able to prepare the (Ge₉)_n^{2−} chain from a mixed alloy of nominal composition Li₂RbGe₁₇.⁷⁵ These studies highlight possible decomposition pathways of the cluster ions and illustrate their viability for the synthesis of germanium containing materials.

The tendency to undergo facile aggregation exemplifies a major drawback when designing catalytically active molecular clusters based on the Ge₉^{4−} scaffold. Porous germanium-containing materials have been prepared using these clusters, starting from well-defined precursors.^{72,76–81} Of note is the formation of hexagonal nanoporous germanium by Tolbert and co-workers, which starts by preparing (Ge₉)_n^{2−} as described by Guloy.^{70,72} Further studies have since found applications of such materials in lithium ion batteries.⁷⁸

Since its isolation, many Zintl clusters have been synthesised from reactions between Ge₉^{4−} and various transition metal precursors.^{26,63,82} It has been shown to both incorporate metal atoms into the centre of the cage to form endohedral clusters (e.g. [Ni@Ge₉]^{3−}, [Fe@Ge₁₀]^{3−} and [Pd₂@Ge₁₈]^{4−}),^{22,45,82–86} as well as add metal–ligand fragments to the cluster surface, with metal–cluster coordination modes changing depending on the electronic requirements of the metal fragment.^{63,87} In most cases, the nonagermanide moiety remains intact upon dissolution.

This increases the predictability of reaction outcomes and for this reason, it is one of the more well studied Zintl ions for metallation.⁴³

Endohedral Ge_9^{4-} derived Zintl clusters, where one or more atoms are confined within a Zintl ion or cluster, have been particularly well studied.²² One seminal example of this is the encapsulation of three nickel atoms inside two nonagermanide cages (Figure 1.5).⁸⁸



Scheme 1.8: Synthesis of $[\text{K(2.2.2-crypt)}]_4[\text{Ni}_3@ \{ \text{Ge}_9 \}_2]$

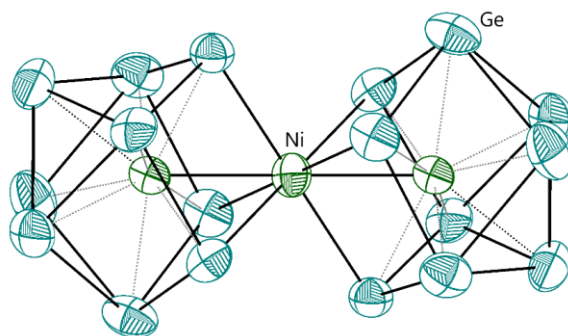


Figure 1.5: Single crystal X-ray structure of $[\text{K(2.2.2-crypt)}]_4[\text{Ni}_3@ \{ \text{Ge}_9 \}_2]$.⁸⁸ $[\text{K(2.2.2-crypt)}]^+$ counterions have been removed for clarity. Ellipsoid probability 50%, connecting lines between atoms do not represent two centre, two electron bonds.

This class of compounds brings to mind endohedral fullerenes which are also of interest to theoretical and computational chemists,^{89,90} since they offer the opportunity to study the electronic properties of a metal atom or fragment restrained inside a cage.^{19,20,22,23,83,91} The non-ligated clusters of this type are sometimes referred to as superatoms due to their spherical-like geometries and high electron delocalisation.²⁶ Although their preparations are relatively recent, there are many examples of these clusters,^{14,18–20,22,23,92–95} allowing the

physical study of fragments observed in laser ablation experiments performed on transition metal–main group metal alloys. They can be synthesised in a number of ways, though the use of metal complexes with weakly bonded ligands is the most popular route. $[\text{Ni}(\text{COD})_2]$, for example, provides a closed shell d^{10} nickel atom to the cage without affecting the overall electron count. In the related chemistry of tin clusters, another interesting route towards endohedral moieties is to start with an intermetallic precursor containing the transition metal. This method was used to produce the open shell *nido*- $[\text{Co}@\text{Sn}_9]^{4-}$ and related metallated *closo* clusters $[\text{Ni}(\text{CO})\{\text{Co}@\text{Sn}_9\}]^{3-}$, $[\text{Ni}(\text{C}_2\text{H}_4)\{\text{Co}@\text{Sn}_9\}]^{3-}$, $[\text{Pt}(\text{PPh}_3)\{\text{Co}@\text{Sn}_9\}]^{3-}$ and $[\text{Au}(\text{Ph})\{\text{Co}@\text{Sn}_9\}]^{3-}$.²¹

Non-endohedral Zintl clusters of germanium do not contain a central metal atom and the transition metal atoms are bonded to the surface of the cluster. Their syntheses are often similar and rely on the reaction of the *nido* nonagermanide tetraanion, $[\text{Ge}_9]^{4-}$, and a transition metal precursor in a polar, redox-active solvent such as 1,2-ethylenediamine. The transition metal then typically takes place in a vacant site to form a *closo* cluster. Depending on the steric and electronics of the transition metal–ligand fragment, the nonagermanide framework has the ability to change its hapticity, resulting in a number of different topologies and binding modes. An interesting example is the formation of open shell clusters $[\text{Ni}(\text{CO})\{\text{Ge}_9\}]^{3-}$ and $[\text{Pd}(\text{PPh}_3)\{\text{Ge}_9\}]^{3-}$ shown in Figure 1.6.^{44,96}

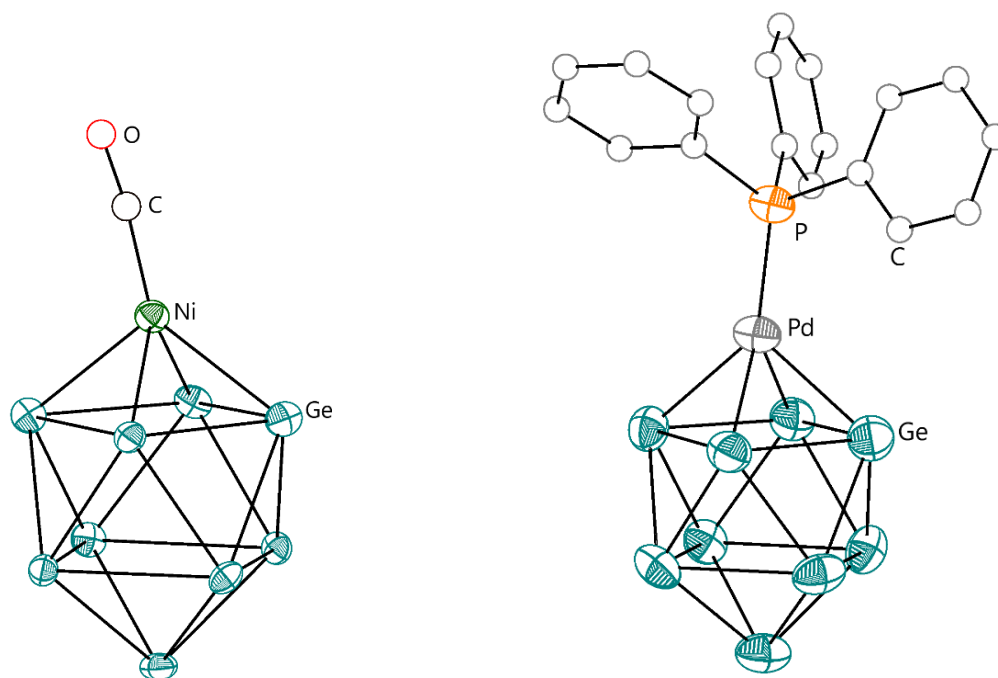


Figure 1.6: Single crystal X-ray structures of $[\text{K}(\text{2.2.2-crypt})]_3[\text{Ni}(\text{CO})\{\text{Ge}_9\}]$ and $[\text{K}(\text{2.2.2-crypt})]_3[\text{Pd}(\text{PPh}_3)\{\text{Ge}_9\}]$.^{44,94} $[\text{K}(\text{2.2.2-crypt})]^+$ counterions have been removed for clarity. Ellipsoid probability 50%, connecting lines between atoms do not represent two centre, two electron bonds. Carbon and oxygen atoms are pictured as spheres of an arbitrary radius, hydrogen atoms have been omitted for clarity.

From a cluster bonding perspective, both are one electron shy of the 22 electrons for a diamagnetic *closo* 10-vertex cluster ($\text{Ge} = 9 \times 2$, $\text{Ni/Pd} = 0$, charge = 3).⁴⁵ Interestingly, their analogous endohedral clusters $[\text{Ni}(\text{CO})\{\text{Ni}@\text{Ge}_9\}]^{2-}$ and $[\text{Pd}(\text{PPh}_3)\{\text{Ni}@\text{Ge}_9\}]^{2-}$ (Figure 1.7) also adopt the same centred tricapped trigonal prismatic geometry where the non-endohedral transition metal is now in a η^3 coordination environment with the nonagermanide cage.

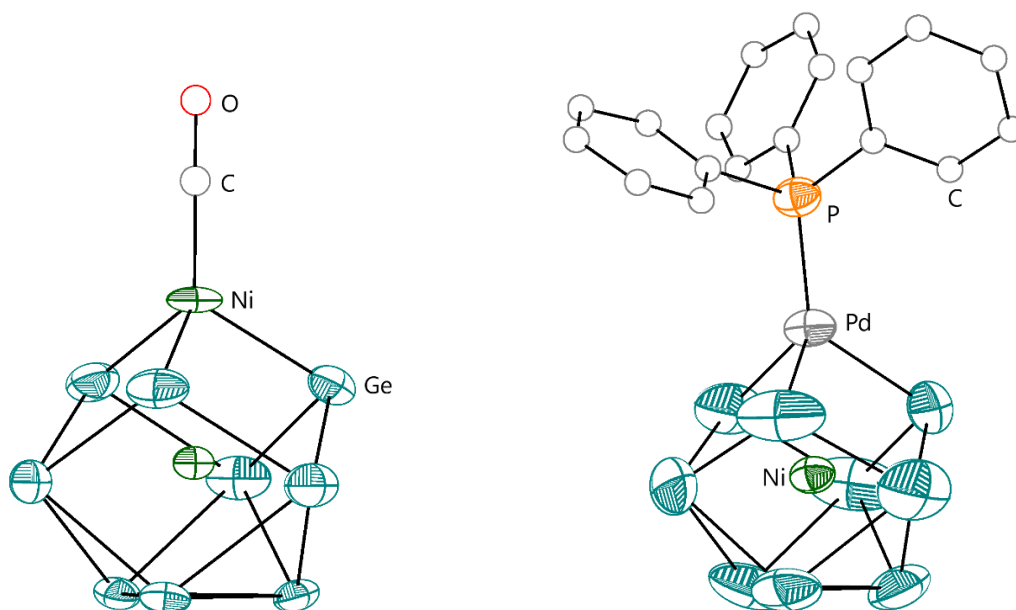


Figure 1.7: Single crystal X-ray structures of $[\text{K}(2.2.2\text{-crypt})]_2[\text{Ni}(\text{CO})\{\text{Ni}@\text{Ge}_9\}]$ and $[\text{K}(2.2.2\text{-crypt})]_2[\text{Pd}(\text{PPh}_3)\{\text{Ni}@\text{Ge}_9\}]$.^{44,96} $[\text{K}(2.2.2\text{-crypt})]^+$ counterions have been removed for clarity. Ellipsoid probability 50%, connecting lines between atoms do not represent two centre, two electron bonds. Carbon and oxygen atoms are pictured as spheres of an arbitrary radius, hydrogen atoms have been omitted for clarity.

Another known coordination mode for transition metal– Ge_9 Zintl clusters is η^1 , where a germanium atom is involved in a two-centre-two-electron *exo* bond with a metal. Such interactions can be found in the tris-functionalised compound $[\text{K}(18\text{-crown-}6)]_4[\{\text{W}(\text{CO})_5\}_3\text{Ge}_9]$ prepared by Xu and co-workers (Figure 1.8).⁹⁷

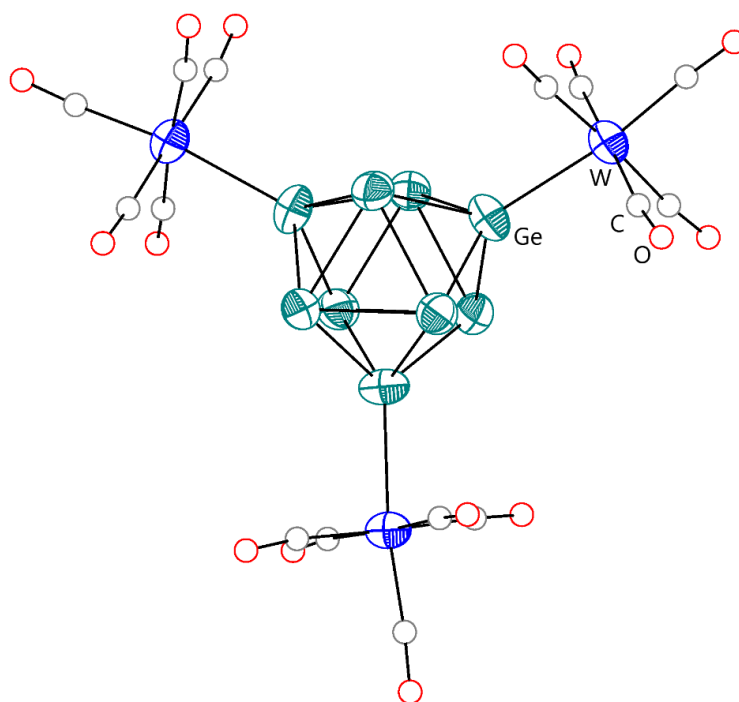
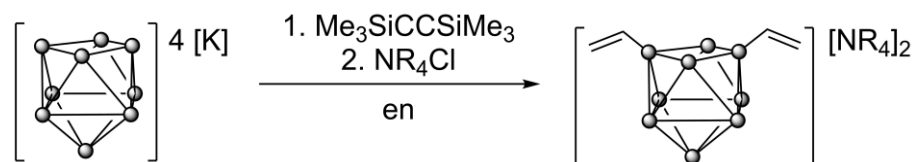


Figure 1.8: Single crystal X-ray structure of $[\text{K}(\text{18-crown-6})]_4[\{\text{W}(\text{CO})_5\}_3\text{Ge}_9]$.⁹⁷ $[\text{K}(\text{2.2.2-crypt})]^+$ counterions have been removed for clarity. Ellipsoid probability 50%, connecting lines between atoms do not represent two centre, two electron bonds. Carbon and oxygen atoms are pictured as spheres of an arbitrary radius, hydrogen atoms have been omitted for clarity.

In comparison to the direct syntheses of these clusters, there has been very little reported in terms of further reactivity and modifications of metallated Zintl clusters.⁴³ This is primarily due to poor solubility, solution instability and a dearth of NMR active nuclei to study solution behaviour beyond what can be gained from mass spectrometry.

1.2.5. Organic Functionalised Zintl Clusters

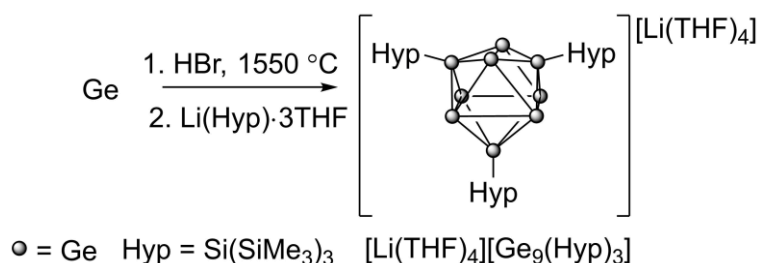
In 2007, Hull et al. reacted 1,2-ethylenediamine solutions of K_4Ge_9 with alkynes, followed by tetraalkyl ammonium halides to form bis-functionalised products that were soluble enough in benzene- d_6 to obtain a ^1H NMR spectrum.⁹⁸ This was a breakthrough paper in the field and introduced the idea of Zintl cluster chemistry in conventional organic solvents (Scheme 1.9).⁹⁹



Scheme 1.9: Synthesis of $[\text{Ge}_9(\text{CHCH}_2)_2]^{2-}$ clusters (R = Me, Pr, Oct)

Interestingly, these clusters were not explored further in terms of their reactivity and coordination chemistry towards transition metals.

In 2003, Schnepf first synthesised the $[\text{Ge}_9(\text{Hyp})_3]^-$ (Hyp = $\text{Si}(\text{SiMe}_3)_3$) ion using germanium(I) bromide as the germanium precursor (Scheme 1.10).¹⁰⁰ The introduction of three hypersilyl substituents provides a spectroscopic handle, allowing the study of such clusters in small scale NMR experiments. This cluster anion is also soluble in toluene and benzene, and therefore allows for the use of many transition metal precursors that are unstable in polar and coordinating solvents such as 1,2-ethylenediamine. In this original synthesis, germanium(I) bromide was formed *in situ*, from liquid germanium metal and HBr at 1550 °C, followed by co-condensation with a toluene: tris-*n*-propylamine mixture at –196 °C. This was then reacted with $\text{Li}(\text{THF})_3(\text{Hyp})$ in toluene at –78 °C to perform the silylation, forming $[\text{Li}(\text{THF})_4][\text{Ge}_9(\text{Hyp})_3]$ (Figure 1.9) in ~9% yield. Although Wade’s rules would predict a *nido* cluster with C_{2v} symmetry, the $[\text{Ge}_9(\text{Hyp})_3]^-$ ion exhibits D_{3h} symmetry which is imposed by the bulky silyl substituents (Figure 1.9).



Scheme 1.10: Synthesis of $[\text{Li}(\text{THF})_4][\text{Ge}_9(\text{Hyp})_3]$ using the GeBr route employed by Schnepf.¹⁰⁰

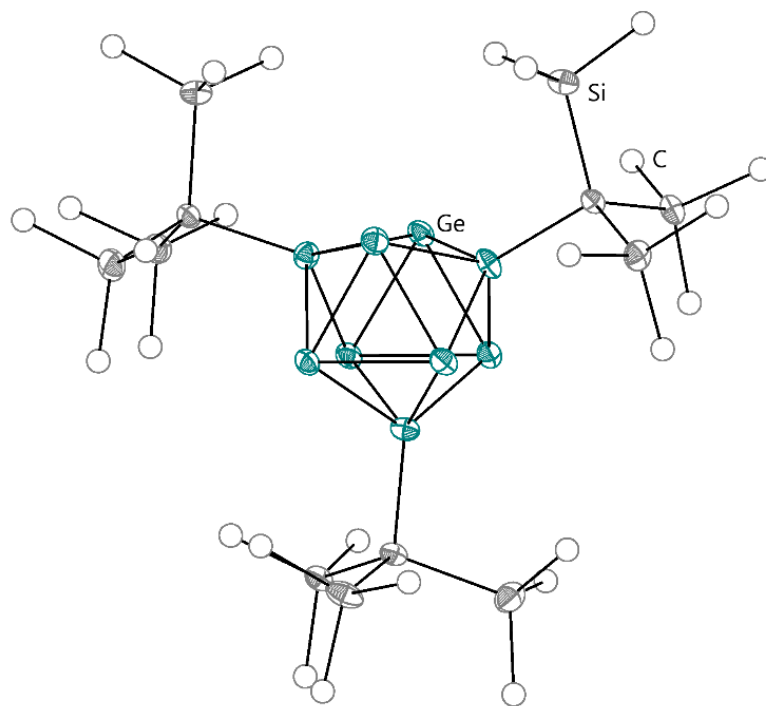
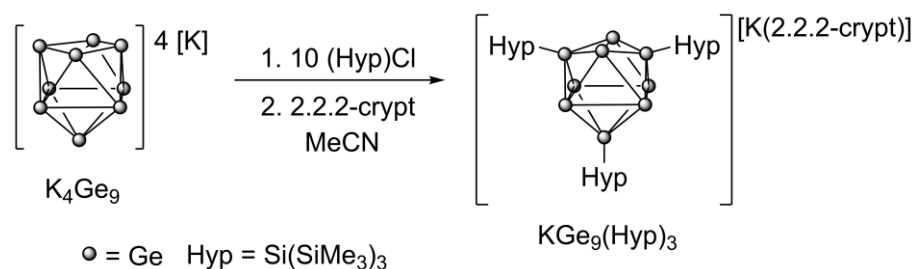


Figure 1.9: Single crystal X-ray structure of the $[\text{Ge}_9(\text{Hyp})_3]^-$ anion.¹⁰⁰ Li^+ counterions and solvent of crystallisation have been removed for clarity. Ellipsoid probability 50%, connecting lines between atoms do not represent two centre, two electron bonds. Carbon atoms are pictured as spheres of an arbitrary radius, hydrogen atoms have been omitted for clarity.

Schnepf's preparation required a bespoke reactor capable of the co-condensation reactions described above. In addition to the low yields, this prevented the further chemistry of $[\text{Ge}_9(\text{Hyp})_3]^-$ from being explored. Li and Sevov reported a milder synthetic route nine years later, starting from the Zintl phase, K_4Ge_9 (Scheme 1.11).¹⁰¹



Scheme 1.11: "Rational" synthesis of the $[\text{Ge}_9(\text{Hyp})_3]^-$ anion.¹⁰¹

Sevov's improved synthesis employed the Zintl phase precursor K_4Ge_9 and silyl halide $(\text{Hyp})\text{Cl}$, which is commercially available. K_4Ge_9 was mixed with an excess of $(\text{Hyp})\text{Cl}$ in MeCN, stirred for two hours at room temperature, filtered, and layered with a solution of 2.2.2-crypt in hexane to afford crystals of $[\text{K}(2.2.2\text{-crypt})][\text{Ge}_9(\text{Hyp})_3]$. Due to the steric hindrance imposed by the large silanes, tetrasubstitution was not observed, even with a ten-fold excess of silyl chloride.

Since this methodology was reported, there have been many publications describing the role of tris-silylated clusters as a ligand for transition metals, and demonstrating that it too can adopt many different coordination modes to suit the transition metal–ligand fragment (Table 1.3). To date there have been no reports of an endohedral cluster of this type, presumably due to the substitution hindering the flexibility of the cage. Notably, the most favourable coordination mode seems to be η^3 , where one or both of the vacant triangular faces of the cluster is used for bonding. The preference of the η^3 coordination mode is presumably due to the reduced steric clash between the hypersilyl substituents and the transition metal moiety.

Table 1.3: Selected examples of different coordination modes of the $[\text{Ge}_9(\text{Hyp})_3]^-$ ion with metal atoms (Cp = cyclopentadienyl; CAAC = 1-(2,6-diisopropylphenyl)-2,2,4,4-tetramethyl-3,4-dihydro-2H-pyrrolidene; IPr = 1,3-bis-(2,6-diisopropylphenyl)imidazolidene).

Hapticity	Examples	Reference
η^1	$[(\text{Cp})\text{Fe}(\text{CO})_2\{\text{Ge}_9(\text{Hyp})_3\}]$, $[\text{Cr}(\text{CO})_5\{\text{Ge}_9(\text{Hyp})_3\}]^-$, $[(\text{Cp})_2\text{Ti}(\text{MeCN})_2\{\text{Ge}_9(\text{Hyp})_3\}]$,	102–104
η^2	$[\text{M}(\text{THF})_2\{\text{Ge}_9(\text{Hyp})_3\}_2]$ (M = Sm, Eu)	105
η^3	$[\text{Cu}(\text{CAAC})\{\text{Ge}_9(\text{Hyp})_3\}]$ (M = Cu), $[\text{M}(\text{IPr})\{\text{Ge}_9(\text{Hyp})_3\}]$ (M = Cu, Ag, Au), $[\text{Mn}\{\text{Ge}_9(\text{Hyp})_3\}_2]$, $[\text{Au}(\text{PR}_3)\{\text{Ge}_9(\text{Hyp})_3\}]$ (R = Et, ^nPr , ^iPr , ^nBu , ^tBu , Cy), $[\text{Ni}(\text{DPPE})\{\text{Ge}_9(\text{Hyp})_3\}]$, $[\text{Pd}\{\text{Ge}_9(\text{Hyp})_3\}_2]^{2-}$	106–109
η^4	No examples prior to this research	
η^5	$[\text{M}(\text{CO})_3\{\text{Ge}_9(\text{Hyp})_3\}]^-$ (M = Cr, Mo, W)	103,110

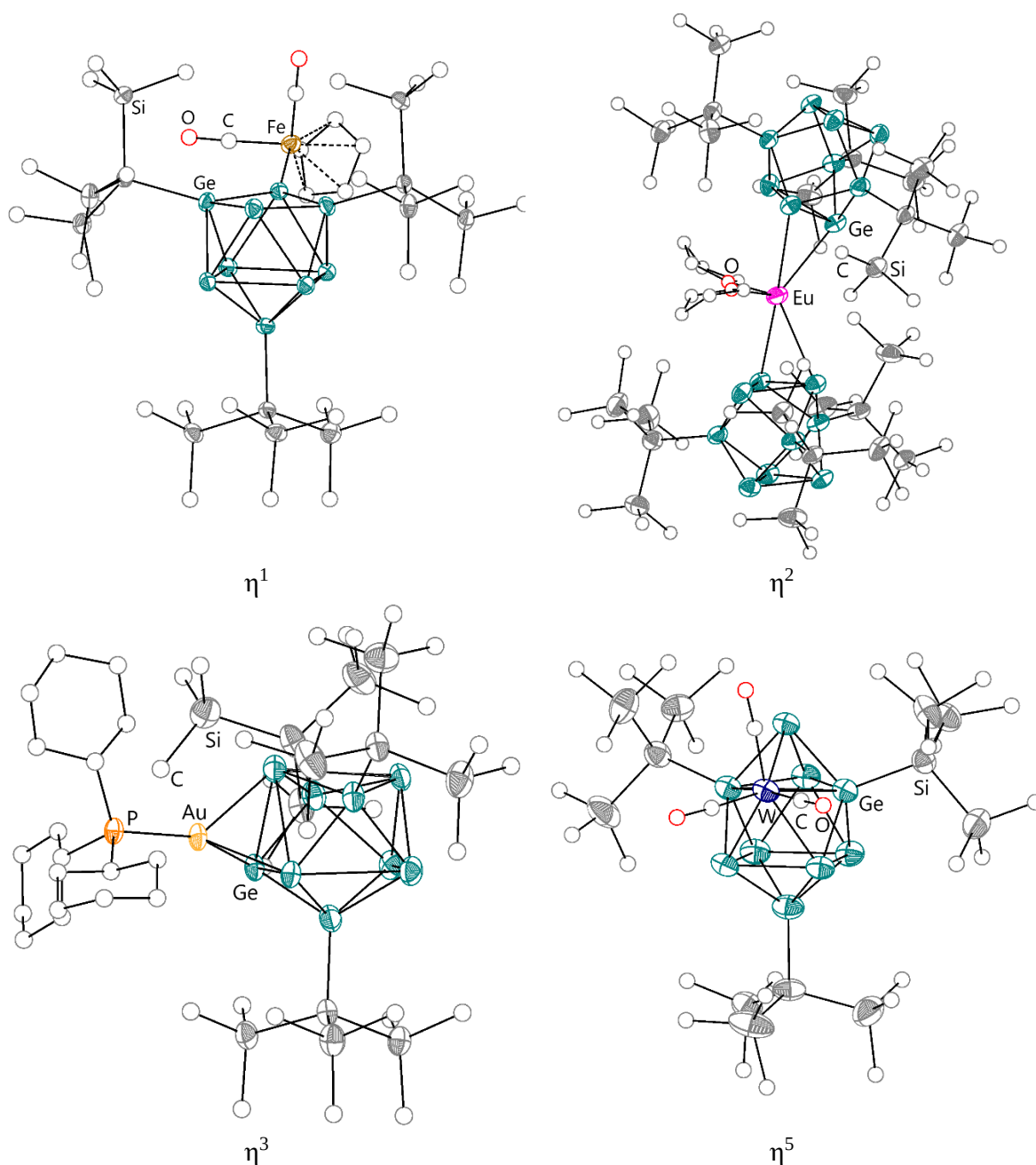


Figure 1.10: Single crystal X-ray structures of $[(\text{Cp})\text{Fe}(\text{CO})_2\{\text{Ge}_9(\text{Hyp})_3\}]$, $[\text{Eu}(\text{THF})\{\text{Ge}_9(\text{Hyp})_3\}_2]$, $[\text{Au}(\text{PCy}_3)\{\text{Ge}_9(\text{Hyp})_3\}]$ and $[\text{Li}(\text{TMEDA})_2][\text{W}(\text{CO})_3\{\text{Ge}_9(\text{Hyp})_3\}]$ (Cy = cyclohexyl, TMEDA = 1,2-bis(dimethylamino)ethane).^{102,105,108,110} Ellipsoid probability 50%, connecting lines between atoms do not represent two centre, two electron bonds. Carbon atoms are pictured as spheres of an arbitrary radius, hydrogen atoms have been omitted for clarity.

With regard to using Zintl clusters as molecular TMMGAs, the large hypersilyl groups featured on the tris-substituted ion $[\text{Ge}_9(\text{Hyp})_3]^-$ increase solubility in non-polar solvents and sterically restrict aggregation pathways. This is in contrast to the “naked” Ge_9^{4-} ion, hence eliminating a possible pathway for cluster decomposition. Furthermore, as mentioned previously, the presence of the hypersilyl substituents allows for reactions and final products to be monitored and characterised by NMR spectroscopy (^1H , ^{13}C , ^{29}Si). All of these factors combined make it an ideal support for the design of hydrocarbon soluble molecular TMMGAs.

1.2.6. Project Aims

The aim of this project is to ultimately emulate the reactivity of TMMGAs using Zintl clusters as molecular models. These can then be studied using conventional techniques used in homogeneous catalysis such as NMR spectroscopy, mass spectrometry and X-ray crystallography to gain an insight into the reactivity of such compounds.

At the start of the project, the first aim was to prepare Zintl clusters based on nickel and bismuth in an effort to mimic the successful use of Ni–Bi TMMGAs in methane dehydrogenation. Since the focus of the project is to develop homogeneous catalysts, the focus of the project was changed to germanium-supported metals because of the aforementioned advantages of known hydrocarbon-soluble derivatives. The core aims of the project were:

- 1) To synthesise a variety of novel, well-defined binary Zintl clusters with variable main group/transition metal ratios, initially chosen to reflect the known successful molten alloy catalysts;
- 2) To explore fundamental studies on C–H activation chemistry at functionalised Zintl clusters;

- 3) To develop such systems in challenging alkane C–H activation chemistry, by taking advantage of single/crystal solid/gas synthesis and catalysis methodologies;
- 4) To deploy these new systems in catalysis, focussing on methane activation and butane dehydrogenation.

1.3. Thesis summary

Due to the enhanced performance of nickel containing TMMGAs in methane dehydrogenation, nickel germanides were first explored. Chapter 2 discusses such work investigating routes to nickel–germanium Zintl clusters, using the $[\text{Ge}_9(\text{Hyp})_3]^-$ ion, though further reactivity was unsuccessful due to solution instability and coordination sphere saturation.

Chapter 3 describes the first use of a Zintl cluster in homogeneous catalysis, employing a $[\text{Rh}(\text{COD})]^+$ (COD = 1,5-cyclooctadiene) fragment on the $[\text{Ge}_9(\text{Hyp})_3]^-$ support. The catalytic hydrogenation of *cis*-cyclooctene and 1,5-cyclooctadiene was studied using kinetic and density functional theory methods to propose a model mechanism. It was found that reactivity was hindered by both a ligand fluctuation process and cluster decomposition in the presence of dihydrogen.

Chapter 4 investigates modifications of the $[\text{Rh}(\text{COD})\{\text{Ge}_9(\text{Hyp})_3\}]$ cluster via ligand substitution at the rhodium centre in order to prepare coordinatively unsaturated systems $[\text{Rh}(\text{L})\{\text{Ge}_9(\text{Hyp})_3\}]$. These clusters were then investigated in catalysis studies involving H–H and C–H bond activation processes.

Chapter 5 explores novel methods for the controlled cluster expansion of either $[\text{Ge}_9(\text{Hyp})_3]^-$ or $[\text{Rh}(\text{COD})\{\text{Ge}_9(\text{Hyp})_3\}]$ with late transition metal complexes. Firstly, to prepare homometallic 11- and 12-vertex species containing additional $[\text{Rh}(\text{alkene})]^+$ fragments, varying the Rh:Ge content. This strategy was then applied in the synthesis of hetero-

multimetallic clusters incorporating $[\text{Ir}(\text{COD})]^+$ or $[\text{Ni}(\text{COD})]$ moieties, as a form of metal doping.

1.4. References

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2. Cluster Expansion and Vertex Substitution Pathways in Nickel Germanide Zintl Clusters

2.1. Background and Introduction

Semiconducting Ni–Ge intermetallic alloys, for example NiGe or Ni₃Ge,¹ have been extensively explored in recent years as catalysts, in microelectronics and in thermoelectric materials.^{1–7} Discrete metalloid clusters are studied as molecular models for such extended solids to investigate their underlying structural and physical properties.^{8,9} Inspired by this, and due to the impressive performance of nickel containing transition metal–main group alloys (TMMGAs) in alkane dehydrogenation,¹⁰ molecular nickel germanide clusters were chosen as the first synthetic targets for the work described in this chapter.

In 2016, Schnepf and co-workers reported the first reactivity studies of [KGe₉(Hyp)₃] (Hyp = Si(SiMe₃)₃) with transition metal halides.¹¹ Reactions between [KGe₉(Hyp)₃] and [MnCl₂] were shown to afford the homoleptic complex [Mn{Ge₉(Hyp)₃}₂] in low yields (7%). By contrast, reaction with [NiCl₂] resulted in the formation of black insoluble solids, presumably due to the oxidative coupling of the [Ge₉(Hyp)₃][–] cage and reduction of the nickel(II) precursor. This assumption was further corroborated by the observed formation of Ge₁₈(Hyp)₆ when [FeCl₂] was reacted with [KGe₉(Hyp)₃].¹² Interestingly, although the large hypersilyl substituents in [Ge₉(Hyp)₃][–] seem to hinder aggregation compared to the unsubstituted systems (i.e. Ge₉^{4–}), a triangular face of the cluster is still sterically accessible for the η³ coordination of suitably unencumbered Lewis acids as highlighted in Figure 2.1.

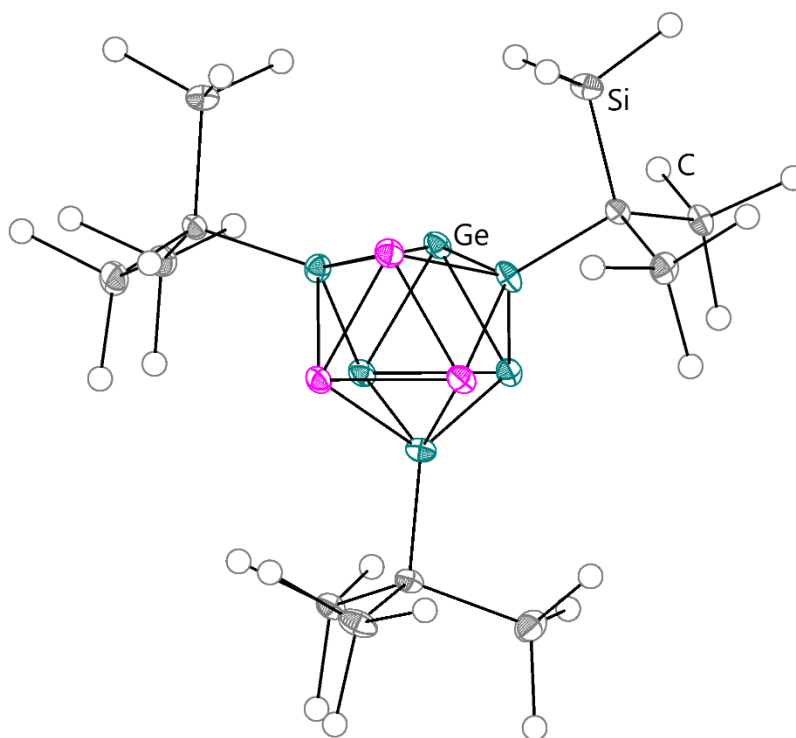
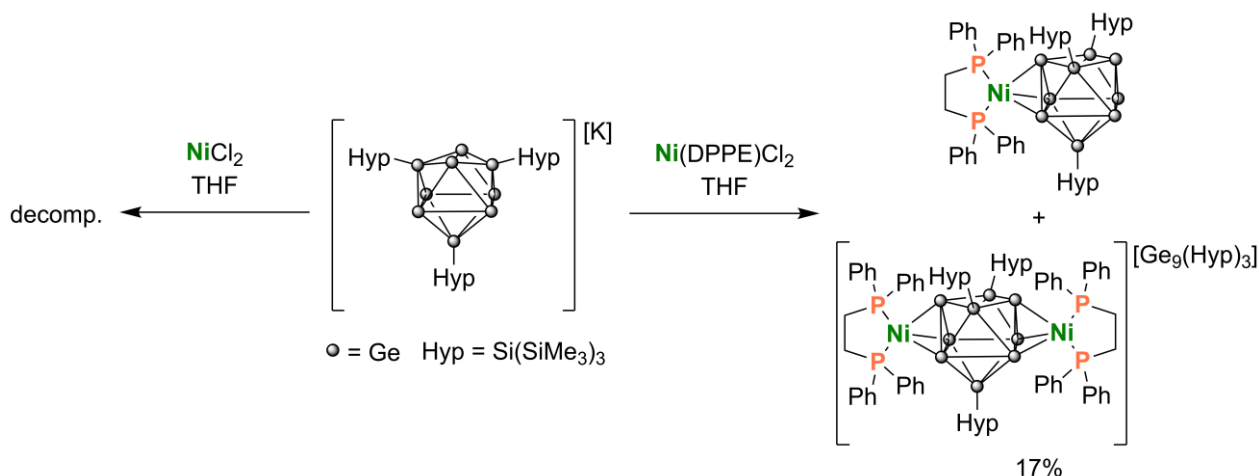


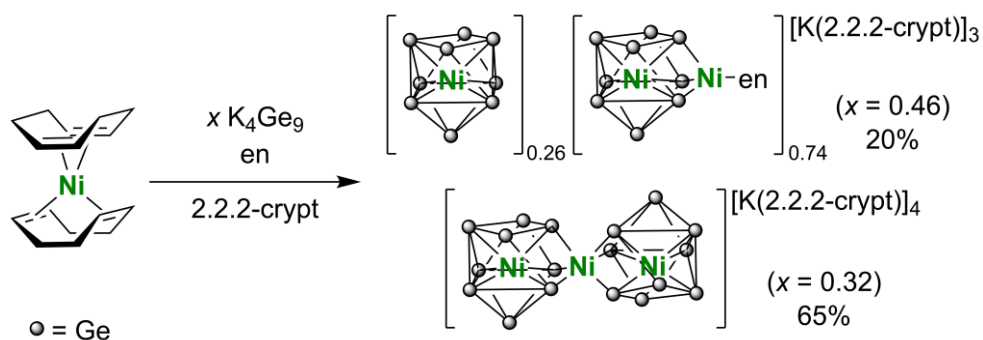
Figure 2.1: Single crystal X-ray structure of the $[\text{Ge}_9(\text{Hyp})_3]^-$ anion,¹³ with one of the triangular faces highlighted in magenta. $[\text{Li}]^+$ counterion has been removed for clarity. Ellipsoid probability 50%. Connecting lines between atoms do not represent two-centre, two-electron bonds. Carbon atoms are pictured as spheres of an arbitrary radius, hydrogen atoms have been omitted for clarity.

Schnepf and co-workers also reported the use of supporting ligands such as DPPE (DPPE = 1,2-bis(diphenylphosphino)ethane), which is a popular chelating ligand, forming complexes from across the d-block of the periodic table.¹⁴ However reactions between $[\text{KGe}_9(\text{Hyp})_3]$ and $[\text{Ni}(\text{DPPE})\text{Cl}_2]$, were unselective and low yielding, affording two products: $[\text{Ni}(\text{DPPE})\text{Ge}_9(\text{Hyp})_3]$ and $[\{\text{Ni}(\text{DPPE})\}_2\text{Ge}_9(\text{Hyp})_3][\text{Ge}_9(\text{Hyp})_3]$, which were obtained in a combined yield of 17% (Scheme 2.1).¹¹



Scheme 2.1: Previously reported reactivity between $[\text{KGe}_9(\text{Hyp})_3]$ and nickel halide complexes, yield reported as the total of both products.¹¹

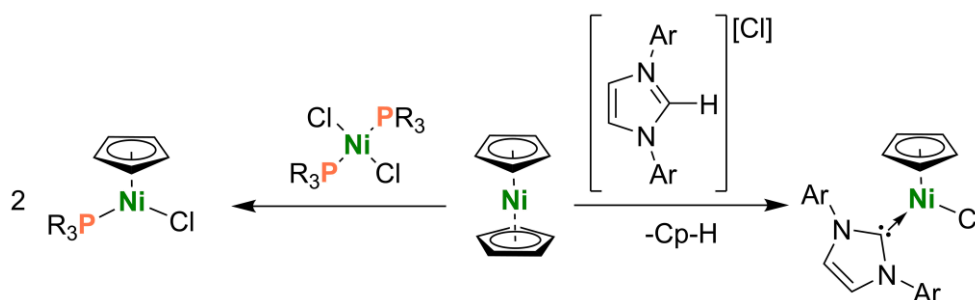
We opted to instead use the nickel organometallic reagents $[\text{Ni}(\text{COD})_2]$ and $[\text{Ni}(\text{Cp})_2]$. $[\text{Ni}(\text{COD})_2]$ is a well-studied nickel(0) source for donor-stabilised complexes such as $[\text{Ni}(\text{COD})(\text{DPPF})]$ ($\text{DPPF} = 1,1'$ -bis(diphenylphosphino)ferrocene).¹⁴ It is most commonly used for the *in situ* preparation of catalysts with a range of ligands (e.g. phosphines, carbenes) for organic C–C coupling reactions.^{14–16} Furthermore, $[\text{Ni}(\text{COD})_2]$ has been used as a single atom source for the preparation of endohedral Zintl clusters containing nickel atoms in the centre of tetrel cages (Scheme 2.2).^{17,18}



Scheme 2.2: Previous uses of $[\text{Ni}(\text{COD})_2]$ towards the synthesis of nickel germanide Zintl clusters.^{15–19}

These studies also provided an opportunity to compare and contrast the reactivity of the well-studied “naked” Ge_9^{4-} ion against its tris-hypersilyl functionalised counterpart. An attractive aspect of using $[\text{Ge}_9(\text{Hyp})_3]^-$ is its solubility in non-polar solvents, which prevents side reactions that might occur between the transition metal precursor and more common solvents used in Zintl cluster chemistry, such as 1,2-ethylenediamine. This allows, firstly, for the possibility of new reaction pathways, and secondly, for the use of precursors not before employed in the formation of Zintl clusters. For example, bis(cyclopentadienyl)nickel, $(\text{Ni}(\text{Cp})_2)$, which may act as a source of $\text{Ni}(\text{Cp})$ vertices, has not been successfully used to incorporate nickel atoms into Zintl clusters previously.

$[\text{Ni}(\text{Cp})_2]$ is a 20 valence electron nickel(II) sandwich complex and its reactivity is typically driven by the stability of resultant 18 valence electron complexes upon loss of a cyclopentadienyl ligand. An example of this is its reactivity towards imidazolium salts to form half sandwich carbene complexes, eliminating $(\text{Cp})\text{H}$.²⁰ Another example is a ligand redistribution reaction with the 16 valence electron complex $[\text{Ni}(\text{PR}_3)_2\text{Cl}_2]$ to produce two equivalents of the 18 valence electron $[(\text{Cp})\text{Ni}(\text{PR}_3)\text{Cl}]$ (Scheme 2.3).²¹



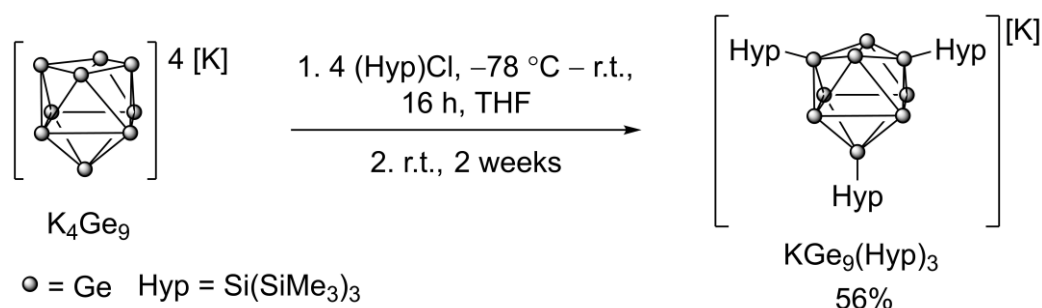
Scheme 2.3: Representative examples of $[\text{Ni}(\text{Cp})_2]$ reactivity resulting in the loss of one cyclopentadienyl ligand.^{20,21}

2.2. Chapter Outline

This chapter will describe the reactivity of $[\text{KGe}_9(\text{Hyp})_3]$ towards the nickel reagents $[\text{Ni}(\text{COD})_2]$ and $[\text{Ni}(\text{Cp})_2]$, which results in two different nickel germanide clusters, by either cluster expansion or vertex substitution. These products were analysed by cyclic voltammetry and showed reversible redox behaviour towards formal nickel(I) complexes.

2.3. Improved Synthesis of $[\text{KGe}_9(\text{Hyp})_3]$

The synthesis of $[\text{KGe}_9(\text{Hyp})_3]$ from K_4Ge_9 and $(\text{Hyp})\text{Cl}$ was previously performed in MeCN with a 10 fold excess of $(\text{Hyp})\text{Cl}$ to avoid the presence of $[\text{K}_2\text{Ge}_9(\text{Hyp})_2]$ in the product (yield not clearly reported).²² Alternatively, the reaction can be carried out in THF with an isolated yield of 28% (relative to K_4Ge_9).²³ This prompted us to optimise the preparation and increase the yield of desolvated, non-sequestered, $[\text{KGe}_9(\text{Hyp})_3]$. The main notable differences with the literature reported syntheses are: 1) the use of a THF solution of $(\text{Hyp})\text{Cl}$; 2) a longer reaction time (2 weeks) due to the insolubility of K_4Ge_9 in THF; and 3) a stepwise workup (Scheme 2.4).



Scheme 2.4: Synthesis of $[\text{KGe}_9(\text{Hyp})_3]$.

In a typical synthesis, freshly ground K_4Ge_9 was dispersed in distilled THF. The mixture was cooled to -78°C and a solution containing 4 equivalents of $(\text{Hyp})\text{Cl}$ in THF was added dropwise over the course of 30 minutes. THF, as opposed to MeCN, has been shown to selectively produce the tris-silylated cluster and not a mixture of bis- and tris-silylated clusters

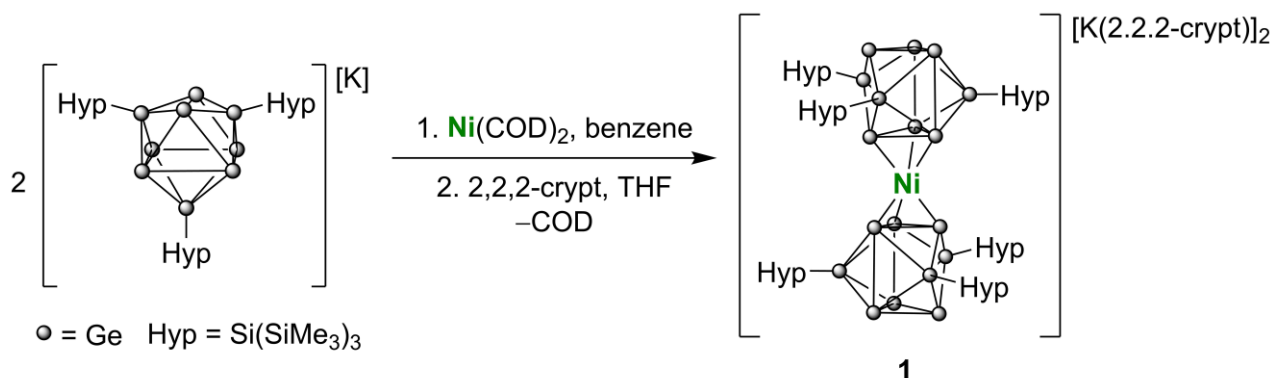
$([\text{Ge}_9(\text{Hyp})_2]^{2-}, [\text{Ge}_9(\text{Hyp})_3]^-)$.²³ The grey suspension was stirred with a glass-coated stir bar, warming slowly to room temperature overnight. The mixture was then stirred for two weeks to produce a grey suspension in a red-orange solution. This was filtered and the THF removed *in vacuo*. The resulting red-orange solid was extracted with toluene and slowly evaporated *in vacuo* over the course of 5 hours to produce large red needle-like crystals of the previously reported solvate complex $[\text{K}(\text{tol})_3][\text{Ge}_9(\text{Hyp})_3] \cdot \text{tol}$, and a red oil.²³ The red oil, containing polysilane by-products, was removed by dissolution in *n*-hexane and filtration. Care must be taken when removing the filter cannula since $[\text{KGe}_9(\text{Hyp})_3]$ is highly pyrophoric and combusts immediately on contact with air, igniting any vapours of solvent that are present. The yellow-orange microcrystalline solid was dried *in vacuo* to obtain pure, desolvated $[\text{KGe}_9(\text{Hyp})_3]$ (yield: ~56% relative to K_4Ge_9) which is a significant improvement compared to the literature. NMR spectroscopic data are consistent with the literature.²³

2.4. $[\text{Ni}\{\text{Ge}_9(\text{Hyp})_3\}_2]^{2-}$ (**1**)

2.4.1. Synthesis of Ion $[\text{K}(2.2.2\text{-crypt})]_2\mathbf{1}$

The reaction of the 18 electron nickel(0) organometallic complex, $[\text{Ni}(\text{COD})_2]$, with two equivalents of $[\text{KGe}_9(\text{Hyp})_3]$ in benzene resulted in the formation of a dark green solution. At first, we proposed the formation of an endohedral cluster, in line with previous studies on the reactivity of unsubstituted Ge_9^{4-} cages and $[\text{Ni}(\text{COD})_2]$ (*vide supra*).^{17,18} The product was unstable in solution for more than 2 days and also if placed under vacuum, forming a brown suspension from which the previously reported $[\text{K}(\text{tol})_3][\text{Ge}_9(\text{Hyp})_3] \cdot \text{tol}$ was recovered.²³ By using a more concentrated reaction mixture (~100 mg/ml), precipitation of a pyrophoric blue-green powder was possible. This solid was unstable to vacuum and partially soluble in toluene. Dissolution of the compound in tetrahydrofuran-*d*₈ (THF-*d*₈) afforded an intense teal solution. ¹H NMR spectroscopy revealed a new resonance at 0.37 ppm, proposed to be

$[\text{K}(\text{THF})_n]_2[\text{Ni}\{\text{Ge}_9(\text{Hyp})_3\}_2]$ ($[\text{K}(\text{THF})_n]_2\mathbf{1}$). This species was unstable in solution, forming $[\text{KGe}_9(\text{Hyp})_3]$ and nickel metal on standing and therefore not isolated.



Scheme 2.5: Preparation of $[\text{K(2.2.2-crypt)}]_2\mathbf{1}$.

Dissolution of $[\text{K}(\text{THF})_n]_2\mathbf{1}$ and 2.2.2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane) in THF, however, resulted in the formation of $[\text{K(2.2.2-crypt)}]_2[\text{Ni}\{\text{Ge}_9(\text{Hyp})_3\}_2]$ ($[\text{K(2.2.2-crypt)}]_2\mathbf{1}$) (Scheme 2.5) which was sufficiently stable for characterisation. Interestingly, although the 2.2.2-crypt seemed to provide some stability to the product, the mixing of $[\text{Ni}(\text{COD})_2]$ and $[\text{K(2.2.2-crypt)}][\text{Ge}_9(\text{Hyp})_3]$ ²² in benzene or THF did not result in a reaction.

2.4.2. Nuclear Magnetic Resonance Spectroscopic Analysis of $[\text{K(2.2.2-crypt)}]_2\mathbf{1}$

The ^1H NMR spectrum of $[\text{K(2.2.2-crypt)}]_2\mathbf{1}$ in $\text{THF-}d_8$ shows a single singlet resonance at 0.38 ppm, which implies that all of the hypersilyl resonances are chemically equivalent. A small (<3%) impurity, $[\text{K(2.2.2-crypt)}][\text{Ge}_9(\text{Hyp})_3]$ at 0.25 ppm is also observed, and increases in concentration upon standing at room temperature, presumably arising from fragmentation/decomposition. No resonances relating to COD are observed.

The $^{29}\text{Si}/^1\text{H}$ HMBC and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra are consistent with one hypersilyl environment. The HMBC spectrum (Figure 2.2) reveals two cross-peaks at -107.10 and -10.48 ppm corresponding to the core $\text{Si}(\text{SiMe}_3)_3$ and $\text{Si}(\text{SiMe}_3)_3$, respectively.

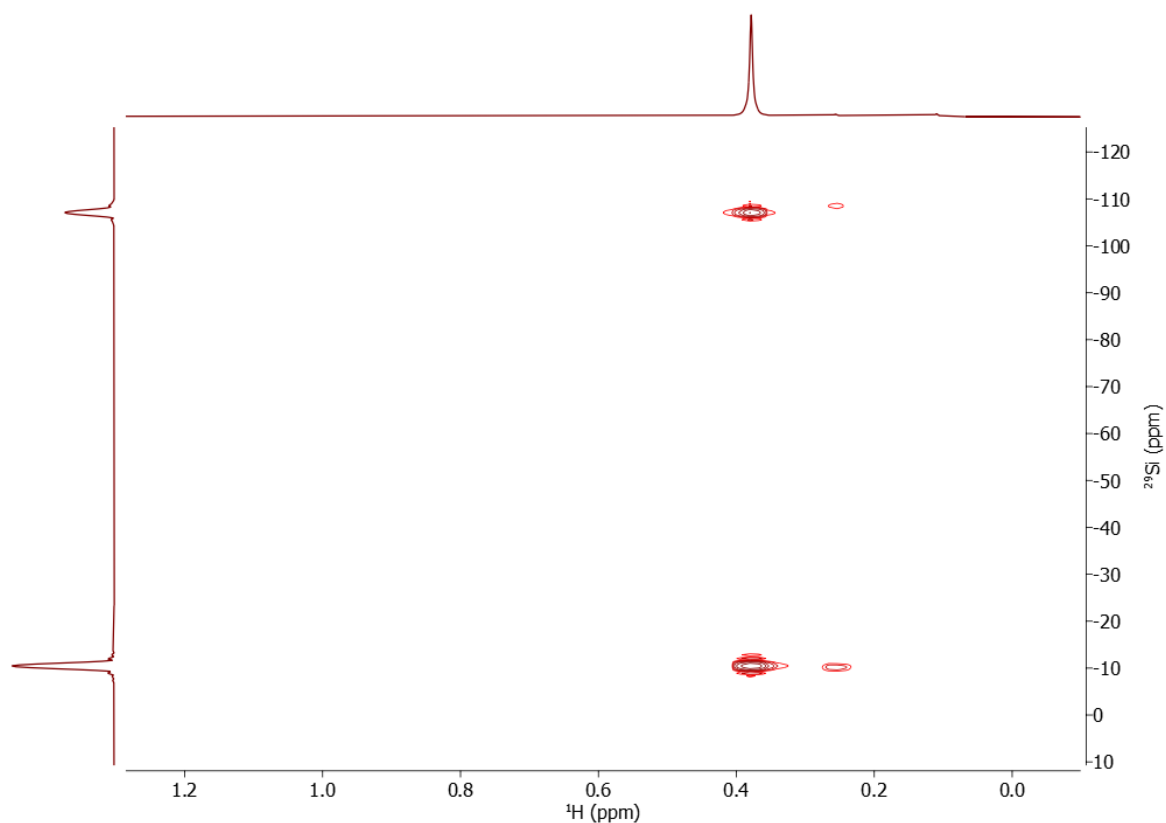


Figure 2.2: $^{29}\text{Si}/^1\text{H}$ HMBC NMR spectrum ($\text{THF}-d_8$, 298 K, 79.5 MHz) of $[\text{K}(\text{2.2.2-crypt})]_2\mathbf{1}$, cross-peaks for the $[\text{K}(\text{2.2.2-crypt})][\text{Ge}_9(\text{Hyp})_3]$ impurity are also shown.

2.4.3. Single Crystal X-ray Structure of $[\text{K}(\text{2.2.2-crypt})]_2\mathbf{1}$

Crystals suitable for single crystal X-ray crystallography were grown from a concentrated THF solution at $-40\text{ }^\circ\text{C}$. Figure 2.3 shows the resulting structure, i.e. a dianionic nickel(0) sandwich compound with D_{3d} symmetry and the nickel atom coordinated to a triangular face (as per Figure 2.1) of each $[\text{Ge}_9(\text{Hyp})_3]^-$ in an octahedral ligand field. There is an elongation of the Ge–Ge distances in the coordinating face compared to the non-coordinating face by $\sim 0.2\text{ \AA}$ (Figure 2.3).

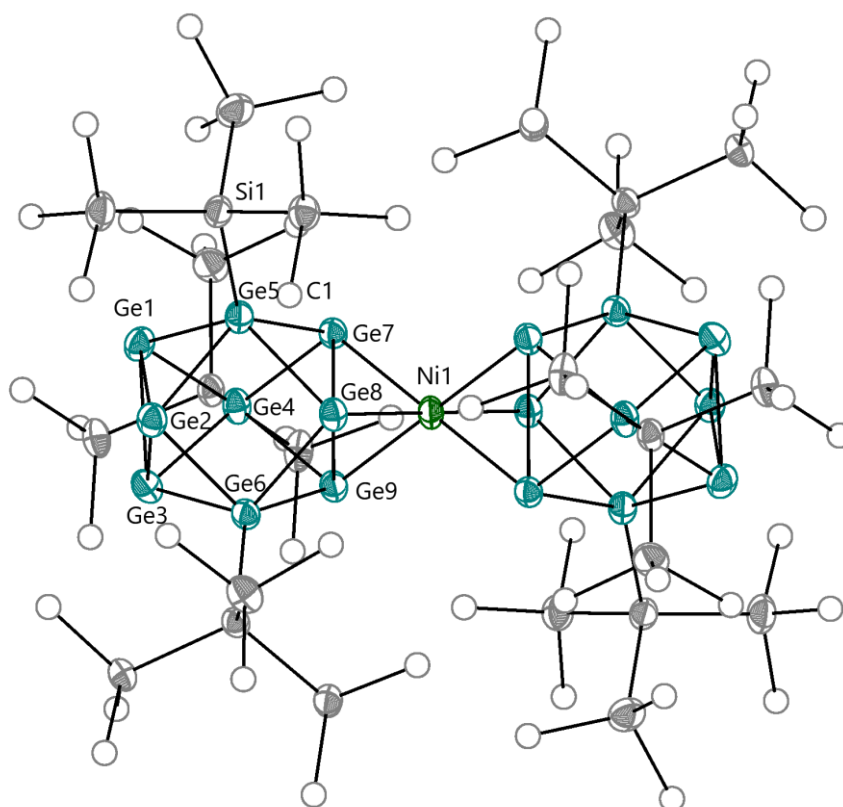


Figure 2.3: Single crystal X-ray structure of $[\text{K}(\text{2.2.2-crypt})]_2 \cdot 2\text{THF}$. Anisotropic displacement ellipsoids are set at 50% probability. Hydrogen atoms, $[\text{K}(\text{2.2.2-crypt})]^+$, and solvent of crystallisation have been omitted for clarity. Carbon atoms are pictured as spheres of an arbitrary radius. One half of the cluster was generated by the symmetry operation: $1-x$, $1-y$, $-z$.

Table 2.1: Selected crystallographic bond distances (Å) of compound [K(2.2.2-crypt)]₂[**1**].

Bond	Distance (Å)
Ni1–Ge7	2.442(1)
Ni1–Ge8	2.436(1)
Ni1–Ge9	2.443(1)
Ge1–Ge2	2.679(1)
Ge1–Ge3	2.643(1)
Ge2–Ge3	2.631(1)
Ge7–Ge8	2.900(1)
Ge7–Ge9	2.830(1)
Ge8–Ge9	2.826 (1)

1 is isostructural and valence isoelectronic to related group 10, 11 and 12 clusters previously reported in the literature, for example [Pd{Ge₉(Hyp)₃}₂]²⁻, [M{Ge₉(Hyp)₃}₂]⁻ (M = Cu, Ag, Au) and [M{Ge₉(Hyp)₃}₂] (M = Zn, Cd, Hg).^{24–27} It is isostructural but not valence isoelectronic to [Mn{Ge₉(Hyp)₃}₂].¹¹ The intense colour and instability could be indicative of a Ni²⁺ complex with metal to ligand charge transfer, featuring two [Ge₉(Hyp)₃]²⁻ ligands.

The structure is also closely related to the previously mentioned unsubstituted cluster [K(2.2.2-crypt)]₄[Ni₃@{Ge₉}₂].¹⁸ The Ge–Ni distances of compound [K(2.2.2-crypt)]₂[**1**] are ca. 0.1 Å shorter in length than those in [K(2.2.2-crypt)]₄[Ni₃@{Ge₉}₂]. This is due to a few factors such as lower overall charge, lack of extra interstitial nickel atoms and differing electron count (*vide infra*).

1 can be described using polyhedral skeletal electron pair theory if treated as two [Ge₉(Hyp)₃]⁻ fragments bonded to a Ni(0) centre, which contributes no valence electrons to cluster bonding. The [Ge₉(Hyp)₃]⁻ has 22 valence electrons for cluster bonding arising from

six unsubstituted germanium vertices (two electrons available for cluster bonding), three Ge(Hyp) vertices (three electrons) and an overall charge of one (one electron). The cluster fragment has $2n + 4$ valence electrons for cluster bonding, where n is the number of vertices, which is in agreement with a *nido* 9-vertex cluster.

This contrasts with the two 20 electron fragments in the $[\text{K}(\text{2.2.2-crypt})]_4[\text{Ni}_3@\{\text{Ge}_9\}_2]$ example ($\text{Ni} = 0 \text{ e}^-$; $\text{Ge} = 9 \times 2 \text{ e}^-$; charge = $2 \times 1 \text{ e}^-$), meaning that although the two are structurally related, they are not valence isoelectronic.

As described for the central atom in $[\text{Ni}_3@\{\text{Ge}_9\}_2]^{4-}$,¹⁸ the d^{10} nickel atom in $[\text{K}(\text{2.2.2-crypt})]_2\mathbf{1}$ does not contribute to cluster bonding and simply provides complementary orbitals for overlap with cluster-based orbitals. This can also be attributed to the solution instability of $[\text{K}(\text{2.2.2-crypt})]_2\mathbf{1}$. Due to the ability for these two compounds to have comparable structures but different valence electron counts, one could also envisage interesting electrochemical behaviour of $[\text{K}(\text{2.2.2-crypt})]_2\mathbf{1}$ without significant structural rearrangement.

2.4.4. Cyclic Voltammetry of $[\text{K}(\text{2.2.2-crypt})]_2\mathbf{1}$

The electrochemistry of $[\text{K}(\text{2.2.2-crypt})]_2\mathbf{1}$ was probed by cyclic voltammetry in THF (Figure 2.4), revealing a reversible oxidation at $E_1^\circ = -1.56 \text{ V vs. Fc}^{0/+}$, which is followed by a second, quasi-reversible oxidation event at $E_2^\circ = -1.20 \text{ V vs. Fc}^{0/+}$. This is followed by a third oxidation, $E_{3\text{pa}} = -0.85 \text{ V vs. Fc}^{0/+}$, which is irreversible at all scan rates ($v = 0.05 - 1 \text{ mV s}^{-1}$).

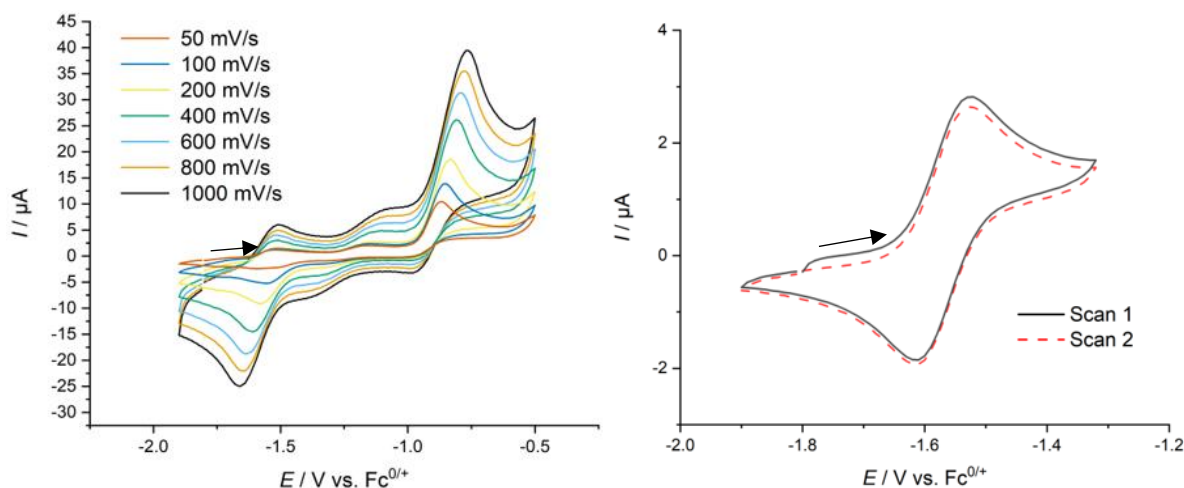


Figure 2.4: Cyclic voltammogram of $[\text{K}(2.2.2\text{-crypt})]_2\mathbf{1}$ (Left: 1.0 mM, 0.2 M $[\text{N}^n\text{Bu}_4][\text{PF}_6]$, THF, room temperature; Right: 100 mV s^{-1} , first oxidative event)

By adjusting the window, the reversibility of the first oxidative event could be analysed (Figure 2.5, Left). On inspection of the voltammogram, the peak current ratio (i_{PA}/i_{PC}) is 0.99 μA , indicating a reversible process. The peak potential separation ($\Delta E_P = E_{PC} - E_{PA}$) is 79.5 mV, which is somewhat larger than the 57 mV (2.22 RT/F ; R = universal gas constant, T = temperature; F = Faraday's constant) expected for a one electron process at room temperature as per the Nernst equation. Plotting peak current against the square root of the scan rate shows a linear relationship, ($R = 0.9987$) which indicates that the redox species are diffusing freely (Figure 2.5, Right).²⁸ From this, one could view $[\text{K}(2.2.2\text{-crypt})]_2\mathbf{1}$ as potentially a strong reducing agent, exhibiting a potential between than that of $[\text{Co}(\text{Cp})_2]$ ($-1.3 \text{ V vs. Fc}^{0/+}$) and $[\text{Co}(\text{Cp}^*)_2]$ ($-1.91 \text{ V vs. Fc}^{0/+}$), two well studied strong organometallic reducing agents.²⁹

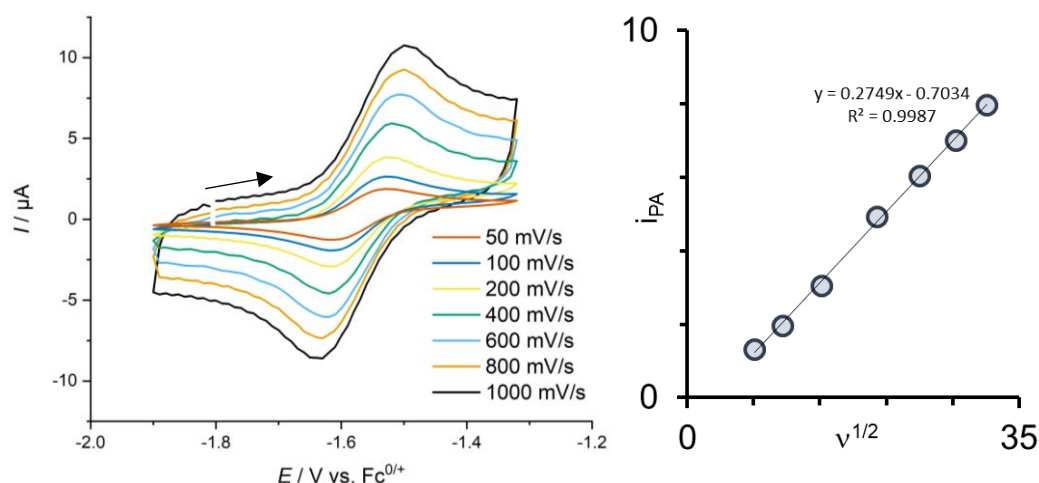


Figure 2.5: Left: Cyclic voltammogram of compound $[K(2.2.2\text{-crypt})]_2\mathbf{1}$, first oxidative event (1.0 mM, 0.2 M $[N(n\text{Bu})_4][PF_6]$, THF, room temperature). Right: Plot of anodic peak intensity as a function of the square root of the scan rate.

Since $[K(2.2.2\text{-crypt})]_2\mathbf{1}$ slowly decomposes into $[K(2.2.2\text{-crypt})][Ge_9(Hyp)_3]$ in solution, CV studies of $[K(2.2.2\text{-crypt})][Ge_9(Hyp)_3]$, were conducted under the same conditions to ensure the observed redox processes arise from the complex (Figure 2.6). This showed one oxidation event, $E_{3pa} = -0.75$ V vs. $Fc^{0/+}$, which is irreversible at all scan rates ($v = 0.05\text{--}1$ mV s^{-1}). This event is 0.1 V anodic compared to the irreversible event for $[K(2.2.2\text{-crypt})]_2\mathbf{1}$.

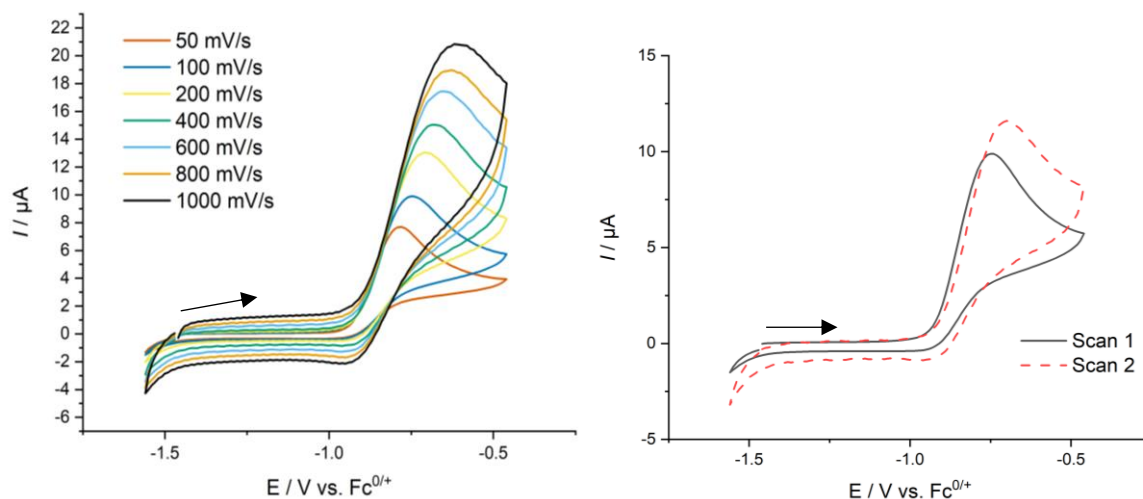


Figure 2.6: Cyclic voltammogram of $[\text{K}(2.2.2\text{-crypt})][\text{Ge}_9(\text{Hyp})_3]$ (Left: 1.0 mM, 0.2 M $[\text{N}^n\text{Bu}_4][\text{PF}_6]$, THF, room temperature; Right: 100 mV s^{-1} , first oxidative event)

2.4.5. Further Reactivity of $[\text{K}(2.2.2\text{-crypt})]_2\mathbf{1}$

The reversibility of the first oxidative process in Figure 2.5 indicates that the one electron oxidation product may be chemically accessible. This was attempted using $[\text{Co}(\text{Cp})_2][\text{PF}_6]$ as an oxidising agent ($-1.3 \text{ V vs. Fc}^{0/+}$ in dimethoxyethane),²⁹ which resulted in a colour change from blue-green to magenta and a loss of the ^1H NMR signals relating to $[\text{K}(2.2.2\text{-crypt})]_2\mathbf{1}$. A paramagnetic species with a g value of 2.03 was observed *in situ* using EPR spectroscopy (Figure 2.7), however the compound could not be isolated due to its instability in solution and to vacuum. The g value and lack of hyperfine coupling is not typical for transition metal-based radicals, indicating a form of ligand oxidation. Cooling of this solution to -40°C and standing for two days produced crystals of $[\text{K}(2.2.2\text{-crypt})]_2\mathbf{1}$. This is presumably due to a disproportionation pathway.

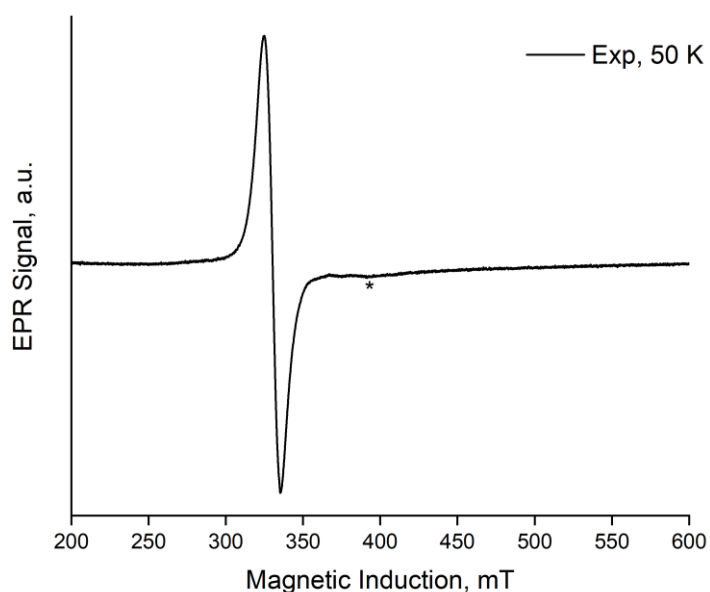
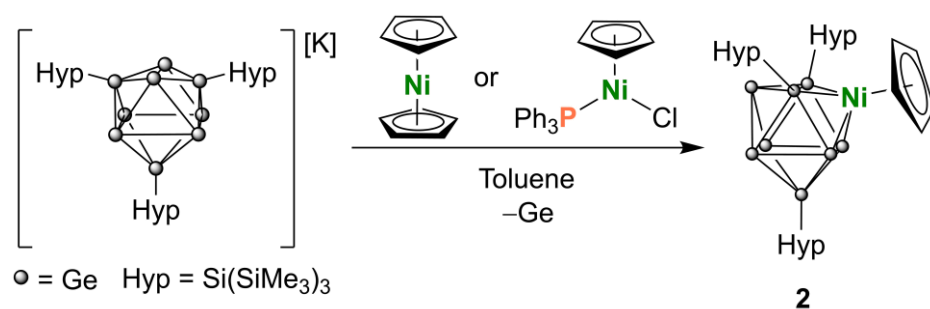


Figure 2.7: EPR spectrum of $[\text{K}(\text{2.2.2-crypt})]_2\mathbf{1}$ and $[\text{Co}(\text{Cp})_2][\text{PF}_6]$ at 50 K in $\text{THF-}d_8$, asterisk shows the residual $[\text{Co}(\text{Cp})_2]$ signal. Data acquired by Dr. Will Myers.

2.5. $[(\text{Cp})\text{Ni}\{\text{Ge}_9(\text{Hyp})_3\}]$ (**2**)

2.5.1. Synthesis of Compound **2**

$[\text{Ni}(\text{Cp})_2]$ (or $[(\text{Cp})\text{Ni}(\text{PPh}_3)\text{Cl}]$) was added as a toluene solution to $[\text{KGe}_9(\text{Hyp})_3]$ at 0 °C and stirred, slowly warming to room temperature overnight, to produce a brown suspension. A green-brown solution was extracted with *n*-hexane, leaving a pyrophoric grey powder (potassium cyclopentadienide + elemental germanium). The solution was concentrated and cooled to −40 °C to produce emerald crystals of the cluster $[(\text{Cp})\text{Ni}\{\text{Ge}_8(\text{Hyp})_3\}]$ (**2**) (Scheme 2.6). Yields of 30% for $[\text{Ni}(\text{Cp})_2]$ and 35% for $[(\text{Cp})\text{Ni}(\text{PPh}_3)\text{Cl}]$ were obtained (after sublimation of the PPh_3 from the latter).



Scheme 2.6: Preparation of $[(\text{Cp})\text{Ni}\{\text{Ge}_8(\text{Hyp})_3\}]$ (**2**).

2.5.2. Single Crystal X-ray Structure of Compound **2**

Emerald-green crystals of compound **2** suitable for single crystal X-ray crystallography were grown from a concentrated solution of toluene. As can be seen in the crystal structure of the product (Figure 2.8), this reaction resulted in a vertex substitution, in which a germanium atom of the nonagermanide core is replaced by a $\text{Ni}(\text{Cp})$ fragment. While previously observed for “naked” $[\text{E}_9]^{4-}$ clusters, which under reducing conditions have been shown to give rise to cluster fragmentation,^{30–32} this is the first evidence of such “vertex-substitution” reactivity in substituted clusters. The cluster exhibits C_s symmetry, with two inequivalent hypersilyl environments. Two of these are bonded to germanium atoms which are also connected to the $\text{Ni}(\text{Cp})$ fragment (Ge1 and Ge2) and the other is connected to Ge7, which is situated two vertices away from the nickel moiety.

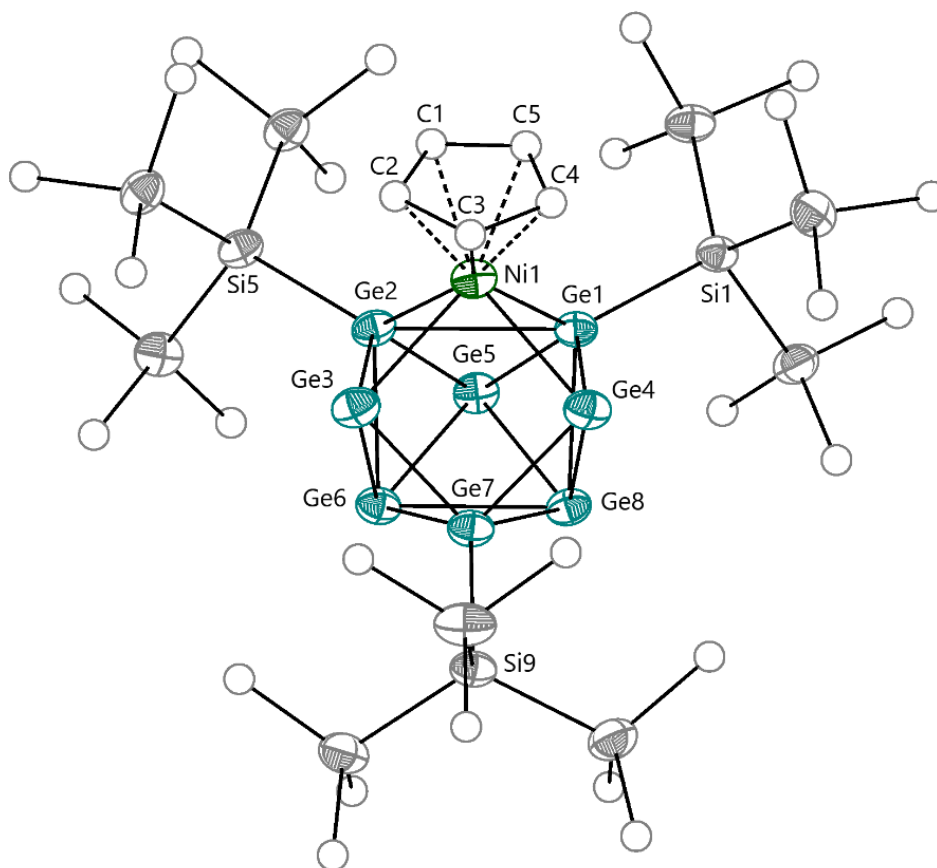
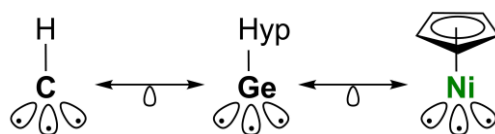


Figure 2.8 Single crystal X-ray structure of compound **2**·1.5toluene. Anisotropic displacement ellipsoids are set at 50% probability. Hydrogen atoms and solvent of crystallisation have been omitted for clarity. Carbon atoms are pictured as spheres of an arbitrary radius.

Table 2.2: Selected crystallographic bond distances (Å) of compound **2**.

Bond	Distance (Å)
Ni1–Ge1	2.400(2)
Ni1–Ge2	2.404(2)
Ni1–Ge3	2.591(2)
Ni1–Ge4	2.580(2)
Ni1–C1	2.082(7)
Ni1–C2	2.094(7)
Ni1–C3	2.096(8)
Ni1–C4	2.109(9)
Ni1–C5	2.107(8)

In order to analyse the bonding in compound **2** using polyhedral skeletal electron pair theory, the isolobal analogy must be invoked to calculate the number of electrons available for cluster bonding at the 18 electron Ni(Cp) fragment. This fragment is isolobal to methine, with three orbitals and three valence electrons available for cluster bonding. This fragment is also isolobal to Ge(Hyp) (Scheme 2.7).³³



Scheme 2.7: Isolobal relationship between methine, Ge(Hyp) and Ni(Cp) fragments.³³

Therefore, compound **2** has 22 electrons for cluster bonding, in line with a *nido* 9-vertex polyhedron (Ni(Cp) = 3 e[−], Ge = 2 e[−], Ge(Hyp) = 3 e[−]).³³ Compound **2** adopts a distorted mono-capped square-antiprismatic geometry, where the Ni(Cp) fragment is at a basal position.

Interestingly, if polyhedral skeletal electron pair theory is used to predict the structure of “(Cp)NiGe₉(Hyp)₃”, our original target compound, the cluster would have a *nido*-geometry with 24 electrons available for cluster bonding. Related *nido* 10-vertex borane and carborane clusters, such as *nido*-B₁₀H₁₄ are known to undergo cage contraction to produce smaller nuclearity polyhedra.³⁴ This link to well-studied borane cluster chemistry may offer an insight into the formation of compound **2**.

Though initially counter-intuitive, it has been postulated by Fässler that vertex substitution or cage contraction is one of the first steps towards cage expansion. On the subject of their 9-vertex tetrel cluster [(Cp)Ti{Sn₈}]³⁻,³¹ they propose that the resulting Sn₈ fragment could be formed as an early intermediate and react with other fragments in the formation of such compounds as [Ir@Sn₁₂]³⁻,³⁵ [{Sn₈}Co{Co@Sn₉}]⁵⁻ and [{Sn₈}Ni{Ni@Sn₉}]⁴⁻.^{36,37} It must be noted however that [(Cp)Ti{Sn₈}]³⁻ is comparatively more “open” to cluster expansion, relative to compound **2**, due to the lack of bulky substituents.

2.5.3. Nuclear Magnetic Resonance Spectroscopic Analysis of Compound **2**

The *nido* deltahedron **2** retains its C_s symmetry in solution, as evidenced by two singlets in both the ¹H (0.49 and 0.60 ppm) and ¹³C{¹H} NMR spectra (3.31 and 4.24 ppm), indicating two inequivalent hypersilyl substituents. In addition, one singlet corresponding to the cyclopentadienyl ligand is observed at 5.18 and 87.73 ppm in the ¹H and ¹³C{¹H} NMR spectra, respectively. Four cross peaks were observed in the ²⁹Si/¹H HMBC NMR spectrum (Figure 2.9) at -101.1 (Si(SiMe₃)₃), -76.1 (Si(SiMe₃)₃) and -8.4 ppm (all Si(SiMe₃)₃). Notably, one of the core hypersilyl silicon environments is significantly shifted downfield due to close proximity with the Ni(Cp) moiety.

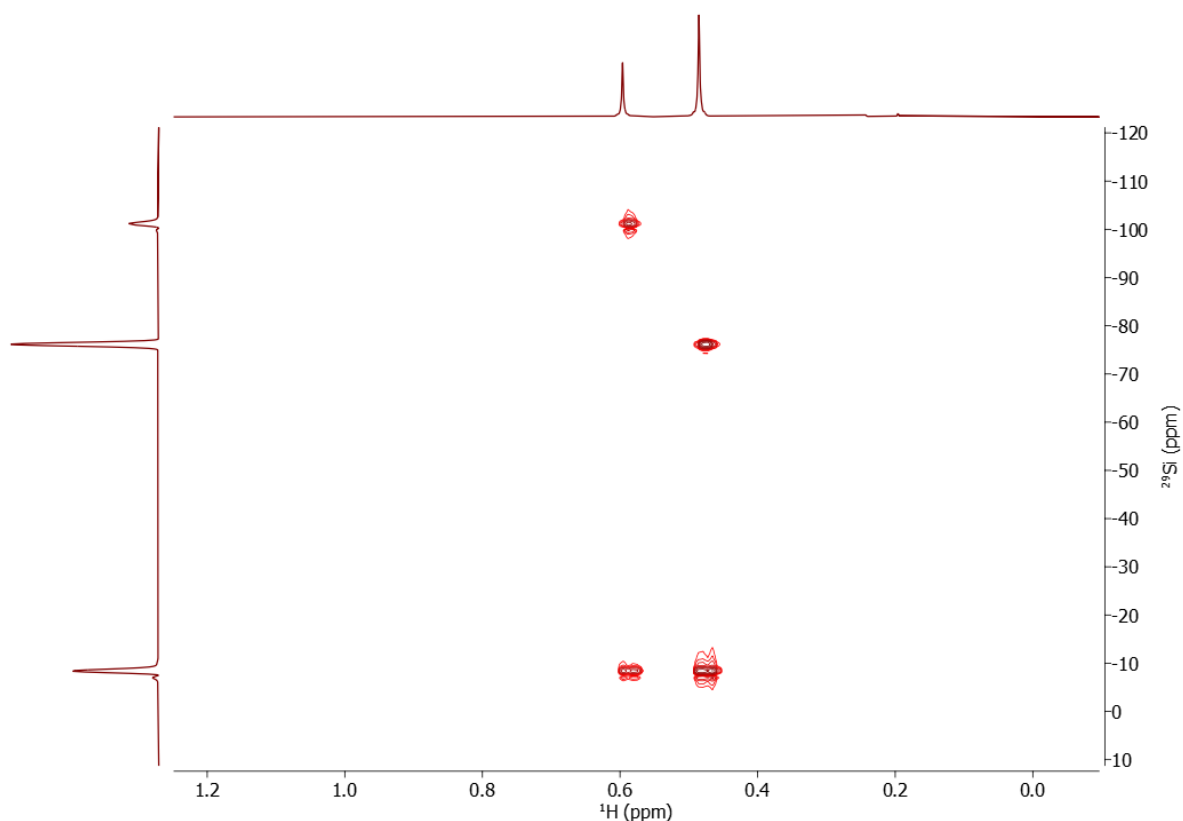


Figure 2.9: $^{29}\text{Si}/^1\text{H}$ HMBC NMR spectrum (C_6D_6 , 298 K, 79.5 MHz) of compound **2**.

2.5.4. Cyclic Voltammetry of Compound **2**

Compound **2** has a structural resemblance to the known cluster $[\text{Fe}(\text{CO})_3\{\text{Ge}_8\}]^{3-}$, however it is a closed shell species with 22 valence skeletal electrons as opposed to the 21 electrons available for cluster bonding in the iron cluster.³² This prompted us to investigate possible redox processes using cyclic voltammetry (Figure 2.10). The voltammogram exhibited a qualitatively reversible reductive event at $E_1^\circ = -2.07$ V (vs. $\text{Fc}^{0/+}$, THF). This is followed by a second reduction at $E_{2\text{pc}} = -2.54$ V, which is irreversible at all scan rates ($\nu = 0.05 - 1$ mV s^{-1}) and is accompanied by two additional irreversible features in the reverse scan ($E^{\text{pa}} = -2.38, -1.21$ V) indicating some form of cluster degradation/rearrangement on over-reduction (Figure 2.10, Right).

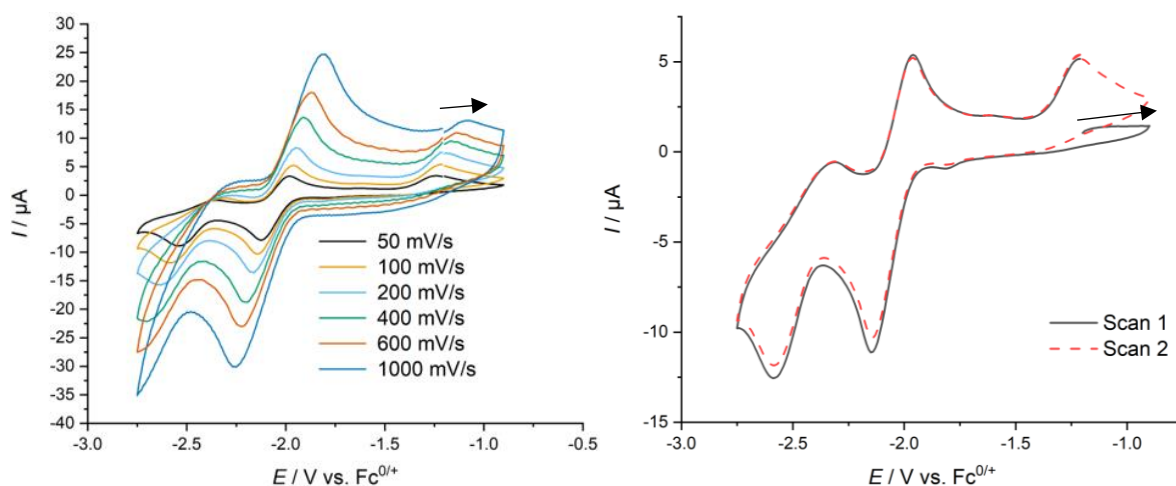


Figure 2.10: Cyclic voltammogram of compound **2** (Left: Scan 2, 1.0 mM, 0.1 M $[\text{N}(\text{nBu})_4][\text{PF}_6]$, THF, room temperature; Right: first and second reductive events at $\nu = 50 \text{ mV s}^{-1}$)

Isolation of the first reduction window removed these features, and shows a quasi-reversible event with a separation (ΔE_p) of 209.7 mV (Figure 2.11). This is very large for a one electron process, indicating a high barrier to electron transfer or structural change in the product, where a higher potential is required to oxidise the reduced species. The peak current ratio (i_{PA}/i_{PC}) was 0.91, also indicating some irreversibility. Due to the closeness of the reduction peak to the $E_2^{\text{pc}} = -2.54 \text{ V}$ peak, a suitable tangent was not measurable at higher scan rates. Therefore, a meaningful plot of peak current against the square root of the scan rate was unattainable.

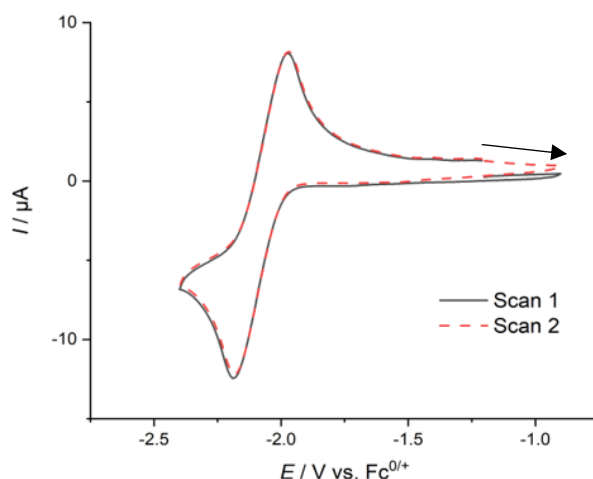


Figure 2.11: Cyclic voltammogram of compound **2** (1.0 mM, 0.1 M $[\text{N}(\text{nBu})_4][\text{PF}_6]$, THF, room temperature; 50 mV s^{-1} , first reductive event)

Although the ΔE_p indicated that the reduced species may be chemically inaccessible, attempts to reduce compound **2** were nevertheless made using Na/Hg ($-2.36 \text{ V vs. Fc}^{0/+}$),²⁹ however, this resulted only in decomposition towards an intractable mixture with a complex ^1H NMR spectrum.

2.5.5. Further Reactivity of Compound **2**

Similarly to compound **1**, whilst multiple oxidation states may be accessible under electrochemical conditions, decomposition pathways seem to render chemical isolation of their redox products inaccessible. Reactions with metal complexes such as $[\text{Ni}(\text{COD})_2]$ or $[\text{Rh}(\text{COD})_2][\text{B}(\text{Ar}^{\text{F}})_4]$ ($\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$) to “cap” the *nido* cluster to a 22 valence electron 10-vertex *closo* cluster were unsuccessful. Removal of the cyclopentadienyl group via protonation with $[\text{H}(\text{OEt}_2)_2][\text{B}(\text{Ar}^{\text{F}})_4]$ was also inconclusive, resulting in the formation of a brown solution which was insoluble in benzene- d_6 and polymerised THF- d_8 .

2.6. Conclusion

In this chapter, two new nickel germanide Zintl clusters were synthesised and analysed by NMR spectroscopy, single crystal X-ray diffraction and cyclic voltammetry. The resulting

structures indicate contrasting reaction pathways. The use of $[\text{Ni}(\text{COD})_2]$ also allowed us to contrast the reactivity of $[\text{Ge}_9(\text{Hyp})_3]^-$ with that of Ge_9^{4-} . These studies showed that substituted endohedral clusters may be more difficult to access, presumably due to a loss in cluster flexibility on functionalisation.

Although further reactivity studies were unsuccessful, an interesting point of note is that both complexes exhibit reversible redox processes towards formal nickel(I) species under electrochemical conditions. Aspects from this chapter were published in *Chemistry Communications*:

Townrow, O. P. E.; Weller, A. S.; Goicoechea, J. M. Cluster Expansion and Vertex Substitution Pathways in Nickel Germanide Zintl Clusters. *Chem. Commun.* **2021**, 57, 7132–7135.

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3. A Neutral Heteroatomic Zintl Cluster for the Catalytic Hydrogenation of Cyclic Alkenes

3.1. Background and Introduction

Since the ultimate goal of this project is alkane dehydrogenation, metals that have shown promise in such processes were considered when designing potential catalysts. Rhodium and iridium complexes have been previously used in hydrogenation catalysis and the microscopic reverse, dehydrogenation catalysis.¹⁻⁸ This is attributed to appropriate orbital overlap, allowing for optimal synergistic bonding between the C-H bond and the metal in an intermediate complex with a three centre-two electron bond. This results in bond scission by formal two electron oxidative addition at the metal centre from the +1 to the +3 oxidation state.⁹

Complexes of both these metals are typically diamagnetic, making them easy to monitor by NMR spectroscopy. There are also a plethora of known coordination environments which have been well studied and tuned towards applications.¹⁰ An example of such ligand field tuning can be found in the study of half sandwich metallocene complexes, which have pushed the boundaries in C-H activation. Examples of complexes with electron-rich pentamethylcyclopentadienyl and trimethylphosphine ligands were some of the first to activate the C-H bonds of alkanes and arenes (Figure 3.1).¹¹⁻²⁰ More recently, isolable rhodium σ -alkane complexes, prepared by the Weller group, have been shown to undergo C-H activation.²¹⁻²³

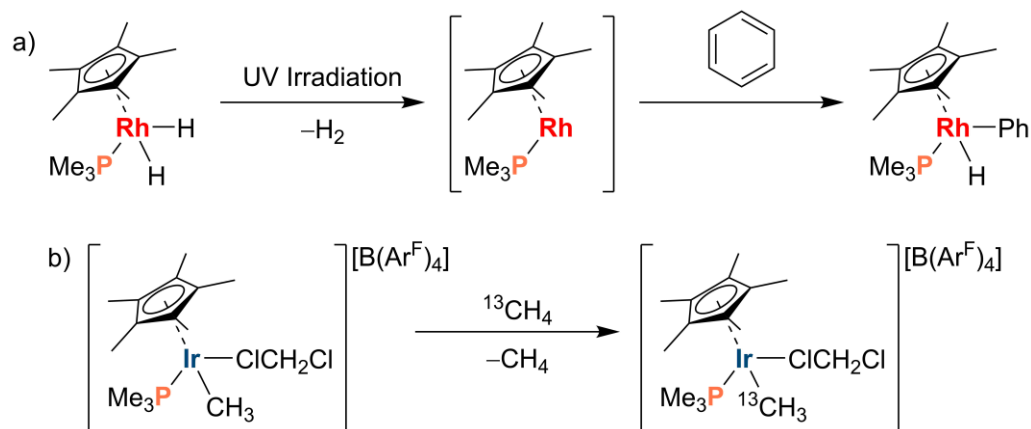


Figure 3.1: Activation of benzene and methane with rhodium or iridium pentamethylcyclopentadienyl complexes.

Furthermore, alkene complexes of the group 9 metals have been intensely studied as homogeneous catalysts for the last 60 years,^{24–26} with reports dating back to Chatt's pioneering work on $[\text{Rh}(\text{COD})\text{Cl}]_2$ (COD = 1,5-cyclooctadiene).²⁷ The rhodium alkene interaction follows the Dewar-Chatt-Duncanson model, characterised by σ -donation from the C=C double bond to the metal, and π -backdonation from the metal to the alkene π^* orbital.^{28,29}

Many examples of rhodium(I) alkene complexes are known and remarkably, some are rather resistant to oxidation in air which makes them attractive pre-catalysts for organic transformations.³⁰ The alkenes are often viewed as labile ligands, and are commonly displaced by more strongly donating phosphines and substrates in catalytic cycles. Sixteen-electron rhodium(I) alkene complexes, in particular, are typically active in dihydrogen activation, and in many cases, able to transfer the hydrogen atoms to the alkene in a formal hydrogenation reaction under mild conditions.³¹ For this reason, many of these complexes are active in hydrogenation catalysis (Figure 3.2).³²

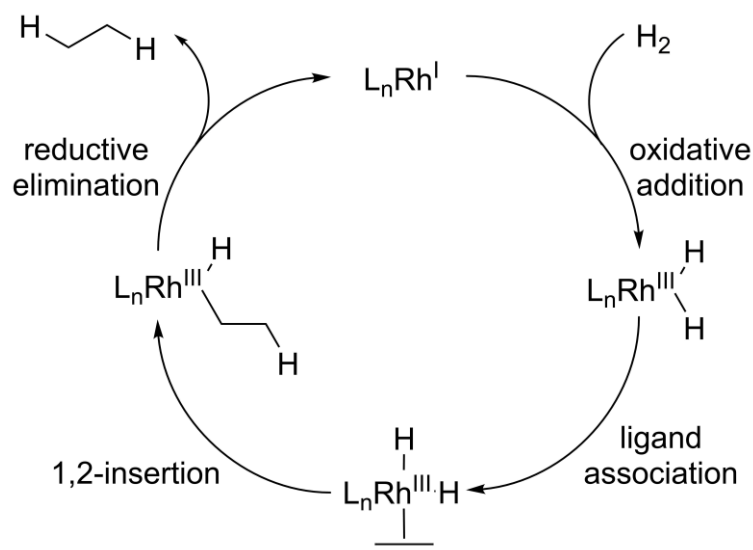


Figure 3.2: Mechanism of alkene hydrogenation at a rhodium centre, modified from Luo et al.³³

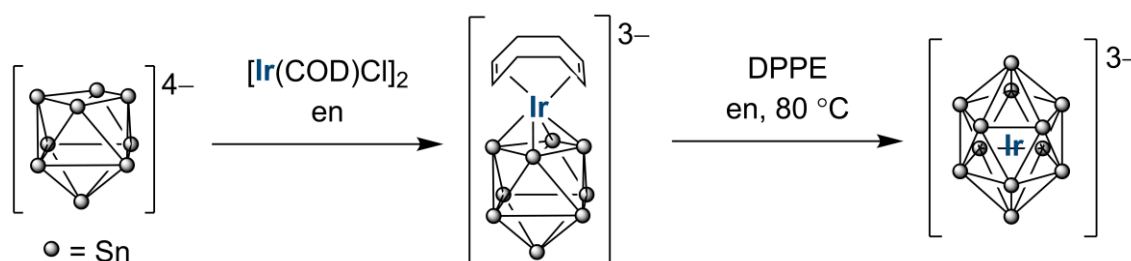
Although applications in catalysis have previously been postulated for Zintl clusters,³⁴ prior to the start of this project, there were no known examples of Zintl cluster-supported catalysts. This led us to design a cluster with a $\text{Rh}(\text{L})_x$ fragment that is known to facilitate catalysis. Such a species would allow us to investigate whether well-established reaction pathways in rhodium chemistry are compatible with Zintl cluster ligand supports.

When choosing the most appropriate $\text{Rh}(\text{L})_x$ fragment for the Zintl ion incorporation, a few factors were considered:

- 1) The metal–ligand fragment must be able to withstand the conditions of synthesis, retaining its ligand, L, in the presence of the *exo* lone pairs at the germanium atoms;³⁵
- 2) The metal–ligand moiety should not be reduced by the cluster support;
- 3) L should also be labile enough for reactivity, so a balance is required in regards to point 1;

- 4) The precursor should preferably also contain a halide ligand in order to both undergo salt metathesis and form a neutrally charged cluster. This provides a thermodynamic driving force for the reaction, and increases the solubility of the product.

We targeted a Zintl cluster containing a $[\text{Rh}(\text{COD})]^+$ fragment, since it offered a potentially labile ligand with many examples of analogues in the literature with which to compare our system.^{36–45} The chelating nature of the COD ligand offers protection from nucleophilic attack by the cluster lone pairs and the low oxidation state of the precursor (+1) protects it from reduction. The isostructural and valence isoelectronic $[\text{Ir}(\text{COD})\text{Cl}]_2$ precursor has been employed in the formation of $[\text{Ir}(\text{COD})\{\eta^4\text{-Sn}_9\}]^{3-}$ by Eichhorn and co-workers,⁴⁶ where the $[\text{Ir}(\text{COD})]^+$ fragment occupies an η^4 coordination site. Subsequent chemistry by Fässler and co-workers allowed access to the endohedral cluster $[\text{Ir}@\text{Sn}_{12}]^{3-}$ on heating $[\text{Ir}(\text{COD})\{\eta^4\text{-Sn}_9\}]^{3-}$ in the presence of 1,2-bis(diphenylphosphino)ethane (DPPE) (Scheme 3.1).⁴⁷



Scheme 3.1: Previously reported use of $[\text{Ir}(\text{COD})\text{Cl}]_2$ in the formation of tetrel Zintl clusters (COD = 1,5-cyclooctadiene; en = 1,2-ethylenediamine; DPPE = 1,2-diphenylphosphinoethane).^{46,47}

These previous studies reveal that the $[\text{Ir}(\text{COD})]^+$ fragment does not interact with the “naked” tin vertices of the cluster or the 1,2-ethylenediamine solvent, and can be displaced by a chelating phosphine. Inspired by this synthesis, $[\text{M}(\text{COD})\text{Cl}]_2$ ($\text{M} = \text{Rh}, \text{Ir}$) were reacted with $[\text{KGe}_9(\text{Hyp})_3]$ ($\text{Hyp} = \text{Si}(\text{SiMe}_3)_3$) to target clusters of form $[\text{M}(\text{COD})\{\text{Ge}_9(\text{Hyp})_3\}]$ ($\text{M} = \text{Rh}, \text{Ir}$).

3.2. Chapter Outline

In this chapter, a $[\text{Rh}(\text{COD})]^+$ fragment is supported on a $[\text{Ge}_9(\text{Hyp})_3]^-$ Zintl ion and the resulting molecular complex tested in alkene hydrogenation. Although alkene hydrogenation has been extensively studied in classic organometallic chemistry, such a transformation is unknown with Zintl cluster ligands. Following the principle of microscopic reversibility, we show that our cluster-based catalyst can support all the elemental steps required for alkane dehydrogenation (the reverse reaction). This chapter details the first report of homogeneous catalysis in the field of Zintl cluster chemistry.

3.3. $[\text{Rh}(\text{COD})\{\text{Ge}_9(\text{Hyp})_3\}]$ (**3**)

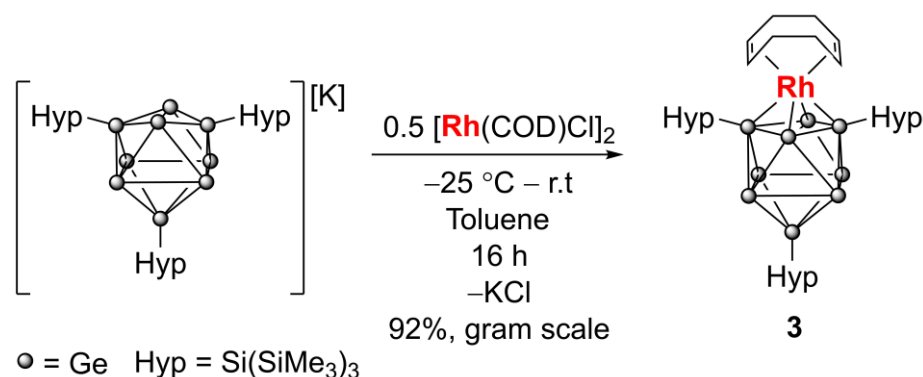
3.3.1. Synthesis of Compound **3**

Half an equivalent of $[\text{Rh}(\text{COD})\text{Cl}]_2$ in toluene was added dropwise to a cooled ($-25\text{ }^\circ\text{C}$) toluene solution of $[\text{KGe}_9(\text{Hyp})_3]$ over the course of 30 minutes under argon.

It was found that the use of more polar solvents, such as THF, or performing the reaction at room temperature significantly decreases the yield of the final product. The use of lower temperatures also reduces the yield due to precipitation of the $[\text{KGe}_9(\text{Hyp})_3]$ precursor, effectively limiting the efficacy of dropwise addition.

The reaction mixture underwent a colour change from red-orange to brown. The brown solution was slowly warmed to room temperature overnight. Filtration of the KCl by-product and subsequent extraction with *n*-hexane yielded an essentially pure red-brown solution of the neutrally charged, hydrocarbon soluble, cluster $[\text{Rh}(\text{COD})\{\text{Ge}_9(\text{Hyp})_3\}]$ (**3**). Upon concentrating and cooling to $-80\text{ }^\circ\text{C}$, red-brown crystals suitable for analysis by single crystal X-ray diffraction could be obtained in an 88% isolated yield. The best isolated yields ($>92\%$) on a preparative scale ($>1\text{ g}$) can be achieved by dissolution of the dried hexane extract into benzene ($\sim 5\text{ ml}$) and subsequent lyophilisation to produce a red-brown powder (Scheme 3.2).

These finely divided powders spontaneously ignite on contact with air, so care must be taken with their manipulation.



Scheme 3.2: Gram scale preparation of $[\text{Rh}(\text{COD})\{\text{Ge}_9(\text{Hyp})_3\}]$ (**3**).

The analogous reaction with $[\text{Ir}(\text{COD})\text{Cl}]_2$ produced a crude reaction mixture containing multiple products by ^1H NMR spectroscopy, none of which could be isolated on a preparative scale.

3.3.2. Nuclear Magnetic Resonance Spectroscopic Analysis of Compound **3**

Analysis of a crystalline sample of compound **3** in benzene- d_6 by ^1H NMR spectroscopy indicates two inequivalent hypersilyl environments at 0.29 and 0.57 ppm in a 2:1 ratio, in addition to peaks at 1.93, 2.31 and 5.48 ppm (each integrating to 4H) corresponding to the COD ligand. Closer inspection of the spectrum reveals that a minor component (~10%) is present, also giving rise to resonances relating to three hypersilyl substituents and a COD ligand. We propose that this component is a structural isomer of compound **3**, as the compound can be obtained as a compositionally pure sample, according to elemental analysis. Variable temperature NMR studies in toluene- d_8 (193 K to 333 K) show that there is no exchange between the two species on the NMR timescale, though it must be noted that the minor component is fluxional in this range (Figure 3.3). Notably, further reactivity studies

described later in this thesis show that both isomers react in stoichiometric reactions to form single products.

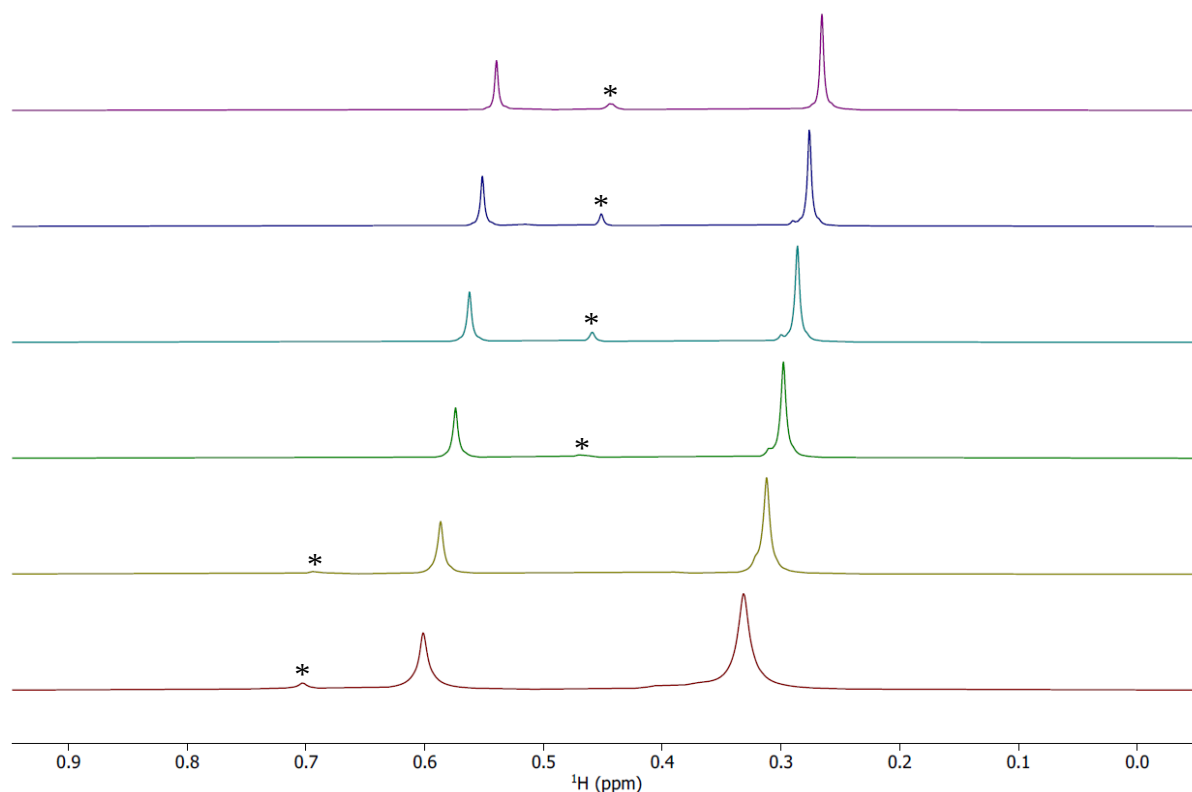


Figure 3.3: Variable temperature ^1H NMR spectrum (C_7D_8 , 400 MHz) of compound **3** highlighting the fluxionality of the minor component in the sample, indicated by an asterisk. From top to bottom: $T = 298, 273, 253, 233, 213$ and 193 K.

Data from $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy supports the ^1H NMR assignment, the alkenic carbon resonances for the major and minor isomers appear as doublets ($^1J_{\text{Rh-C}} = 8.0$ Hz, 9.3 Hz respectively) due to coupling to ^{103}Rh ($I = \frac{1}{2}$, 100%). The coupling constants are more consistent with cationic species such as $[\text{Rh}(\text{COD})_2]^+$ ($^1J_{\text{Rh-C}} = 7.6$ Hz) and $[(\text{GaCp}^*)_3\text{Rh}(\text{COD})]^+$ ($\text{Cp}^* = \text{pentamethylcyclopentadienyl}$) ($^1J_{\text{Rh-C}} = 8.7$ Hz),^{48,49} than that of other neutral complexes, for example $[(\text{Cp})\text{Rh}(\text{COD})]$ and $[(\text{Tp})\text{Rh}(\text{COD})]$ ($\text{Cp} = \text{cyclopentadienyl}$; $\text{Tp} = \text{tris-pyrazolylborate}$) ($^1J_{\text{Rh-C}} = 14.3$ Hz and $^1J_{\text{Rh-C}} = 13.2$ Hz, respectively).^{36,50,51} Interestingly, the anionic 11-vertex cluster $[\text{Rh}(\text{COD})\{\text{C}_2\text{B}_{10}\text{H}_{12}\}]^-$ ($^1J_{\text{Rh-C}}$

$c = 11$ Hz), has similar Rh–C bond metrics (*vide infra*). Further functionalisation with transition metals can lower the coupling constant of the carborane cluster to 9 Hz.⁵²

The $^{29}\text{Si}/^1\text{H}$ HMBC NMR spectrum (Figure 3.4) shows four cross peaks for the major isomer. Interestingly, the hypersilyl ^{29}Si signal for the germanium-bonded silicon atoms differ in chemical shift significantly depending on whether they are adjacent to the rhodium atom or opposite (Figure 3.5). Two cross-peaks can also be observed for the minor isomer. The ^{29}Si NMR resonances corresponding to the single hypersilyl substituent could not be resolved.

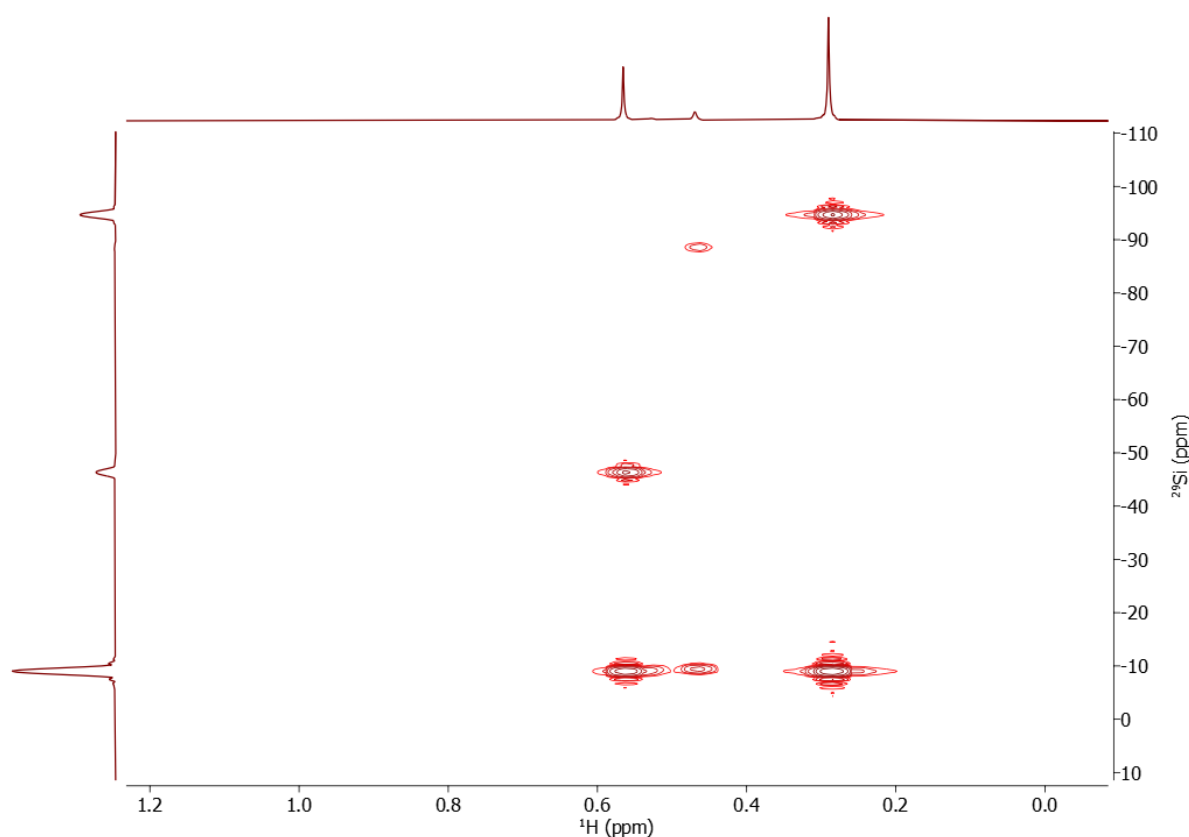


Figure 3.4: $^{29}\text{Si}/^1\text{H}$ HMBC NMR spectrum (C_6D_6 , 298 K, 79.5 MHz) of compound **3**.

3.3.3. Single Crystal X-ray Structure of Compound **3**

The symmetry observed in the solution phase is also retained in the solid, and was confirmed by single crystal X-ray diffraction (Figure 3.5). The asymmetric unit contains two crystallographically inequivalent clusters with comparable bond metrics (Table 3.1).

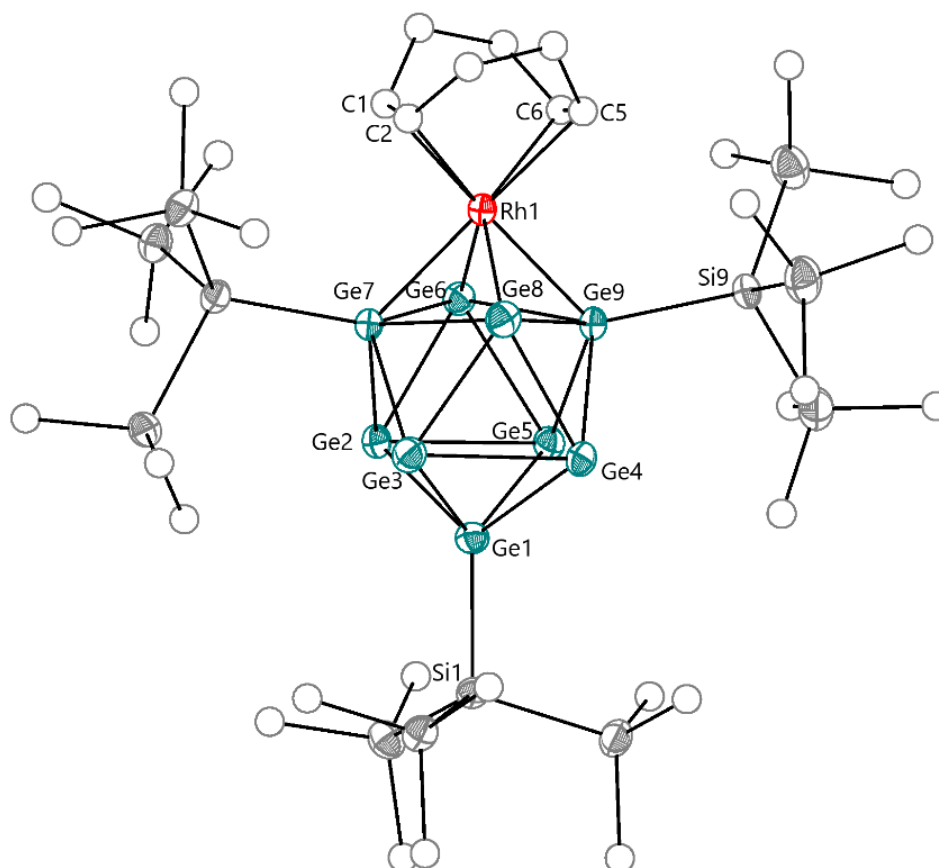
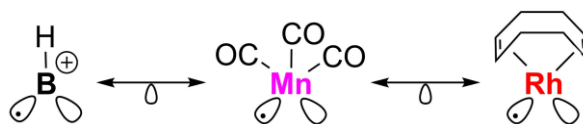


Figure 3.5: Single crystal X-ray structure of compound **3**. Anisotropic displacement ellipsoids set at 50% probability. All carbon atoms are pictured as spheres of an arbitrary radius. Hydrogen atoms are omitted for clarity. Only one of two crystallographically independent molecules is shown.

Compound **3** is a *closo* 10-vertex deltahedron with 22 electrons available for cluster bonding ($[\text{Rh}(\text{COD})] = 1 e^-$, $\text{Ge} = 2 e^-$, $\text{Ge}-(\text{Hyp}) = 3 e^-$) and has a bicapped square antiprismatic geometry of non-crystallographically imposed C_{2v} symmetry.

Determining the number of electrons available for cluster bonding at the $[\text{Rh}(\text{COD})]$ fragment was achieved by applying the isolobal analogy. A $[\text{BH}]^+$ fragment is isolobal and valence isoelectronic to a $[\text{Mn}(\text{CO})_3]$ fragment (Scheme 3.3). Therefore, $[\text{Rh}(\text{COD})]$ only donates one electron for cluster bonding.⁵³



Scheme 3.3: Electron counting of [Rh(COD)] using the isolobal analogy.

Table 3.1: Selected crystallographic bond distances (Å) of **3** comparing the crystallographically inequivalent clusters in the asymmetric unit.

Bond	Cluster 1 Distance (Å)	Cluster 2 Distance (Å)
Rh1–Ge6	2.549(2)	2.598(2)
Rh1–Ge7	2.496(2)	2.496(2)
Rh1–Ge8	2.581(2)	2.553(2)
Rh1–Ge9	2.514(2)	2.503(2)
Rh1–C1	2.192(13)	2.212(11)
Rh1–C2	2.168(11)	2.201(11)
Rh1–C5	2.218(12)	2.204(10)
Rh1–C6	2.168(11)	2.174(10)
Ge6–Ge7	2.715(2)	2.696(2)
Ge6–Ge9	2.725(2)	2.712(2)
Ge7–Ge8	2.723(2)	2.735(2)
Ge8–Ge9	2.709(2)	2.721(2)

The rhodium atom is bonded to [Ge₉(Hyp)₃][−] in an η⁴ coordination mode. Compound **3** is the first example of an η⁴ coordination with a [Ge₉R₃][−] cluster, however this bonding mode is well known in the chemistry of the unsubstituted clusters.⁵⁴ The Rh–C distances in the Rh(COD) fragment (mean distance 2.192 Å) are typical for Rh(COD) complexes (Table 3.2).

Table 3.2: Comparison of mean Rh–C (COD) distances and $^1J_{\text{Rh-C}}$ (COD) coupling constants for selected [(L)Rh(COD)] complexes. Cp = cyclopentadienyl; Tp = tris-pyrazolylborate; Cp* = pentamethylcyclopentadienyl; Ar^F = 3,5-(CF₃)₂C₆H₃; DCPE = 1,2-bis(dicyclohexylphosphino)ethane.^{36,42,44,48,49,51,52,55}

Compound	Rh–C Mean Distance (Å)	$^1J_{\text{Rh-C}}$ (Hz)
[(Tp)Rh(COD)]	2.109	13.2
[(Cp)Rh(COD)]	2.113	14.3
[N(PPh ₃) ₂][(C ₂ B ₁₀ H ₁₂)Rh(COD)]	2.170	11.0
3	2.192	8.0
[(GaCp*) ₃ Rh(COD)][B(Ar ^F) ₄]	2.205	8.7
[(DCPE)Rh(COD)][B(Ar ^F) ₄]	2.241	N.A.
[Rh(COD) ₂][Al{(OC(CF ₃) ₃) ₃ } ₄]	2.241	7.6

The differences in Rh–C bond metrics and coupling constants between compound **3** and the selected literature examples (Table 3.2) are most likely due to a combination of the delocalised nature of cluster bonding and electronegativity differences between heavier main-group elements (Ga, Ge) when compared to classical organometallic ligands.

3.3.4. Catalytic Studies of Compound **3**

In preliminary experiments, a benzene-*d*₆ solution of compound **3** was exposed to an atmosphere of H₂, which resulted in cluster decomposition. This was evidenced by the loss of defined hypersilyl ¹H NMR signals, and more notably the production of cyclooctane (COA) by complete hydrogenation of the COD ligand. No upfield signals (<0 ppm), indicating the presence of metal hydrides or dihydrogen complexes were observed. Presumably, the decomposition pathway proceeds by ligand hydrogenation, followed by C–H, Si–C and/or Si–Si of the hypersilyl substituents at the rhodium centre (Scheme 3.4).

H₂ was added using a Schlenk line, set at an overpressure of 1 bar, into the NMR tube which was cooled in liquid nitrogen. Interestingly, the only change observed in the ¹H NMR spectra was the conversion of substrate to product, and steady decomposition of compound **3**. Compound **3** appeared to be the catalyst resting state as no other peaks were visible corresponding to intermediates. It must be noted here that recharging with reagents after the decomposition of compound **3** did not result in further turnover, thus suggesting that cluster decomposition was H₂ promoted and led to a product which was inactive in catalysis.

The concentrations of compound **3** and COD were then varied and analysed in terms of initial rates kinetics by ¹H NMR spectroscopy (Figure 3.7). These initial studies indicated a positive order in [**3**] and [COD]. The rate dependence on the concentration of compound **3** is almost linear (first order) at low concentrations, then almost zero order at higher concentrations, suggesting that the rate is limited by diffusion of H₂ which is a common problem with NMR scale reactions involving gases.³²

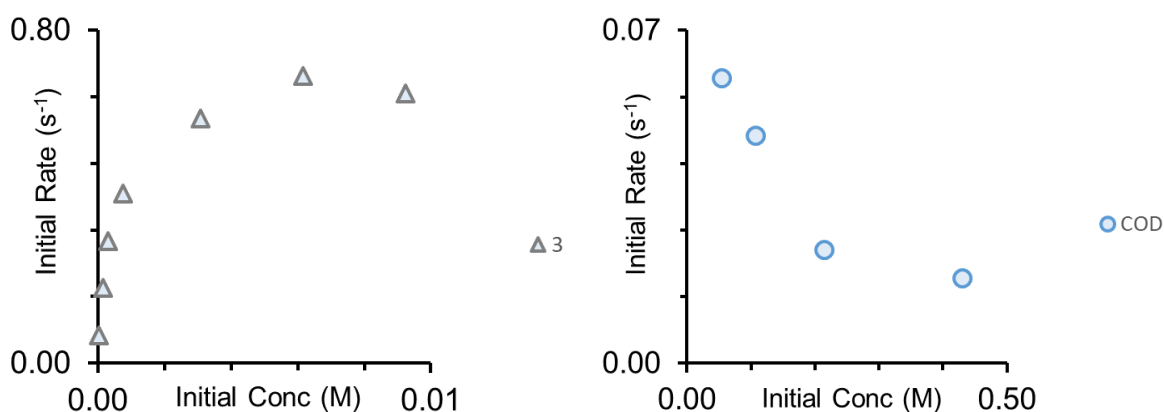


Figure 3.7: Variation of [**3**] and [COD] and comparison by initial rates kinetics.

These experiments were then repeated with *cis*-cyclooctene (COE) under the same conditions to compare reaction rates and temporal profiles (Figure 3.8).

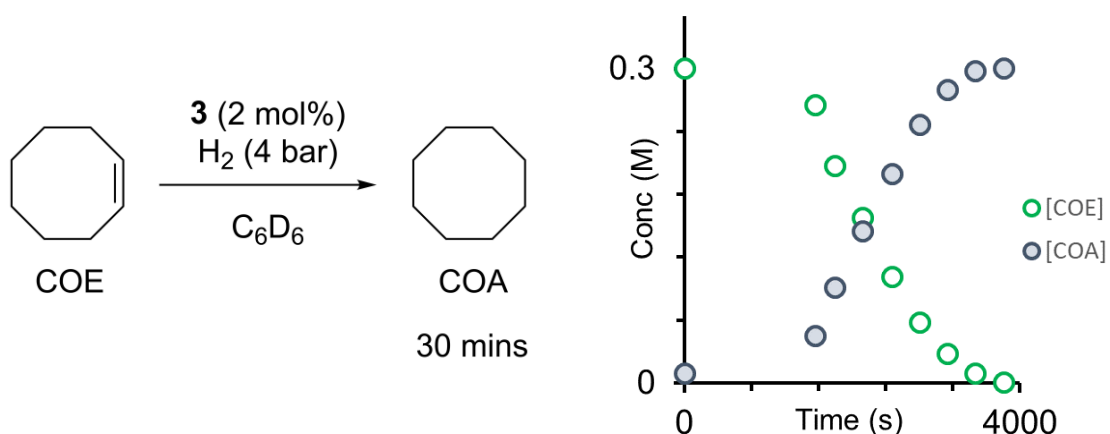


Figure 3.8: Catalytic hydrogenation of COE, 2 mol% catalyst loading, 4 bar H₂.

This reaction was found to be approximately 16 times faster than the COD hydrogenation under similar reaction conditions and, like COD hydrogenation, the rate was found to be limited by H₂ diffusion. Due to this, initial rates kinetics and meaningful kinetic profiles could not be obtained, however, qualitatively it appears that there is an induction period, which is not present in COD hydrogenation. Interestingly, COE hydrogenation was also observed at low catalyst loadings (0.01 mol%).

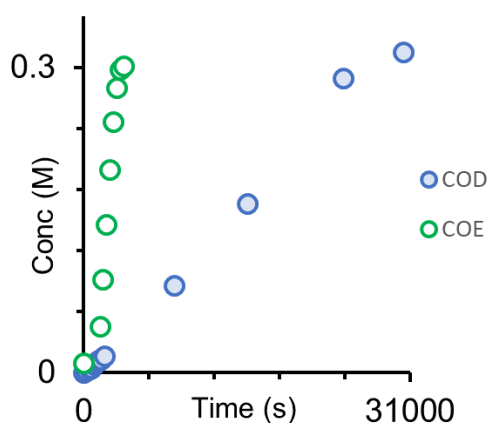


Figure 3.9: Comparison of COA production in COD and COE hydrogenation, 2 mol% catalyst loading, 4 bar H₂.

3.3.5. Kinetics Studies

In light of the problems with H₂ diffusion, we changed our methodology to collect the data for the kinetics analysis. These experiments were stirred in an ampoule fitted with a J. Young stopcock and open to a constant flow of H₂ (1 bar). Individual time/concentration datapoints were collected for separate experiments which were quenched at the desired reaction time and measured using ¹H NMR spectroscopy. Under these conditions, although the surface area of the solution was larger, the reduced pressure of H₂ caused the reactions to proceed much slower, indicating a positive order in [H₂] (Figure 3.10).

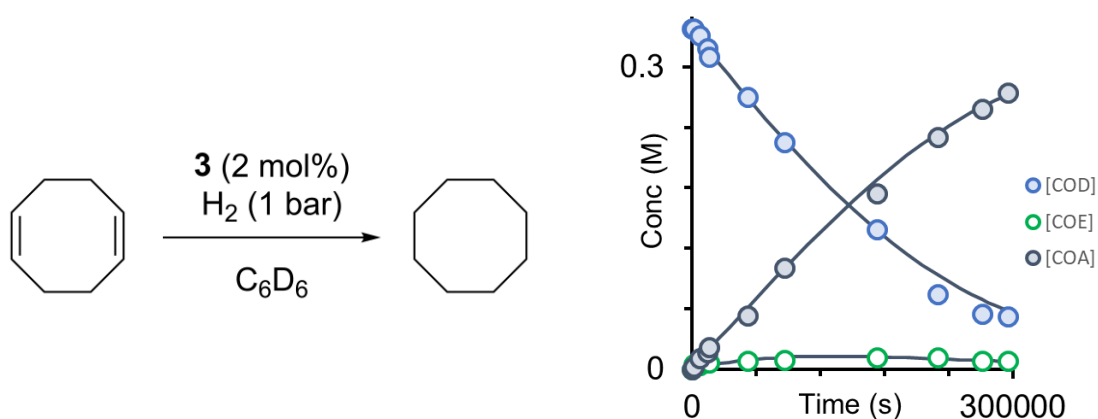


Figure 3.10: Catalytic hydrogenation of COD, 2 mol% catalyst loading, 1 bar H₂. Circles = experimental data; Lines = simulated data.

Close inspection of the ¹H NMR spectra from COD hydrogenation showed the formation of a small amount of COE during the reaction, suggesting an equilibrium whereby COD can compete with H₂ at a Rh(COE) intermediate, releasing COE and potentially regenerating compound **3**.

The same process was repeated with COE as the substrate. This time, the setup allowed for meaningful kinetics to be obtained (Figure 3.11).

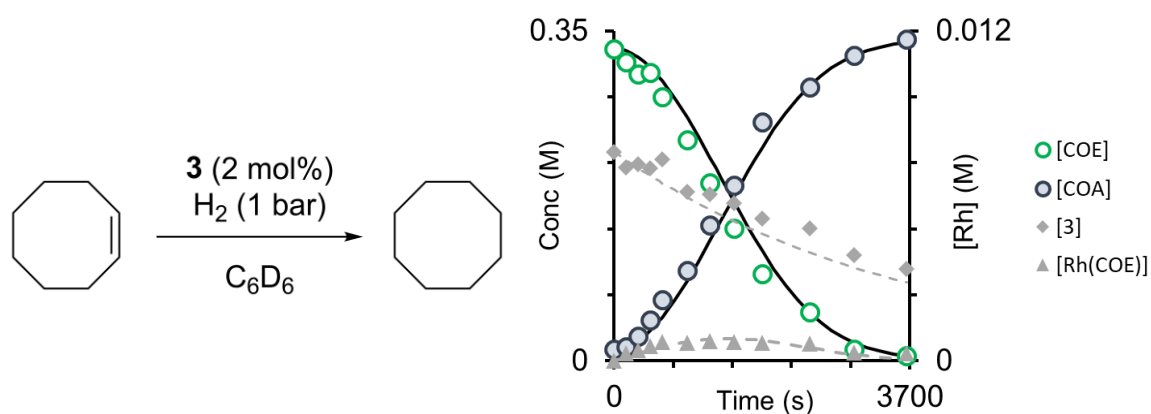


Figure 3.11: Catalytic hydrogenation of COE, 2 mol% catalyst loading, 1 bar H₂. Circles = experimental data; Lines = simulated data.

On inspection of the ¹H NMR spectra during COE hydrogenation, a new species unique to COE hydrogenation appeared in low concentrations during the reaction and was consumed by the end of the reaction. Although the relative integrations could not be assigned due to overlap with other signals, using the chemical shifts we postulate that this species is a rhodium–COE containing intermediate of form Rh(COE)_n[Ge₉(Hyp)₃] (n = 1, 2). Unfortunately, attempts to prepare this compound independently have been unsuccessful.

To discount the formation of a colloidal catalyst, a mercury drop test was performed (Figure 3.12), showing that the catalysis is most likely not catalysed by rhodium nanoparticles. Other tests,⁵⁷ such as the PMe₃ test were not appropriate due to reactivity between compound **3** and PMe₃, which has been investigated and will be discussed further in Chapter 4.

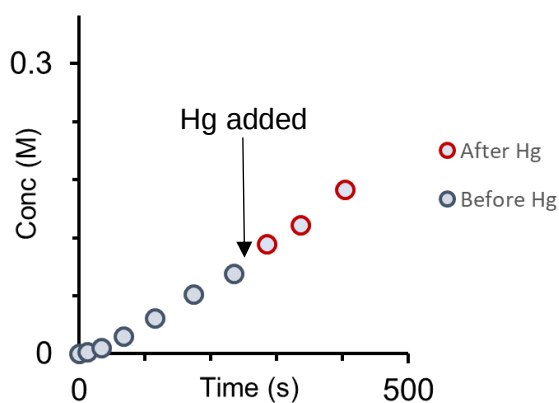


Figure 3.12: Mercury drop test showing COA production. Blue circles: before the addition of elemental mercury; Red circles: after the addition of elemental mercury.

The temporal profiles of COD and COE hydrogenation were then compared (Figures 3.10 and 3.11). COD follows a steady deceleration of COD conversion and COA production, whereas COE hydrogenation looks more complex with three distinct stages: induction, acceleration and deceleration.

In order to gain additional information from these observations, we modelled the kinetics data using the COPASI software package.⁵⁸ All COPASI simulations were performed by Prof. Andrew S. Weller. The single simulated kinetic model (Figure 3.13) shows good agreement with the experimental data for both COD and COE hydrogenation, even with the differences in their temporal profiles.

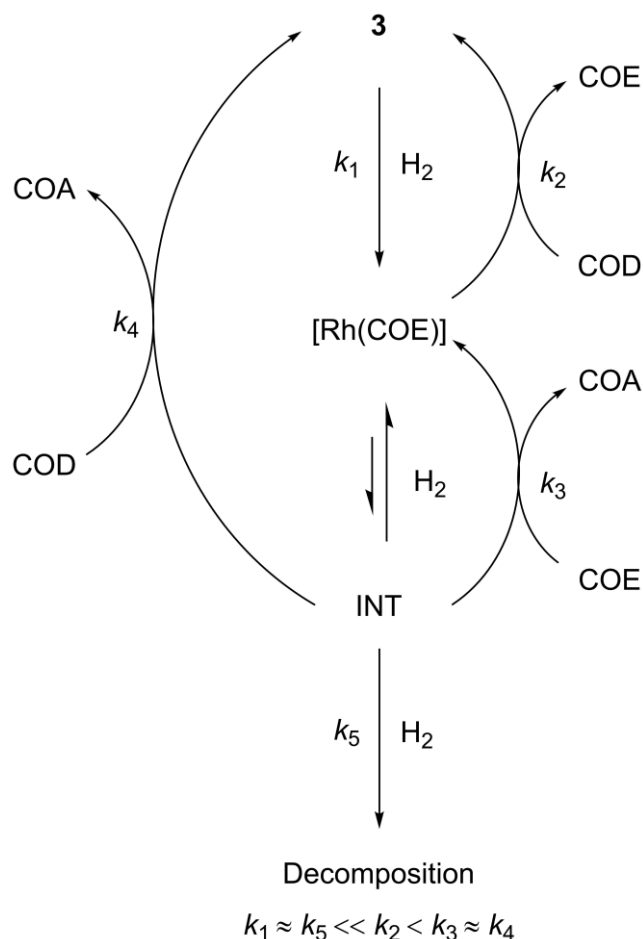


Figure 3.13: Simulated kinetic model mechanism for COD and COE hydrogenation. Simulation courtesy of Prof. Andrew S. Weller.

This model proposes that compound **3** reacts with a molecule of H_2 (k_1) to form an intermediate, assumed to be $\text{Rh}(\text{COE})[\text{Ge}_9(\text{Hyp})_3]$ ($[\text{Rh}(\text{COE})]$), which was observed in very low concentrations during COE hydrogenation. This intermediate can undergo either: ligand substitution with COD (k_2), which is observed by NMR spectroscopy by the formation of free COE; or reaction with a second molecule of H_2 to form a second intermediate, INT. This second intermediate can undergo ligand displacement with either COE, towards $[\text{Rh}(\text{COE})]$ (k_3) or ligand displacement with COD, towards the reformation of compound **3** (k_4). Alternatively, it can undergo an off-cycle reaction with H_2 to form COA and cluster decomposition (k_5) (observed as steady decline in **[3]** and deceleration at the end of both reactions).

In the case of COE hydrogenation, the changes in rate of reaction (acceleration, deceleration) also seem to coincide with concentration of observed $[\text{Rh}(\text{COE})]$ (Figure 3.11). To model this, the COPASI derived model data was differentiated and plotted as its first derivative, comparing to the modelled $[\text{Rh}(\text{COE})]$ data (Figure 3.14). This qualitatively showed very good correlation, indicating that the observed intermediate may be the (more) active catalytic species in the hydrogenation of COE.

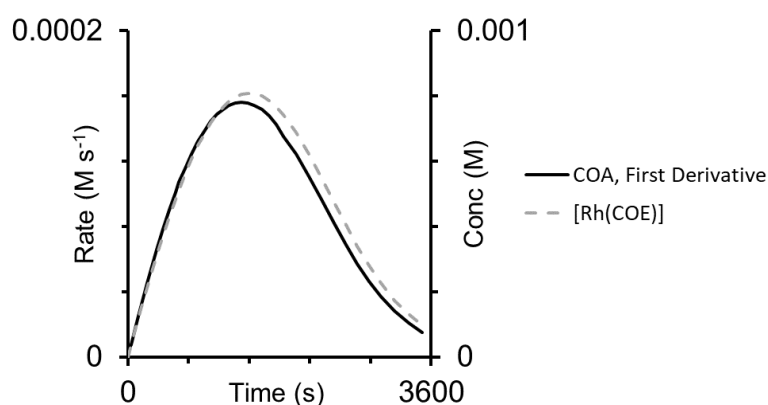


Figure 3.14: Plot of the first derivative of COA production from COE and the concentration of the observed intermediate $\text{Rh}(\text{COE})[\text{Ge}_9(\text{Hyp})_3]$ ($[\text{Rh}(\text{COE})]$).

3.3.6. Density Functional Theory Calculations

In order to probe the mechanism more intricately, density functional theory (DFT) was employed. This allowed us to compute possible structures for the intermediates postulated in the simulated kinetics model. To choose the appropriate level of theory, some benchmarking was done by performing a geometry optimisation and frequency calculation on one of the molecules of compound **3** from the crystal structure, varying the functional and basis set (Table 3.3).

Table 3.3: Benchmarking analysis for DFT geometry optimisation and frequency calculation for compound **3**. Top: basis set variation;^{59–66} Bottom: functional variation.^{67–76} RMSD = root mean square distances.

Entry	Functional	Basis Set (Rh)	Basis Set (Ge, Si)	Basis Set (C,H)	CPU Time (h)	RMSD (Relative to Entry 3)
1	BP86	LanL2DZ	6-31g(d,p)	6-31g(d,p)	213	0.170
2	BP86	LanL2DZ	LanL2DZ	6-31g(d,p)	103	0.086
3	BP86	SDD	SDD(d)	6-31g(d,p)	145	0
4	BP86	SDD(f)	SDD(d)	6-31g(d,p)	152	0.004
5	B3LYP	SDD	SDD(d)	6-31g(d,p)	235	0.066
6	BLYP	SDD	SDD(d)	6-31g(d,p)	141	0.114
7	M06L	SDD	SDD(d)	6-31g(d,p)	354	0.201
8	M06	SDD	SDD(d)	6-31g(d,p)	448	0.209
9	PBE	SDD	SDD(d)	6-31g(d,p)	169	0.050
10	PBE0	SDD	SDD(d)	6-31g(d,p)	296	0.103
11	TPSS	SDD	SDD(d)	6-31g(d,p)	237	0.054
12	TPSSh	SDD	SDD(d)	6-31g(d,p)	325	0.073
13	ω b97xd	SDD	SDD(d)	6-31g(d,p)	394	0.201

For the basis set testing, the BP86 functional was used for all experiments. Two Effective Core Potential (ECP) basis sets were then selected for Si, Ge and Rh: LanL2DZ or SDD (with and without polarisation functions); alongside 6-31g(d,p) for C and H. The use of 6-31g(d,p) for Si and Ge was also tested. The combination of basis sets in entry 3 seemed appropriate in terms of CPU time and purpose (geometry optimisation) and produced a very similar energy and optimised geometry (RMSD = 0.0037) to entry 4, which includes f orbital polarisation

for rhodium atoms. For the functional testing, the combination of basis sets in entry 3 was used to compare BP86 against different functionals.

It has been noted before that the most appropriate functional type for main group cluster compounds is a “pure” Generalised Gradient Approximation (GGA) functional (for example BP86). Hybrid functionals (for example B3LYP), as well as being computationally expensive, are advised against due to problems dealing with metallic-like bonding.⁷⁷

It was concluded that the BP86/SDD/6-31g(d,p) level of theory was adequate for geometry optimisation, frequency and subsequent polarised continuum model (PCM) calculations. This computationally cheap combination allowed the calculation of a model mechanism in a reasonable timeframe. To increase the accuracy and generate the reported energies, a single point energy calculation at the BP86/Def2-TZVP level of theory was performed on each optimised geometry.⁷⁸

Since the rhodium centre is assumed to be a coordinatively saturated 18 electron rhodium(I) complex in compound **3**, the first step to model was an η^4 to η^2 coordination of the COD ligand to allow for the oxidative addition of dihydrogen. This was done by performing a potential energy surface scan calculation, gradually lengthening one of the alkenic Rh–C distances (Figure 3.15).

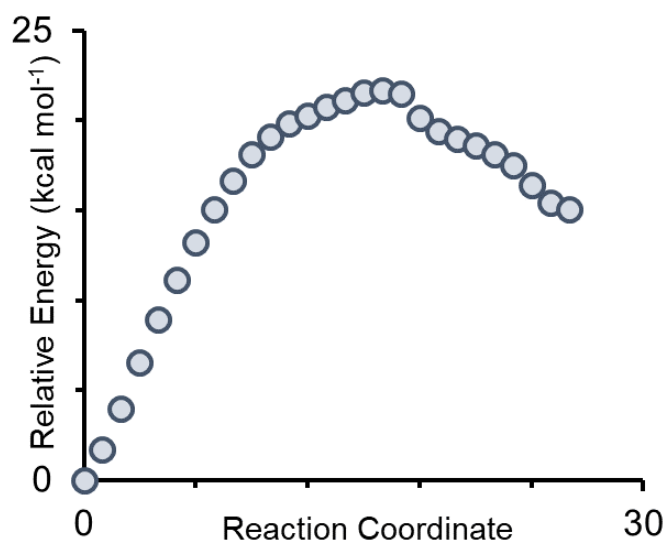


Figure 3.15: Potential energy surface scan of η^4 to η^2 dissociation at the COD ligand. Energies relative to the optimised geometry of compound **3**.

On inspection of this profile, geometries around the maximum were further optimised to find an accessible transition state TS(A–B) at +19.6 kcal mol⁻¹; a subsequent frequency calculation revealed a single negative eigenvalue, indicative of a saddle point, rather than a minimum. This was further tested using intrinsic reaction coordinate (IRC) calculations. The resulting displacements were optimised to produce geometries A and B. The minimum (reaction coordinate 26) was also optimised to geometry B, with a relative free energy of +12.9 kcal mol⁻¹ containing no negative eigenvalues. From this we can conclude that B is likely kinetically accessible via TS(A–B) at room temperature (Figure 3.16). Considering the relative energies and the equilibrium constant for this process at room temperature, $k_{eq} = e^{-\Delta G^0/RT} = 2.98 \times 10^{-10}$, this agrees with NMR spectroscopic data that under the conditions of excess COD, the observed resting state is A.

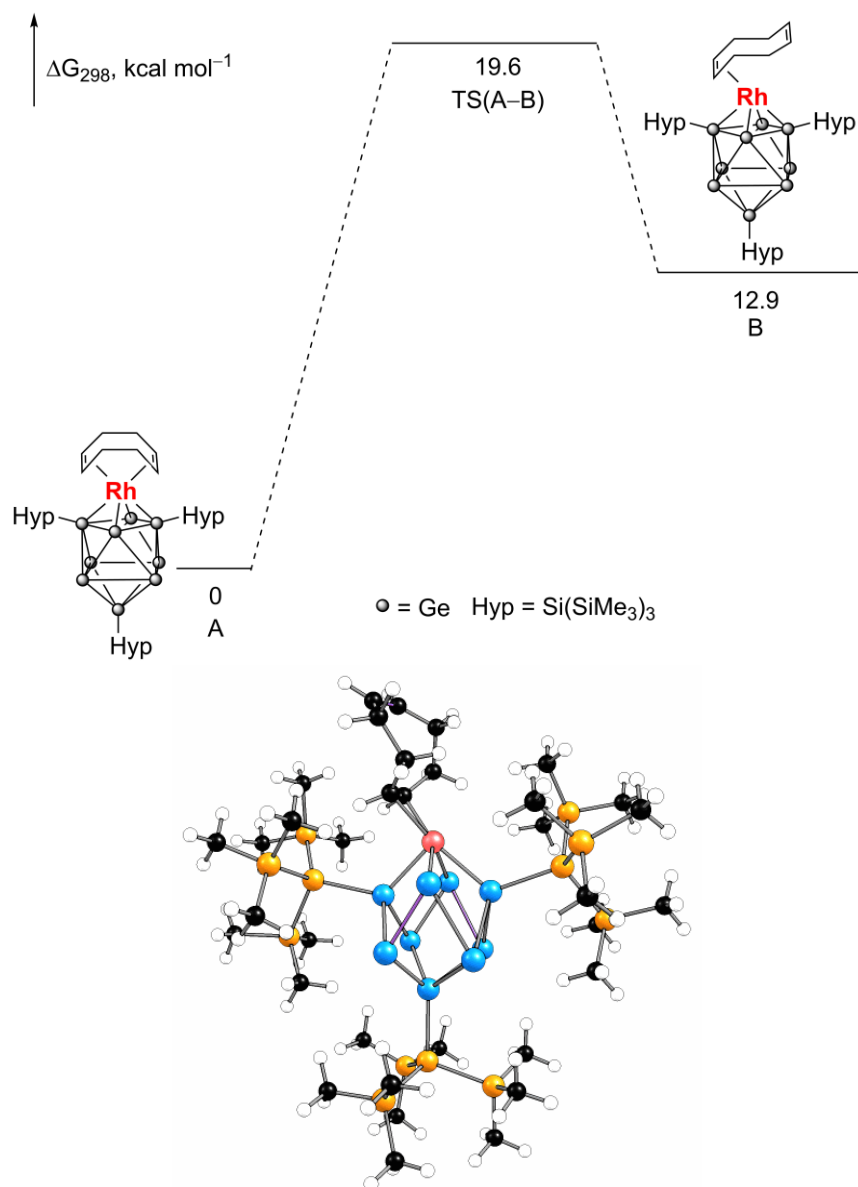


Figure 3.16: η^4 to η^2 dissociation at the COD ligand, allowing access to a coordinatively unsaturated rhodium centre. Top: reaction coordinates ($\Delta G_{298}, \text{ kcal mol}^{-1}$); Bottom: Optimised geometry of intermediate B.

Next, oxidative addition of H_2 at the rhodium centre, via dihydrogen complex C to produce a rhodium(III) dihydride complex (D) was modelled. These processes were determined to be essentially barrierless (Figure 3.17).

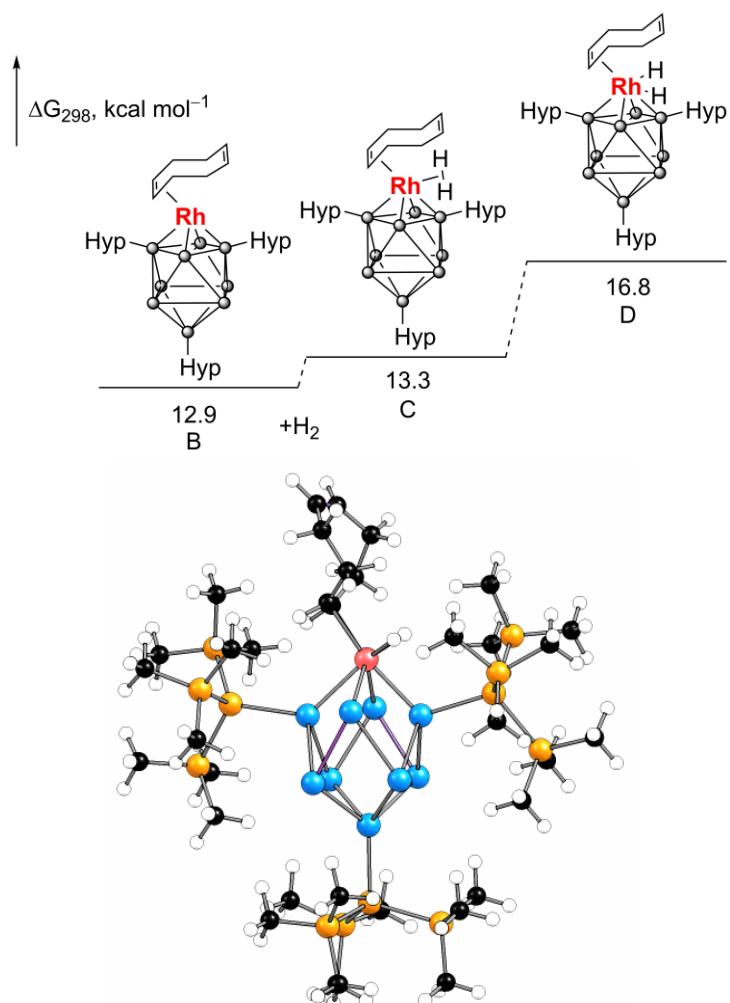


Figure 3.17: Oxidative addition of dihydrogen to produce Rh(III) dihydride complex D, Top: reaction coordinates (ΔG_{298} , kcal mol^{-1}); Bottom: Optimised geometry of intermediate D.

A migratory insertion was then modelled, which was found to operate via agostically stabilised intermediate E. Breaking of the agostic interaction towards the rhodium(III) alkyl hydride complex F resulted in the transition state TS(E–F), which was the highest overall barrier for the mechanism (Figure 3.18).

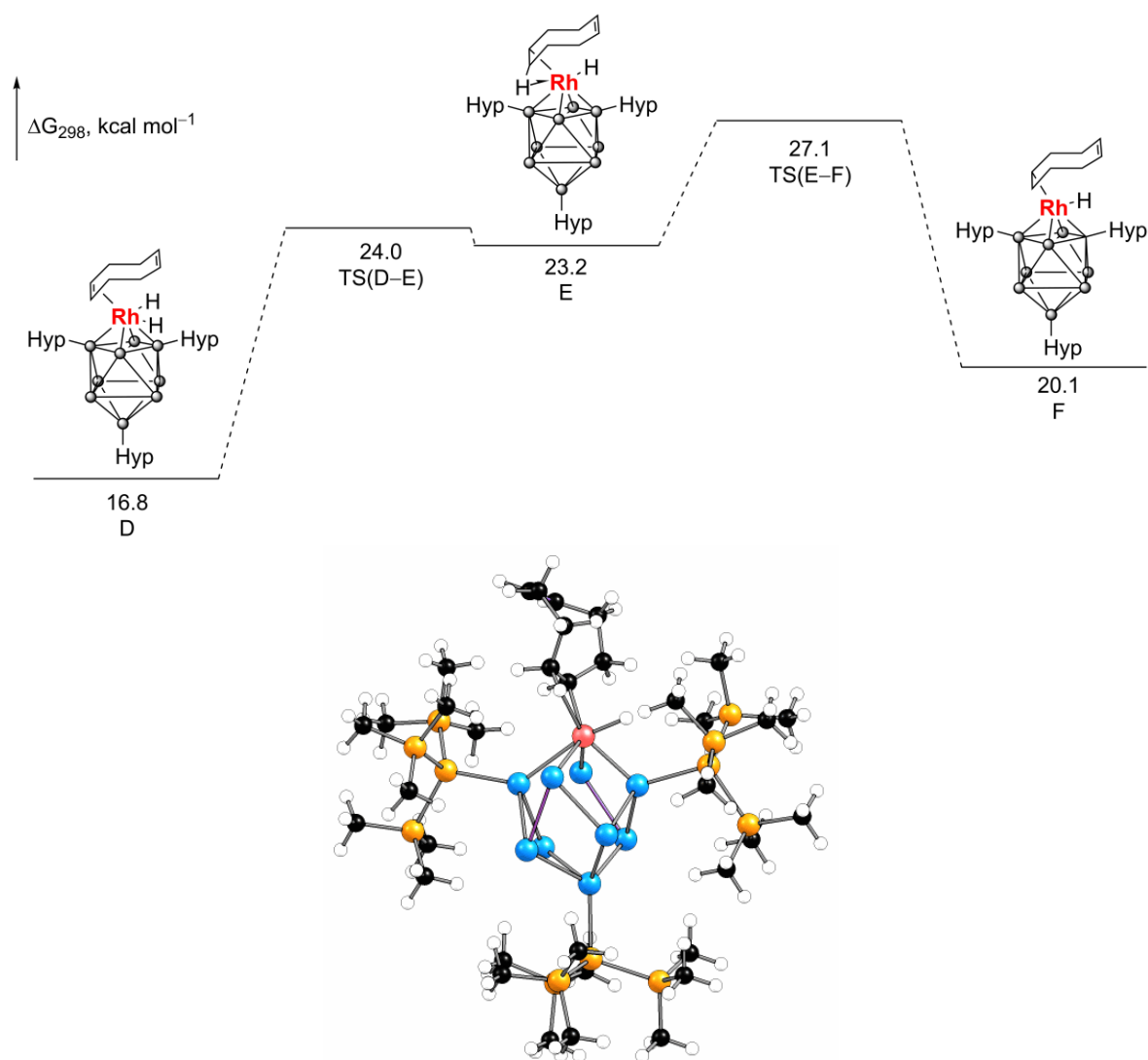


Figure 3.18: Hydride transfer to produce a rhodium(III) alkyl hydride complex via an agostically stabilised intermediate, Top: reaction coordinates (ΔG_{298} , kcal mol^{-1}); Bottom: Optimised geometry of the highest energy transition state TS(E-F).

From F, a reductive elimination and reassociation step was modelled, producing H at a relative energy of $-1.9 \text{ kcal mol}^{-1}$. We propose that this intermediate is the experimentally observed $[\text{Rh}(\text{COE})]$ (H) and that exergonic process A-H can be characterised under the rate constant k_1 . This correlates well with the simulated mechanism, since the highest overall barrier must precede the formation of the rhodium COE complex, i.e. displacement of the COD to release the active catalyst, and accounts for the induction period and faster rate observed during COE hydrogenation.

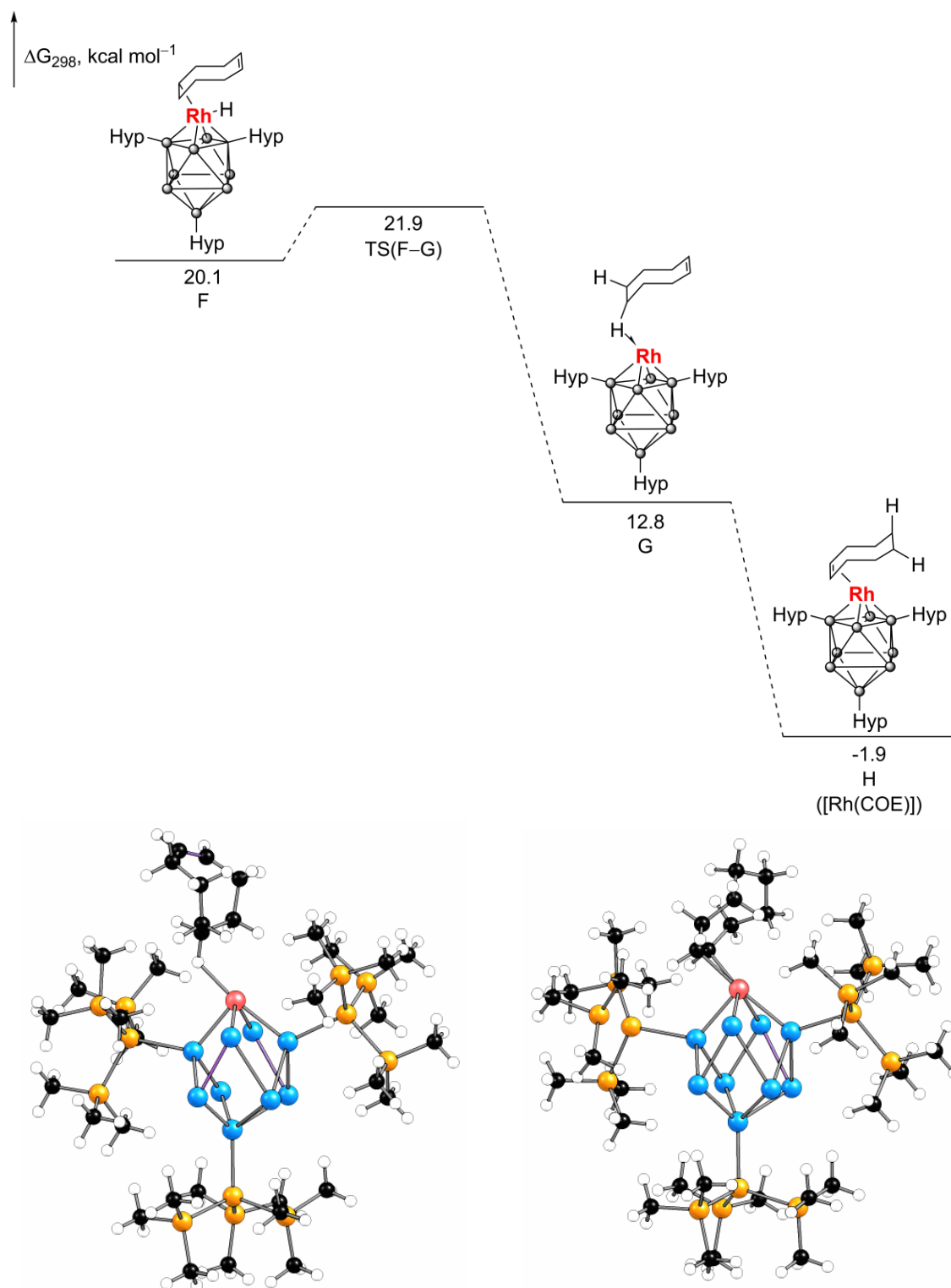


Figure 3.19: Reductive elimination towards the proposed intermediate H ($\text{Rh}(\text{COE})[\text{Ge}_9(\text{Hyp})_3]$) via sigma complex G (ΔG_{298} , kcal mol⁻¹) Top: reaction coordinates (ΔG_{298} , kcal mol⁻¹); Bottom: Optimised geometries of intermediates sigma complex G (Left) and H (Right).

A similar mechanism was modelled for the second hydrogenation (Figure 3.20), the most noticeable difference being that the overall barrier is much lower, by approximately the same energy required for η^4 to η^2 complexation at the COD ligand (A–B). From this finding, we could predict that the synthesis of a isolable analogue of H would be a far superior catalyst.

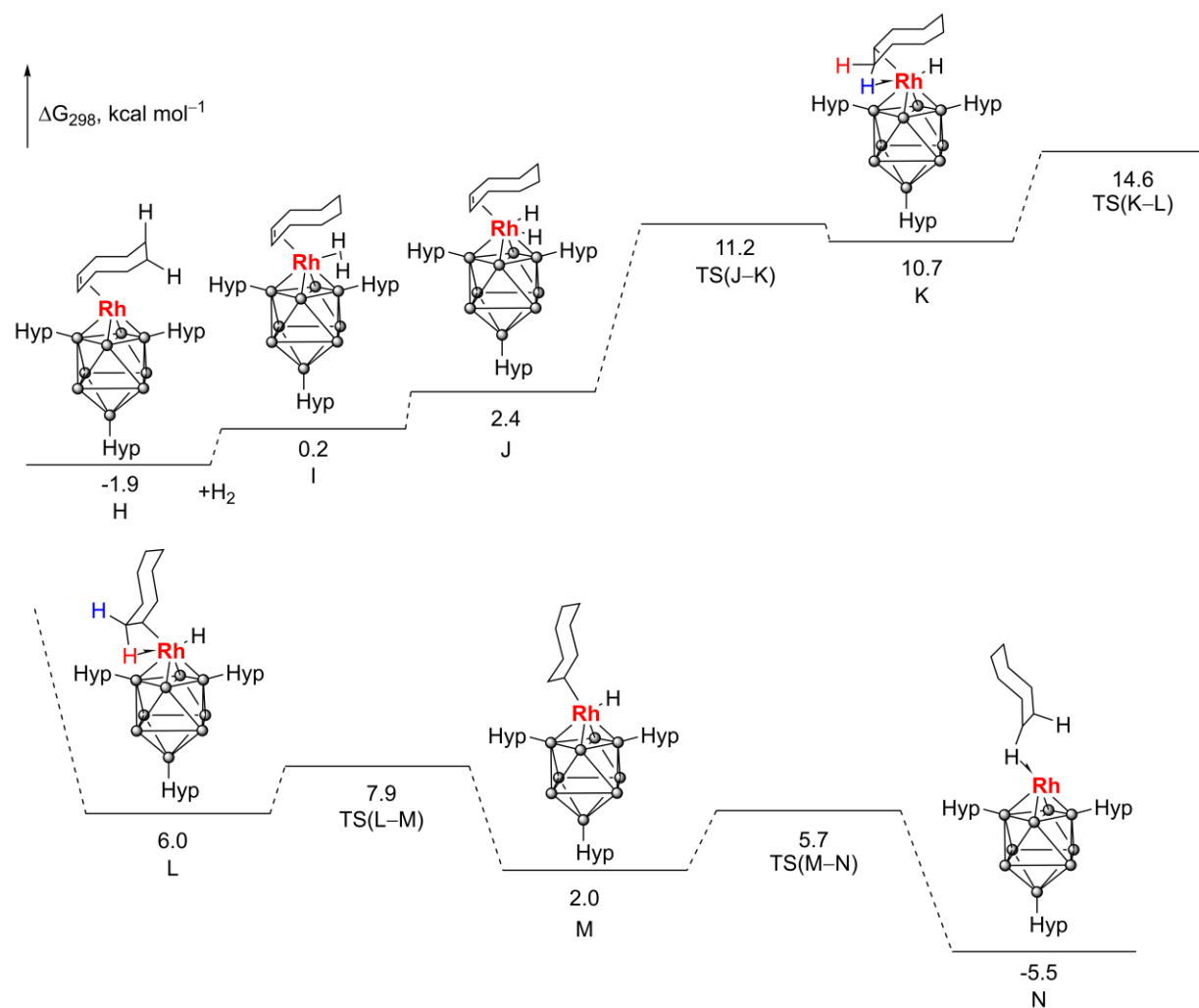


Figure 3.20: Hydrogenation of the [Rh(COE)] complex intermediate, H (ΔG_{298} , kcal mol⁻¹).

The substrate (COD or COE) is then introduced again to easily displace the sigma-bound COA and start the cycle at A or H respectively. This model accounts for the increased rate of COE hydrogenation.

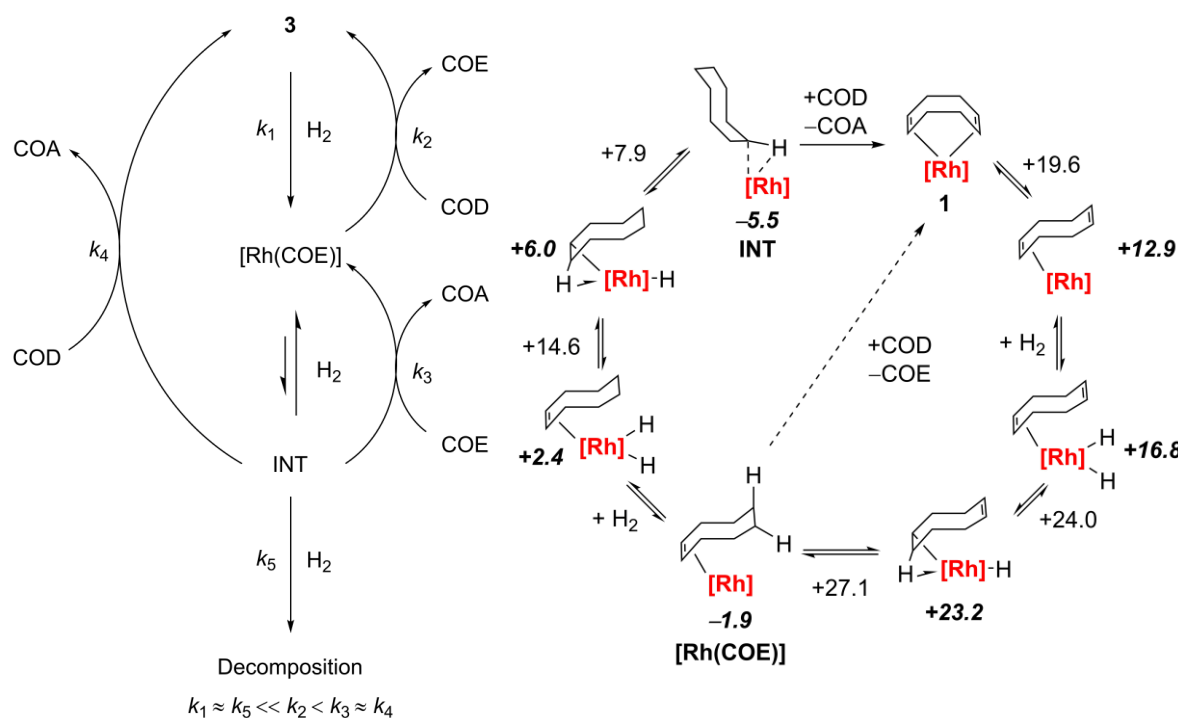


Figure 3.21: Simulated (left) and condensed calculated (right) mechanisms for COD or COE hydrogenation at compound **3** (ΔG_{298} , kcal mol⁻¹).

3.4. Conclusion

In conclusion, a *closo* 10-vertex Zintl cluster, $[\text{Rh}(\text{COD})\{\text{Ge}_9(\text{Hyp})_3\}]$ (**3**), has been synthesised by a salt metathesis reaction between $[\text{KGe}_9(\text{Hyp})_3]$ and $[\text{Rh}(\text{COD})\text{Cl}]_2$. This was then used as the first Zintl cluster based homogeneous catalyst in the hydrogenation of cyclic alkenes (*cis*-cyclooctene and 1,5-cyclooctadiene). A kinetics study was performed in tandem with DFT calculations to determine a suitable model mechanism, which is applicable to both substrates. This preliminary study will act as a platform for modification of both the transition metal and main group components in the studies described in subsequent chapters.

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3.5. References

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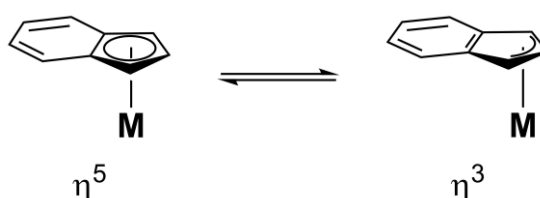
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4. Synthesis and Reactivity of Coordinatively Unsaturated Zintl clusters

4.1. Background and Introduction

The ability of a ligand to support a transition metal centre *and* dynamically react to its steric and electronic requirements can lower the energies of intermediates and transition states in catalytic cycles.^{1–5} This can, in turn, affect catalyst selectivity, lifetime, and reaction rates.⁶ Such structurally responsive ligands can be found in nature, most notably in the active sites of metalloenzymes, where the functional groups of flanking amino acid residues are used to stabilise the coordination sphere of the metal centre.^{7–9}

In organometallic chemistry, archetypal examples of this include hemilabile phosphine ligands,¹⁰ where one or more donor sites can dissociate from the metal centre, and indenyl ligands which can undergo facile “ring slip” hapticity changes between η^5 and η^3 coordination modes (Scheme 4.1).^{11–13}

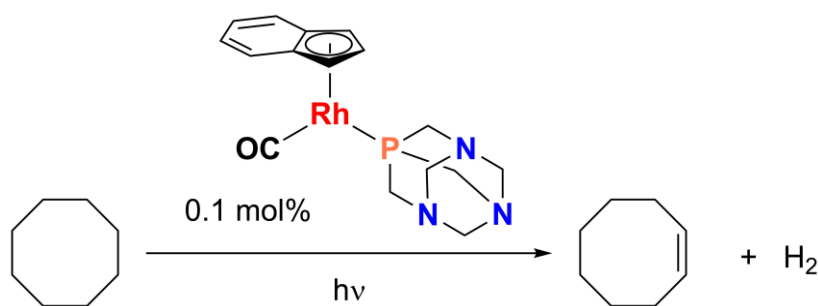


Scheme 4.1: “Ring slippage” of indenyl ligands.

This indenyl effect has been observed for metal–indenyl complexes across the periodic table and exploited in their further coordination chemistry and applications in catalysis.¹² In the specific context of rhodium catalysed reactions, some of the first studies using rhodium–indenyl complexes investigated the [2+2+2] cycloaddition of alkynes.^{14,15} These studies showed that indenyl complexes had enhanced activity compared to their cyclopentadienyl analogues and it was proposed that the indenyl effect allowed for an extra ligand to coordinate

to the metal centre. Computational methods were later used to compare the mechanisms of these complexes, finding that the highest energy barrier in the mechanism was the coordination of the third equivalent of alkyne.¹⁶ The more facile slipping of the indenyl ligand lowers this barrier by 34% (43.2 to 28.5 kcal mol⁻¹), which is in agreement with experimental studies showing an increased catalyst turnover number and activity at lower temperatures.¹²

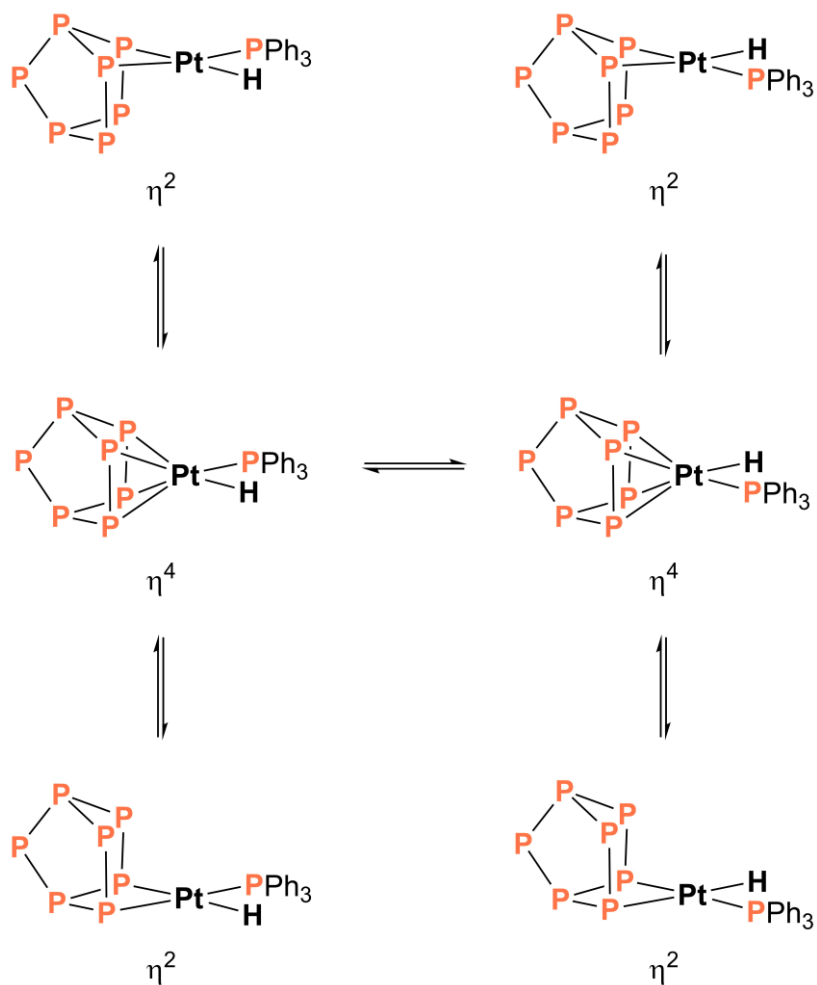
The complex [(Ind)Rh(CO)(PTA)] (Ind = indenyl; PTA = 1,3,5-triaza-7-phosphaadamantane) has been employed in the acceptorless dehydrogenation of alkanes under photolytic conditions (Scheme 4.2).¹⁷



Scheme 4.2: Acceptorless dehydrogenation of cyclooctane using a rhodium indenyl complex.¹⁷

Compared to the cyclopentadienyl analogue, [(Cp)Rh(CO)(PTA)] (Cp = cyclopentadienyl), both conversion and turnover frequency were increased from 20.4% to 33.6% and 34 h⁻¹ to 56 h⁻¹, respectively, in favour of the indenyl complex. Once again, this serves to highlight the utility of a ligand which can undergo facile changes in hapticity.^{12,17}

Such processes are also known in the field of Zintl clusters. In 2000, Eichhorn and co-workers reported the dynamic exchange present in the clusters [Pt(H)(PPh₃){E₇}]²⁻ (E = P, As).¹⁸ Using 2D EXSY NMR spectroscopy, they were able to propose an $\eta^2 - \eta^4$ mechanism, at the platinum–cluster interface (Scheme 4.3).



Scheme 4.3: Exchange pathways in $[\text{Pt}(\text{H})(\text{PPh}_3)\{\text{P}_7\}]^{2-}$, reproduced from Kesanli et al.¹⁸

The dynamic exchange between η^4 and η^5 coordination modes in $[\text{M}(\text{CO})_3\{\text{E}_9\}]^{4-}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{E} = \text{Sn}, \text{Pb}$) Zintl clusters has also been studied through spectroscopic and computational methods.^{19,20} In studies by Kesanli et al., crystalline samples of $[\text{W}(\text{CO})_3\{\eta^4\text{-Sn}_9\}]^{4-}$ and $[\text{W}(\text{CO})_3\{\eta^5\text{-Sn}_9\}]^{4-}$ were mixed and dissolved in *N,N*-dimethylformamide (DMF), before studying in solution by ^{13}C and ^{119}Sn NMR spectroscopy. This produced a single set of ^{119}Sn NMR resonances and a single resonance for the carbonyl carbon atoms, indicating a fast dynamic process on the NMR timescale between the two hapticities.²⁰

Analogous processes on metallated $[\text{Ge}_9(\text{Hyp})_3]^-$ ($\text{Hyp} = \text{Si}(\text{SiMe}_3)_3$) clusters are also known. An example of this is the solution behaviour of $[\text{M}(\text{CO})_3\{\eta^5\text{-Ge}_9(\text{Hyp})_3\}]^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), where despite the C_s solid-state symmetry, all three hypersilyl substituents are equivalent on

the NMR timescale. This indicates that low energy fluxional pathways are accessible on the $[\text{Ge}_9(\text{Hyp})_3]^-$ support in solution.²¹

Following the results of Chapter 3, where dissociation of COD was found to limit the rate of hydrogenation catalysis (increasing the barrier for the transformation by ca. 13 kcal mol⁻¹), we proposed that a hapticity change could lower this energy. Inspired by the facile hapticity changes in Zintl cluster supported transition metal complexes, and the advantages of such processes in established organometallic systems, we aimed to synthesise new clusters exhibiting these properties in the pursuit of more efficient catalysts.

4.2. Chapter Outline

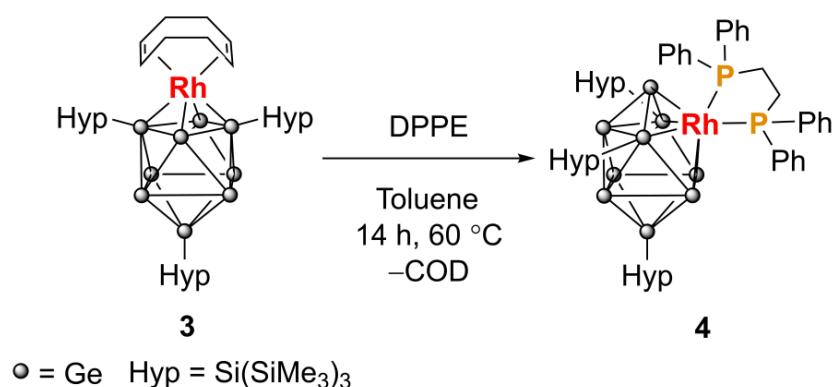
This chapter describes how the Zintl cluster $[\text{Rh}(\text{COD})\text{Ge}_9(\text{Hyp})_3]$ (**3**) was modified at the rhodium centre by ligand substitution chemistry to produce clusters $[\text{Rh}(\text{L})\{\text{Ge}_9(\text{Hyp})_3\}]$ (L = phosphine, carbene, alkyne). All reactions resulted in coordination mode changes at the Rh–cluster interface. Depending on the ligand in question, these reactions can be used to access coordinatively unsaturated rhodium centres. These clusters were then explored in terms of their coordination chemistry and aptitude towards H–H and C–H bond activation reactions. Employment of *parahydrogen* and density functional theory were used to gain further insights into the bond activation processes.

4.3. $[\text{Rh}(\text{DPPE})\{\eta^5\text{-Ge}_9(\text{Hyp})_3\}]$ (**4**)

To explore the coordination chemistry of **3**, which bears the “L₂ type” ligand 1,5-cyclooctadiene (COD) bound in an η^4 fashion,²² 1,2-bis(diphenylphosphino)ethane (DPPE) was added to displace the COD ligand without affecting the electron count. Dissolving equimolar quantities of compound **3** and DPPE in benzene-*d*₆ and heating the solution to reflux in an NMR tube overnight under a static vacuum resulted in the formation of a new doublet resonance in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 43.8 ppm with a coupling constant $^1J_{\text{P-}}$

$\nu_{\text{Rh}} = 160.4$ Hz, due to coupling with ^{103}Rh ($I = \frac{1}{2}$, 100%). The two signals relating to the inequivalent hypersilyl protons observed for compound **3** converged to a single peak, and signals relating to free COD were observed in the ^1H NMR spectrum. This data suggested that a significant fluxional process was occurring. Notably, both of the major and minor components observed in the ^1H NMR spectrum for **3** converted to the single product compound **4**.

4.3.1. Synthesis of Compound **4**



Scheme 4.4: Preparation of $[\text{Rh}(\text{DPPE})\{\eta^5\text{-Ge}_9(\text{Hyp})_3\}]$ (**4**) (DPPE = 1,2-bis(diphenylphosphino)ethane).

On a preparative scale, the reaction was performed in toluene at 60 °C overnight. The solution was dried *in vacuo* and extracted with *n*-pentane. The dark red pentane solution was then concentrated and cooled to –80 °C to yield dark red crystals suitable for X-ray crystallography. Although a typical crystalline isolated yield was 65 %, conversion by NMR spectroscopy appears to be quantitative.

4.3.2. Single Crystal X-ray Structure of Compound **4**

Single crystal X-ray diffraction revealed that compound **4**, like precursor **3**, adopts a bicapped square antiprismatic geometry, however the coordination of the rhodium centre to the cluster support has changed from η^4 to η^5 (Figure 4.1).

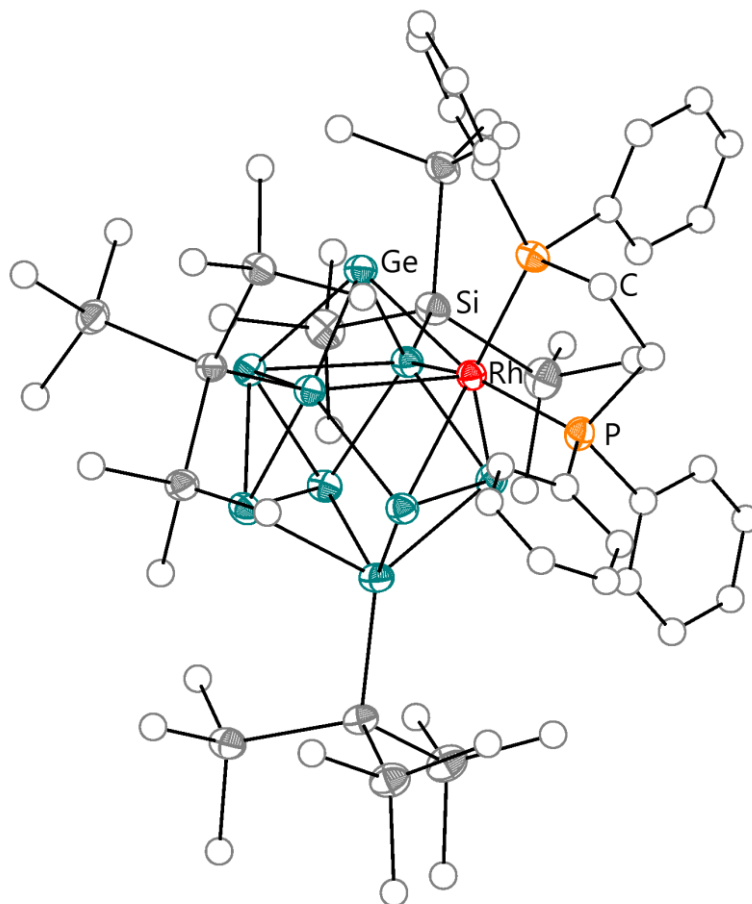
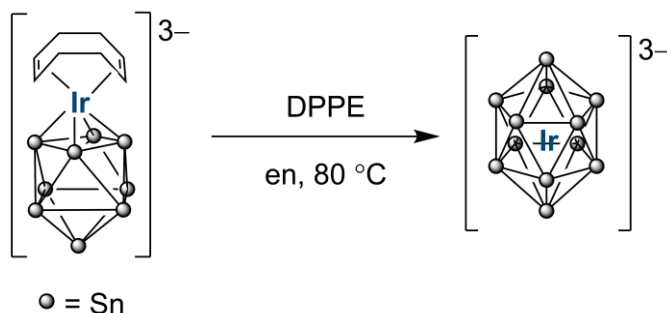


Figure 4.1: Single crystal X-ray structure of compound **4**. Anisotropic displacement ellipsoids set at 50% probability. All carbon atoms are pictured as spheres of an arbitrary radius. Hydrogen atoms are omitted for clarity.

In comparison to the synthesis of $[\text{Ir}@\text{Sn}_{12}]^{3-}$, which was produced by heating the valence isoelectronic $[\text{Ir}(\text{COD})\{\eta^4\text{-Sn}_9\}]^{3-}$ in the presence of DPPE (Scheme 4.5),²³ this reaction builds on the results in Chapter 2 to give further evidence that substituted cages cannot form endohedral clusters and are less prone to fragmentation/reformation pathways.



Scheme 4.5: Synthesis of $[\text{Ir}@\text{Sn}_{12}]^{3-}$ (en = 1,2-ethylenediamine; DPPE = 1,2-diphenylphosphinoethane).^{23,24}

Compound **4** is a *closo* 10-vertex deltahedron with 22 electrons available for cluster bonding ($[\text{Rh}(\text{DPPE})] = 1 \text{ e}^-$, $\text{Ge} = 2 \text{ e}^-$, $\text{Ge}(\text{Hyp}) = 3 \text{ e}^-$) with C_s cluster symmetry. This is analogous to compound **3** since metal–cluster connectivity does not change the electron count of a fragment.²⁵

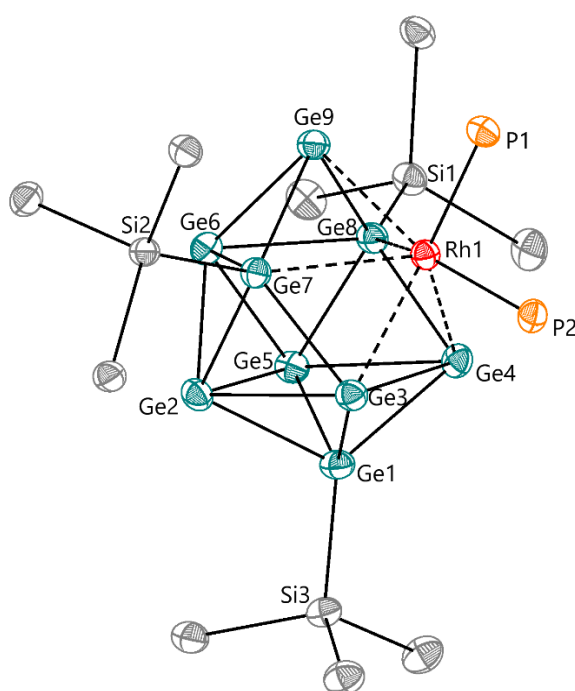
The rhodium atom is in an η^5 coordination mode with the germanium support and is isostructural and valence isoelectronic to literature reported compounds such as the $[\text{M}(\text{CO})_3\{\eta^5\text{-Ge}_9(\text{Hyp})_3\}]^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) series reported by Schnepf.^{21,26}

The structural rearrangement between compounds **3** and **4** shows that although the number of electrons available for cluster bonding is unchanged, the germanium support is structurally responsive to accommodate the steric and electronic demands of the rhodium centre. This species can be compared to the metalloborane $[\text{Rh}(\text{CO})_3\{\text{B}_9\text{H}_9\}]^-$, which is also a 10-vertex cluster with 22 electrons available for cluster bonding.²⁷

Whilst $\eta^4 - \eta^5$ equilibria are documented in the chemistry of $[\text{M}(\text{CO})_3\{\text{Sn}_9\}]^{4-}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) clusters,²⁰ this represents the first example of ligand exchange induced isomerisation at a functionalised Zintl cluster.²⁸ The Rh–P distances in the Rh(DPPE) fragment (mean distance 2.321 Å) (Table 4.1) are typical for Rh(DPPE) complexes when compared to the literature (Table 4.2). For example, $[\text{Rh}(\text{DPPE})(\text{NBD})][\text{BF}_4]$, which exhibits a mean Rh–P distance of

2.279 Å.²⁹ Interestingly, the two Rh–P distances differ from each other by 0.07 Å, consistent with *trans* influence from the different number of germanium atoms on the cage *trans* to each phosphorus atom.

Table 4.1: Selected crystallographic bond lengths (Å) of compound **4**. A truncated molecular model is included as a key.



Bond	Distance (Å)
Ge3–Rh1	2.596(1)
Ge4–Rh1	2.561(1)
Ge7–Rh1	2.743(1)
Ge8–Rh1	2.837(1)
Ge9–Rh1	2.672(1)
Rh1–P1	2.356(1)
Rh1–P2	2.286(1)
Ge1–Si1	2.395(1)
Ge7–Si5	2.416(1)
Ge8–Si9	2.429(1)

4.3.3. Nuclear Magnetic Resonance Spectroscopic Analysis of Compound **4**

Analysis of a crystalline sample of compound **4** dissolved in benzene-*d*₆ by ¹H NMR spectroscopy indicates a single hypersilyl environment at 0.46 ppm (81 H). In addition, a doublet resonance is observed at 1.68 ppm, relating to the DPPE ethane bridge and three resonances relating to the DPPE phenyl groups were observed in the aromatic region. The ¹³C{¹H} NMR spectrum was consistent with the presence of a single hypersilyl environment. The difference between solid-state and solution symmetry is similar to that of the isostructural

$[\text{M}(\text{CO})_3\{\eta^5\text{-Ge}_9(\text{Hyp})_3\}]^-$,²¹ where the ^1H NMR signals relating to the three hypersilyl groups are also equivalent (0.30 ppm). Dissociative processes involving the rapid and reversible formation of the separated ion pair $[\text{Rh}(\text{DPPE})(\eta^6\text{-arene})][\text{Ge}_9(\text{Hyp})_3]$, which would also have three equivalent hypersilyl environments, were discounted due to the observation of compound **4** by NMR spectroscopy in aliphatic solvents such as cyclohexane.

Variable temperature ^1H NMR experiments (193 K to 298 K) in toluene- d_8 were performed in attempt to slow down any fluxional processes. This resulted in negligible change to the hypersilyl chemical shifts, suggesting a very low barrier for this process. At 193 K, significant precipitation occurred (see Chapter 7).

$^{29}\text{Si}/^1\text{H}$ HMBC NMR experiments (Figure 4.2) showed two ^{29}Si environments with two cross peaks (−84.38 and −9.76 ppm) corresponding with a $\text{Si}(\text{SiMe}_3)_3$ and a $\text{Si}(\text{SiMe}_3)_2$ environments, respectively. This is consistent with three equivalent hypersilyl substituents.

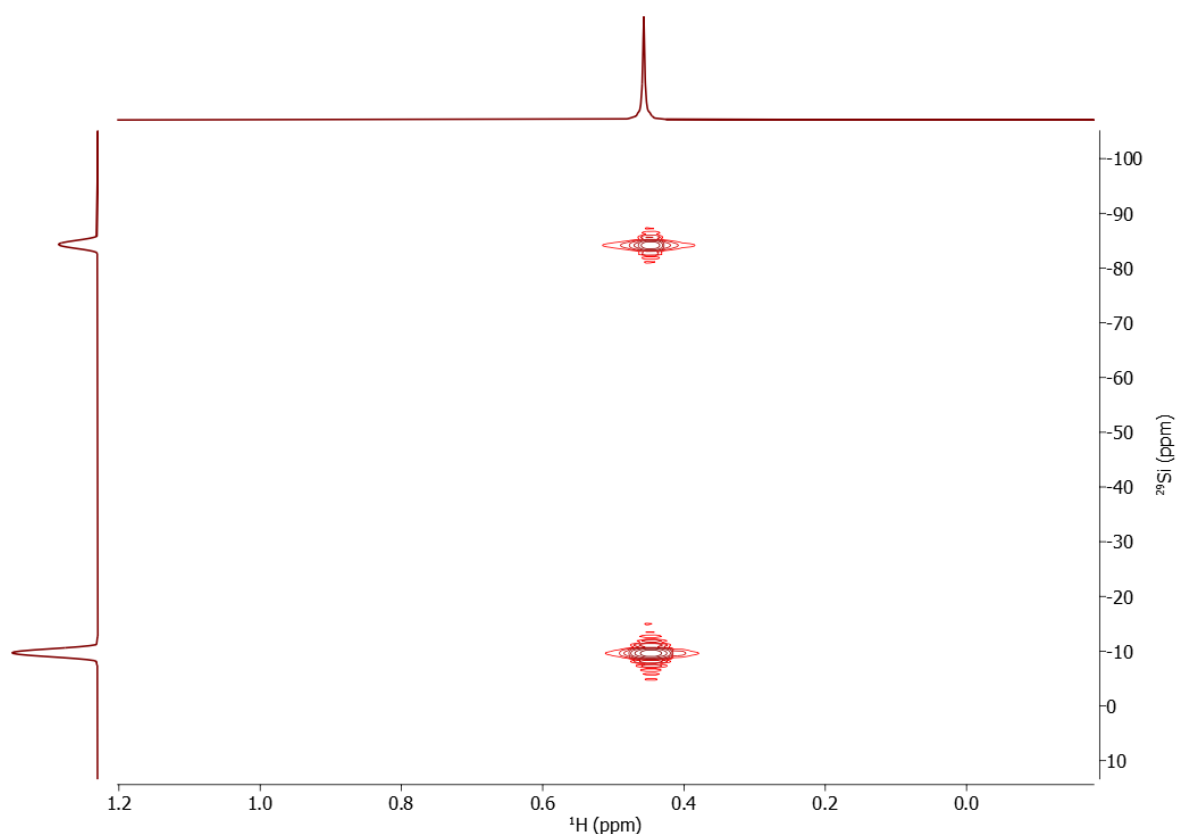


Figure 4.2: $^{29}\text{Si}/^1\text{H}$ HMBC NMR spectrum (C_6D_6 , 298 K, 79.5 MHz) of compound **4**.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of compound **4** exhibits a single doublet resonance at 43.85 ppm with a coupling constant $^1J_{\text{P-Rh}} = 160.4$ Hz, consistent with those of related compounds such as 2-Ph-*closo*-1,2,3,4-Rh(dppe) $\text{C}_3\text{B}_7\text{H}_9$ (57.5 ppm; $^1J_{\text{P-Rh}} = 166$ Hz).³⁰ This indicates that the DPPE is bound to the rhodium in solution and that both phosphorus atoms are magnetically equivalent on the NMR timescale. Comparison of this signal to fully characterised $[\text{Rh}(\text{DPPE})(\eta^6\text{-benzene})]^+$ complexes in the literature, which exhibit $^{31}\text{P}\{^1\text{H}\}$ resonances in the range of 75–77 ppm with coupling constants of $^1J_{\text{P-Rh}} = 203\text{--}205$ Hz further supports that it is not a separated ion pair.³¹

Comparing the $^1J_{\text{P-Rh}}$ coupling constants and mean bond lengths with other rhodium(I) DPPE complexes in the literature (Table 4.2), one can see that although the structure is fluxional and in an atypical ligand field, it has comparable metrics to established systems.

Table 4.2: Comparison of mean Rh–P distances and $^1J_{\text{P-Rh}}$ coupling constants for selected (L)Rh(DPPE) complexes. ^a[BF₄], ^b[B(Ar^F)₄]. Cp = cyclopentadienyl; Ar^F = 3,5-(CF₃)₂C₆H₃; NBD = norbornadiene; py = pyridine.^{30–35}

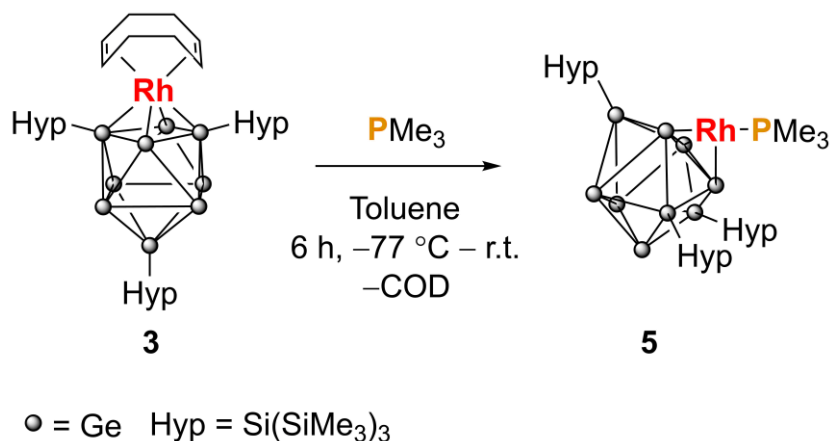
Compound	Rh–P Mean Distance (Å)	$^1J_{\text{P-Rh}}$ (Hz)
[Rh(DPPE) ₂][BF ₄]	2.303	133
[Rh(DPPE)-3-(py)- <i>closo</i> -1,2-SB ₉ H ₈]	2.26	150
[Rh(DPPE)(NBD)] ⁺	2.28 ^a	157 ^b
4	2.32	160
Rh(DPPE)-2-Ph- <i>closo</i> -1,2,3,4-C ₃ B ₇ H ₉	2.26	166
[Rh(DPPE)(η ⁶ -benzene)][BF ₄]	2.22	203
[(Cp)Rh(DPPE)]	N.A.	220

4.4. [Rh(PMe₃){η³-Ge₉(Hyp)₃}] (**5**)

4.4.1. Synthesis of Compound **5**

In an effort to access into the low coordinate species postulated in Chapter 3, one equivalent of a PMe₃ solution in benzene-*d*₆ was vacuum transferred to solid compound **3**, before thawing under an atmosphere of H₂ in an NMR tube. This resulted in a small amount of decomposition. It was found that, as with the synthesis of compound **4**, the two ¹H NMR resonances arising from the hypersilyl environments of compound **3** converged to a single resonance. Resonances for free COD were observed. In the ³¹P{¹H} NMR spectrum, a new doublet resonance was observed at –13.47 ppm, ($^1J_{\text{P-Rh}}$ = 210.3 Hz), indicating the formation of a rhodium phosphine complex.

On a preparative scale, a toluene solution of PMe_3 was added to a cooled ($-77\text{ }^\circ\text{C}$) solution of compound **3** dropwise under argon. This produced a product with identical ^1H and ^{31}P NMR signals to the aforementioned NMR tube scale experiment. This compound was characterised as $[\text{Rh}(\text{PMe}_3)\{\text{Ge}_9(\text{Hyp})_3\}]$ (**5**) (Scheme 4.6).



Scheme 4.6: Preparation of $[\text{Rh}(\text{PMe}_3)\{\eta^3\text{-Ge}_9(\text{Hyp})_3\}]$ (**5**).

The brown solution was dried *in vacuo* to remove COD and any excess PMe_3 before extracting in *n*-hexane and lyophilizing from benzene (typical isolated yield = 93%). The resulting brown powder is suitable for further synthesis, though care must be taken as even it will spontaneously combust on contact with air. Crystals suitable for single crystal X-ray diffraction were grown by extraction into *n*-hexane and cooling to $-40\text{ }^\circ\text{C}$ for two days.

4.4.2. Nuclear Magnetic Resonance Spectroscopic Analysis of Compound **5**

Analysis of a crystalline sample of compound **5**, which was dissolved in benzene- d_6 , by ^1H NMR spectroscopy indicates a single hypersilyl environment at 0.51 ppm, in addition to a doublet at 1.13 ppm, relating to the coordinated PMe_3 ligand. $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy is consistent with the presence of a single hypersilyl environment which, as for compound **4**, suggests a highly fluxional species. $^{29}\text{Si}/^1\text{H}$ HMBC NMR spectroscopy (Figure 4.3) shows two ^{29}Si environments with two cross peaks, as expected for the equivalent hypersilyl substituents. The ^{29}Si chemical shifts are similar to those of **4**.

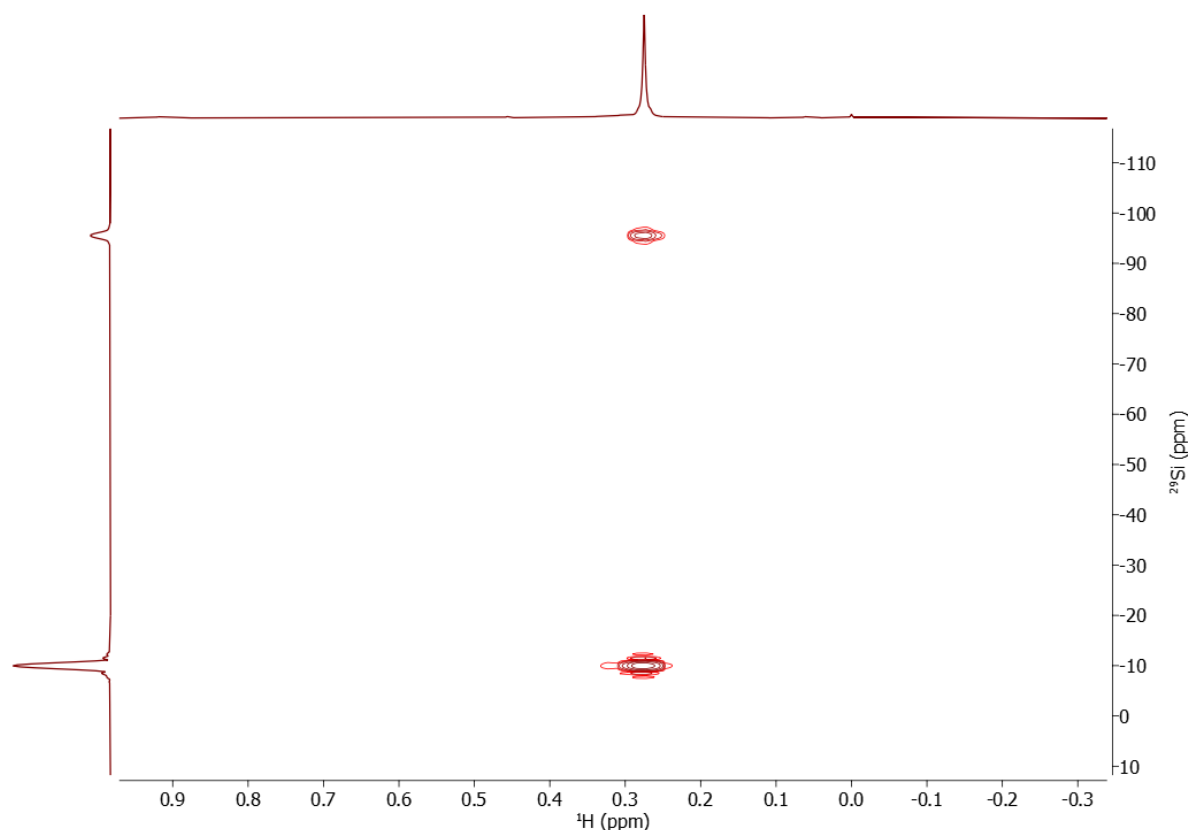


Figure 4.3: $^{29}\text{Si}/^1\text{H}$ HMBC NMR spectrum (C_6D_6 , 298 K, 79.5 MHz) of compound **5**.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a doublet resonance at -13.47 ppm ($^1J_{\text{P-Rh}} = 210.3$ Hz), comparable to other rhodium(I) trimethylphosphine complexes such as $[(\text{Cp}^*)\text{Rh}(\text{PMe}_3)_2]$ ($\text{Cp}^* = \text{pentamethylcyclopentadienyl}$; $^1J_{\text{P-Rh}} = 216$ Hz).³⁶

4.4.3. Single Crystal X-ray Structure of Compound **5**

Single crystal X-ray diffraction revealed that compound **5** adopts a *hypercloso* cluster geometry with C_s symmetry.²⁸ The rhodium centre is coordinated in an η^3 fashion to the cluster support, and is now coordinatively unsaturated (Figure 4.4). Comparing to **4**, which resembles $[\text{Rh}(\text{CO})_3\{\text{B}_9\text{H}_9\}]^-$, the geometry of **5** resembles $[\text{Rh}(\text{CO})_3\{\text{B}_9\text{H}_9\}]^+$, where the removal of an electron pair affords a system with n skeletal electron pairs (as opposed to $n+1$ for a *closo* cluster) resulting in a similar topological distortion.²⁷ The reverse of this transformation has also been observed in the formation of *closo*-(PET_3) $_3\text{RuC}_2\text{B}_7\text{H}_9$ from

hypercloso-(PEt₃)₂RuC₂B₇H₉ on addition of PEt₃, which donates an extra skeletal electron pair to the system.^{37,38}

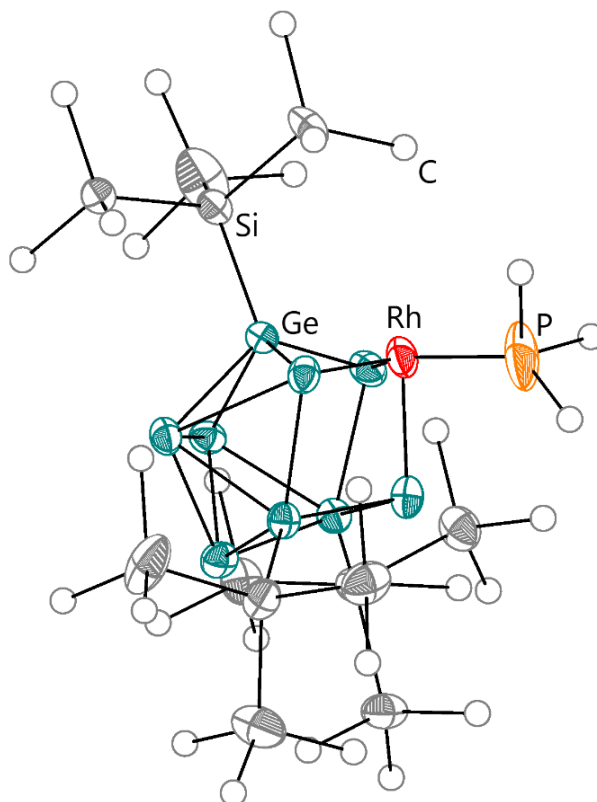
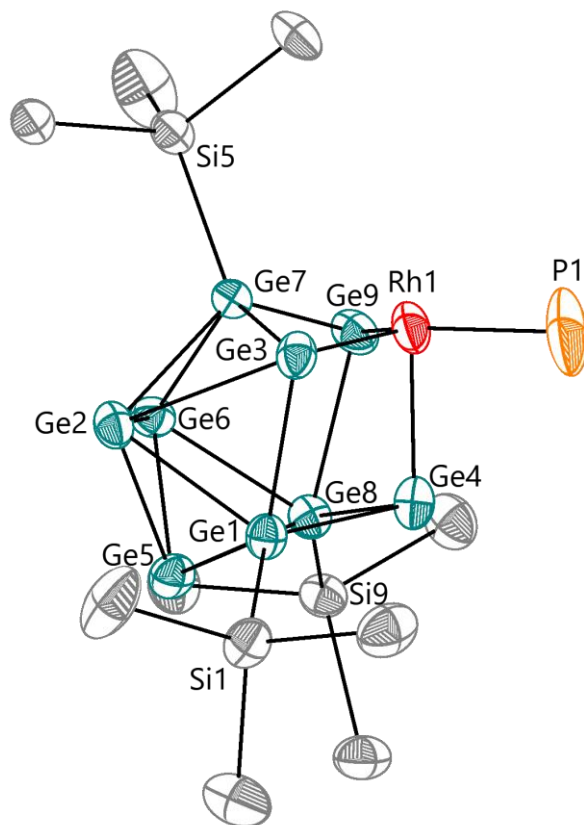


Figure 4.4: Single crystal X-ray structure of compound **5**. Anisotropic displacement ellipsoids set at 50% probability. All carbon atoms are pictured as spheres of an arbitrary radius. Hydrogen atoms are omitted for clarity.

Though the asymmetric unit contains one crystallographically unique cluster, two disordered components were modelled, accounting for two orientations of the cluster (related by rotation) with relative occupancies of 62% and 38%. In the major component, the three Rh–Ge distances are in the range 2.394(8) – 2.433(8) Å, with a close Rh–Ge contact of 2.517(7) Å (Table 4.3). Interestingly, this contact is significantly shorter than the range of the two longer Rh–Ge distances in the η^5 cluster **4** (2.743(1) and 2.837(1) Å). One could therefore describe this as an alternative η^4 coordination mode, though will be described as η^3 for consistency with literature examples of related *hypercloso* clusters.^{28,39}

Table 4.3: Selected crystallographic bond lengths (Å) of compound 5 comparing the two disorder components in the asymmetric unit. A truncated molecular model is included as a key.

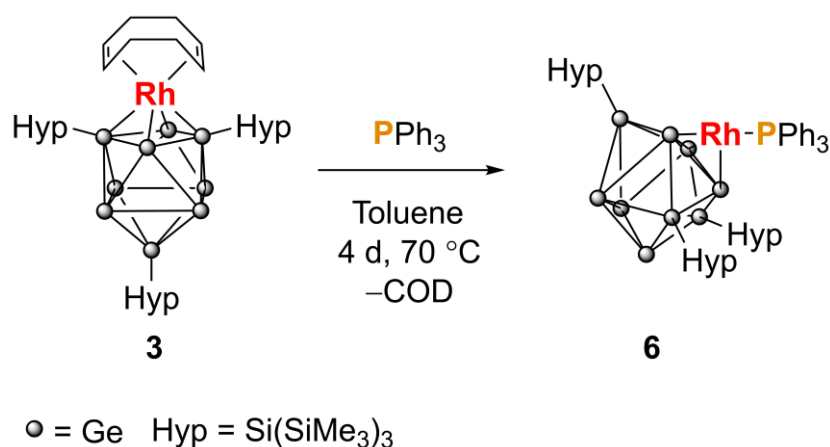


Bond	Major Component (Å)	Bond	Minor Component (Å)
Ge3–Rh1	2.415(3)	Ge3A–Rh1A	2.378(12)
Ge4–Rh1	2.433(8)	Ge4A–Rh1A	2.434(15)
Ge7–Rh1	2.517 (7)	Ge7A–Rh1A	2.502(11)
Ge9–Rh1	2.394(8)	Ge9A–Rh1A	2.469(6)
Rh1–P1	2.299(2)	Rh1A–P1	2.446(18)
Ge1–Si1	2.537(7)	Ge1A–Si9	2.395(10)
Ge7–Si5	2.454(5)	Ge7A–Si1	2.466(10)
Ge8–Si9	2.389(6)	Ge8A–Si5	2.258(9)

4.5. [Rh(PPh₃){η³-Ge₉(Hyp)₃}] (**6**)

Following the synthesis of compound **5**, the analogous triphenylphosphine ligated cluster was targeted. Due to reduced σ-donation and increased steric hindrance, the triphenylphosphine ligand is more labile than its trimethyl analogue.^{40–42} We reasoned that this would provide the opportunity to allow coordination of substrates by both fluctuation at the rhodium–cluster interface and also by the reversible coordination of PPh₃.^{40–44}

4.5.1. Synthesis of Compound **6**



Scheme 4.7: Preparation of [Rh(PPh₃){η³-Ge₉(Hyp)₃}] (**6**).

Toluene was added to an equimolar mixture of compound **3** and triphenylphosphine at room temperature, and the brown solution was stirred for 3 hours before heating to 70 °C for 4 days. The solvent and COD were removed *in vacuo* and the product was extracted in *n*-pentane, dried *in vacuo* and lyophilized from benzene to yield compound **6** as a brown powder (typical yields ~84%). Fine dry powders of compound **6** ignite spontaneously in air. Black-brown crystals suitable for X-ray crystallography were obtained by dissolving the solid in *n*-hexane and cooling to –40 °C.

Given that high temperatures are typically required for alkane dehydrogenation (see Chapter 1.1.), any viable catalyst must be stable under such harsh conditions. Thermal stability tests

on compound **6** were performed either in *n*-dodecane solution or in the solid-state. These revealed that compound **6** was stable for over 10 hours in solution at 190 °C (or 240 °C for over a minute in the solid-state), as determined by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Unfortunately, GC-MS analysis of the dodecane solution showed no indication of solvent dehydrogenation, such as traces of unsaturated alkanes.

4.5.2. Nuclear Magnetic Resonance Spectroscopic Analysis of Compound **6**

As in the case of compound **5**, the ^1H NMR spectrum of compound **6** exhibits one resonance (0.46 ppm) relating to the 81 equivalent hypersilyl protons, indicating again a fluxional process which is fast on the NMR timescale. Interestingly, this is the same chemical shift as in compound **4**, however the ^{29}Si signals, obtained by $^{29}\text{Si}/^1\text{H}$ HMBC NMR spectroscopy do differ slightly (−94.2, −9.6 ppm). A new doublet resonance at 49.29 ppm ($^1J_{\text{P-Rh}} = 214$ Hz) was observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. This compares favourably to other examples of rhodium(I) triphenylphosphine complexes such as $[(\text{Cp})\text{Rh}(\text{PPh}_3)_2]$ ($^1J_{\text{P-Rh}} = 222$ Hz) and $[(\text{Cp})\text{Rh}(\text{PPh}_3)(\eta^2\text{-C}_2\text{H}_4)]$ ($^1J_{\text{P-Rh}} = 210$ Hz).^{45,46}

4.5.3. Single Crystal X-ray Structure of Compound **6**

Although black-brown crystals of compound **6** could be grown from concentrated *n*-hexane solutions, due to a lack of high angle diffraction, the data was of insufficient quality for a detailed description of the bond lengths and angles. Nevertheless, a preliminary structure (Figure 4.5) can be obtained which qualitatively shows a similar geometry to that exhibited by compound **5**, indicating that the preference for an η^3 coordination mode at the rhodium–cluster interface in the solid-state is controlled by the nature of the Rh(L) fragment.

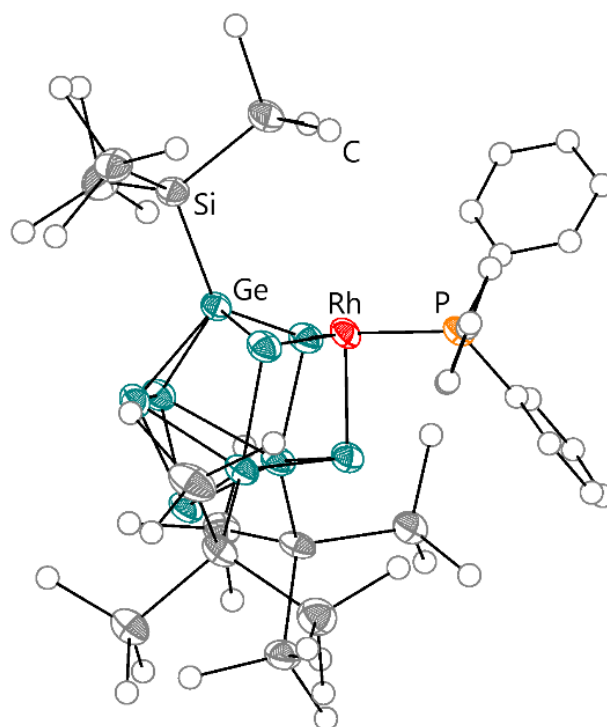


Figure 4.5: Single crystal X-ray structure of compound **6**.

4.5.4. Density Functional Theory Analysis of Compound **6**

The fluxional behaviour of compound **6** was probed using density functional theory (DFT) at the BP86/SDD/6-31g(d,p)//Def2-TZVP level of theory.^{47–55} The optimised ground state geometry retains the *hypercloso* C_s symmetry observed in the solid-state structure. From this, a potential energy surface scan calculation was performed, exploring the effect of elongating the Rh–Ge distance highlighted by a dotted line in Figure 4.6, Left. Compounds **5** and **6** produced qualitatively similar results however, the increased size of the phosphine ligand in compound **6** allowed for a more defined potential energy plot.

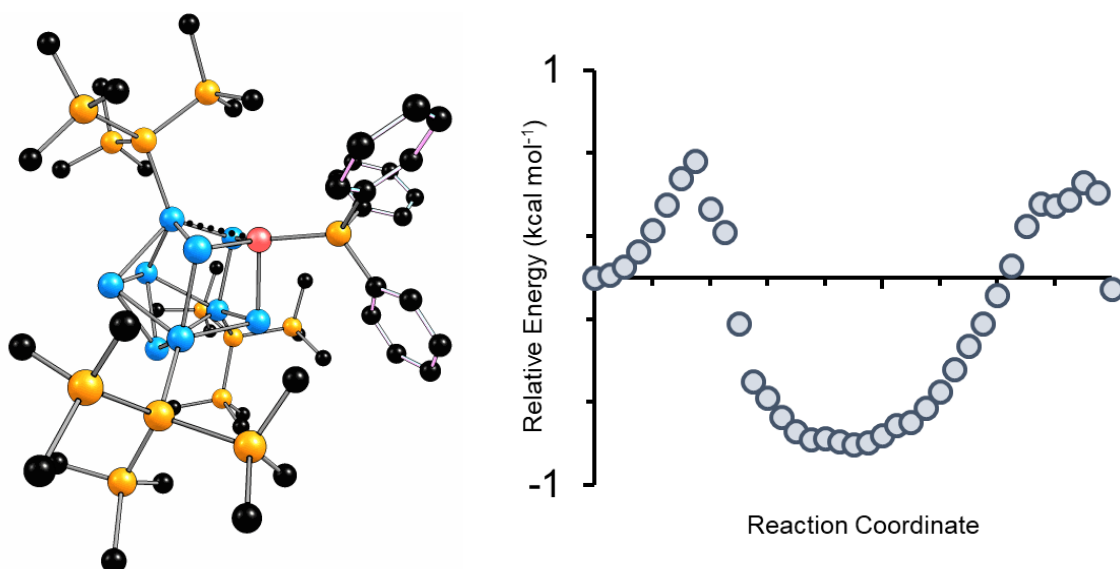
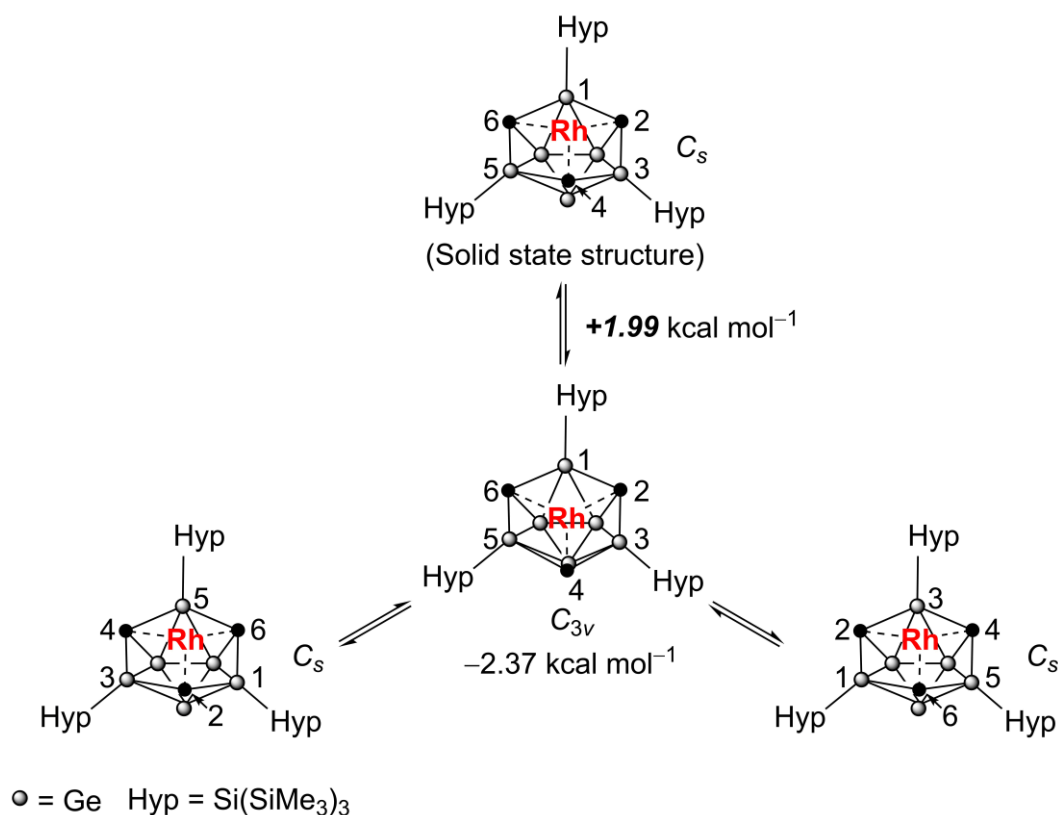


Figure 4.6, Left: DFT optimised geometry of compound **6** (BP86/SDD/6-31g(d,p)), highlighting the variable Rh–Ge distance; Right: Potential energy surface plot (BP86/SDD/6-31g(d,p)) on elongating the variable distance. Energies relative to the optimised solid-state structure of compound **6**.

Figure 4.6, Right shows a plot of total self-consistent field (SCF) energy relative to the optimised solid-state structure of compound **6** as a function of the highlighted Rh–Ge interatomic distance. This exhibits three notable features: two approximately equal maxima, indicative of possible transition states, and a minimum separating the two maxima. Optimisation of the maximum stationary point converged to a geometry with a relative energy of $+1.99 \text{ kcal mol}^{-1}$ above the optimised geometry of compound **6**. This was subsequently characterised using a frequency calculation to be a transition state by one negative eigenvalue (-14.9 cm^{-1}). Optimisation of the two intrinsic reaction coordinate (IRC) displacements reproduced the starting geometry and produced the C_{3v} symmetric minimum stationary point with comparable energies. The minimum was also optimised to produce a C_{3v} symmetric geometry with a relative energy of $-2.37 \text{ kcal mol}^{-1}$ and no negative eigenvalues, indicating an intermediate that is lower in energy to that observed in the solid-state. Interestingly, this

geometry is isostructural to the known *hypercloso* Zintl clusters $[\text{Ni}(\text{L})\{\eta^3\text{-Ni@Ge}_9\}]^{2-}$ ($\text{L} = \text{CO}, \text{PPh}_3$) and $[\text{Pd}(\text{PPh}_3)\{\eta^3\text{-Ni@Ge}_9\}]^{2-}$.^{39,56,57}



Scheme 4.8: DFT calculated fluxional processes for compound **6** (BP86-D3/Def2-TZVP) showing how three isomers of the solid-state structure can be linked via a single intermediate. Coordinated PPh_3 omitted for clarity.

This intermediate links all three possible isomers (Scheme 4.8), and the low energy barriers accounts for the C_{3v} symmetry observed in solution by NMR spectroscopy. Since the differences in energy are very small, the C_s symmetry observed in the solid-state could be due to crystal packing effects, and are also within the error of DFT.

Inspection of the frontier molecular orbitals for the C_{3v} symmetric structure of compound **6** reveals that the HOMO is a fully occupied, doubly degenerate set of e orbitals, whereas the LUMO an a_1 symmetric orbital (Figure 4.7).

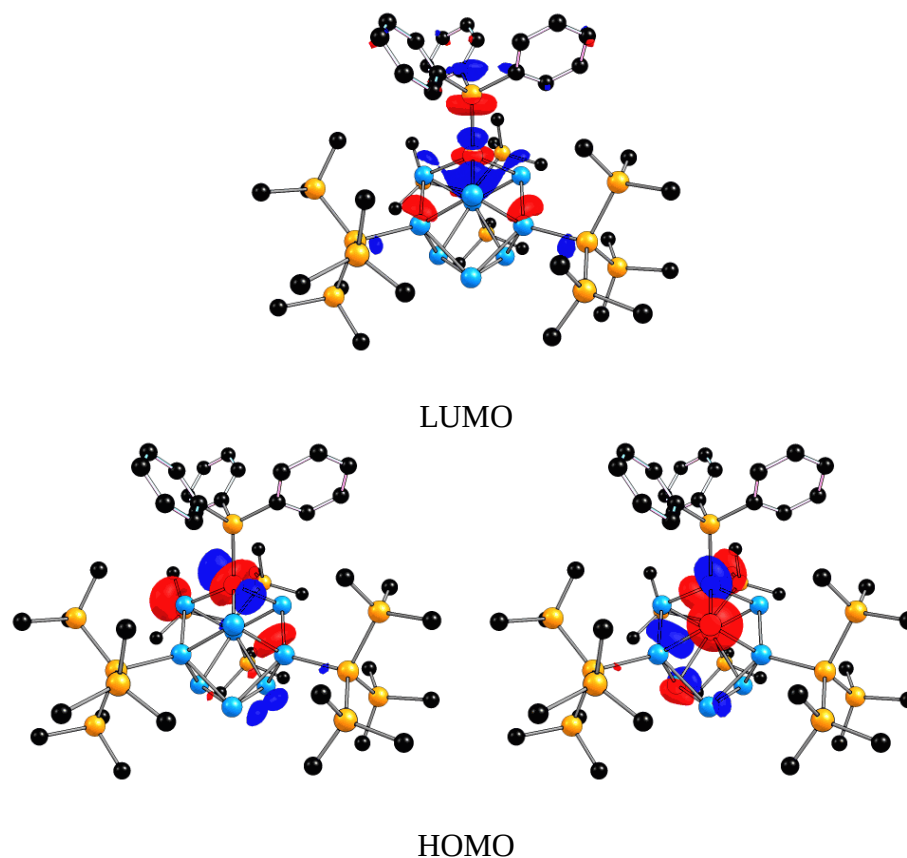


Figure 4.7: DFT calculated molecular orbitals (BP86/Def2-TZVP, isovalue 0.04) of the calculated C_{3v} symmetric geometry.

4.5.5. Ligand Exchange Reactions

In order to assess the lability of the triphenylphosphine ligand, phosphines DPPE, PMePh_2 and $\text{P}(p\text{-tol})_3$ were added to compound **6**, dissolved in benzene- d_6 (Scheme 4.9). In the case of DPPE, almost quantitative conversion to compound **4** and free PPh_3 was observed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy at room temperature within three hours (Figure 4.8).

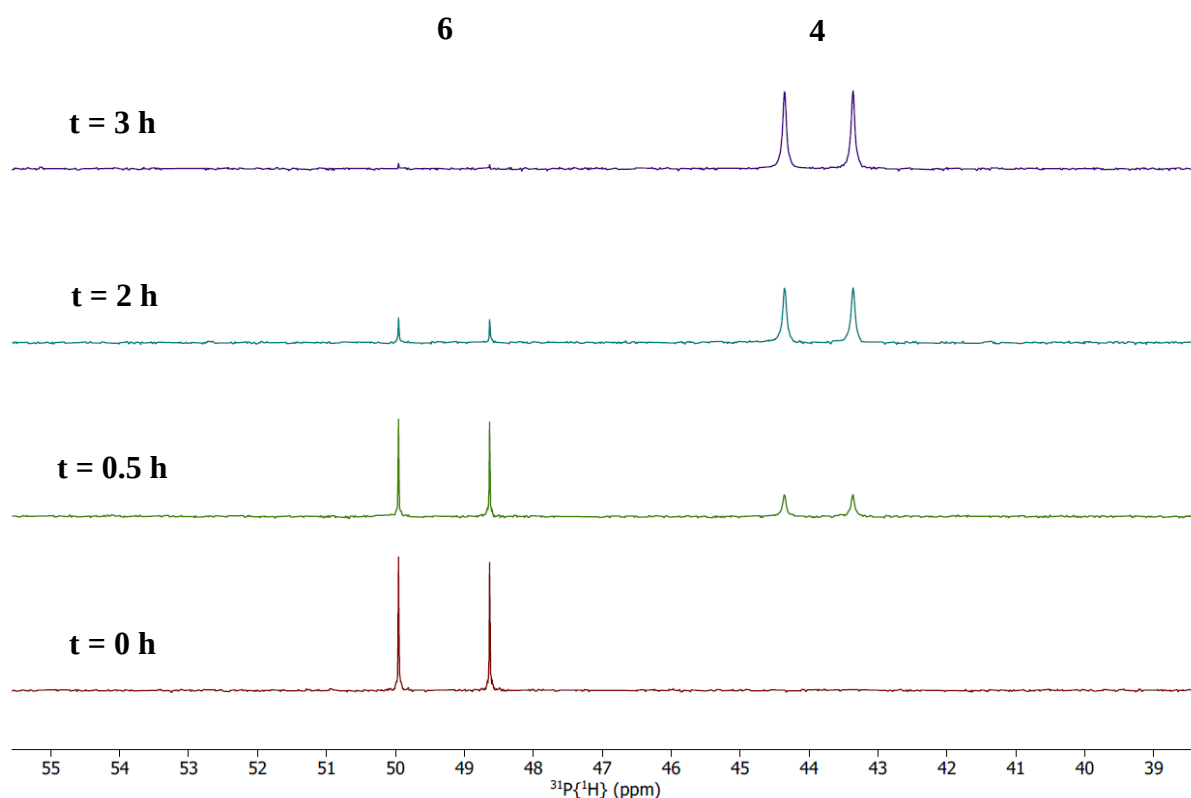
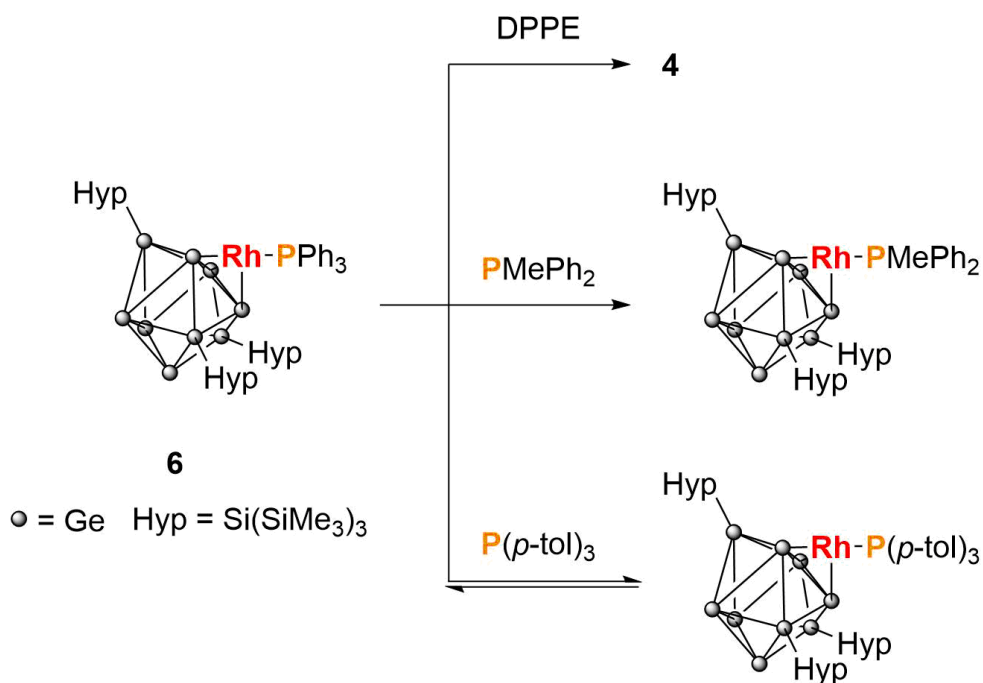


Figure 4.8: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (C_6D_6 , 298 K, 162 MHz) showing the conversion of compound **6** to compound **4** on addition of DPPE.

This is in contrast to the synthesis of compound **4** from compound **3**, which requires elevated temperatures and long reaction times. Since the facile reaction of compound **6** with DPPE may be justified by the chelate effect driving reactivity, the monophosphine PMePh_2 was next employed. This was found to quantitatively displace PPh_3 immediately at room temperature to produce the compound $[\text{Rh}(\text{PMePh}_2)\{\text{Ge}_9(\text{Hyp})_3\}]$, as evidenced by a new ^1H NMR resonance relating to the hypersilyl substituents at 0.48 ppm, as well as a doublet of doublet resonance ($^2J_{\text{H-P}} = 8.2$ Hz; $^3J_{\text{H-Rh}} = 1.8$ Hz) with a relative integration of 3H. A new doublet resonance was observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 22.72 ppm ($^1J_{\text{P-Rh}} = 208.0$ Hz).



Scheme 4.9: Summary of NMR scale ligand exchange reactions on reaction of compound **6** with phosphines.

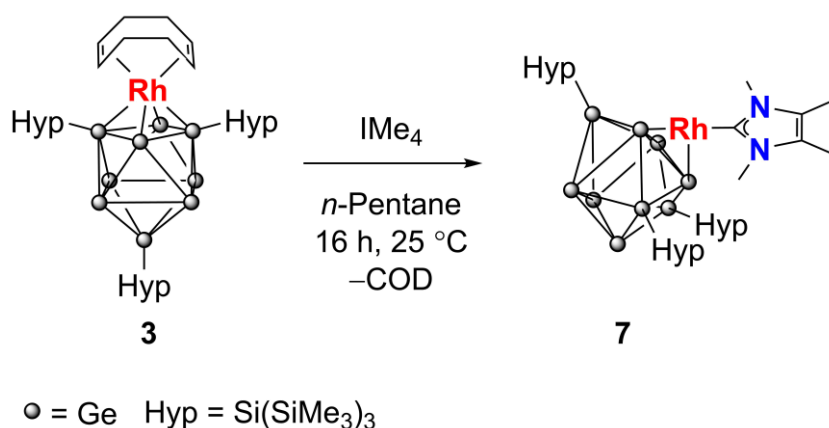
To investigate these ligand displacement reactions further, a monophosphine that is more electronically similar to PPh_3 was reacted with compound **6**. Addition of one equivalent of tris-*para*-tolylphosphine, $\text{P}(p\text{-tol})_3$, to a benzene- d_6 solution of compound **6** resulted in the formation of a mixture containing $[\text{Rh}(\text{P}(p\text{-tol})_3)\{\text{Ge}_9(\text{Hyp})_3\}]$ and unreacted starting material within 5–10 minutes after the addition of $\text{P}(p\text{-tol})_3$. The ratios of each component were measured over the next three days by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, finding that the relative ratios were unchanged after 1 day. The equilibrium constant, K_{eq} , was calculated to be 1.12, which is consistent with the increased σ -donation from $\text{P}(p\text{-tol})_3$.⁴² A new singlet resonance relating to the hypersilyl substituents at 0.48 ppm in the ^1H NMR spectrum and a new doublet resonance at 45.94 ppm ($^1J_{\text{P-Rh}} = 212.7$ Hz) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum were observed for the new product. It was subsequently shown that varying the amounts of either phosphine resulted in correlated changes in the relative concentrations of the two complexes, meaning that the two clusters are in equilibrium.

Due to the similarity of triphenylphosphine and tris-*para*-tolylphosphine, we can assume from this experiment that PPh₃ can reversibly dissociate from compound **6** in solution. ³¹P{¹H} exchange spectroscopy (EXSY) NMR was used to investigate whether the exchange between compound **6** and one equivalent of PPh₃ was observable on the NMR timescale at room temperature. Unfortunately, no cross-peaks between the coordinated and free triphenylphosphine was observed at all tested mixing rates. This data and the time to reach equilibrium in the competition experiments suggest that the exchange is slow on the NMR timescale.

4.6. [Rh(Ime₄){η³-Ge₉(Hyp)₃}] (**7**)

With a synthetic strategy to fluxional clusters bearing monodentate and bidentate phosphine ligands in hand, other ancillary ligands were explored to probe trends at the metal–cluster interface. Complexes of rhodium bearing *N*-heterocyclic carbene (NHC) ligands have been used extensively in recent years in the catalysis of organic reactions,^{58–62} they are considered to be strongly σ-donating and poorly π-accepting compared to phosphines.^{63,64} We therefore investigated the coordination of an NHC ligand to compound **3**.

4.6.1. Synthesis of Compound **7**



Scheme 4.10: Synthesis of [Rh(Ime₄){η³-Ge₉(Hyp)₃}] (**7**).

Compound **3** was dissolved in *n*-pentane and added to a suspension of 1,3,4,5-tetramethylimidazol-2-ylidene (IMe₄) in *n*-pentane at room temperature. The brown suspension was stirred for 16 hours before filtering to remove a black precipitate. The solution was then concentrated and cooled to −40 °C producing black crystals of compound **7** (crystalline yield 58%) which were suitable for crystallography. Compound **7** can be synthesized in aromatic solvents, however this is accompanied by the formation of unidentified by-products with similar solubility.

4.6.2. Single Crystal X-ray Structure of Compound **7**

The asymmetric unit of compound **7** features two crystallographically unique clusters with comparable bond metrics (Table 4.4). As with previous clusters **5** and **6**, the rhodium centre is in a trigonal pyramidal ligand field with *C_s* symmetry (Figure 4.9).

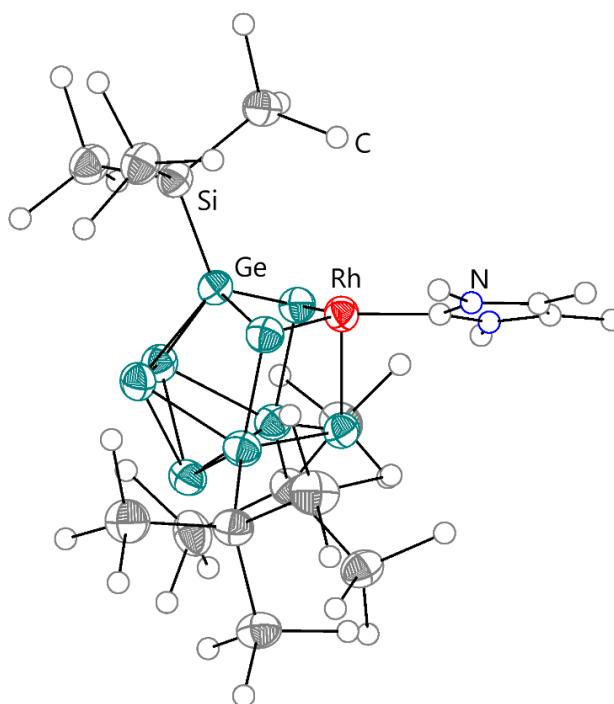
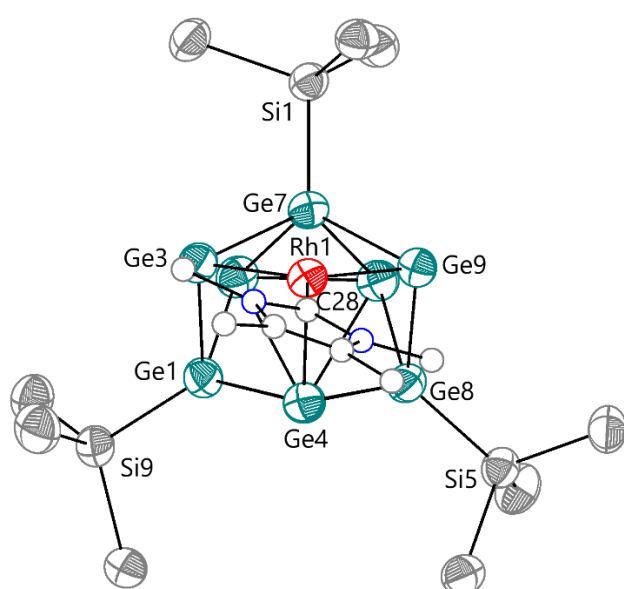


Figure 4.9: Single crystal X-ray structure of compound **7**. Anisotropic displacement ellipsoids set at 50% probability. All carbon and nitrogen atoms are pictured as spheres of an arbitrary radius. Hydrogen atoms are omitted for clarity. Only one of two crystallographically independent molecules is shown.

The Rh–Ge distances are within the range of 2.397(6) and 2.418(5) Å, for the three unsubstituted Ge centres, with a short Rh–Ge contact to a substituted Ge(Hyp) vertex (2.667(7) Å). The Rh–C distances in both clusters (2.036(4) and 2.044(4) Å) are typical for other rhodium NHC complexes, for example, [(COD)Rh(Ime₄)₂][Cl] (2.04(4), 2.05(4) Å).⁶⁵

Table 4.4: Selected crystallographic bond lengths (Å) of compound **7** comparing the crystallographically inequivalent moieties in the asymmetric unit. A truncated molecular model is included as a key.



Bond	Cluster 1 Distance (Å)	Cluster 2 Distance (Å)
Rh1–Ge3	2.397(6)	2.398(7)
Rh1–Ge4	2.418(5)	2.417(5)
Rh1–Ge7	2.667(7)	2.664(7)
Rh1–Ge9	2.399(7)	2.397(6)
Rh1–C28	2.036(4)	2.044(4)
Ge1–Si9	2.395(1)	2.391(1)
Ge7–Si1	2.381(9)	2.382(9)
Ge8–Si5	2.556(7)	2.396(1)

4.6.3. Nuclear Magnetic Resonance Spectroscopic Analysis of Compound **7**

Inspection of the ¹H NMR spectrum of compound **7** in benzene-*d*₆ shows a single resonance (0.55 ppm) for the hypersilyl protons. This correlates well with the two silicon environments found in the ²⁹Si/¹H HMBC NMR spectrum. In addition, two resonances appear at 1.16 and

3.38 ppm relating to the four NHC methyl groups. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum exhibits a doublet ($^1J_{\text{C-Rh}} = 76.0$ Hz) resonance at 171.4 ppm assigned to the carbene carbon. Comparison of compound **7** to other rhodium NHC complexes reveals that while the Rh–C bond length is similar, the ^{13}C NMR chemical shift and coupling constant are more sensitive to the electronic environment at the rhodium centre (Table 4.5).

Table 4.5: Selected examples of IMe_4 and $\text{I}^i\text{Pr}_2\text{Me}_2$ rhodium complexes (COD = 1,5-cyclooctadiene; IMe_4 = 1,3,4,5-tetramethylimidazol-2-ylidene; $\text{I}^i\text{Pr}_2\text{Me}_2$ = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene; Cp^* = 1,2,3,4,5-pentamethylcyclopentadienyl; Mes^* = 2,4,6-tri-*tert*-butylbenzene).^{65–68}

Compound	Rh–C Distance (Å)	$\delta^{13}\text{C}_{\text{carbene}}$ (ppm)	$^1J_{\text{Rh-C}}$ (Hz)
$[(\text{CO})\text{Rh}(\text{IMe}_4)\text{Cl}]$	N.A.	182.9	41
$[(\text{CO})\text{Rh}(\text{I}^i\text{Pr}_2\text{Me}_2)_3][\text{PF}_6]$	2.07(13), 2.08(13)	179.2, 178.3	43, 47
$[(\text{COD})\text{Rh}(\text{IMe}_4)\text{Cl}]$	2.02	178.8	51
$[(\text{COD})\text{Rh}(\text{IMe}_4)_2][\text{Cl}]$	2.04(4), 2.05(4)	178.7	53
$[(\text{Cp}^*)\text{Rh}(\text{I}^i\text{Pr}_2\text{Me}_2)(\text{PMes}^*)]$	2.04(2)	185.0	63.7
7	2.036(4)	171.4	76

The $^1J_{\text{C-Rh}}$ coupling constant for the ^{13}C NMR chemical shift of compound **7** is significantly larger than the literature examples. This is attributed to decreased σ -donation and increased π -backbonding in the Rh–C interaction, indicative of a higher electron density at rhodium.^{69,70}

Variable temperature NMR experiments at 193 K were performed in toluene- d_8 to “trap” the C_s symmetry observed in the solid-state, which would result in divergence of the hypersilyl proton signals into a 2:1 ratio whilst retaining symmetric environments for the NHC ligand.

These were unsuccessful, showing no broadening of the resonance, indicating a very low energy process that is fast on the NMR timescale.

4.6.4. Density Functional Theory Analysis of Compound 7

DFT methods were employed to investigate the electronic structure, as well as the fluxionality found by NMR spectroscopy. Firstly, calculation of the frontier molecular orbitals elucidated a lone pair of electrons situated in an orbital with significant d-orbital parentage (Figure 4.10).

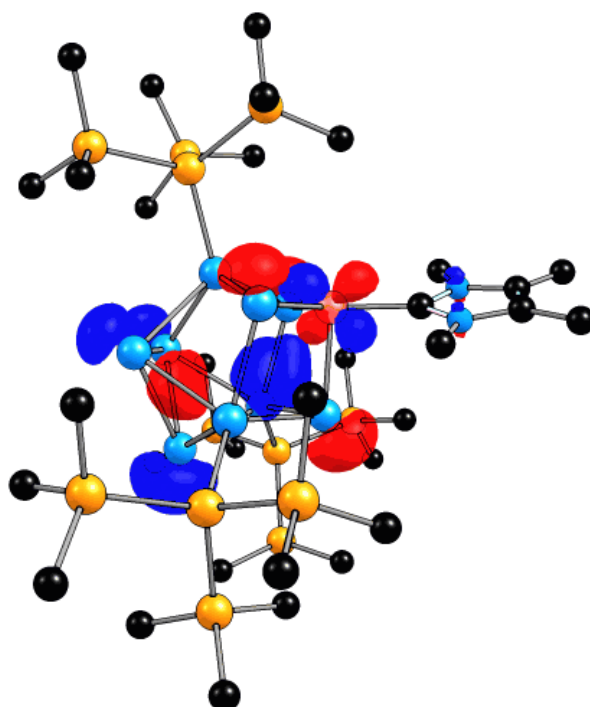


Figure 4.10: Highest occupied molecular orbital of 7 (BP86/Def2-TZVP, isovalue 0.04).

As with compound 6, a potential energy surface scan calculation (BP86/SDD/6-31g(d,p)) was performed to probe a possible fluctuation pathway. The resulting plot (Figure 4.11, Right) exhibits only a maximum between two equivalent isomers of compound 7, in contrast to the C_{3v} symmetric structure found in the case of compound 6. This transition state was optimised to find a converged saddle-point with a single negative vibrational frequency at -23.27 cm^{-1} . Extrapolation of this vibration using IRC calculations produced the two isomeric geometries observed in the scan.

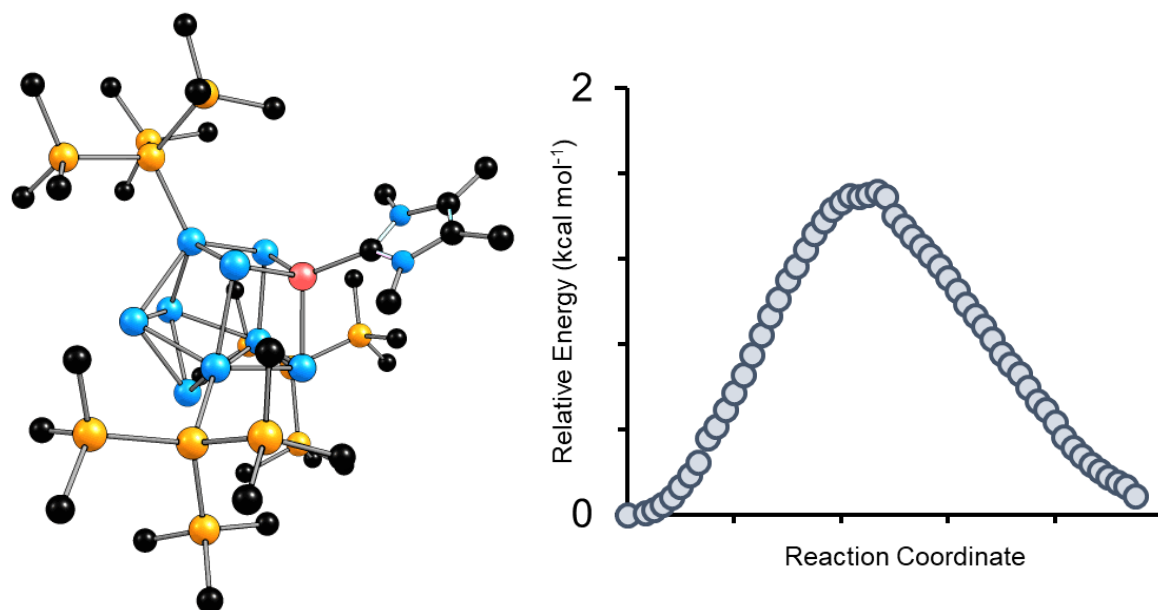
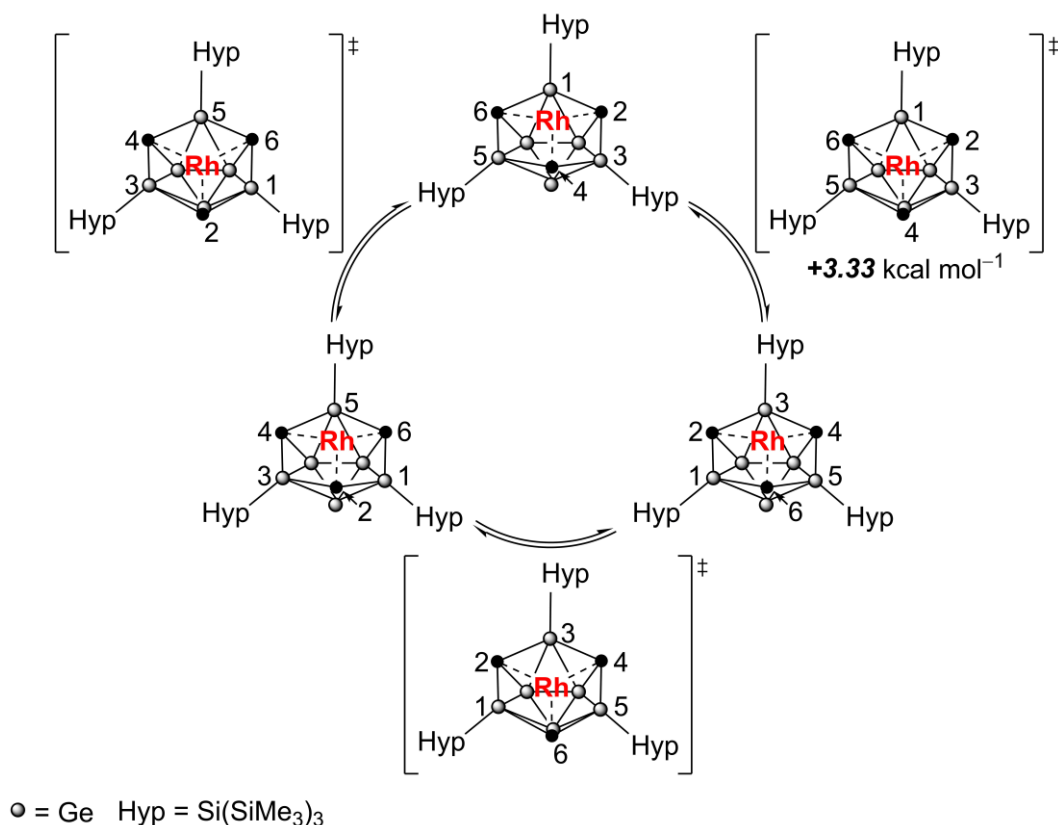


Figure 4.11, Left: DFT optimised transition state for the fluctuation pathway found in compound 7. Right: Potential energy surface plot on elongating the variable distance (BP86/SDD/6-31g(d,p)). Energies relative to the ground state optimised geometry of compound 7.

In this transition state, the rhodium moiety has deviated from its original trigonal pyramidal geometry observed in its solid-state towards a tetrahedral geometry with an overall C_s symmetry. With a calculated activation energy of $\Delta G_{298}^\ddagger = 3.33 \text{ kcal mol}^{-1}$, this process would not be slowed down enough by VT NMR to observe. The small discrepancy between the converged activation energy and that in the potential energy scan plot can be explained by the larger basis set and dispersion correction used in the converged transition state energy. This process allows the $\text{Rh}(\text{IME}_4)$ fragment to move towards any $\text{Ge}(\text{Hyp})$ vertex via three equivalent transition states, making the hypersilyl substituents equivalent (Scheme 4.11).



Scheme 4.11: DFT calculated fluxional processes for compound **7** (BP86-D3/Def2-TZVP). Coordinated IMe₄ omitted for clarity.

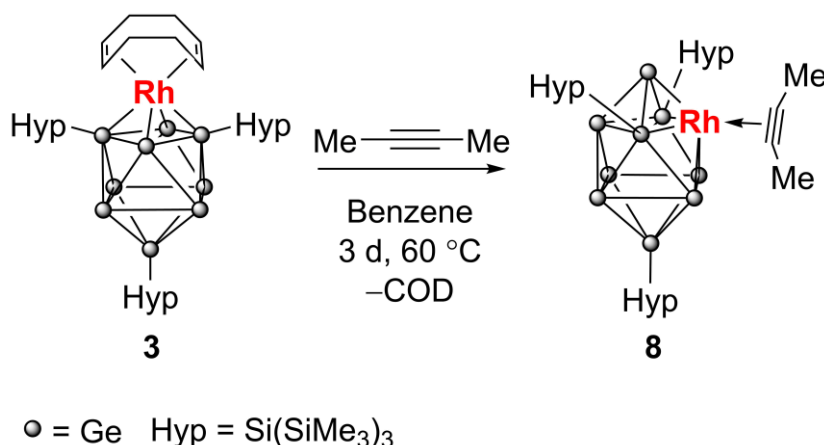
4.7. [Rh(η^2 -C₂Me₂){ η^5 -Ge₉(Hyp)₃}] (**8**)

The results described in Chapter 3 predict that [Rh(COE){Ge₉(Hyp)₃}] (COE = cyclooctene) is a better catalyst than compound **3**, owing to removal of the barrier imposed by η^4 - η^2 opening of the COD ligand. Although the direct synthesis of a mono-alkene complex was found to be unattainable, the synthesis of a mono-acetylene complex was attempted. In addition, alkynes typically bind stronger than alkenes to the metal centres due to an additional set of π orbitals which can provide extra stabilisation, allowing them to act as four electron donors.⁷¹ The alkyne compound would, in theory, be able to act in the same way as the proposed [Rh(COE){Ge₉(Hyp)₃}] cluster however with increased ligand sphere stabilisation.

2-butyne was chosen as a ligand for this reaction due to its small size and lack of a terminal alkynyl C–H bond, which may result in undesirable *sp* C–H activation. Due to the tendency

to undergo [2+2+2] cycloaddition reactions to produce hexamethylbenzene,⁷² only a few “side-on” rhodium 2-butyne complexes are known.^{73–75} Only one example, [(Tp')Rh(PMe₃)(η²-C₂Me₂)] (Tp' = tris(3,5-dimethyl-1-pyrazolyl)borate), has been crystallographically characterised. It cannot be prepared by simple ligand substitution, though interestingly, the complex can C–H activate benzene at room temperature.⁷³

4.7.1. Synthesis of Compound **8**



Scheme 4.12: Synthesis of [Rh(η²-C₂Me₂){η⁵-Ge₉(Hyp)₃}] (**8**).

Compound **3** was dissolved in benzene, producing a red-brown solution. 10 equivalents of 2-butyne were then added before heating the reaction mixture at 60 °C for four days. The solution was lyophilised to a red powder, containing analytically pure compound **8**. To obtain crystalline material, this powder was dissolved in a minimum of *n*-pentane and cooled to –40 °C for two days yielding large black-red crystals suitable for X-ray crystallography (83% yield).

In contrast to the synthesis of [(Tp')Rh(PMe₃)(η²-C₂Me₂)], no C–H activation of benzene or alkyne is observed during the reaction.⁷³

4.7.2. Nuclear Magnetic Resonance Spectroscopic Analysis of Compound **8**

Analysis of compound **8** by NMR spectroscopy revealed a similar set of spectra to compounds **4–7**. A single singlet resonance for the ^1H and ^{13}C nuclei, and two ^{29}Si environments relating to the hypersilyl substituents were observed in the respective NMR spectra. Notably, in the ^1H NMR spectrum, a doublet resonance at 2.27 ppm ($^3J_{\text{H-Rh}} = 2.23\text{ Hz}$) relating to the methyl groups of the alkyne ligand coupling to the ^{103}Rh nucleus (Figure 4.12) was observed. This coupling constant is relatively large when compared to literature examples. The methyl protons in the previously mentioned $[(\text{Tp}')\text{Rh}(\text{PMe}_3)(\eta^2\text{-C}_2\text{Me}_2)]$ are reported as a singlet. $[\text{RhCl}(\text{P}^i\text{Pr}_3)(\eta^2\text{-C}_2\text{Me}_2)]$, $[(\text{Cp})\text{Rh}(\text{P}^i\text{Pr}_3)(\eta^2\text{-C}_2\text{Me}_2)]$ and $[(\text{Cp})\text{Rh}(\eta^2\text{-C}_2\text{H}_4)(\eta^2\text{-C}_2\text{Me}_2)]$, the only other three monomeric examples, are reported with $^3J_{\text{H-Rh}}$ constants of 1.3 Hz, 1.3 Hz and 1.1 Hz, respectively.^{73–75}

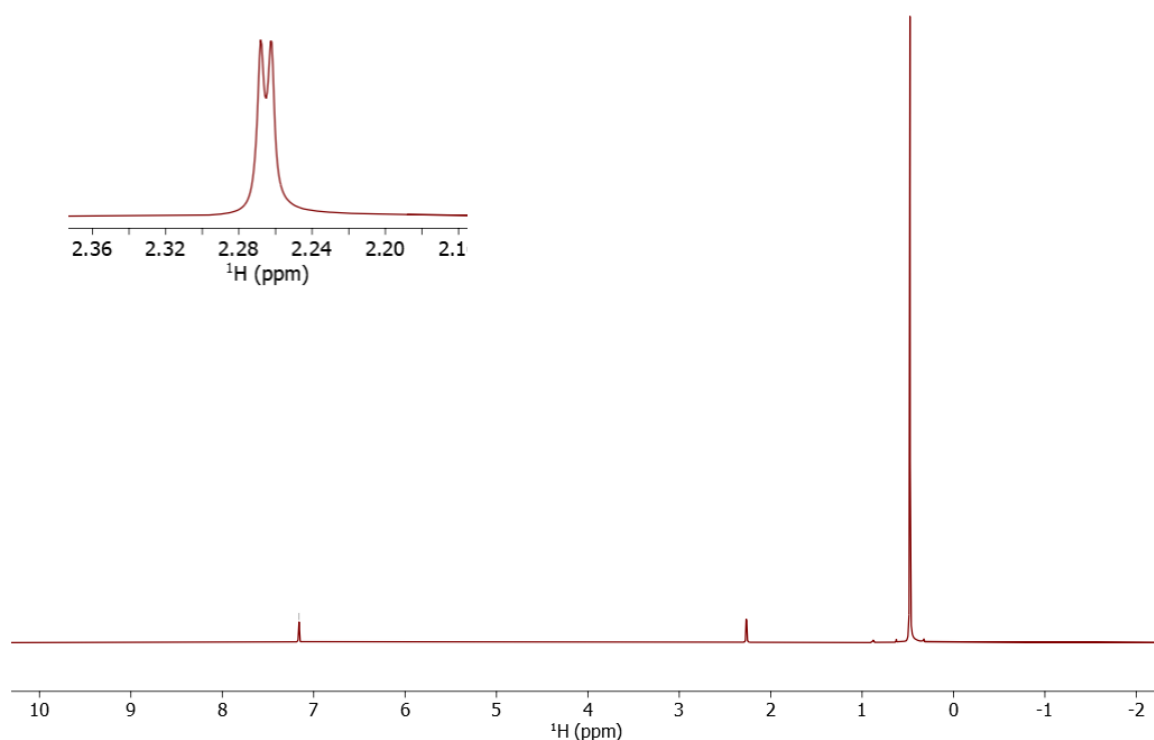


Figure 4.12: ^1H NMR spectrum (C_6D_6 , 298 K, 400.16 MHz) of compound **8**.

In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, two doublet signals are observed for the 2-butyne ligand at 17.14 and 103.36 ppm (Figure 4.13), exhibiting ^{13}C – ^{103}Rh coupling constants of 18.5 and 1.6 Hz for the alkynyl and methyl carbons, respectively.

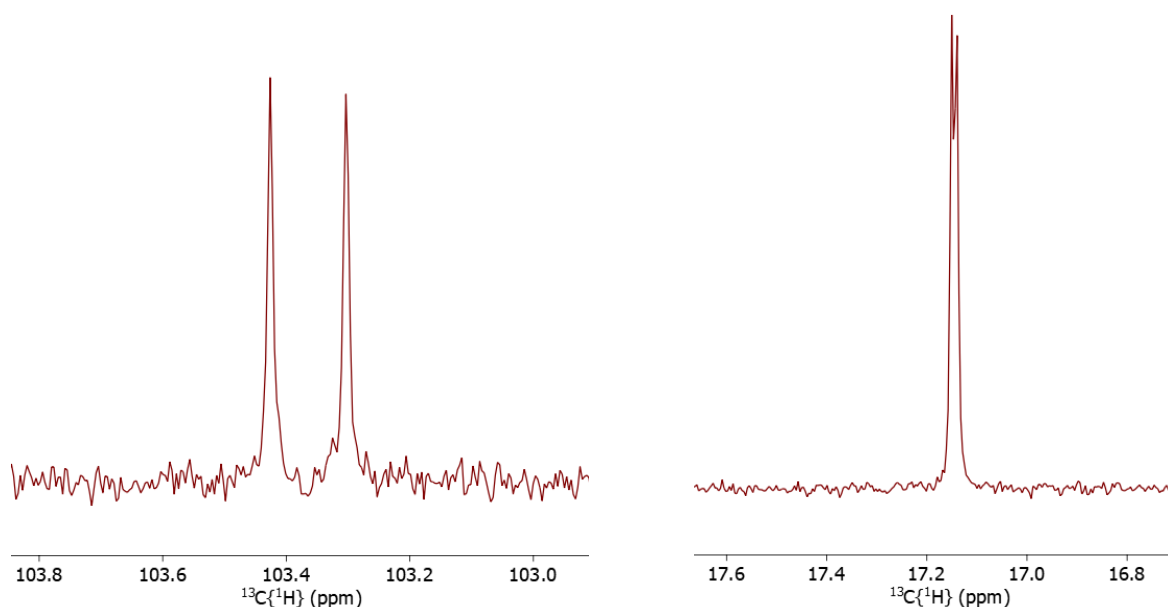


Figure 4.13: Excerpts showing the doublet resonances present in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (C_6D_6 , 298 K, 151 MHz) of compound **8**.

Unfortunately, there are no reported $^{13}\text{C}\{^1\text{H}\}$ NMR spectra in the literature for rhodium 2-butyne complexes with which to compare these values. However, the ^{13}C NMR chemical shifts for four electron donor alkyne ligands typically appear at around 160 ppm,^{76–79} rather than 100 ppm, which is more consistent with two electron donation.^{80,81}

4.7.3. Single Crystal X-ray Structure of Compound **8**

Single crystal X-ray crystallography revealed that compound **8** bears a striking resemblance with compound **4** and displays similar bond metrics (Table 4.6). It also bears a bicapped square antiprismatic *closo* geometry and the rhodium centre is coordinated in an η^5 coordination mode by the cluster (Figure 4.14). Conversely to the NMR data, this indicates that the alkyne may be acting as a four-electron donor ligand. Distortion of the alkyne is

observed by measuring bond angles C1-C2-C3 ($148.2(2)^\circ$) and C4-C3-C2 ($148.6(2)^\circ$) and bond length C2-C3 ($1.269(3)$ Å); (the C-C distance in free 2-butyne is $1.213(1)$ Å),⁸² showing that the π -manifold is weakened by the interaction towards sp^2 . This could either result from four electron donation to the metal or π -backbonding from the metal, as described for $[(Tp')Rh(PMe_3)(\eta^2-C_2Me_2)]$, which exhibits bond angles of $146.1(8)^\circ$ and $143.9(8)^\circ$, a C-C bond length of $1.275(10)$ Å and a Rh-C distances of $2.044(8)$ and $2.057(8)$.⁷³

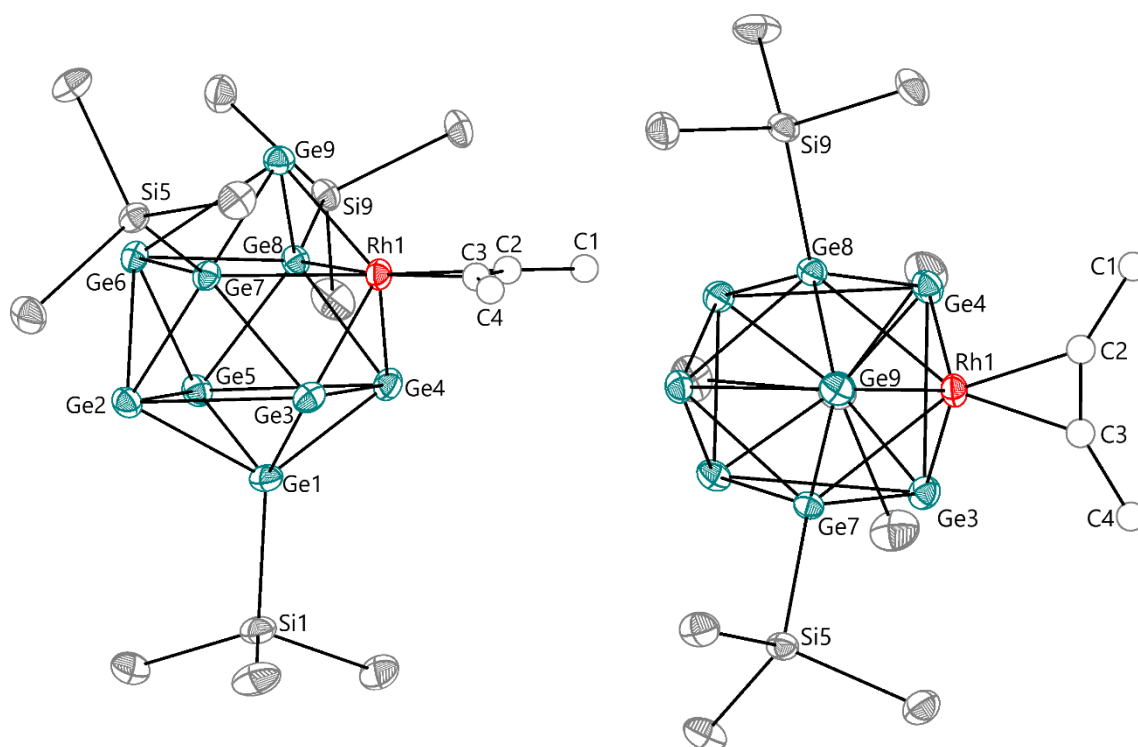


Figure 4.14: Single crystal X-ray structure of compound **8**. Anisotropic displacement ellipsoids set at 50% probability. Carbon atoms are pictured as spheres of an arbitrary radius. Hydrogen atoms and carbon atoms attached to the hypersilyl substituents are omitted for clarity.

Table 4.6: Selected bond metrics from the crystal structure of compound **8**.

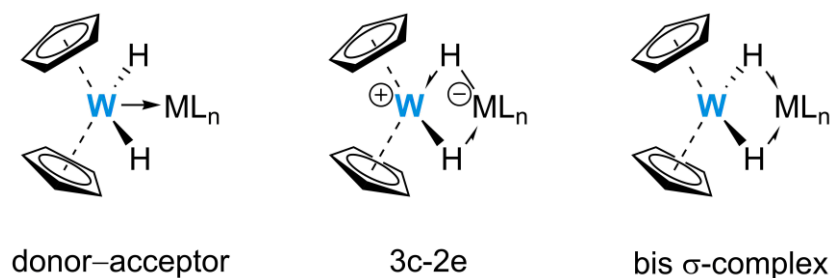
Bond	Distance (Å)
Ge3–Rh1	2.472(5)
Ge4–Rh1	2.466(6)
Ge7–Rh1	2.811(6)
Ge8–Rh1	2.809(7)
Ge9–Rh1	2.439(5)
Rh1–C2	2.025(2)
Rh1–C3	2.025(2)
C2–C3	1.269(3)
Ge1–Si1	2.390(5)
Ge7–Si5	2.401(7)
Ge8–Si9	2.389(7)

4.8. $[\text{Rh}(\mu\text{-H})_2\text{W}(\text{Cp})_2\{\eta^3\text{-Ge}_9(\text{Hyp})_3\}]$ (**9**)

The reaction of compound **3** with various ‘L type’ ligands has been rather reliable in producing *closo* and *hypercloso* clusters of type $[\text{Rh}(\text{L})\{\eta^3\text{-Ge}_9(\text{Hyp})_3\}]$, provided that L can outcompete COD. It was therefore proposed to use this strategy to build bimetallic complexes with reactive Lewis basic transition metal complexes, which act as L type ligands. The empty coordination site at rhodium could then, in theory, be used to coordinate substrates and release products, whilst performing transformations at the Rh–M interface.

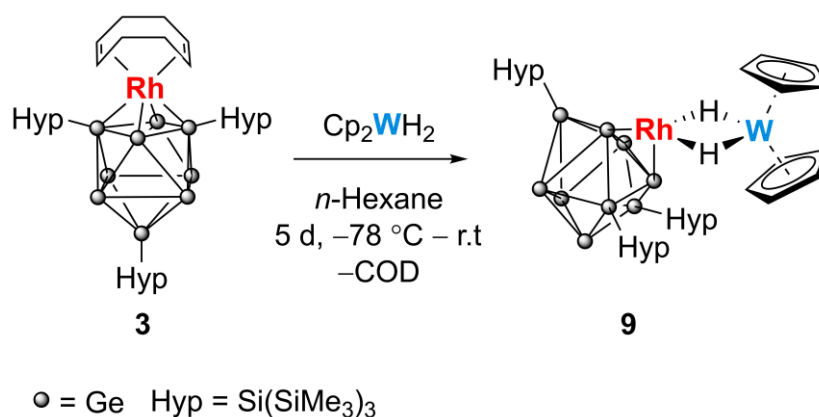
The coordinatively saturated 18-electron complex $[(\text{Cp})_2\text{WH}_2]$ has very rich reactivity,^{83–87} especially under photolytic conditions, where H_2 can be extruded to provide $[(\text{Cp})_2\text{W}]$ *in situ*.^{88–94} It is also known to act as a Lewis base towards transition metal,^{95–103} rare earth

metal,¹⁰⁴ and group 13 centres.^{105,106} Depending on the coordinated metal, this can be described as a donor–acceptor interaction, using the lone pair of electrons at tungsten; a 3-centre-2-electron interaction; or a bis σ -complex type interaction, where the hydrides are donating electron density (Scheme 4.13).^{84,101}



Scheme 4.13: Bonding extremes in $[(\text{Cp})_2\text{WH}_2]$ adducts.

4.8.1. Synthesis of Compound **9**



Scheme 4.14: Preparation of $[\text{Rh}(\mu\text{-H})_2\text{W}(\text{Cp})_2\{\eta^3\text{-Ge}_9(\text{Hyp})_3\}]$ (**9**).

A pale-yellow suspension of $[(\text{Cp})_2\text{WH}_2]$ in *n*-hexane was added slowly to a cooled ($-78\text{ }^\circ\text{C}$) solution of compound **3**. This was stirred overnight at room temperature, by which time all reagents had fully dissolved. The volume was then reduced by 90% *in vacuo* and the suspension stirred for four days under a static vacuum before removing the supernatant, containing mostly unreacted starting material. The product was isolated as a pyrophoric brown powder after washing with cold ($-78\text{ }^\circ\text{C}$) *n*-pentane in approx. 70% yield. Black

crystals suitable for X-ray crystallography were obtained by dissolving in a 1:10 mixture of toluene and *n*-pentane and cooling the solution to $-40\text{ }^{\circ}\text{C}$.

If the reaction is performed in an aromatic solvent such as benzene or toluene, the reaction reaches a maximum of 70% conversion after 4 days, and the product cannot be suitably isolated from the starting materials. Attempts to heat the reaction to above $45\text{ }^{\circ}\text{C}$ or stir the reaction longer (~ 1 week) resulted in decomposition. $[(\text{Cp})_2\text{WH}_2]$ was also unable to displace PPh_3 in compound **5** to produce compound **9**.

4.8.2. Nuclear Magnetic Resonance Spectroscopic Analysis of Compound **9**

Inspection of the ^1H NMR spectrum of compound **9** reveals a single singlet resonance for the hypersilyl protons indicating that it is also fluxional. This is accompanied by a singlet resonance for the ten cyclopentadienyl protons and a doublet resonance with doublet satellites at -16.15 ppm ($^1J_{\text{H-Rh}} = 26.2\text{ Hz}$; $^1J_{\text{H-W}} = 76.0\text{ Hz}$) owing to two equivalent ^1H nuclei bridging between ^{103}Rh ($I = \frac{1}{2}$, 100%) and ^{183}W ($I = \frac{1}{2}$, 14.31%) (Figure 4.15).

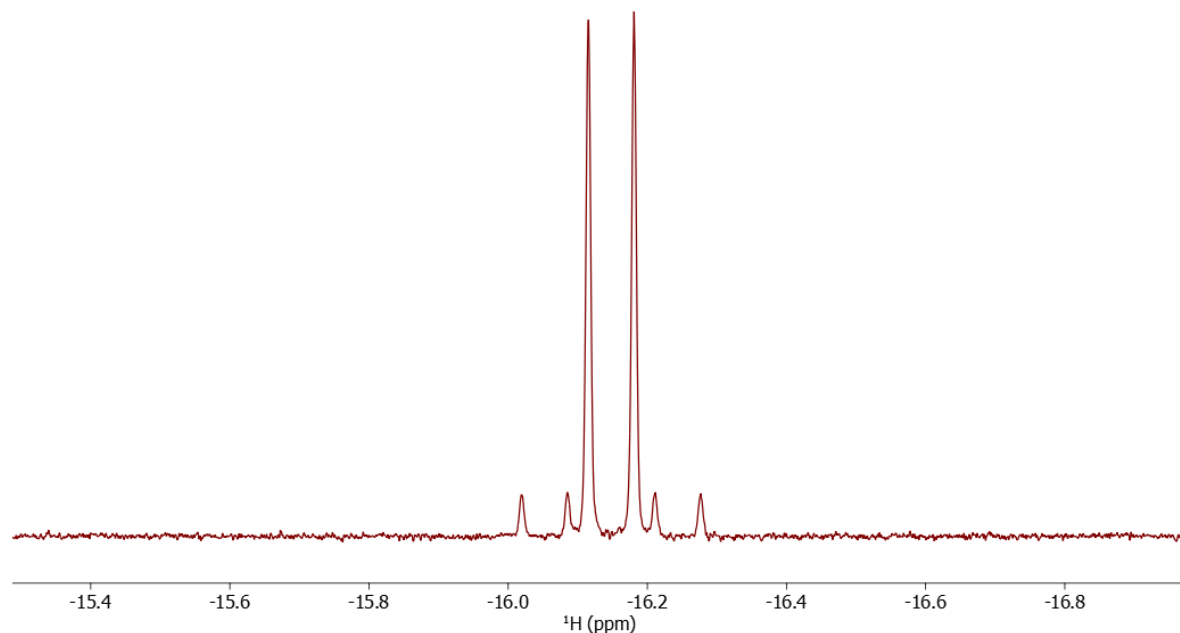


Figure 4.15: ^1H NMR spectrum (C_6D_6 , 298 K, 400.16 MHz) of compound **9** showing the bridging hydride resonance.

The data is consistent with the two literature known examples of $[\text{Rh}](\mu\text{-H})_2\text{W}(\text{Cp})_2$ complexes (*vide infra*), of which only one has been structurally characterised.^{96,102,103} The chemical shift appears further downfield and although $^1J_{\text{H-Rh}}$ is similar, $^1J_{\text{H-W}}$ is different. This could however be due to the steric and electronic differences between the $[\text{Ge}_9(\text{Hyp})_3]$ ligand in compound **9** and arylphosphine ligands in the literature examples. The dihydride signals in the ^1H NMR spectra of $[(\text{PPh}_3)_2\text{Rh}(\mu\text{-H})_2\text{W}(\text{Cp})_2][\text{PF}_6]$ and $[((-)\text{DIOP})\text{Rh}(\mu\text{-H})_2\text{W}(\text{Cp})_2][\text{PF}_6]$ (DIOP = 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane) appear as a doublet of triplets (due to $^2J_{\text{H-P}}$ coupling) at -18.11 and -17.99 ppm, respectively, which is similar to that of compound **9**. Both literature compounds exhibit the same coupling constants for this signal ($^1J_{\text{H-Rh}} = 29$ Hz; $^1J_{\text{H-W}} = 107$ Hz; $^2J_{\text{H-P}} = 10$ Hz).^{96,103} The large coupling constants to both metals (especially rhodium), indicate a bridging hydride (bis σ -complex) interaction, rather than a donor-acceptor interaction where the hydrides are non-bridging. For reference, an example of the latter is $[(\text{CO})_5\text{W}(\mu\text{-H})_2\text{W}(\text{Cp})_2]$, which exhibits two distinct sets of doublet resonances ($^1J_{\text{H-W}} = 63$ Hz; $^2J_{\text{H-W}} = 19.2$ Hz).¹⁰⁷

4.8.3. Single Crystal X-ray Structure of Compound **9**

The crystal structure of compound **9** shows one cluster in the asymmetric unit (Figure 4.16), although as in the case of compound **5**, it is disordered over two orientations. These are related by rotation and chemically equivalent with relative occupancies of 85% and 15%.

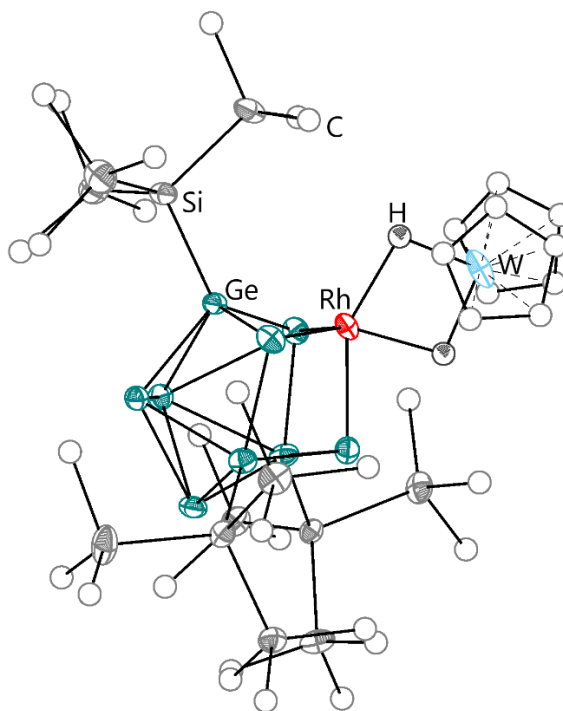
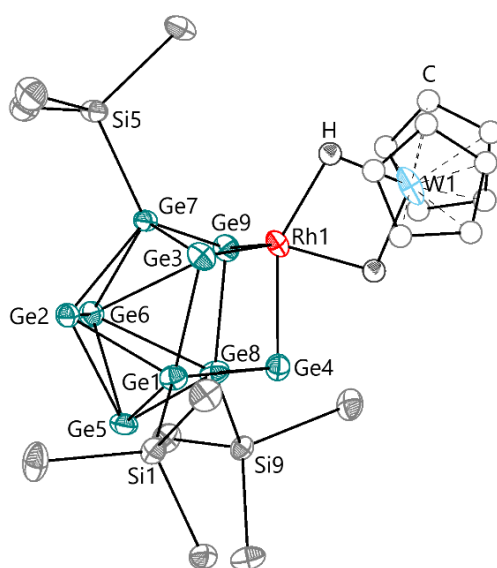


Figure 4.16: Single crystal X-ray structure of **9**. Anisotropic displacement ellipsoids set at 50% probability. Carbon atoms are pictured as spheres of an arbitrary radius. Hydrogen atoms bonded to carbon are omitted for clarity.

The Rh–W distance (2.859(5) Å) is longer than that of the structurally authenticated compound $[(PPh_3)_2Rh(\mu-H)_2W(Cp)_2][PF_6]$, which has a Rh–W distance of 2.721(3) Å.^{102,103} This gives further evidence of a bridging hydride interaction in compound **9**.

Comparing the Rh–Ge distances (2.411(14) – 2.430(5) Å), and the short Rh⋯Ge contact of 2.644(11) Å, one can see that these are similar to those of the PMe_3 and IMe_4 ligated complexes.

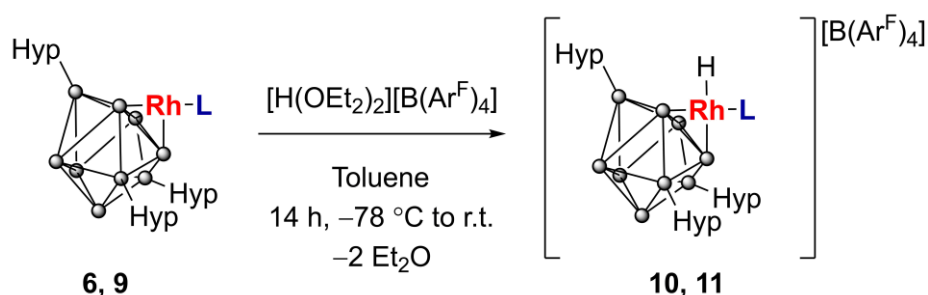
Table 4.6: Selected crystallographic bond lengths (Å) of compound **9**.



Bond	Distance (Å)
Ge3–Rh1	2.421(5)
Ge4–Rh1	2.430(5)
Ge7–Rh1	2.644(11)
Ge9–Rh1	2.411(14)
Rh1–W1	2.852(5)
Ge1–Si1	2.384(11)
Ge7–Si5	2.376(12)
Ge8–Si9	2.421(10)

4.9. Protonation of Compounds **6** and **9**

In order to probe the coordinative unsaturation and redox chemistry of $[\text{Rh}(\text{L})\{\text{Ge}_9(\text{Hyp})_3\}]$, compounds **6** and **9** ($\text{L} = \text{PPh}_3$ and $[(\text{Cp})_2\text{WH}_2]$, respectively) were reacted with one equivalent of Brookhart's acid ($[\text{H}(\text{OEt}_2)_2][\text{B}(\text{Ar}^{\text{F}})_4]$; $\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$) in toluene.



○ = Ge Hyp = Si(SiMe₃)₃ $[\text{B}(\text{Ar}^{\text{F}})_4]^- = [\text{B}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_4]^-$ $\text{L} = \text{PPh}_3$ (**6**, **10**), $\text{H}_2\text{W}(\text{Cp})_2$ (**9**, **11**)

Scheme 4.15: Protonation of unsaturated compounds **6** and **9** to their respective conjugate hydrides $[\text{RhH}(\text{PPh}_3)\{\eta^3\text{-Ge}_9(\text{Hyp})_3\}][\text{B}(\text{Ar}^{\text{F}})_4]$ (**10**) and $[\text{RhH}\{(\mu\text{-H})_2\text{W}(\text{Cp})_2\}\{\eta^3\text{-Ge}_9(\text{Hyp})_3\}][\text{B}(\text{Ar}^{\text{F}})_4]$ (**11**).

This resulted in the formation of cationic rhodium(III) hydride complexes $[\text{RhH}(\text{PPh}_3)\{\eta^3\text{-Ge}_9(\text{Hyp})_3\}][\text{B}(\text{Ar}^{\text{F}})_4]$ (**10**) and $[\text{RhH}\{(\mu\text{-H})_2\text{W}(\text{Cp})_2\}\{\eta^3\text{-Ge}_9(\text{Hyp})_3\}][\text{B}(\text{Ar}^{\text{F}})_4]$ (**11**) as evidenced by the observation of a new resonance at negative chemical shifts in the ^1H NMR spectra of the resulting compounds. Removal of the solvent *in vacuo* in both syntheses produced red (**10**) or red-brown (**11**) oils.

4.9.1. Nuclear Magnetic Resonance Spectroscopic Analysis of Compound **10**

In the case of compound **10**, ^1H NMR spectroscopy in benzene- d_6 revealed two new broad singlet resonances at 0.07 and 0.33 ppm (in a 1:2 ratio) relating to the hypersilyl substituents. This indicates that protonation has stopped the fluxional processes observed for compound **6**. In addition, a new doublet of doublets at -1.48 ppm ($^2J_{\text{H-P}} = 3.4$ Hz, $^1J_{\text{H-Rh}} = 12.6$ Hz) arising from the hydride was observed. Since the signal features both $^1J_{\text{H-Rh}}$ and $^2J_{\text{H-P}}$ coupling, $^1\text{H}\{^{31}\text{P}\}$ NMR spectroscopy was used to unequivocally assign the coupling constants. This shift is further downfield than expected for a terminal rhodium hydride, for example the rhodium(III) hydride complex $[(\text{Cp}^*)\text{RhH}(\text{PMe}_3)_2][\text{PF}_6]$ exhibits a triplet of doublets at -13.35 ppm ($^2J_{\text{H-P}} = 23.4$ Hz, $^1J_{\text{H-Rh}} = 34.9$ Hz).³⁶ The hydride resonance in the triphenylphosphine analogue $[(\text{Cp}^*)\text{RhH}(\text{PPh}_3)_2][\text{PF}_6]$ appears as a doublet of triplets at -11.05 ppm ($^2J_{\text{H-P}} = 30$ Hz, $^1J_{\text{H-Rh}} = 18$ Hz).¹⁰⁸

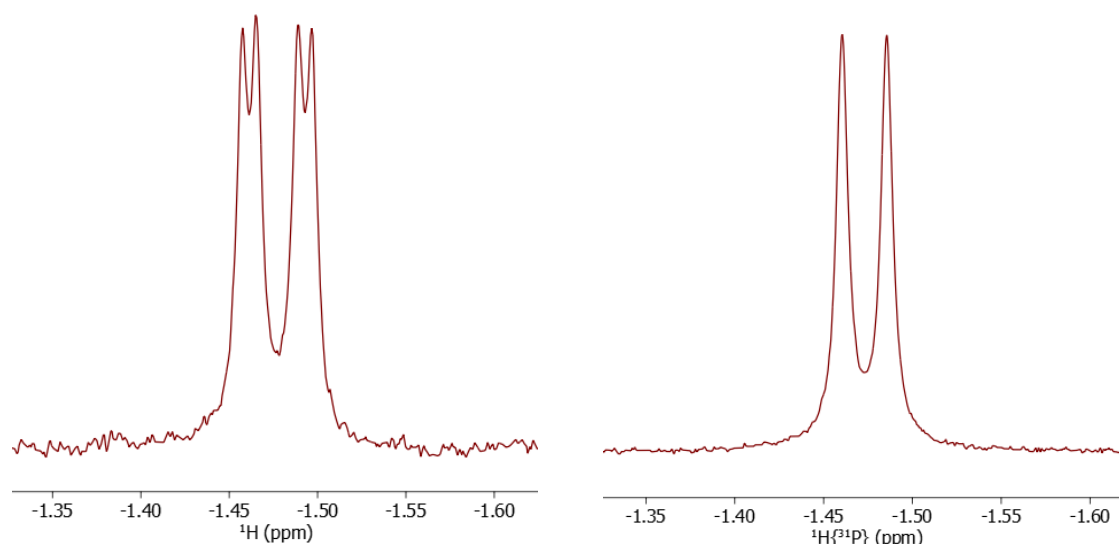


Figure 4.17: ^1H (Left) and $^1\text{H}\{^{31}\text{P}\}$ (Right) NMR spectra (C_6D_6 , 298 K, 400.16 MHz) of compound **10** showing the terminal hydride resonance.

The $^{31}\text{P}\{^1\text{H}\}$ NMR signal for the PPh_3 ligand of compound **6**, also shifted from 49.28 ($^1J_{\text{P-Rh}} = 214.0$ Hz) to 41.39 ppm ($^1J_{\text{P-Rh}} = 188.9$ Hz) upon protonation. The change in coupling constant is consistent with the change in oxidation state at rhodium, as $^1J_{\text{P-Rh}}$ is generally smaller for rhodium(III) compounds than those of rhodium(I). For example $[(\text{Cp}^*)\text{Rh}(\text{PMe}_3)_2]$ has a larger $^1J_{\text{P-Rh}}$ coupling constant than its conjugate hydride $[(\text{Cp}^*)\text{RhH}(\text{PMe}_3)_2][\text{PF}_6]$ (216 Hz compared to 137 Hz).³⁶ Attempts to identify $^2J_{\text{P-H}}$ coupling to the hydride using ^{31}P NMR spectroscopy were unsuccessful due to overlap with the resonances arising from coupling to the aryl protons.

Due to the poor solubility of compound **10** in aromatic solvents and its incompatibility with other more polar solvents, we were unable to explore the reactivity of this species towards substrates, or to collect variable temperature NMR data.

4.9.2. Single Crystal X-ray Structure of Compound **10**

Dark red crystals of compound **10** suitable for X-ray crystallography were grown by vigorously dispersing the resulting red oil in *n*-hexane and standing overnight. Notably,

solvent diffusion methods or cooling concentrated solutions in diethyl ether did not afford a solid sample, giving rise instead to red oils.

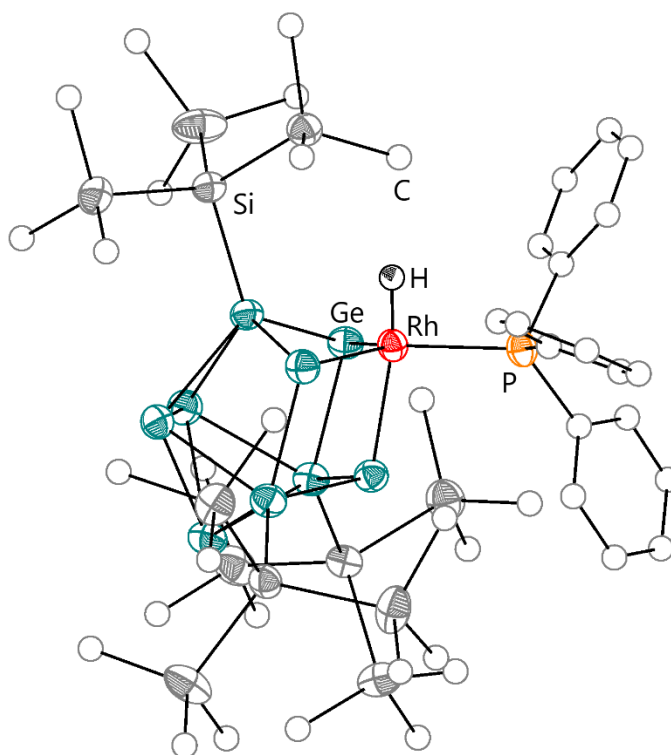
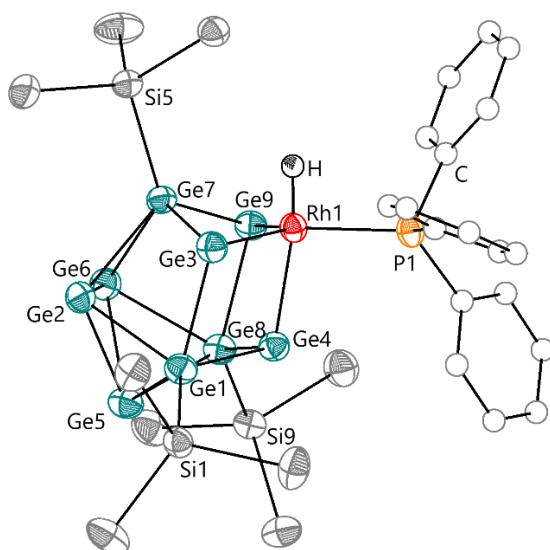


Figure 4.18: Single crystal X-ray structure of compound **10**. Anisotropic displacement ellipsoids set at 50% probability. Carbon atoms and hydrogen atoms bonded to metals are pictured as spheres of an arbitrary radius. Hydrogen atoms bonded to carbon, solvent of crystallisation and $[B(Ar^F)_4]^-$ counter ion have been omitted for clarity.

The asymmetric unit of compound **10** contains a single crystallographically unique cationic cluster, $[RhH(PPh_3)\{\eta^3\text{-}Ge_9(\text{Hyp})_3\}]^+$, similar to compounds **5**, **6** and **9**. However, due to protonation, the rhodium centre adopts a trigonal bipyramidal geometry with a hydride in one of the apical positions. Due to the formal two electron oxidation of the rhodium centre, the Rh–Ge distances are contracted by ca. 0.03 Å when compared to compounds **5**, **6** and **9**.

Table 4.7: Selected crystallographic bond lengths (Å) of compound **10**. A truncated molecular model is included as a key.



Bond	Distance (Å)
Ge3–Rh1	2.397(4)
Ge4–Rh1	2.365(4)
Ge7–Rh1	2.676(6)
Ge9–Rh1	2.396(6)
Rh1–P1	2.322(6)
Ge1–Si1	2.380(11)
Ge7–Si5	2.388(11)
Ge8–Si9	2.386(11)

4.9.3. Nuclear Magnetic Resonance Spectroscopic Analysis of Compound **11**

The ^1H NMR spectrum of compound **11** in benzene- d_6 revealed two new sharp singlet resonances at 0.21 and 0.42 ppm (in a 1:2 ratio) relating to the hypersilyl substituents, indicating, as with compound **10**, no fluxional process is taking place on the NMR timescale. In addition to this, a new downfield doublet resonance (-0.03 ppm; $^1J_{\text{H-Rh}} = 12.2$ Hz) is observed, indicating a terminal hydride. The bridging hydride resonance also shifts from -16.15 ppm ($^1J_{\text{H-Rh}} = 26.2$ Hz, $^1J_{\text{H-W}} = 76.0$ Hz) to -15.41 ppm ($^1J_{\text{H-Rh}} = 27.8$ Hz, $^1J_{\text{H-W}} = 83.3$ Hz). Interestingly, no $^2J_{\text{H-H}}$ or $^3J_{\text{H-W}}$ coupling is observed.

4.9.4. Single Crystal X-ray Structure of Compound **11**

Large black-red crystals of compound **11** suitable for single crystal X-ray crystallography were grown by dissolving the oil in diethyl ether, concentration of the solution by slow evaporation and cooling to -40 °C for two days.

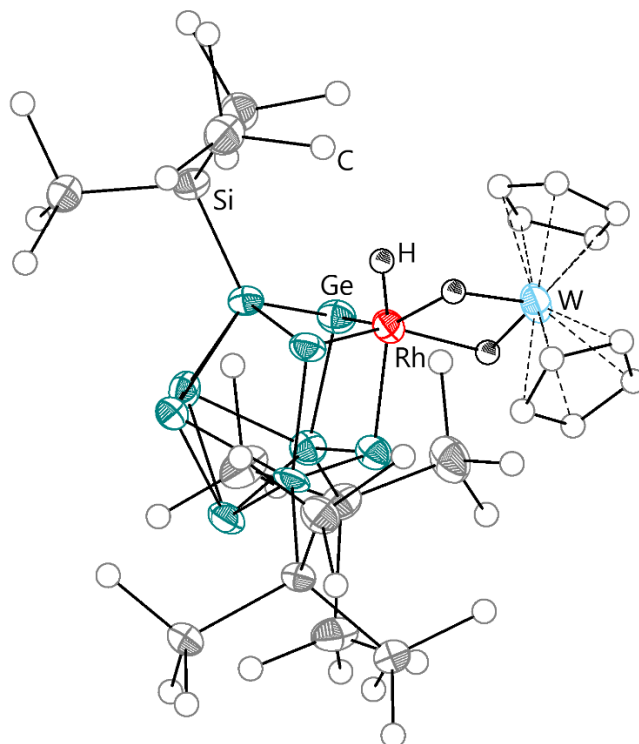
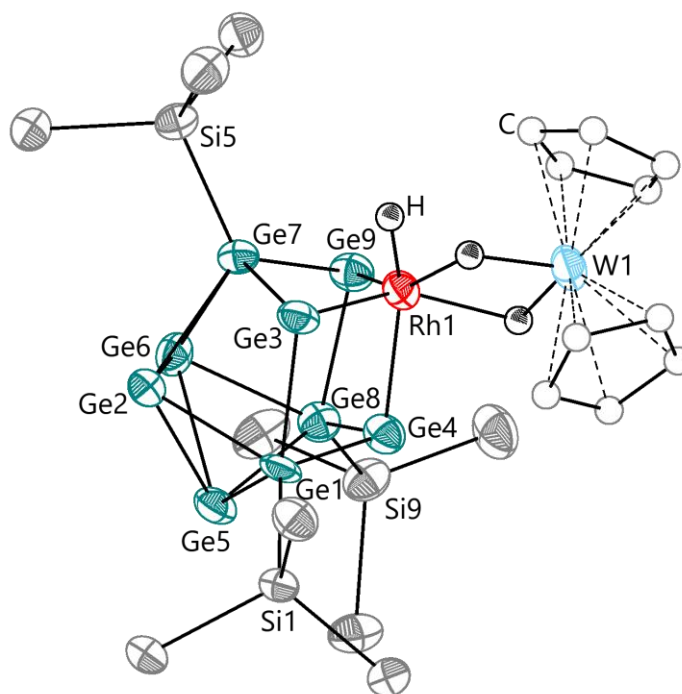


Figure 4.19: Single crystal X-ray structure of compound **11**. Anisotropic displacement ellipsoids set at 50% probability. Carbon atoms and hydrogen atoms bonded to metals are pictured as spheres of an arbitrary radius. Hydrogen atoms bonded to carbon, solvent of crystallisation and $[B(Ar^F)_4]^-$ counter ion are omitted for clarity.

The asymmetric unit of compound **11** contains, like **10**, a single crystallographically unique cationic cluster, $[RhH((\mu-H)_2W(Cp)_2)\{\eta^3-Ge_9(Hyp)_3\}]^+$, again with positional disorder.

Comparing the structure to that of compound **9**, protonation at the rhodium metal centre has caused the tungstenocene moiety to rotate around dihedral angle Ge4-Rh1-W1-(Cp) by ca. 40° (Cp = calculated centroid of the 5 cyclopentadienyl carbon atoms). Direct comparison of the Rh–Ge, Ge–Si and Rh–W distances between compound **9** and its conjugate hydride **11** shows a contraction of Rh–Ge distances, most significantly Rh1–Ge4 which is contracted by ca. 0.05 Å, and slight elongation of the Rh1–Ge7 short contact. Whilst the average of the Ge–Si distances remains almost unchanged, the Rh1–W1 distance is contracted by 0.054 Å.

Table 4.8: Selected crystallographic bond lengths (Å) of compound **11**, compared to **9**. A truncated molecular model is included as a key.



Bond	9 (Å)	11 (Å)
Ge3–Rh1	2.421(5)	2.400(2)
Ge4–Rh1	2.430(5)	2.379(13)
Ge7–Rh1	2.644(11)	2.674(3)
Ge9–Rh1	2.411(14)	2.405(16)
Rh1–W1	2.852(5)	2.798(19)
Ge1–Si1	2.384(11)	2.422(3)
Ge7–Si5	2.376(12)	2.366(3)
Ge8–Si9	2.421(10)	2.379(4)

4.10. H–H and C–H Bond Activation

Due to the thermal stability of compound **6** and bimetallic nature of compound **9**, the two clusters were chosen for further study. Compound **4** was also chosen to measure the effect of increased coordination number on the reactivity of compound **6**.

4.10.1. Reactivity of Compounds **4** and **6** with H₂ and/or D₂

To begin investigating the reactivity of these clusters, we first explored an oxidative addition of dihydrogen at the unsaturated rhodium(I) centre. Addition of H₂ or D₂ (1 bar) to a toluene-*d*₈ solution of compounds **6** or **4** resulted in no observed change in either the ¹H or ³¹P{¹H} NMR spectra between the temperatures of 193 K and 298 K. However, if either complex is placed under a mixture of H₂ and D₂, the immediate formation of HD is observed, albeit ca. 50% slower for compound **4** as determined by the H₂:HD ratio. This indicates H/D scrambling catalysis by fast H₂ and D₂ activation on the NMR timescale. Although no H₂ or D₂ activation is directly observable by NMR spectroscopy, this indirectly indicates that it must be taking place and that it is reversible. In regard to the core project aims, similar tests employing a mixture of CH₄ and D₂ were explored but resulted in no reaction.

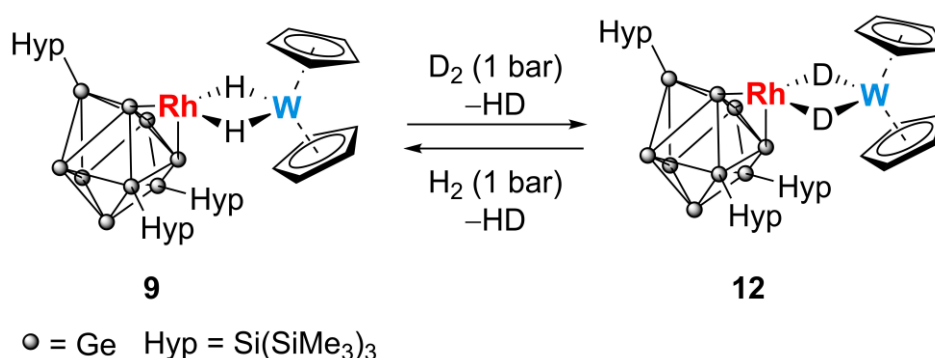
Mechanistically speaking, it was postulated that an η⁶-toluene complex intermediate may be responsible for this catalysis upon dissociation of either: the phosphine ligand, forming [Rh(η⁶-toluene){Ge₉(Hyp)₃}]; or the [Ge₉(Hyp)₃][−] moiety, forming [Rh(L)(η⁶-toluene)][Ge₉(Hyp)₃] (L = PPh₃, DPPE). Therefore, the reactions were repeated in cyclohexane-*h*₁₂ and analysed using unlocked ¹H NMR spectroscopy, showing again the formation of HD. The H₂ and HD ¹H NMR peaks are well enough separated from the solvent signal, thus allowing qualitative confirmation for the formation of HD.

It was attempted to probe possible mechanisms for H/D scrambling using DFT, however, all modelled pathways encountered energies which were too large to reasonably operate at room

temperature ($\Delta G_{298} > 28 \text{ kcal mol}^{-1}$). This typically occurred once the second molecule of H_2 was introduced, or when a phosphine ligand was dissociated, so could arise from the known problems of entropy and bond dissociation energy overestimation with DFT.^{109,110} Lower connectivity than η^3 at the germanium support also resulted in high energy pathways.

4.10.2. Reactivity of Compound **9** with H_2 or D_2

To test bimetallic reactivity, a benzene- d_6 solution of compound **9** was placed under an atmosphere of D_2 (1 bar). The doublet ^1H NMR signal for the bridging hydrides immediately started to decrease in intensity and dissolved H_2 and HD was observed.



Scheme 4.16: Reversible activation of H_2 and D_2 at heterobimetallic compound **9**.

The reaction was mixed by tumbling for 3 hours, resulting in a low intensity peak containing two overlapping doublet resonances. This is consistent with a mixture of compound **9**, an isotropically shifted hydrido-deuteride complex $[\text{Rh}(\mu\text{-H})(\mu\text{-D})\text{W}(\text{Cp})_2\{\text{Ge}_9(\text{Hyp})_3\}]$ and the unobserved dideuteride complex $[\text{Rh}(\mu\text{-D})_2(\text{Cp})_2\{\text{Ge}_9(\text{Hyp})_3\}]$ (**12**). Replacing the atmosphere with H_2 then resulted in complete regeneration of compound **9** and the observation of dissolved HD over the course of a day (Figure 4.20). It must be noted that this reactivity does not occur when $[(\text{Cp})_2\text{WH}_2]$ is placed under D_2 , indicating that the reaction does not proceed at a dissociated $[(\text{Cp})_2\text{WH}_2]$ fragment.

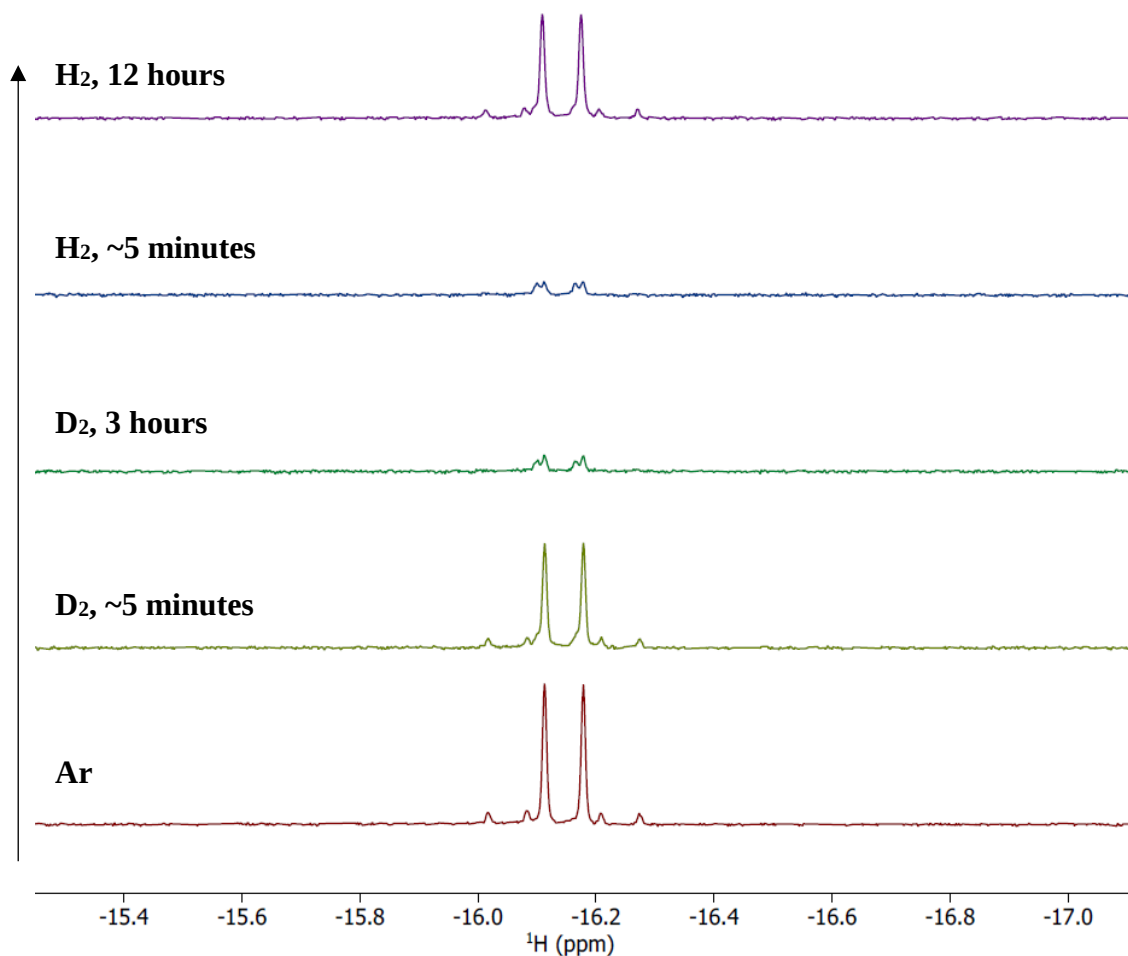


Figure 4.20: ^1H NMR spectra (C_6D_6 , 298 K, 400.16 MHz) of the bridging hydride showing the reversible activation of H_2 and D_2 on changing the atmosphere. From Bottom to Top: Ar, D_2 , D_2 (3 hours tumbled), H_2 , H_2 (12 hours tumbled).

When compound **9** was mixed by tumbling under D_2 in an NMR tube overnight, complete loss of the bridging ^1H signals was observed, due to the conversion of compound **9** and $[\text{Rh}(\mu\text{-H})(\mu\text{-D})\text{W}(\text{Cp})_2\{\text{Ge}_9(\text{Hyp})_3\}]$ to compound **12**. The presence of a bridging D_2 complex was confirmed by ^2H NMR spectroscopy which showed a doublet at -16.07 ppm exhibiting coupling to ^{103}Rh ($^1J_{\text{D-Rh}} = 4.1$ Hz). This resonance was accompanied by satellites exhibiting a $^1J_{\text{D-W}}$ coupling constant of ~ 12 Hz (Figure 4.21).

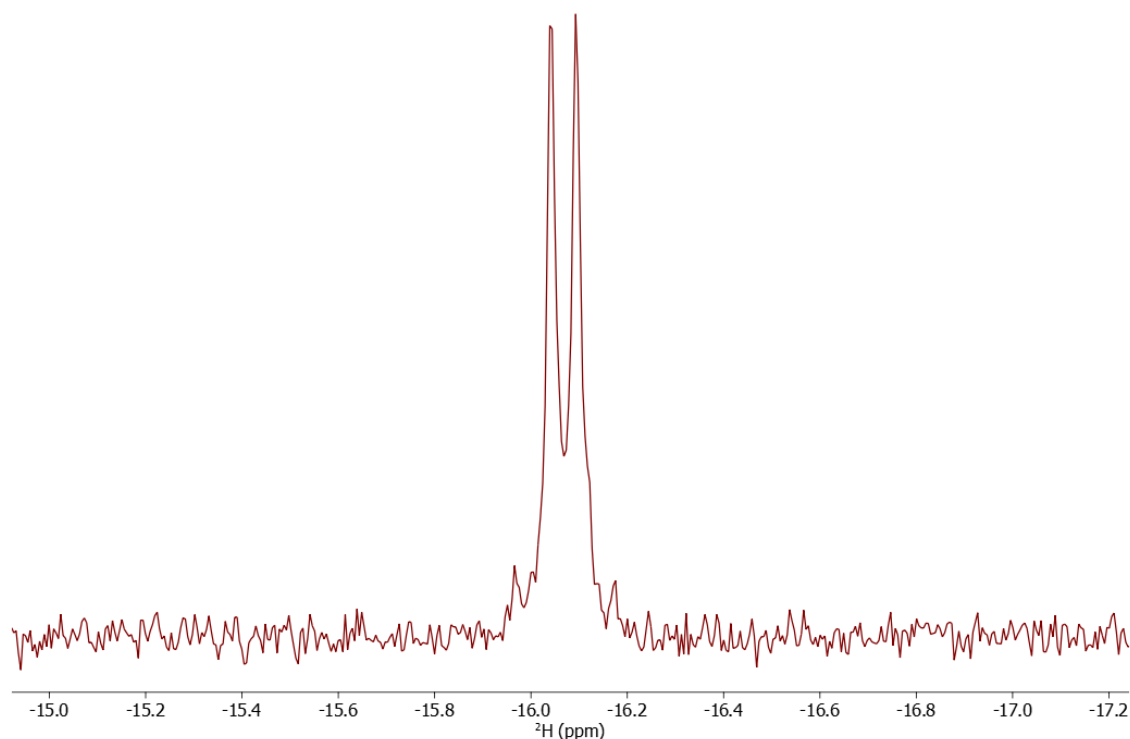


Figure 4.21: ^2H NMR spectrum (C_7H_8 , 298 K, 76.74 MHz) of compound **12** showing the bridging deuteride resonance.

This agrees well with the doublet observed in the ^1H NMR spectrum of compound **9**, both in terms of the chemical shift and coupling constants, considering the different gyromagnetic ratios of ^1H and ^2H ($^2\text{H}/^1\text{H} = 0.154$).¹¹¹ This complex can be isolated as a brown powder by removal of the solvent *in vacuo*, which can be used to test stoichiometric reactivity with substrates by deuterium incorporation.

4.10.3. Reactivity with Parahydrogen

Although further reactivity and catalysis (*vide supra*) implies that H–H activation occurs, no NMR resonances relating to new rhodium hydride complexes were observed. To gain an insight into the interactions of H_2 with compounds **4**, **6** and **9**, experiments were performed using *parahydrogen* ($p\text{H}_2$) in collaboration with Prof. Simon Duckett at the University of York.

H₂ is a highly symmetric molecule with coupled, equivalent and magnetically active centres ($I = \frac{1}{2}$). Because of this, it exists in different, isomeric, spin arrangements: *ortho* and *para* hydrogen. *Orthohydrogen* (*o*H₂) exists in three triply degenerate symmetric states: $\alpha\alpha$, $\beta\beta$ and $\alpha\beta+\beta\alpha$ and is NMR active. *Parahydrogen* (*p*H₂), the lowest energy form of dihydrogen and exists as the antisymmetric linear combination $\alpha\beta-\beta\alpha$, which has no overall angular momentum and is thus NMR silent (Figure 4.22).

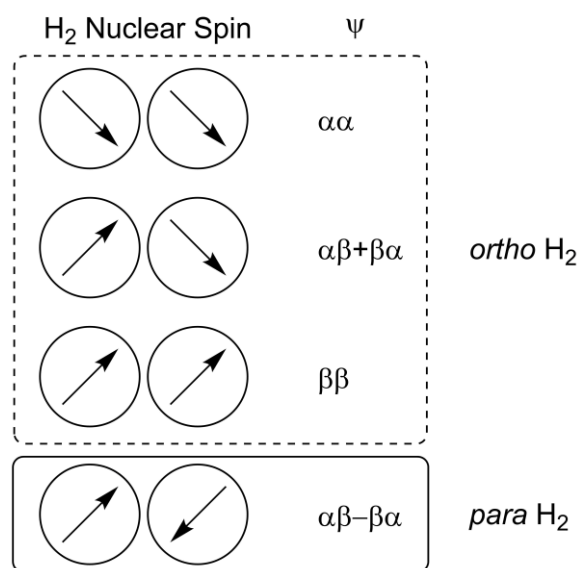


Figure 4.22: Schematic showing the nuclear spin states of dihydrogen.

Pure *p*H₂ (>99.8 %) is formed by storing H₂ over iron oxide or activated charcoal at cryogenic temperatures (~18 K). Interconversion between *p*H₂ and *o*H₂ is spin forbidden, allowing for enriched *p*H₂ to be stored at room temperature for several hours. This also means that any H₂ observed at approximately 4.5 ppm in a ¹H NMR spectrum is due to conversion by the reaction mixture.

For the oxidative addition of “normal” H₂, which gives rise to two inequivalent metal hydrides, the resulting NMR spectra should have two signals in a normal Boltzmann population distribution. However, by transferring *parahydrogen* to a metal centre via oxidative addition, only the $\alpha\beta$ and $\beta\alpha$ spin states in the resulting dihydride complex are

populated. This population difference results in a bias in spin relaxation pathways, which causes large increases in signal intensities (hyperpolarisation) (Figure 4.23).¹¹² For this reason, *Para*Hydrogen Induced Polarisation (PHIP) is a powerful technique to search for short-lived, low concentration intermediates in reaction mechanisms.^{113–115} It has also been explored as a technique in MRI to enhance signal intensities.¹¹⁶

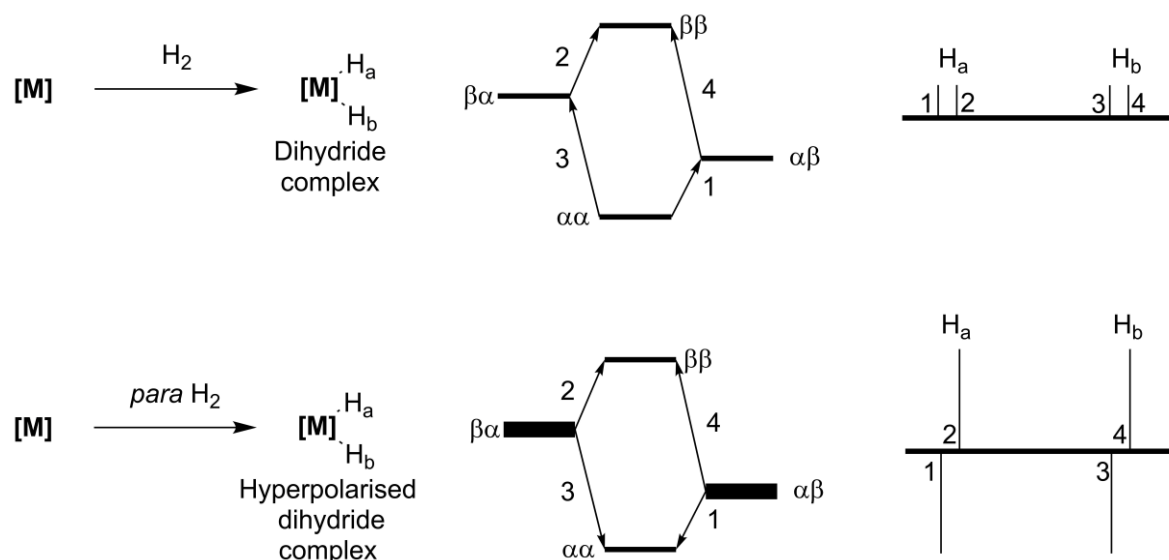


Figure 4.23: Polarization of hydride ^1H NMR signals by $p\text{H}_2$ in PHIP experiments, reproduced from Blazina et al.¹¹²

As well as enhanced signal intensities, population of specific nuclear spin states results in an antiphase character to the signal, this polarisation is short lived and will relax towards a typical Boltzmann distribution of spin states over time. However, adjusting the temperature, concentration and measurement time allows the observation of these products before spin state conversion.

Toluene- d_8 solutions of compounds **4**, **6** and **9**, were exposed to $p\text{H}_2$ (3 bar) in a J. Young NMR tube and analysed by ^1H NMR spectroscopy. In the case of compound **9**, instant conversion (to $o\text{H}_2$) was observed at all concentrations and conditions, due to fast oxidative addition and reductive elimination.

This was also observed with higher concentrations of compound **6** (0.005 mmol/ml) at room temperature and 263 K. When a more dilute solution of compound **6** (0.0005 mmol/ml) was cooled to 263 K in the NMR spectrometer, removed from the magnet and shaken under $p\text{H}_2$ (3 bar) then returned, no new hydride signals were observed. However, a signal with Partially Negative Lineshape (PNL) was observed at 4.56 ppm (Figure 4.24).

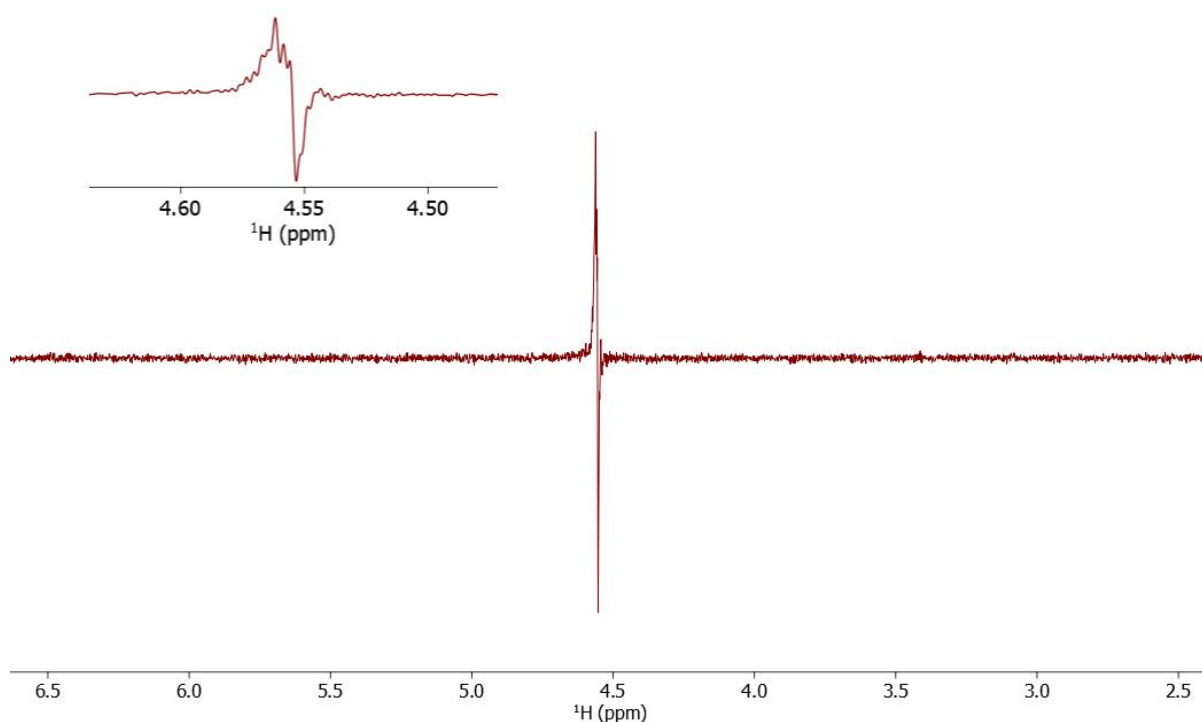
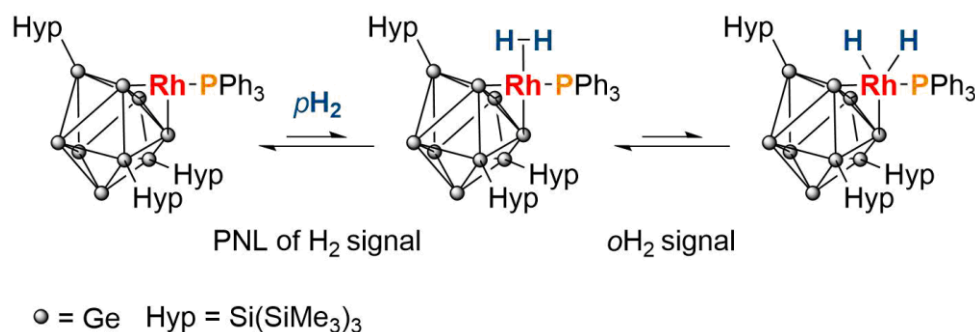


Figure 4.24: ^1H NMR spectrum (C_7D_8 , 400 MHz) of compound **6** (0.0005 mmol/ml) under $p\text{H}_2$ (3 bar), 263 K, acquisition time 0.87 s (1 scan, $d_1 = 0.1$ s). Data acquired by Prof. Simon Duckett.

The PNL phenomenon is related to a reversible coordination and disassociation of $p\text{H}_2$ without oxidative addition, and can be used as an indirect observation for a metal dihydrogen complex.^{113,114} This species also has a lifetime of around <5 s, after which, only $o\text{H}_2$ was observed, so a single scan (acquisition time 0.87 s) was required in order to observe it. Since $p\text{H}_2$ was still in high concentration in the headspace and diffusion of gases in NMR tubes on

standing is slow,¹¹⁷ the PNL can be regenerated on shaking the tube again. From these experiments, both a dihydrogen and dihydride complex can be indirectly inferred (Scheme 4.17).



Scheme 4.17: Reversible formation of dihydrogen and dihydride complexes, indirectly indicated by PNL and spin state conversion of $p\text{H}_2$ to $o\text{H}_2$.

In an effort to inhibit the spin state conversion of $p\text{H}_2$ to $o\text{H}_2$, and investigate the ligand field of the transient complexes formed *in situ*, an excess of 1-octyne was added to the initial, more concentrated, solution of compound **6** (0.005 mmol/ml) and the $p\text{H}_2$ experiments were repeated. This resulted in PNL from the association and disassociation of $p\text{H}_2$ in addition to the hyperpolarization of hydrogenated product, 1-octene, characterized by two new resonances at 5.00 ppm and 5.77 ppm. These exhibit the anti-phase character associated with hyperpolarized products of PHIP (Figure 4.25).

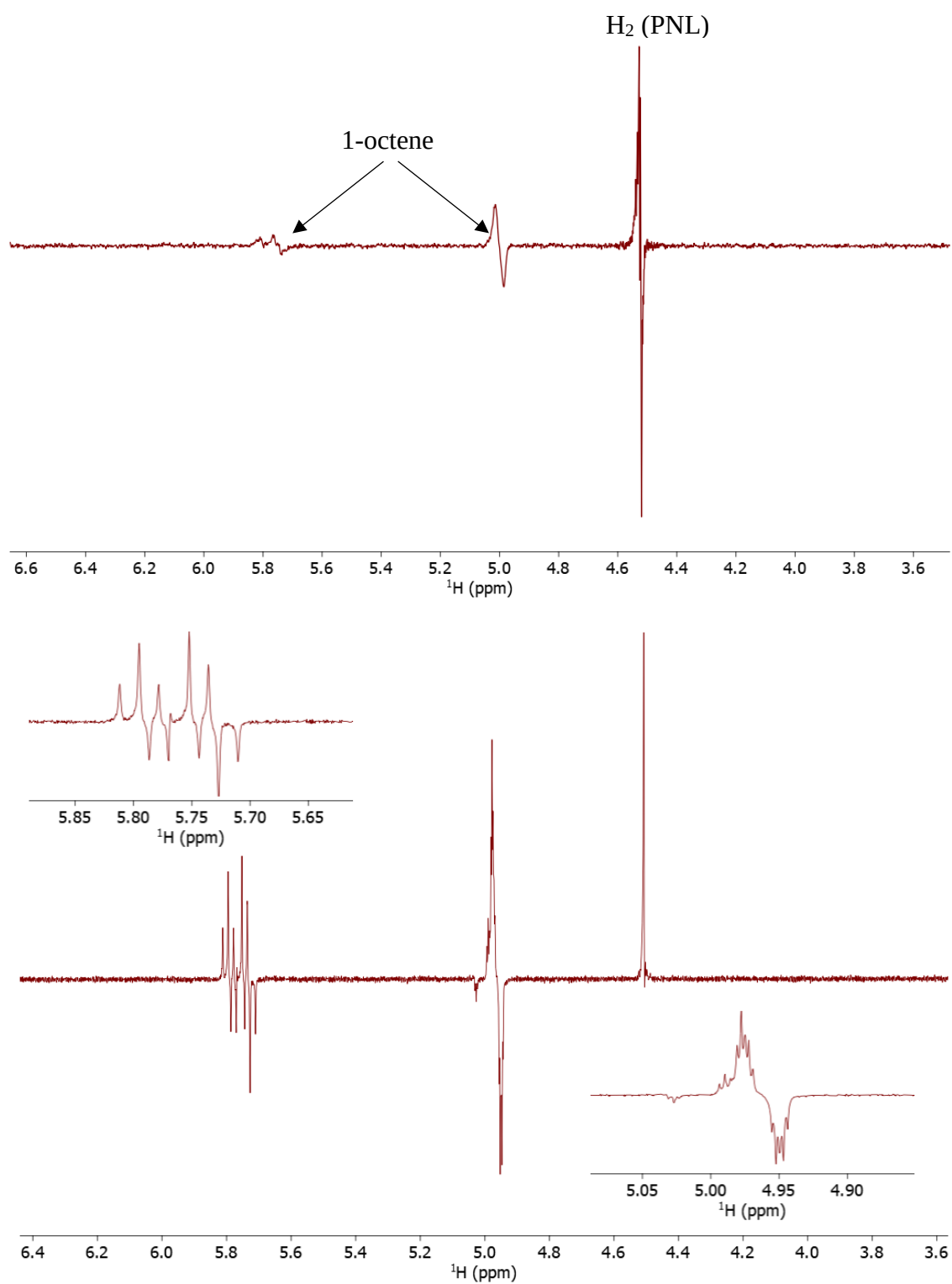


Figure 4.25: ^1H NMR spectra (C_7D_8 , 400 MHz) of compound **6** (0.005 mmol/ml) and 1-octyne under $p\text{H}_2$ (3 bar). Top: 263 K, acquisition time 0.87 s (1 scan, $d_1 = 0.1$ s). Bottom: 298 K, acquisition time 3.99 s (1 scan, $d_1 = 0.1$ s). Data acquired by Prof. Simon Duckett.

On warming the sample to room temperature and increasing the acquisition time to 4 s, the PNL relating to the association-disassociation equilibrium was no longer visible, now showing only oH_2 . In addition, an increased signal intensity and resolution of the hyperpolarised 1-octene was observed (Figure 4.25, Bottom).

Analysis of this spectrum shows a single hyperpolarized vinyl CH signal and two inequivalent resonances for the terminal CH_2 which both exhibit hyperpolarization with a ratio of 1:28. This allows an insight into the mechanism of pH_2 transfer to the alkyne, since for 1-octene, the ratio should be 1:1. Therefore, these results indicate that a *cis*-addition of pH_2 to the substrate is favoured over *trans*-addition (Figure 4.26).¹¹⁸ It must be noted that rapid isomerization of the *cis* product at the metal centre cannot be discounted for the formation of the *trans* product.¹¹⁹

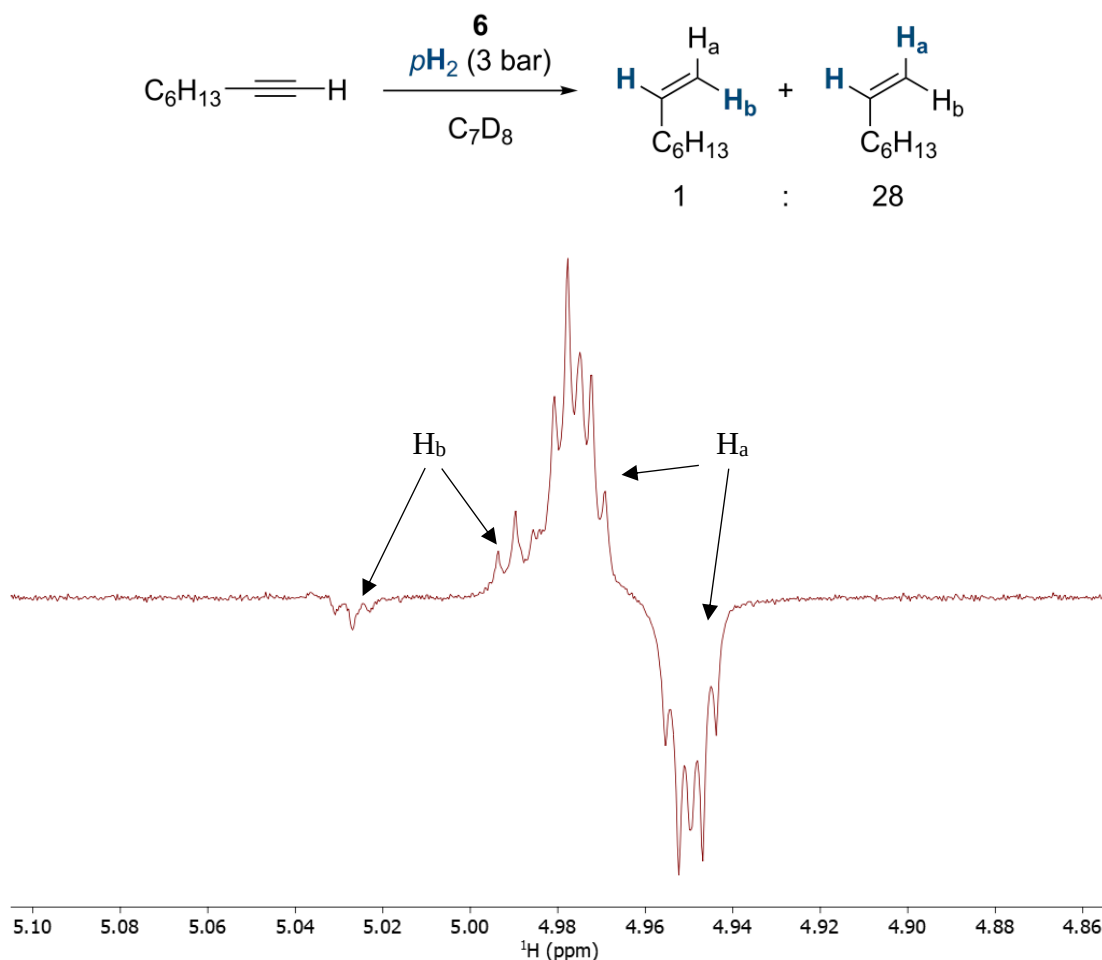


Figure 4.26: Expansion of NMR spectrum in Figure 4.25, Bottom; highlighting the *cis* and *trans* addition products from 1-octyne hydrogenation with $p\text{H}_2$.

Due to its bidentate ligand, compound **4** has one less coordination environment than compound **6** available for the coordination of H_2 , and is a slower catalyst for H/D scrambling (*vide supra*). Therefore, it was used in an attempt to observe a metal hydride intermediate.

At the higher concentration (0.005 mmol/ml) condition where no PNL was observed with compound **6**, PNL was now observed with compound **4**. This shows that the extra phosphine inhibits the conversion of $p\text{H}_2$, much like compound **6** in the presence of an alkyne. This effect is enhanced at the lower concentration (0.0005 mmol/ml). The reduced rate of $p\text{H}_2$ conversion is consistent with the H/D scrambling experiments (Figure 4.27). However, no resonances indicative for hydrides were observed.

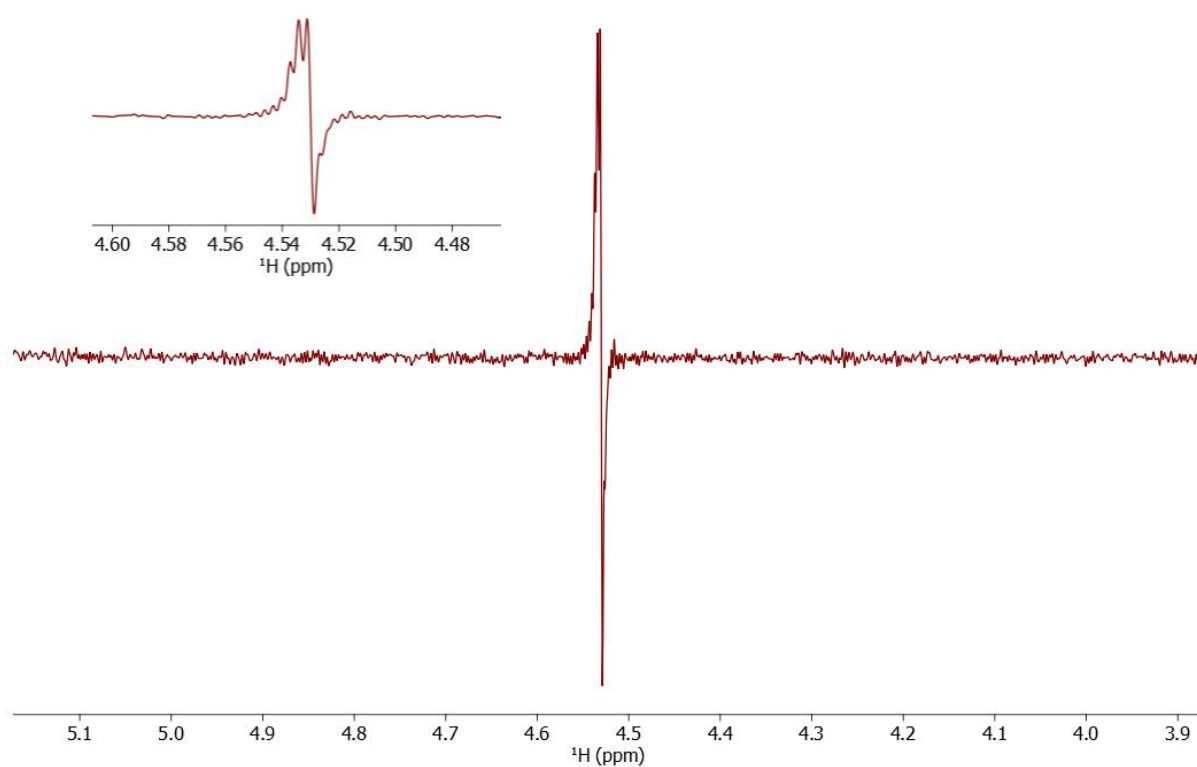


Figure 4.27: ^1H NMR spectrum (C_7D_8 , 400 MHz) of compound **4** (0.0005 mmol/ml) under $p\text{H}_2$ (3 bar), 263 K, acquisition time 0.87 s (1 scan, $d_1 = 0.1$ s). Data acquired by Prof. Simon Duckett.

4.10.4. Catalysis Involving Unsaturated Substrates

Following these experiments, some preliminary studies into the hydrogenation of alkynes were conducted. These were set up in a thick wall NMR tube containing compound **6**, substrate (1-octyne), internal standard (SiMe_4) and H_2 (~4 bar).

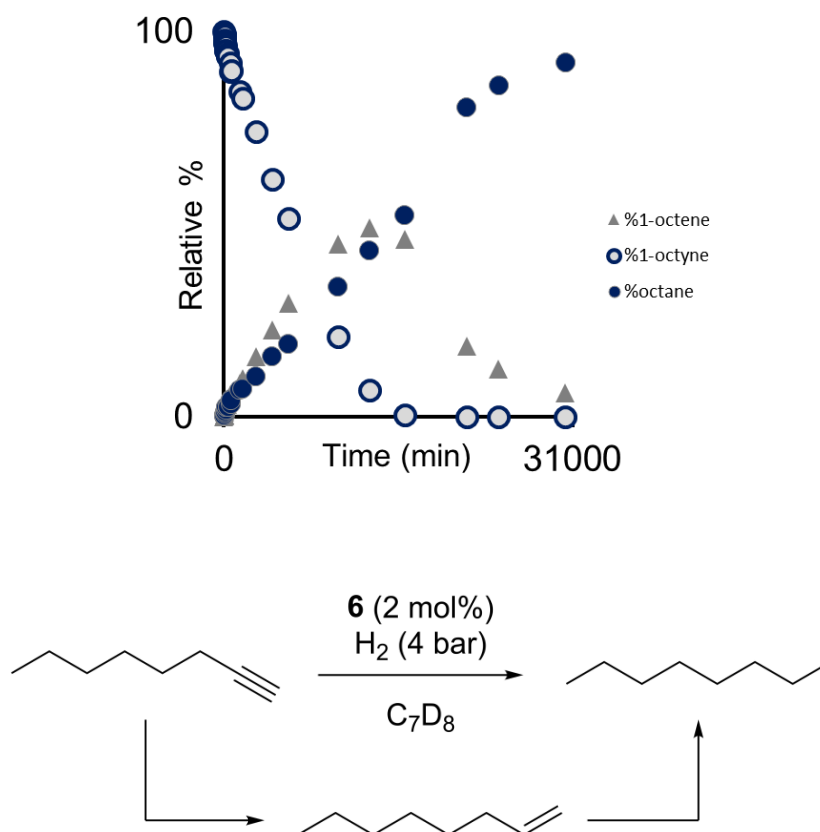


Figure 4.28: Preliminary studies into the catalytic hydrogenation of 1-octyne using compound **6**.

Although very slow, this experiment shows that compound **6** is catalytically active in alkyne hydrogenation, firstly to the terminal alkene and then to the resulting alkane. A small quantity (~2%) of 2-octene is also observed once the alkyne had been used up, indicating that compound **6** may be also active in alkene isomerisation catalysis.

To probe the activity of compound **6** in alkene isomerisation, it was reacted with 1-hexene in the absence of H₂ and shown to produce a mixture of *cis* and *trans* 2-hexene (Figure 4.29). Although the reaction is rather slow, this demonstrates that the cluster is able to perform a C–H activation, a major goal of the project, since alkene isomerizations involving coordinatively unsaturated, non-hydridic late transition metal complexes are known to proceed via an allyl-hydride intermediate, rather than a metal alkyl.^{120–122}

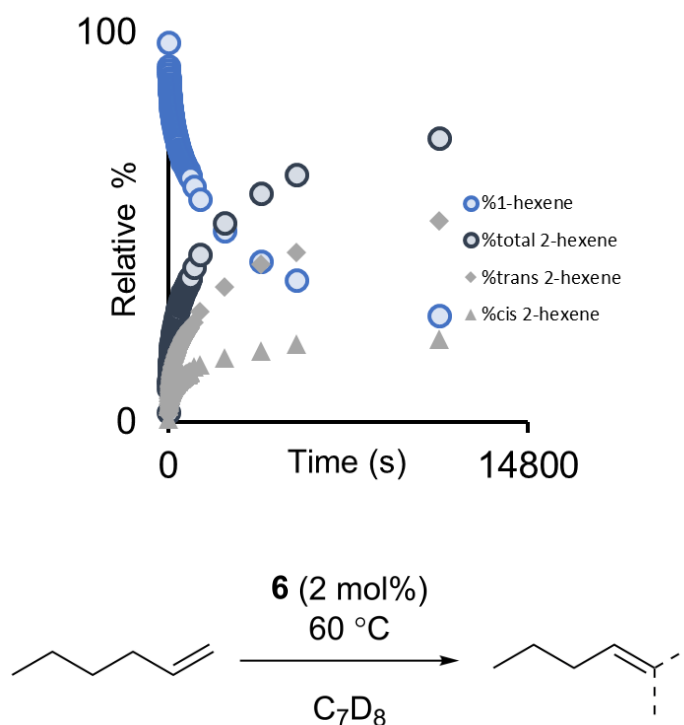


Figure 4.29: Preliminary studies into the catalytic isomerisation of 1-hexene.

4.11. Conclusion

To conclude, this chapter shows that ligand substitution reactions are possible in metal-functionalised Zintl cluster cages. Addition of L_2 type ligands form *closo* clusters of type $[Rh(L_2)\{\eta^5\text{-Ge}_9(\text{Hyp})_3\}]$ which exhibit fluxional behaviour in solution. However, addition of monodentate L type ligands afford *hypercloso* clusters $[Rh(L)\{\eta^3\text{-Ge}_9(\text{Hyp})_3\}]$, allowing access to coordinatively unsaturated rhodium centres, which are catalytically active in H–H and C–H bond activation reactions. Notably, this allowed access to the heterobimetallic complex $[Rh(\mu\text{-H})_2W(\text{Cp})_2\{\eta^3\text{-Ge}_9(\text{Hyp})_3\}]$ (**9**), which was converted to complexes $[RhH\{(\mu\text{-H})_2W(\text{Cp})_2\}\{\eta^3\text{-Ge}_9(\text{Hyp})_3\}][B(\text{Ar}^F)_4]$ (**11**) and $[Rh(\mu\text{-D})_2W(\text{Cp})_2\{\text{Ge}_9(\text{Hyp})_3\}]$ (**12**) by protonation or reaction with D_2 . Reactivity towards the substrates were probed by isotope labelling and *para*hydrogen experiments to gain insights into the mechanisms involved.

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5. Controlled Expansion at a Zintl Cluster Surface

5.1. Background and Introduction

Element ratios are routinely varied when screening the catalytic efficacy of TMMGAs.^{1–5} An example of this, reported by Raman et al.,⁶ showed that for Rh–Ga alloys, those with lower rhodium content (Rh:Ga = 1:125) had the highest productivity for the dehydrogenation of propane. The authors attributed this to the more liquid nature of the catalyst. At intermediate ratios (Rh:Ga = 1:25), intermetallic species at the liquid surface are postulated (Figure 5.1).

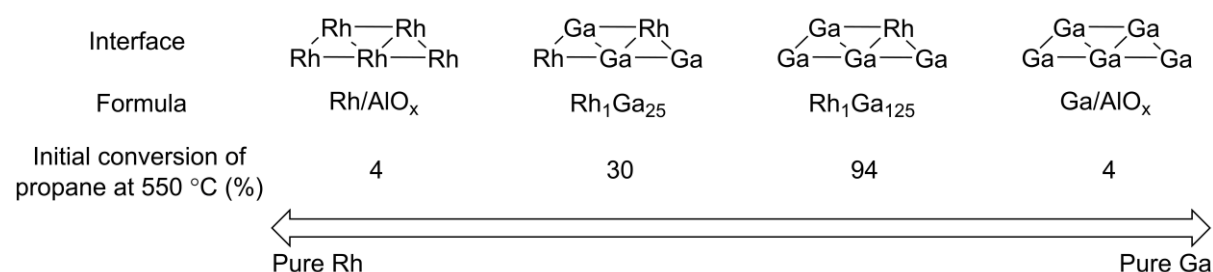
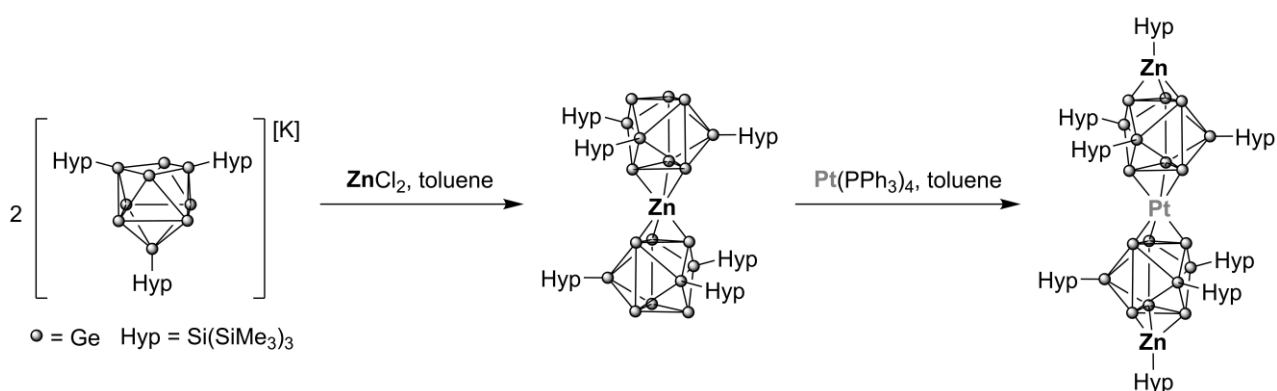


Figure 5.1: Effect of Rh:Ga ratio on the catalytic interface and conversion of propane to propylene. Modified from Raman et al.⁶

Bimetallic complexes of the transition metals have been known since the 1960s when Cotton reported the synthesis and structure [Re₂Cl₈]^{2–}.⁷ They have seen a renaissance in recent years due to an interest in harnessing the unique properties of two metal centres in close proximity.^{8–10} Examples have been reported for elemental combinations spanning most of the periodic table, many of which exhibit cooperativity at the metal–metal bond and can be used in catalytic processes.^{8–15} Unlike varying the metal content in TMMGAs, controllably building multimetallic complexes typically requires bespoke ligand design to support multiple metal centres.¹⁵

In the field of Zintl cluster chemistry, compounds containing more than one transition metal centre are common.^{16,17} Many of these clusters are formed by the serendipitous recombination

of main group and transition metal fragments, resulting in various ratios of each element in the product.^{18,19} Whilst multimetallic cluster growth has been intricately studied,²⁰ the controlled post-modification of these clusters to vary the transition metal content remains relatively unexplored.²¹ For instance, the only known example of a bimetallic compound based on the $[\text{Ge}_9(\text{Hyp})_3]^-$ ion scaffold is $[\text{Pt}\{\text{Zn}(\text{Hyp})\text{Ge}_9(\text{Hyp})_3\}_2]$,²² which features platinum and zinc centres coordinated in an η^3 fashion to the triangular faces of the cage (Scheme 5.1).



Scheme 5.1: Preparation of $[\text{Pt}\{\text{Zn}(\text{Hyp})\text{Ge}_9(\text{Hyp})_3\}_2]$ by Kysliak et al.²²

Despite the non-stoichiometric nature of the reaction, this example shows that $[\text{Ge}_9(\text{Hyp})_3]^-$ clusters can sequentially coordinate more than one transition metal.

A core aim of this project is to build soluble molecular models for TMMGAs, that allow for the transition metal – main group element ratio to be varied. Therefore, we explored the concept of controlled Zintl cluster modification by cluster expansion with late transition metal alkene complexes.

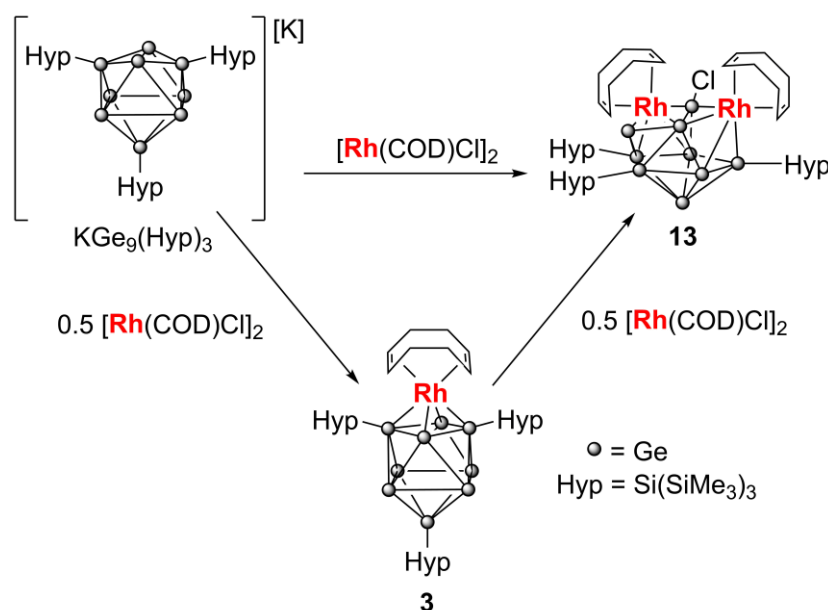
5.2. Chapter Outline

This chapter will describe the use of cluster expansion in the synthesis of homo- and hetero-bimetallic Zintl clusters containing multiple late transition metal alkene fragments.

5.3. $[\{\text{Rh}(\text{COD})\}_2\{\text{Ge}_9(\text{Hyp})_3\text{Cl}\}]$ (**13**)

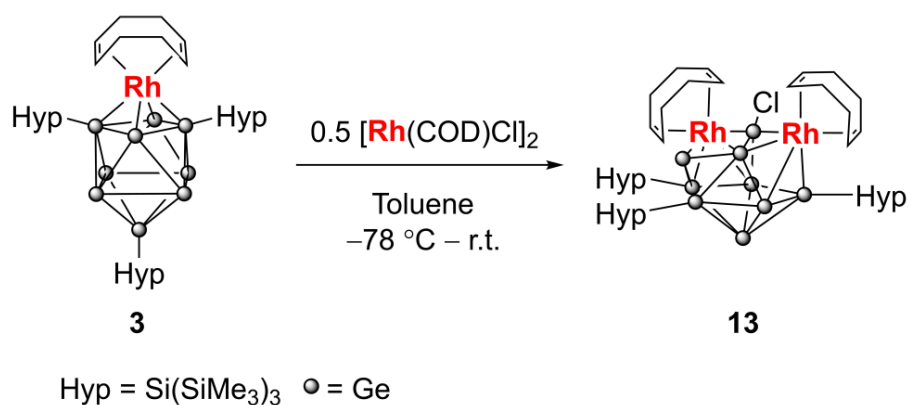
5.3.1. Synthesis of Compound **13**

Initially, $[\text{KGe}_9(\text{Hyp})_3]$ was reacted with one equivalent of $[\text{Rh}(\text{COD})\text{Cl}]_2$ at $-78\text{ }^\circ\text{C}$ in toluene to yield a mixture of products, from which $[\text{Rh}(\text{COD})\{\text{Ge}_9(\text{Hyp})_3\}]$ (**3**) and a new species $[\{\text{Rh}(\text{COD})\}_2\{\text{Ge}_9(\text{Hyp})_3\text{Cl}\}]$ (**13**) were isolated in low yields. This reaction was accompanied by extensive decomposition (Scheme 5.2).



Scheme 5.2: Synthetic pathways to $[\{\text{Rh}(\text{COD})\}_2\{\text{Ge}_9(\text{Hyp})_3\text{Cl}\}]$ (**13**).

To avoid decomposition, compound **13** can be instead selectively prepared using a stepwise synthesis starting from compound **3** (Scheme 5.3). This indicates that compound **13** is most likely assembled by the reaction of two “ $\text{Rh}(\text{COD})\text{Cl}$ ” monomers, rather than one $[\text{Rh}(\text{COD})\text{Cl}]_2$ dimer.



Scheme 5.3: Preparation of [$\{\text{Rh}(\text{COD})\}_2\{\text{Ge}_9(\text{Hyp})_3\text{Cl}\}$] (**13**).

To access on a preparative, a toluene solution of compound **3**, cooled to $-78\text{ }^{\circ}\text{C}$, was added to a toluene solution of $[\text{Rh}(\text{COD})\text{Cl}]_2$ (0.5 eq.) at $-78\text{ }^{\circ}\text{C}$. This was warmed to room temperature over the course of an hour and further stirred at room temperature for three hours, producing compound **13** in an 88% yield. It must be noted that this reaction only proceeds cleanly at low temperatures ($< -30\text{ }^{\circ}\text{C}$), otherwise resulting in an intractable product mixture.

Due to the inherent stability of *closo* clusters, this reaction is a rare instance of a *closo* to *closo* cluster expansion reaction.^{16,23} Similar transformations are known in the chemistry of carboranes, although they tend to proceed via reduced *nido* species formed *in situ*.²⁴

5.3.2. Nuclear Magnetic Resonance Spectroscopic Analysis of Compound **13**

Inspection of the ^1H NMR spectrum of compound **13** shows the complete loss of resonances relating to the hypersilyl substituents of compound **3** at 0.29 and 0.57 ppm and the appearance of new signals at 0.50, 0.54 and 0.69 ppm (in a 1:1:1 ratio). This indicates loss of the C_{2v} cluster symmetry to a complex that is not fluxional on the NMR timescale. In addition to this, multiple new resonances between 1.4 and 5.7 ppm are present which integrate in accordance with two inequivalent COD ligands. The $^{29}\text{Si}/^1\text{H}$ HMBC NMR spectrum exhibits four inequivalent ^{29}Si environments at -79.74 , -74.85 , -62.92 and -8.16 ppm and six cross peaks, confirming three inequivalent hypersilyl substituents (Figure 5.2).

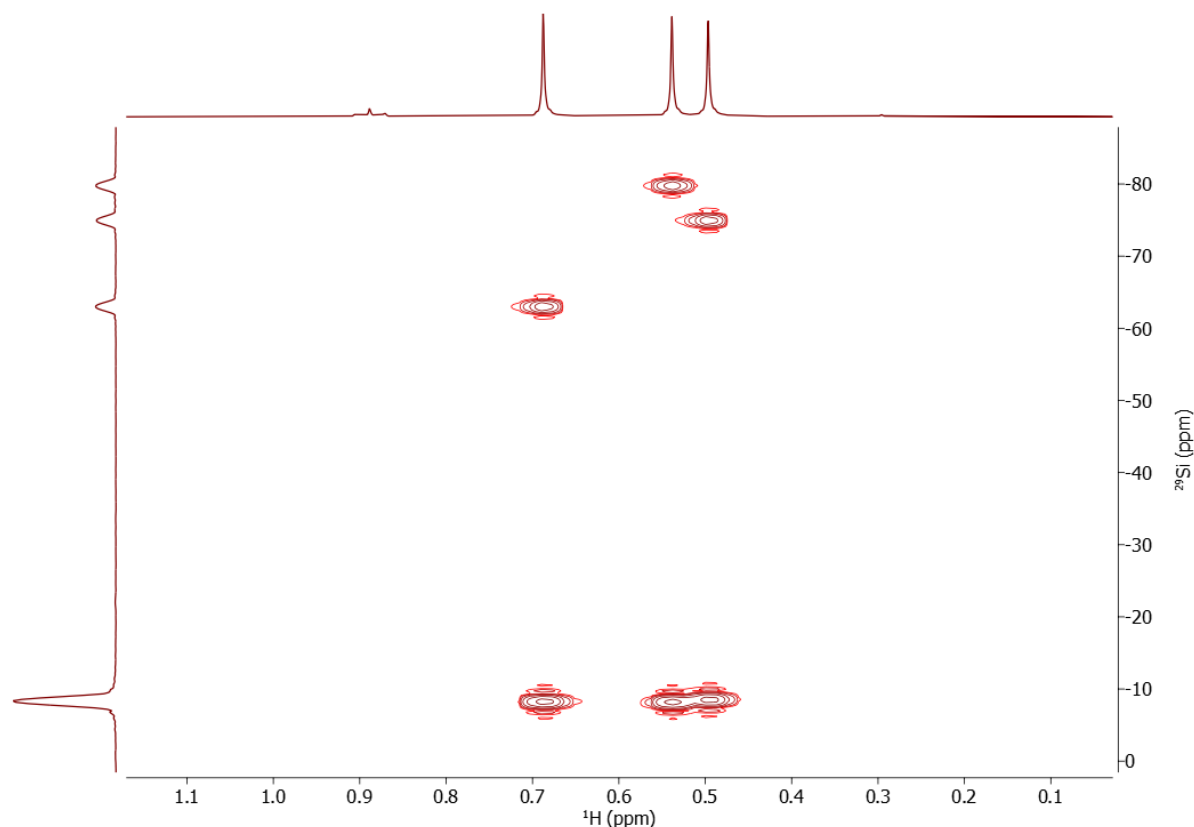


Figure 5.2: $^{29}\text{Si}/^1\text{H}$ HMBC NMR spectrum (C_6D_6 , 298 K, 79.5 MHz) of compound **13**.

5.3.3. Single Crystal X-ray Structure of Compound **13**

Red-brown crystals of compound **13** suitable for single-crystal X-ray diffraction were obtained from an *n*-hexane solution stored at $-40\text{ }^\circ\text{C}$. The asymmetric unit contains one molecule of compound **13** and half a molecule of *n*-hexane. As can be seen in the crystal structure of the product (Figure 5.3), this reaction resulted in a vertex addition, in which a new Rh(COD) fragment has been introduced and a chloride has been transferred onto a proximal germanium atom.

The cluster core adopts an asymmetric, edge-contracted icosahedral geometry containing two Rh(COD) vertices bridged by two germanium vertices. One Rh(COD) vertex (Rh1) takes place in an η^5 coordination site of the cage, complementary to $[\text{Rh}(\text{DPPE})\{\eta^5\text{-Ge}_9(\text{Hyp})_3\}]$ (**4**) and the $[\text{M}(\text{CO})_3\{\eta^5\text{-Ge}_9(\text{Hyp})_3\}]^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) series reported by Schnepf.^{25,26} The

second Rh(COD) fragment is coordinated in an η^4 mode to the germanium support (Rh2), in a similar fashion to the precursor, compound **3**.

The chloride (Cl1), originating from the $[\text{Rh}(\text{COD})\text{Cl}]_2$ precursor, is retained in the product and has been transferred to an adjacent germanium atom (Ge5). The hypersilyl substituents have also rearranged, two of which are now attached to adjacent germanium atoms. Though it is not clear whether the Ge(Hyp) vertices are rearranging or the hypersilyl substituents are moving over the surface of the cage. Some evidence for the latter has been presented by Sevov for the addition of a $\text{Pt}(\text{PPh}_3)$ vertex to the tetrafunctionalised cluster $[\text{Ge}_9(\text{Hyp})_3\text{Et}]$.²⁷

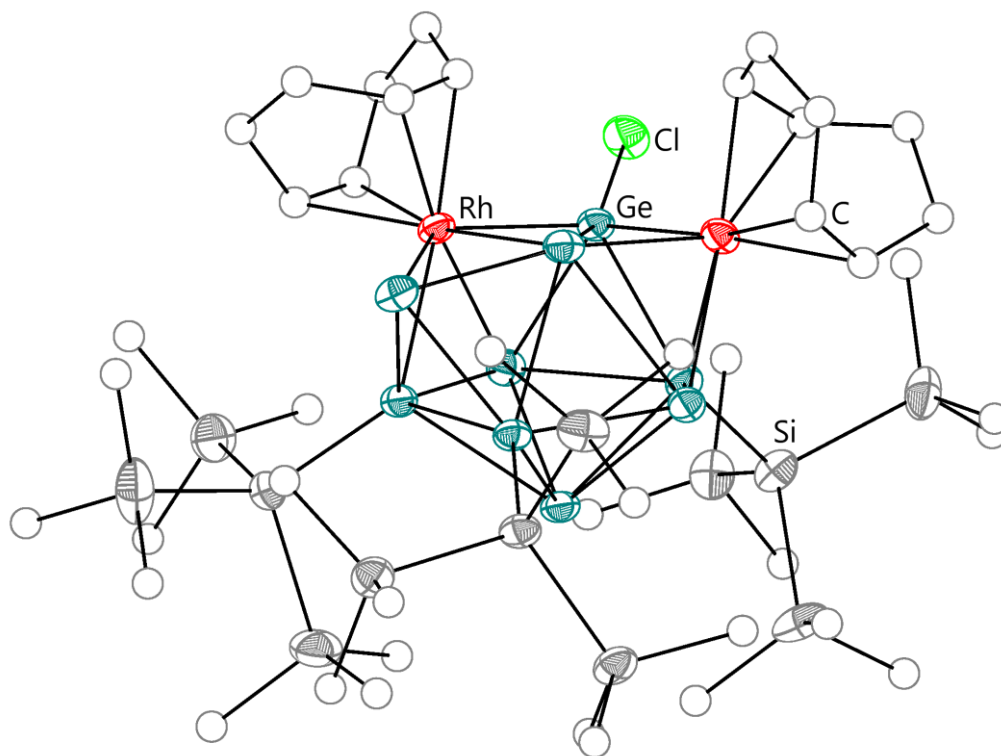
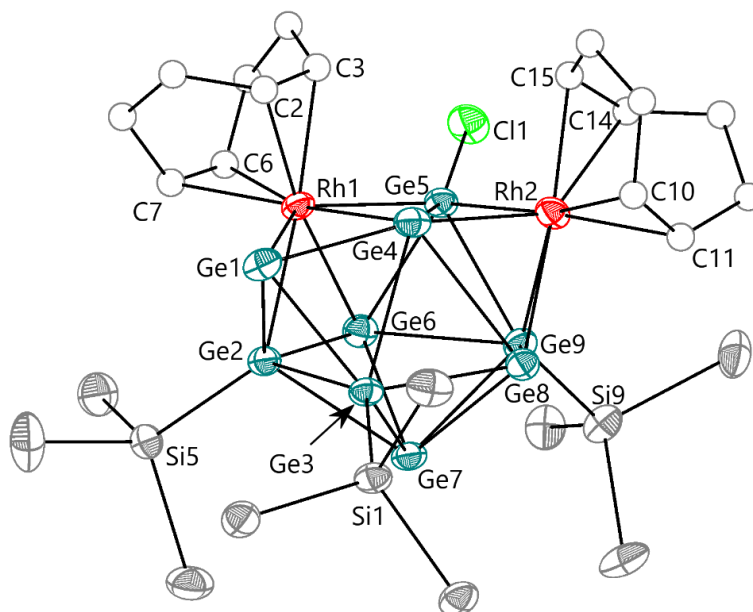


Figure 5.3: Single crystal X-ray structure of **13** in the solid-state. Anisotropic displacement ellipsoids set at 50% probability. All carbon atoms are pictured as spheres of an arbitrary radius. Hydrogen atoms are omitted for clarity.

Rh–Ge distances in compound **13** are in the range of 2.380(1) – 2.687(1) Å and 2.415(1) – 2.861(1) Å at the η^4 and η^5 positions respectively. These are comparable to the η^4 and η^5

coordination modes found in compounds **3** (2.496(2) – 2.581(2) Å) and **4** (2.561(1) – 2.837(1) Å). The Rh–C distances vary between 2.166(7) – 2.254(7) Å, which compares well with those of compound **3** (2.168(11) – 2.218(12) Å).

Table 5.1: Selected crystallographic bond distances (Å) of compound **13**. A truncated molecular model is included as a key.



Bond	Distance (Å)	Bond	Distance (Å)
Ge1–Rh1	2.614 (1)	Ge4–Rh2	2.535(1)
Ge2–Rh1	2.514(1)	Ge5–Rh2	2.380(1)
Ge4–Rh1	2.681(1)	Ge8–Rh2	2.592(1)
Ge5–Rh1	2.415(1)	Ge9–Rh2	2.687(1)
Ge6–Rh1	2.861(1)	Rh1–C10	2.251(6)
Rh1–C2	2.166(7)	Rh1–C11	2.254(7)
Rh1–C3	2.210(1)	Rh1–C14	2.197(7)
Rh1–C6	2.244(8)	Rh1–C15	2.189(7)
Rh1–C7	2.216(8)	Ge2–Si5	2.457(1)
Ge3–Si1	2.418(1)	Ge9–Si9	2.420(1)

Compound **13** is a *closo* 11-vertex deltahedron with 24 valence electrons available for cluster bonding ($\text{Rh}(\text{COD}) = 1 \text{ e}^-$, $\text{Ge} = 2 \text{ e}^-$, $\text{Ge}(\text{Hyp}) = 3 \text{ e}^-$, $\text{Ge}(\text{Cl}) = 3 \text{ e}^-$). It is isostructural and valence isoelectronic to the only two structurally characterised edge-contracted icosahedral clusters $[\text{B}_{11}\text{H}_{11}]^{2-}$ and $[\text{B}_{11}\text{H}_{10}(\text{SMe}_2)]^-$.^{28,29} Zintl clusters with 11 vertices are rare and none of the examples reported to date have a *closo* electron count.^{19,30}

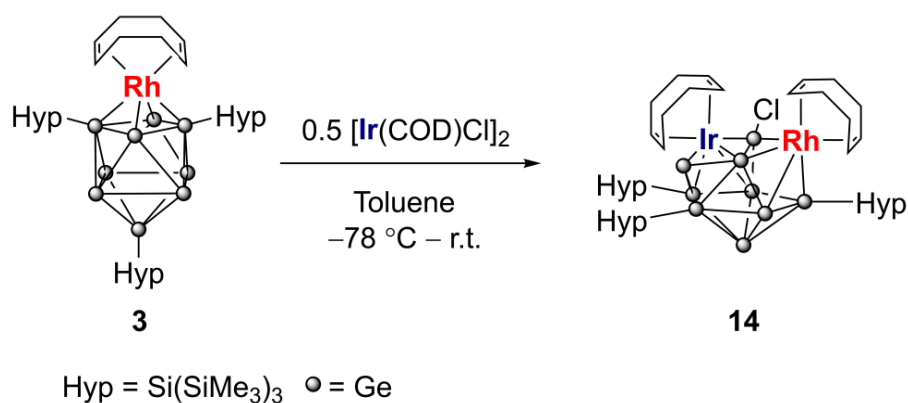
5.3.4. Further Chemistry of Compound **13**

Further chemistry has focussed on attempts to displace the chloride substituent and to probe the reversibility of the cluster expansion transformation. All attempts so far have been unsuccessful. These include: halide abstraction with $\text{Na}[\text{B}(\text{Ar}^{\text{F}})_4]$ ($\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$), reduction with various reducing agents (e.g.: KC_8 , bis(^{Mes}NacNac)dimagnesium (^{Mes}NacNac = mesityl[3-(mesitylamino)-1-methyl-2-butenylidene]amide)), reactions with organoalkali reagents (for example: $\text{Na}(\text{Cp})$, KBz and NaCCMe), bis(pinacolato)diboron, or $[\text{KGe}_9(\text{Hyp})_3]$. All of these attempts showed either no evidence of reactivity, or gave rise to intractable mixtures. As with compound **3**, compound **13** decomposes on exposure to dihydrogen.

5.4. $[\{\text{Rh}(\text{COD})\}\{\text{Ir}(\text{COD})\}\{\text{Ge}_9(\text{Hyp})_3\text{Cl}\}]$ (**14**)

5.4.1. Synthesis of Compound **14**

Interested in extending the methodology used for the synthesis of compound **13**, we attempted to access heterobimetallic complexes with a complementary topology. We proposed that using a different metal reagent would allow us to determine which of the rhodium clusters in compound **13** was originally present in the precursor, compound **3**. The second metal should contribute the same number of electrons and have a similar steric profile to $\text{Rh}(\text{COD})$ to retain the *closo* 24 valence electron count. For this purpose, $[\text{Ir}(\text{COD})\text{Cl}]_2$ was used as the precursor in the synthesis of a Rh/Ir heterobimetallic complex, **14** (Scheme 5.4).



Scheme 5.4: Preparation of [$\{\text{Rh}(\text{COD})\}\{\text{Ir}(\text{COD})\}\{\text{Ge}_9(\text{Hyp})_3\text{Cl}\}$] (**14**).

A toluene solution of compound **3** cooled to -78°C was added to a toluene suspension of $[\text{Ir}(\text{COD})\text{Cl}]_2$ at -78°C under the exclusion of light. This was stirred for 1 hour cold, then for 3 hours in the dark at room temperature. The brown solution was dried *in vacuo* and extracted in *n*-pentane to remove a small amount of black solid. The solvent was removed *in vacuo* and the resultant brown solid lyophilised from benzene. Solids of compound **14** are extremely air sensitive and ignite spontaneously in air. It was found that performing the reaction and workup in the dark improved yields and decreased the formation of black insoluble decomposition products. Compound **14** is moderately unstable in solution and decomposes within a few days at room temperature to an intractable mixture, indicated by broadening and subsequent loss of the ^1H NMR resonances relating to the hypersilyl substituents, which limited the study of further reactivity.

5.4.2. Nuclear Magnetic Resonance Spectroscopic Analysis of Compound **14**

Analysis of a crystalline sample of compound **14** by ^1H NMR spectroscopy revealed a similar spectrum to that of compound **13**. Three peaks, relating to three inequivalent hypersilyl resonances were observed at 0.48, 0.55 and 0.70 ppm (in a 1:1:1 ratio) indicating, again, the loss of C_{2v} cluster symmetry. In addition to this, multiple resonances between 1.1 and 5.7 ppm were present, consistent with two inequivalent COD ligands.

Similarly to compound **13**, the $^{29}\text{Si}/^1\text{H}$ HMBC NMR spectrum of compound **14** shows four inequivalent ^{29}Si environments at -78.36 , -74.64 , -64.28 and -8.34 ppm and six cross peaks, indicative of three inequivalent hypersilyl substituents (Figure 5.4). This spectrum is qualitatively similar to that of **13** (Figure 5.2).

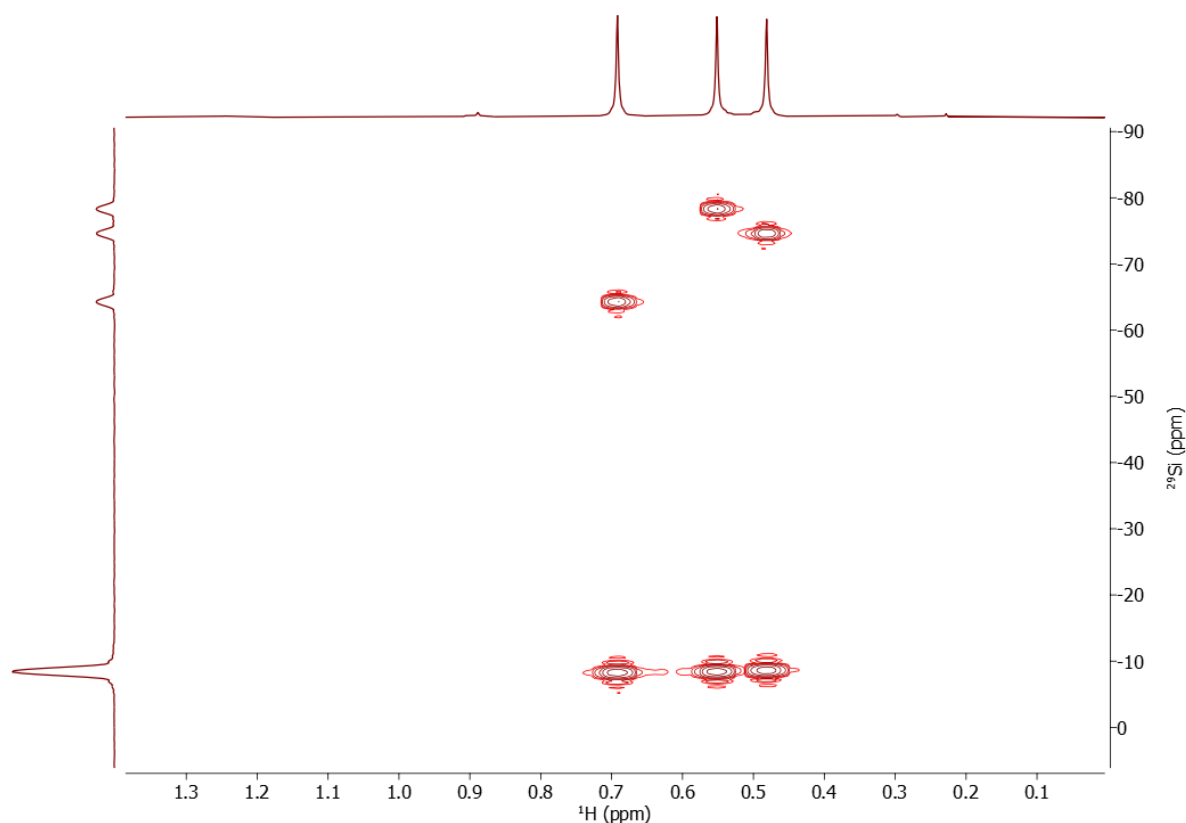


Figure 5.4: $^{29}\text{Si}/^1\text{H}$ HMBC NMR spectrum (C_6D_6 , 298 K, 79.5 MHz) of compound **14**.

5.4.3. Single Crystal X-ray Structure of Compound **14**

Dark red crystals of compound **14** suitable for single-crystal X-ray diffraction were obtained from an *n*-hexane solution stored at -40 °C. On initial inspection, the unit cell parameters of compounds **13** and **14** are almost identical, differing by $3 \text{ \AA}^3$ in volume. Both clusters crystallise in space group $P2_1/c$. The asymmetric unit contains one molecule of compound **14** and half a molecule of *n*-hexane. The Single crystal X-ray structure (Figure 5.5) exhibits the same cluster topology as compound **13** with the two transition metal centers occupying unique sites, confirming incorporation of an Ir(COD) vertex.

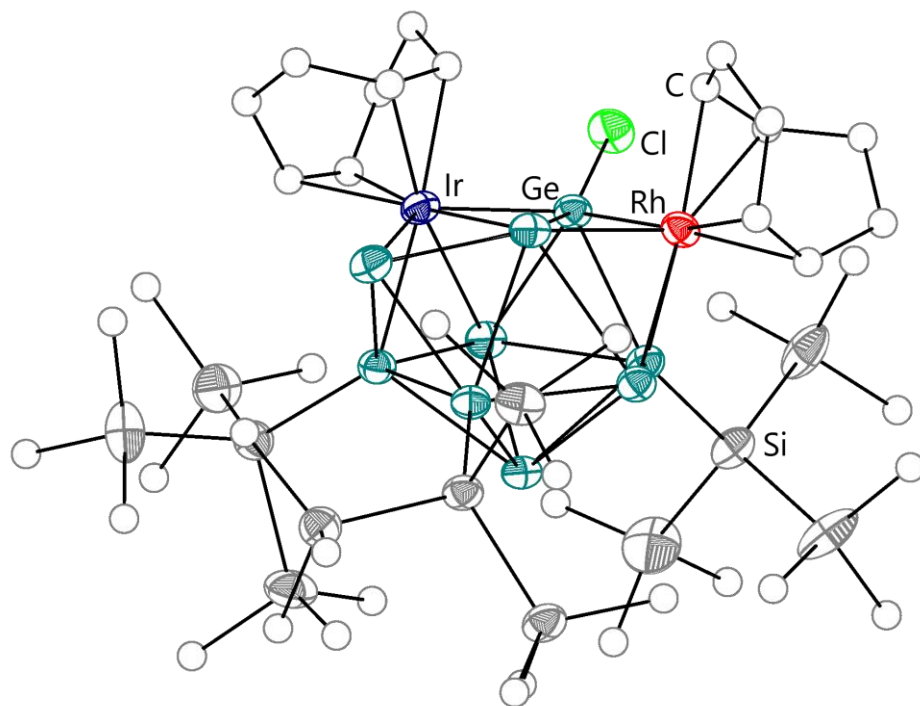
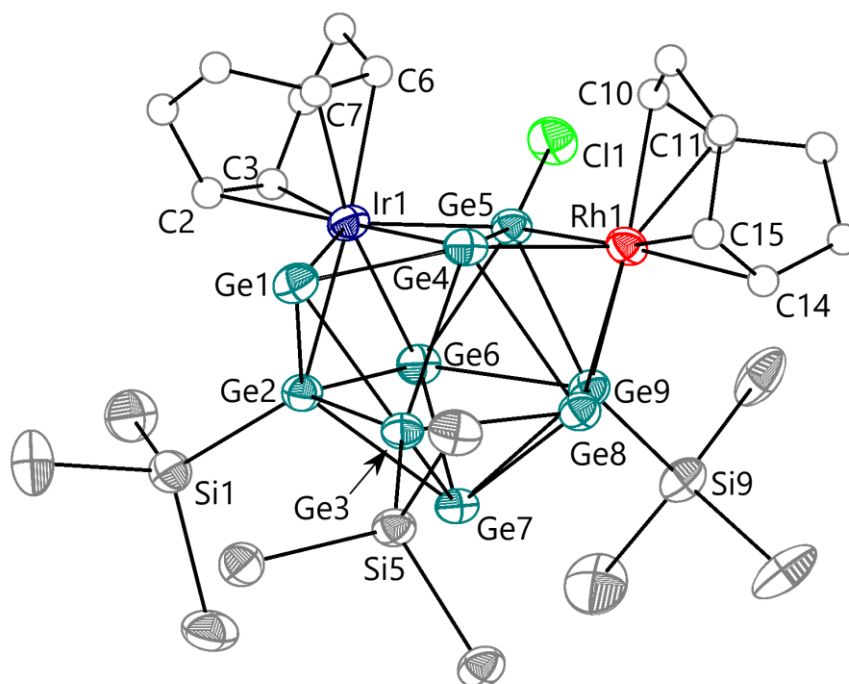


Figure 5.5: Single crystal X-ray structure of compound **14**. Anisotropic displacement ellipsoids set at 50% probability. All carbon atoms are pictured as spheres of an arbitrary radius. Hydrogen atoms are omitted for clarity.

At the η^4 coordinated Rh(COD) vertex, all bond lengths are similar to compound **13**, differing by no more than ± 0.01 Å in either the Rh–Ge or Rh–C distances. The η^5 coordinated Ir(COD) vertex is also similar to its rhodium counterpart in compound **13**, accounting for the slight increase in radius (~ 0.02 Å).³² There is almost no difference in the Ge–Si bond lengths, which accounts for the very similar ^{29}Si NMR chemical shifts.

Table 5.2: Selected crystallographic bond distances (Å) of compound **14**. A truncated molecular model is included as a key.



Bond	Distance (Å)	Bond	Distance (Å)
Ge1–Ir1	2.606(1)	Ge4–Rh1	2.541(1)
Ge2–Ir1	2.519(1)	Ge5–Rh1	2.375 (1)
Ge4–Ir1	2.700(1)	Ge8–Rh1	2.588(1)
Ge5–Ir1	2.424(1)	Ge9–Rh1	2.691(1)
Ge6–Ir1	2.861(1)	Rh1–C10	2.200(7)
Ir1–C2	2.214(7)	Rh1–C11	2.198(7)
Ir1–C3	2.180(8)	Rh1–C14	2.253(6)
Ir1–C6	2.201(9)	Rh1–C15	2.252(6)
Ir1–C7	2.170 (7)	Ge3–Si5	2.417(1)
Ge2–Si1	2.458(1)	Ge9–Si9	2.412(1)

Since the Ir(COD) fragment is valence isoelectronic to Rh(COD), compound **14** has the same electronic structure as of compound **13** and can be classified as an 11-vertex *closo* deltahedron with 24 valence electrons available for cluster bonding.

Given the similar covalent and ionic size of rhodium(I) and iridium(I),^{32,33} previous reports of η^4 bound Ir(COD) fragments on tetrel Zintl clusters,^{23,34} and absence of scrambling over the η^4 and η^5 sites in the crystal structure of compound **14**, we can deduce that the Rh(COD) moiety at the η^4 vertex in both compounds **13** and **14** most likely originates from compound **3**.

Due to the solution instability of compound **14** (*vide supra*), it was not subjected to further chemistry.

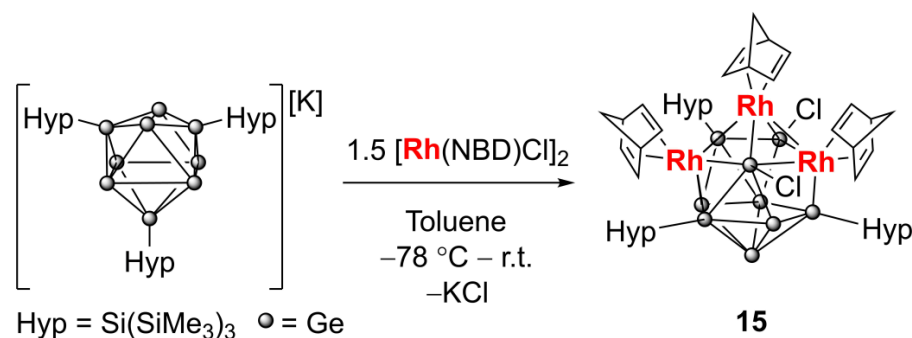
5.5. $[\{\text{Rh}(\text{NBD})\}_3\{\text{Ge}_9(\text{Hyp})_3\text{Cl}_2\}]$ (**15**)

5.5.1. Synthesis of Compound **15**

Due to the peculiar 11-vertex structure of compound **13**, it was proposed that a second *closo* to *closo* cluster expansion may yield a 12-vertex *closo* icosahedron, a geometry that is ubiquitous in cluster chemistry.¹⁷ However, adding further equivalents of $[\text{Rh}(\text{COD})\text{Cl}]_2$ to compound **13** resulted in no change by ^1H NMR spectroscopy. We reasoned that this was due to the bulky COD ligands sterically restricting further reactivity. Therefore, $[\text{Rh}(\text{NBD})\text{Cl}]_2$ (NBD = norbornadiene), which contains a smaller diene, was used as the rhodium precursor.

Initially a stepwise synthesis was attempted by first targeting the complex $[\text{Rh}(\text{NBD})\{\text{Ge}_9(\text{Hyp})_3\}]$, the NBD analogue of compound **3**, by adding 0.5 equivalents of $[\text{Rh}(\text{NBD})\text{Cl}]_2$ to $[\text{KGe}_9(\text{Hyp})_3]$. Analysis of the reaction mixture by ^1H NMR spectroscopy, however, did not display two hypersilyl resonances in a 2:1 ratio between 0 and 1 ppm for the expected product. Instead, unreacted $[\text{KGe}_9(\text{Hyp})_3]$ was observed, in addition to three

peaks in a 1:1:1 ratio. Addition of $[\text{Rh}(\text{NBD})\text{Cl}]_2$ (1 eq.) to this mixture consumed the excess $[\text{KGe}_9(\text{Hyp})_3]$, and increased the intensities of the three new hypersilyl NMR resonances.



Scheme 5.5: Preparation of $[\{\text{Rh}(\text{NBD})\}_3\{\text{Ge}_9(\text{Hyp})_3\text{Cl}_2\}]$ (**15**).

Repeating this experiment with one and a half equivalents of $[\text{Rh}(\text{NBD})\text{Cl}]_2$ overnight in toluene at -78°C (Scheme 5.5), followed by crystallization from *n*-pentane at -80°C produced dark red crystals of $[\{\text{Rh}(\text{NBD})\}_3\{\text{Ge}_9(\text{Hyp})_3\text{Cl}_2\}]$ (**15**) in an 80% isolated yield.

5.5.2. Nuclear Magnetic Resonance Spectroscopic Analysis of Compound **15**

Analysis of the ^1H NMR spectrum of compound **15** revealed three peaks of equal intensity at 0.59, 0.60 and 0.64 ppm, relating to three inequivalent hypersilyl environments. In addition, nine broad signals relating to NBD ligands were observed. Six of the resonances appear within the range 3.85 – 4.84 ppm, relating to the alkenic protons, though $^2J_{\text{H-Rh}}$ coupling could not be resolved.

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum is consistent with this, exhibiting three peaks relating to the hypersilyl substituents. In addition, three singlet resonances for the NBD methylene bridge and two sets of three doublets were observed for the NBD olefinic and R_3CH environments. The $^{29}\text{Si}/^1\text{H}$ HMBC spectrum is consistent with three inequivalent hypersilyl environments, much like compounds **13** and **14**, exhibiting four ^{29}Si signals with asymmetry at the $\text{Si}(\text{SiMe}_3)_3$ environment and resulting overlapping of cross-peaks (Figure 5.6).

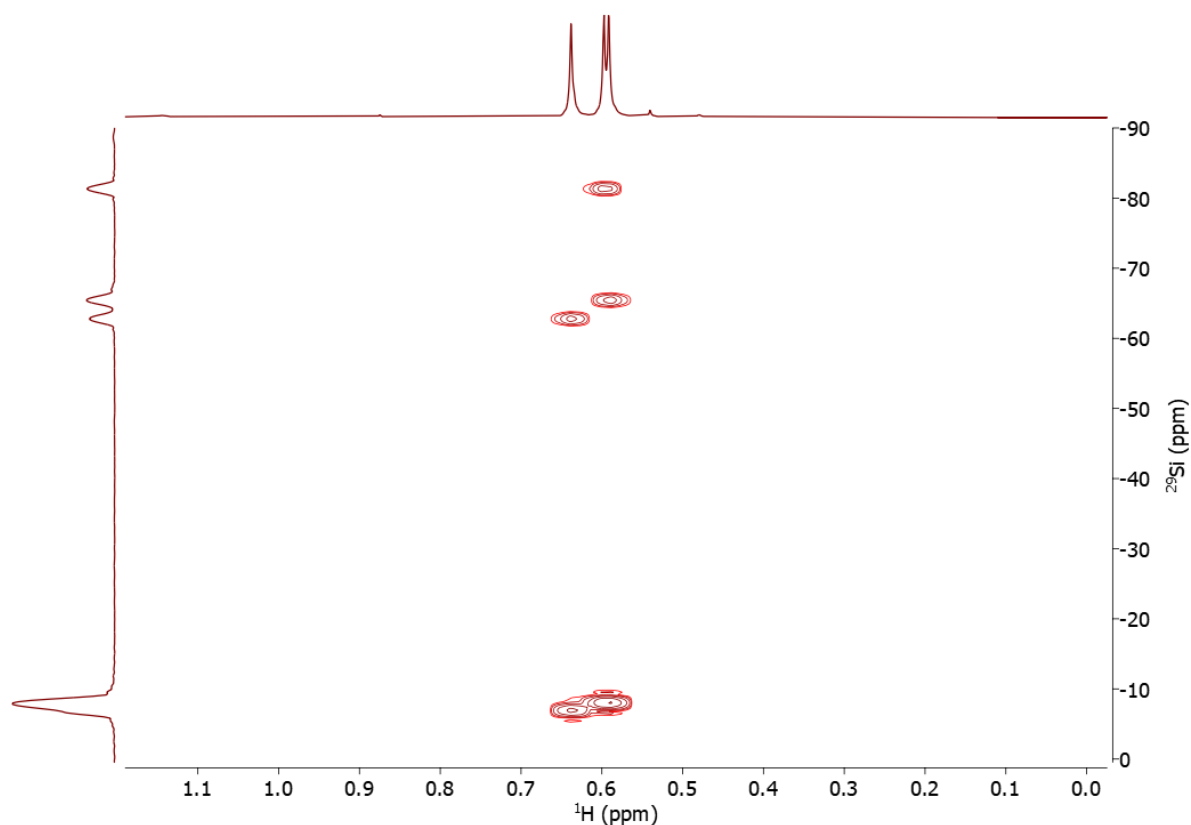


Figure 5.6: $^{29}\text{Si}/^1\text{H}$ HMBC NMR spectrum (C_6D_6 , 298 K, 79.5 MHz) of compound **15**.

5.5.3. Single Crystal X-ray Structure of Compound **15**

The asymmetric unit contains one crystallographically unique molecule of compound **15** and 1.5 equivalents of *n*-pentane as solvent of crystallisation (Figure 5.7). The cluster has a distorted *closo* 12-vertex icosahedral geometry and can be electron counted as a *closo* deltahedron with 26 valence electrons available for cluster bonding ($\text{Rh}(\text{NBD}) = 1\text{ e}^-$, $\text{Ge} = 2\text{ e}^-$, $\text{Ge}(\text{Hyp}) = 3\text{ e}^-$, $\text{Ge}(\text{Cl}) = 3\text{ e}^-$).

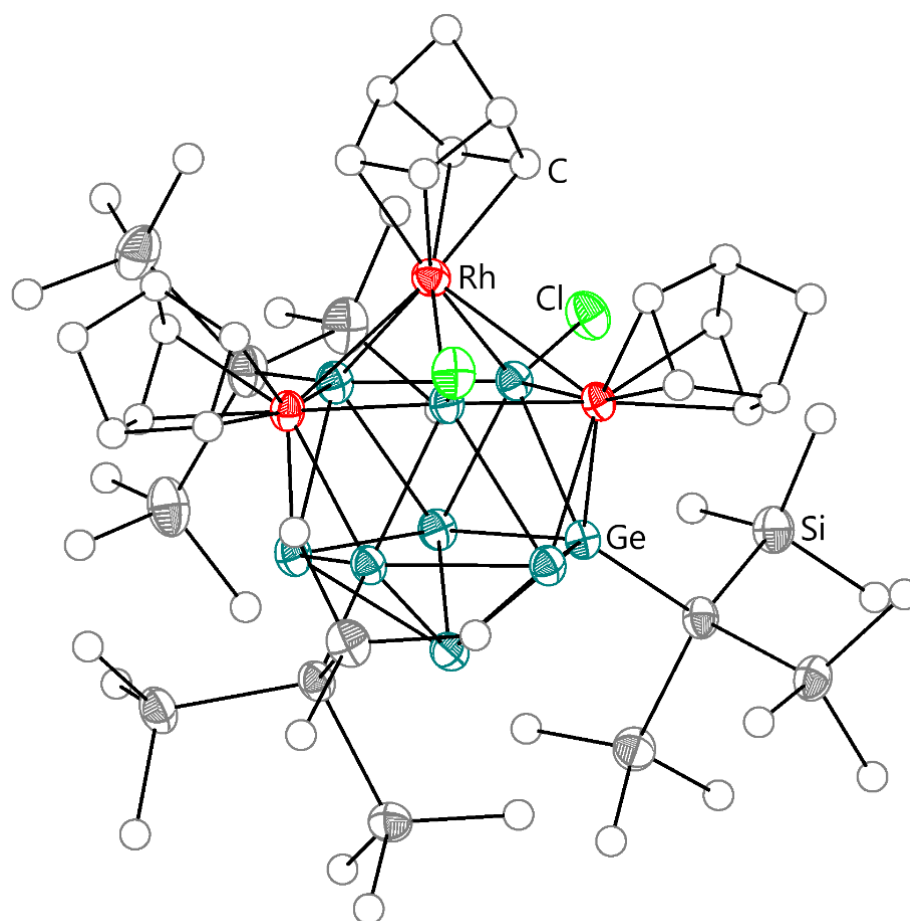
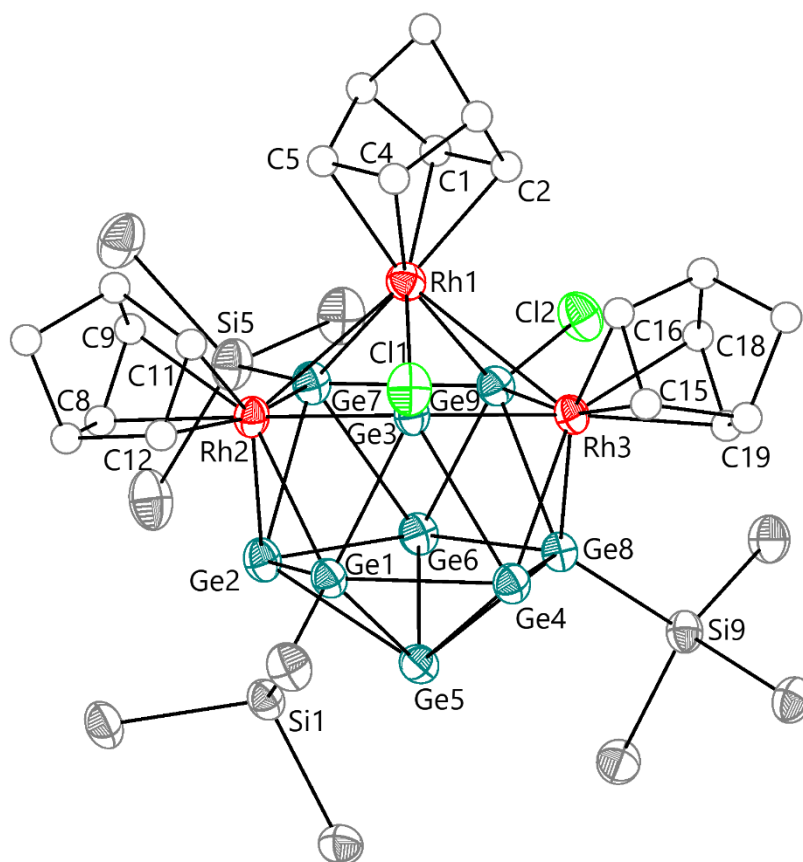


Figure 5.7: Single crystal X-ray structure of compound **15**. Anisotropic displacement ellipsoids set at 50% probability. All carbon atoms are pictured as spheres of an arbitrary radius. Hydrogen atoms are omitted for clarity.

The structure shows two Rh(NBD) fragments coordinated in an η^5 mode by four germanium atoms and the central rhodium atom with Rh–Ge distances in the range of 2.415(1) – 2.551(1) Å. The central Rh(NBD) fragment is capping the edge-contracted icosahedron in an η^5 coordination mode, bonding to three germanium atoms and two flanking rhodium atoms with Rh–Ge distances in the range of 2.418(1) – 2.723(1) Å. The rhodium vertices are separated by 2.989(1) and 3.119(1) Å, which are longer than predicted for a discrete single bond.³² Two chlorides have been transferred to adjacent germanium atoms.

Table 5.3: Selected crystallographic bond distances (Å) of compound **15**. A truncated molecular model is included as a key.



Bond	Distance (Å)	Bond	Distance (Å)	Bond	Distance (Å)
Ge3–Rh1	2.499(1)	Ge1–Rh2	2.606(1)	Ge3–Rh3	2.418(1)
Ge7–Rh1	2.551(1)	Ge2–Rh2	2.723(1)	Ge4–Rh3	2.682(1)
Ge9–Rh1	2.415(1)	Ge3–Rh2	2.470(1)	Ge8–Rh3	2.542(1)
Rh3–Rh1	3.120(1)	Ge7–Rh2	2.482(1)	Ge9–Rh3	2.489(1)
Rh1–C1	2.186(5)	Rh1–Rh2	2.989(1)	Rh3–C15	2.197(4)
Rh1–C2	2.174(5)	Rh2–C8	2.191(4)	Rh3–C16	2.196(5)
Rh1–C4	2.170(5)	Rh2–C9	2.187(4)	Rh3–C18	2.186(3)
Rh1–C5	2.180(5)	Rh2–C11	2.186(6)	Rh3–C19	2.206(3)
Ge3–Cl1	2.243(1)	Rh2–C12	2.204(4)	Ge9–Cl2	2.210(1)
Ge7–Si5	2.457(1)	Ge1–Si1	2.419(1)	Ge8–Si9	2.428(1)

The Rh–C distances range between 2.170(5) – 2.206(3) Å and are, on average, slightly shorter for the central Rh(NBD) than the flanking Rh(NBD) environments. These bond lengths are comparable to Rh(NBD) complexes in the literature, for example: [Rh(NBD)(Ind)] (2.07(1) – 2.15(1) Å) (Ind = indenyl),³⁵ [Rh(NBD)(Tol)][SbF₆] (2.09(2) – 2.13(1) Å),³⁶ and [Rh(NBD)(DPPE)][BF₄] (2.207(3) – 2.236(3) Å).³⁷

Much like compound **13**, salt metathesis reactions to further functionalise compound **15** were also unsuccessful. In addition, mixed COD/NBD 12-vertex clusters were found to be inaccessible, for example, by adding [Rh(NBD)Cl]₂ to compound **3**. Compound **15** is of interest to future catalytic studies, given the presence of three rhodium alkene centres in close proximity.

5.6. [{Rh(COD)}{Ni(COD)}₂{Ge₉(Hyp)₃}] (**16**)

Density functional theory calculations performed on [Rh(COD){η⁴-Ge₉(Hyp)₃}] (**3**) revealed that the occupied molecular orbitals, HOMO and HOMO–1, have germanium lone pair character at the open triangular faces (Figure 5.8). This suggested that the cluster may allow for additional coordination at these sites.

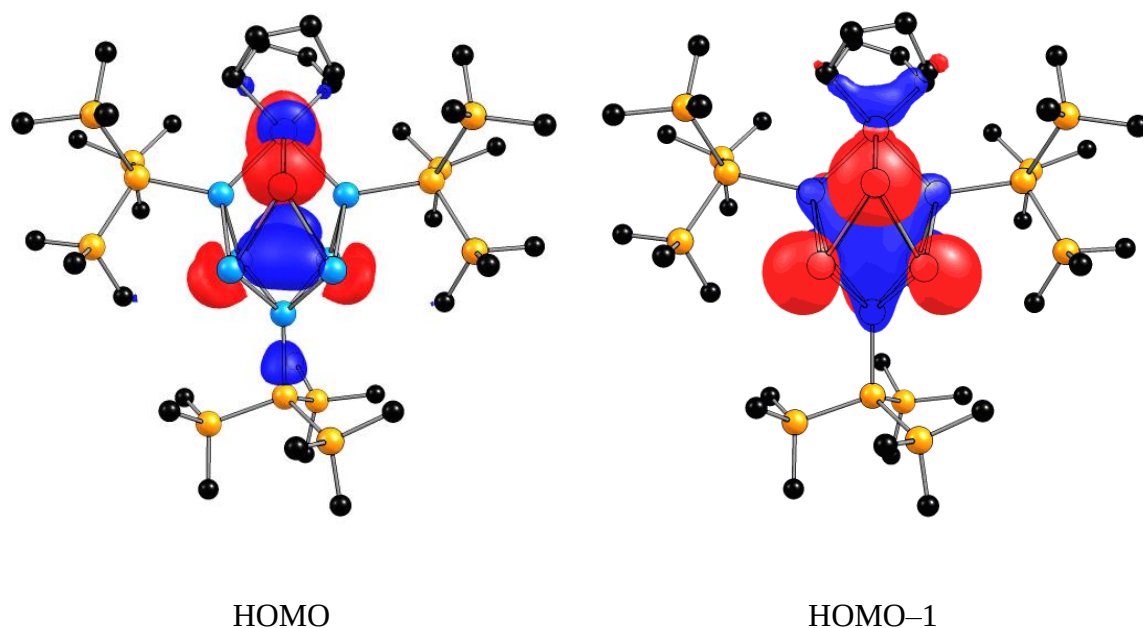
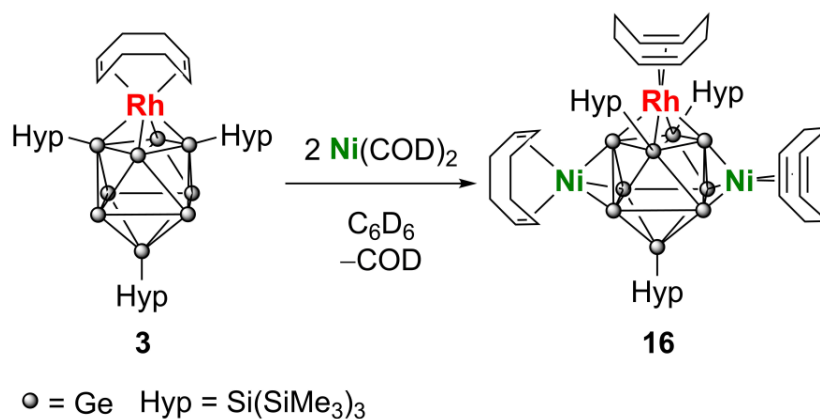


Figure 5.8: Highest occupied molecular orbitals of **3** (BP86/Def2-TZVP).^{38–41}

Nickel has been shown before to have an affinity for coordination at the triangular faces of $[\text{KGe}_9(\text{Hyp})_3]$.^{42,43} In addition, $[\text{Ni}(\text{COD})_2]$ is a well-known nickel(0) source for donor ligand stabilised catalysts of general formula $[\text{Ni}(\text{COD})(\text{L})_2]$, where L is a phosphine or carbene.^{44–46} Therefore $[\text{Ni}(\text{COD})_2]$ was chosen to probe the accessibility of these coordination sites on the *exo* surface of the cluster in the synthesis of a group 9/10 heterobimetallic cluster.

5.6.1. Synthesis of Compound **16**



Scheme 5.6: Preparation of $[\{\text{Rh}(\text{COD})\}\{\text{Ni}(\text{COD})\}_2\{\text{Ge}_9(\text{Hyp})_3\}]$ (**16**).

Benzene- d_6 was added to a solid mixture containing two equivalents of Ni(COD)_2 and one equivalent of compound **3**. This was stirred overnight, resulting in a blood-red solution. The solvent and displaced COD were removed *in vacuo* before dissolving in *n*-pentane for crystallisation (Scheme 5.6). Though the reaction was quantitative by NMR spectroscopy, the isolated crystalline yield was 66% due to the high solubility of the product. Both the major and minor components of compound **3** converged to a single product.

5.6.2. Nuclear Magnetic Resonance Spectroscopic Analysis of Compound **16**

Inspection of the ^1H NMR spectrum of compound **16** showed that the resonances relating to the hypersilyl substituents in compound **3** (0.29 and 0.57 ppm) moved to 0.51 and 0.70 ppm, indicating the formation of a new cluster which retains C_{2v} symmetry. This is consistent with the three ^{29}Si NMR environments and four crosspeaks observed in the $^{29}\text{Si}/^1\text{H}$ HMBC NMR spectrum (Figure 5.9).

In addition to this, peaks relating to two inequivalent COD ligands were observed, in a 2:1 ratio. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum exhibited two alkenic ^{13}C NMR environments at 80.55 and 95.19 ppm. The former is a doublet ($^1J_{\text{C-Rh}} = 8.3$ Hz) and the latter a singlet. This is consistent with the coordination of two $[\text{Ni(COD)}]$ fragments to compound **3**.

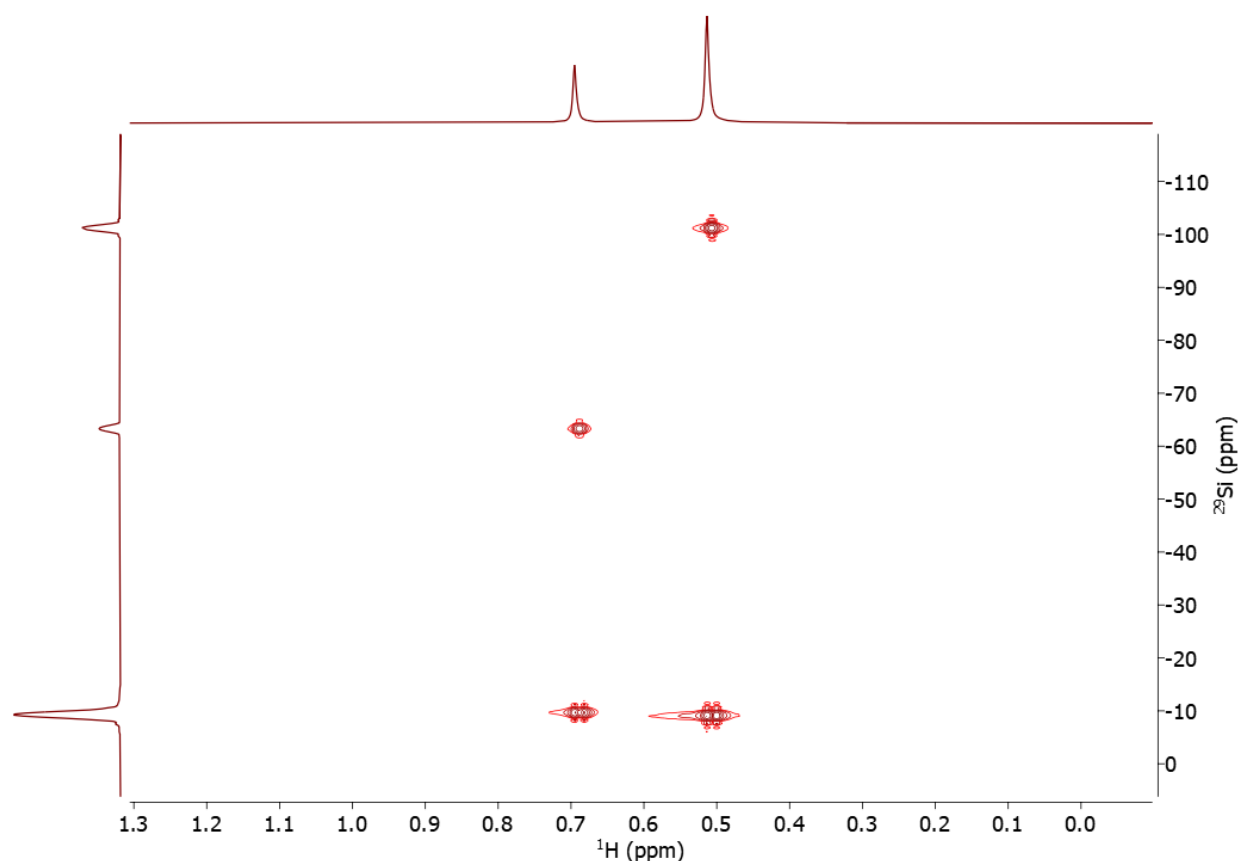


Figure 5.9: $^1\text{H}/^{29}\text{Si}$ HMBC NMR spectrum (C_6D_6 , 298 K, 79.5 MHz) of compound **16**.

5.6.3. Single Crystal X-ray Structure of Compound **16**

Crystals suitable for single crystal X-ray diffraction were grown from *n*-pentane. The crystal structure shows that the $[\text{Rh}(\text{COD})\{\eta^4\text{-Ge}_9(\text{Hyp})_3\}]$ core is intact, with new $\text{Ni}(\text{COD})$ fragments coordinated to the triangular faces (Figure 5.10).

This structure is complementary to the cluster $[\{\text{Ni}(\text{DPPE})\}_2\text{Ge}_9(\text{Hyp})_3][\text{Ge}_9(\text{Hyp})_3]$, reported by Schnepf, which also exhibits two $\text{Ni}(\text{L})_2$ fragments bound to the triangular faces of the *tris*- functionalised nonagermanide cage.⁴² However, this is reported to contain two nickel(I) centres due to the $[\text{Ge}_9(\text{Hyp})_3]^-$ counter ion, making the cluster positively charged. Compound **16**, however, contains two nickel(0) fragments due to the neutral charge.

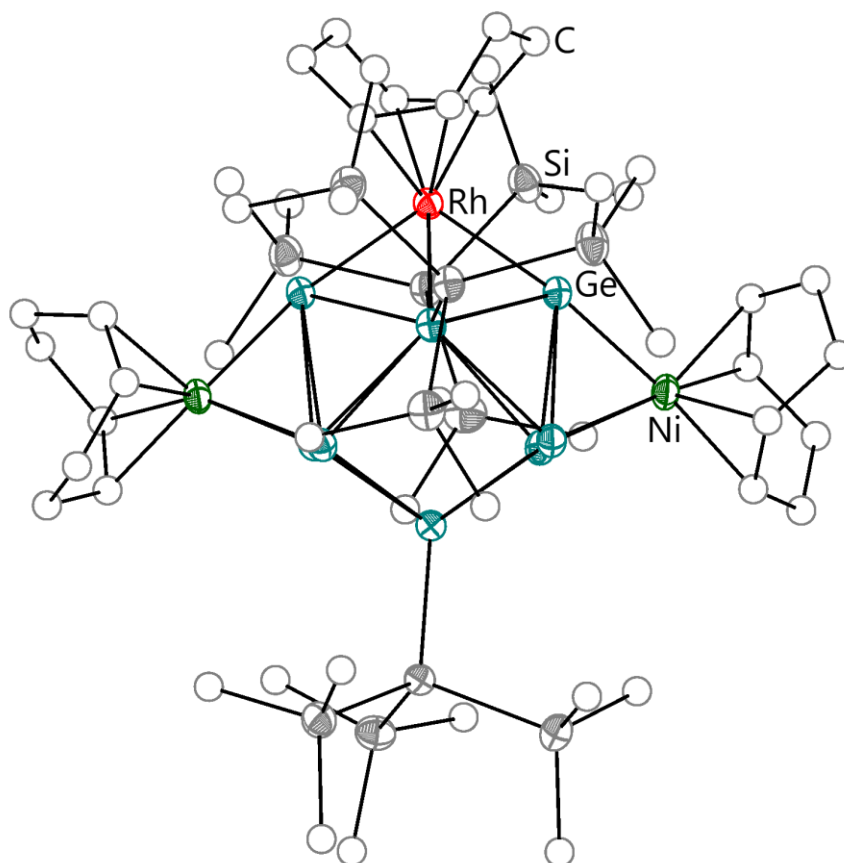
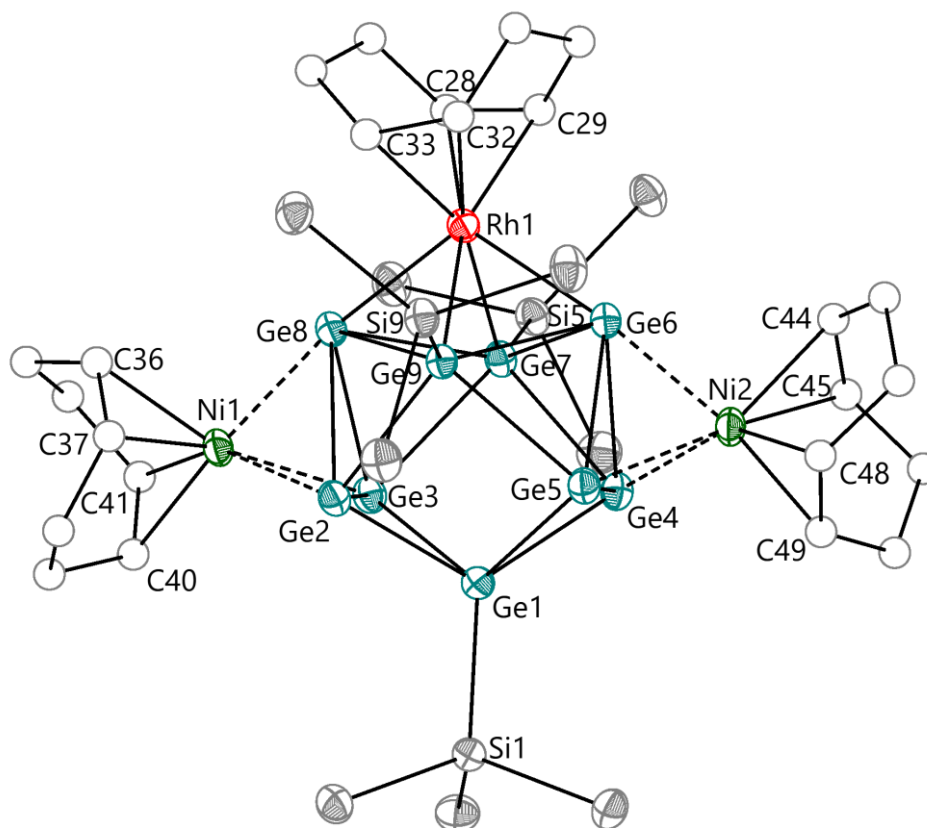


Figure 5.10: Single crystal X-ray structure of compound **16**. Anisotropic displacement ellipsoids are set at 50% probability. Hydrogen atoms have been omitted for clarity. Carbon atoms are pictured as spheres of an arbitrary radius.

The distance between the two triangular faces is elongated by ~ 0.13 Å, presumably due to the fact that the Ge–Ni interactions withdraw electron density used for cluster bonding. Compared to compound **3**, the Rh–Ge distances are now longer for the Ge(Hyp) vertices than the unsubstituted Ge vertices, (which were the shorter of the four distances in compound **3**). The Rh–C distances are also slightly shorter in compound **16**, owing to the change in electronics of the cluster core.

Table 5.4: Selected crystallographic bond distances (Å) of compound **16**. A truncated model is included as a key.



Bond	Distance (Å)	Bond	Distance (Å)	Bond	Distance (Å)
Ge6–Rh1	2.451(1)	Ge2–Ni1	2.450(1)	Ge4–Ni2	2.455(1)
Ge7–Rh1	2.604(1)	Ge3–Ni1	2.425(1)	Ge5–Ni2	2.448(1)
Ge8–Rh1	2.438(1)	Ge8–Ni1	2.301(1)	Ge6–Ni2	2.307(1)
Ge9–Rh1	2.556(1)	Ni1–C36	2.170(3)	Ni2–C44	2.149(3)
Rh1–C28	2.210(3)	Ni1–C37	2.139(3)	Ni2–C45	2.142(4)
Rh1–C29	2.196(3)	Ni1–C40	2.084(4)	Ni2–C48	2.099(3)
Rh1–C32	2.192(3)	Ni1–C41	2.104(3)	Ni2–C49	2.109(3)
Rh1–C33	2.171(3)	Ge1–Si1	2.416(1)	Ge8–Si9	2.436(1)
Ge7–Si5	2.440(1)				

The Ni–C distances (2.084(4) – 2.170(3) Å) are comparable to other nickel(0) COD compounds the literature, for example, Ni(COD)₂ (2.1136(6) – 2.1365(6) Å),⁴⁷ Ni(DCPE)(COD) (2.086(2) – 2.124(2) Å) (DCPE = 1,2-bis(dicyclohexylphosphino)-ethane),⁴⁸ and Ni(C₂Ph₂)(COD) (2.085(6) – 2.115(5) Å).⁴⁹

5.6.3. Further Chemistry of Compound **16**

Compound **16** was compared to compound **3** in the hydrogenation of COD, where it was found to be catalytically active, albeit slower. Interestingly, significant build-up of free COE is observed during the reaction (COE:COA at [COD]₀/2 = 9:1). The reasons for this, however, are unclear.

In future chemistry, it would be interesting to test compound **16** in organic transformations that would partner the catalytic reactivities of rhodium(I) and nickel(0) centres. For example, one could envisage a C–C cross-coupling reaction (nickel(0) chemistry), followed by the hydrogenation of the product by applying a H₂ atmosphere (rhodium(I) chemistry).

5.7. Conclusion

In contrast to the results reported in Chapter 4, where all modifications occur at the transition metal centre, this chapter describes the controlled expansion of [Rh(L){Ge₉(Hyp)₃}] (L = diene) clusters by reactions at the cluster core, showing that the Zintl cluster support can take part in further reactivity.

By reacting [KGe₉(Hyp)₃] or compound **3** with various late transition metal alkene complexes, we were able to prepare a range of novel homo- and hetero-multimetallic clusters, retaining their diene ligands, which is advantageous for follow-up chemistry and their use in catalysis. This demonstrates some unique capabilities of a Zintl cluster based complex over traditional transition metal compounds featuring organic ligands as molecular models for TMMGAs.

Some of the work was published in the following communication in the *Journal of the American Chemical Society*:

Townrow, O. P. E.; Chung, C.; Macgregor, S. A.; Weller, A. S.; Goicoechea, J. M. A Neutral Heteroatomic Zintl Cluster for the Catalytic Hydrogenation of Cyclic Alkenes. *J. Am. Chem. Soc.* **2020**, *142*, 18330–18335.

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6. Conclusions and Future Work

6.1. Conclusions

This thesis reports on the reactivity of the tris-hypersilyl substituted nonagermanide Zintl cluster $[\text{KGe}_9(\text{Hyp})_3]$ ($\text{Hyp} = \text{Si}(\text{SiMe}_3)_3$) towards group 9 and 10 transition metal organometallic complexes. The resulting Zintl clusters were then modified and tested in catalysis as molecular models for transition metal–main group element alloys (TMMGAs).

Due to the impressive reactivity of nickel containing TMMGAs in light alkane activation,^{1–3} nickel germanide clusters were chosen as the first synthetic targets. This work highlighted contrasting reaction pathways which depended on the nickel organometallic source, resulting in vertex addition and substitution. Electrochemical studies were performed to investigate their redox chemistry, finding that both complexes **1** and **2** exhibit reversible redox processes towards formal nickel(I) species under electrochemical conditions.

The introduction of a rhodium centre was next explored in the synthesis of the *closo*-cluster $[\text{Rh}(\text{COD})\{\text{Ge}_9(\text{Hyp})_3\}]$ (**3**), featuring a $\text{Rh}(\text{COD})$ moiety coordinated to the nonagermanide support in an η^4 mode. To investigate whether well-established reaction pathways in rhodium chemistry are compatible with Zintl cluster ligand supports, compound **3** was employed as the first Zintl cluster based homogeneous catalyst in the catalytic hydrogenation of cyclic alkenes *cis*-cyclooctene and 1,5-cyclooctadiene.

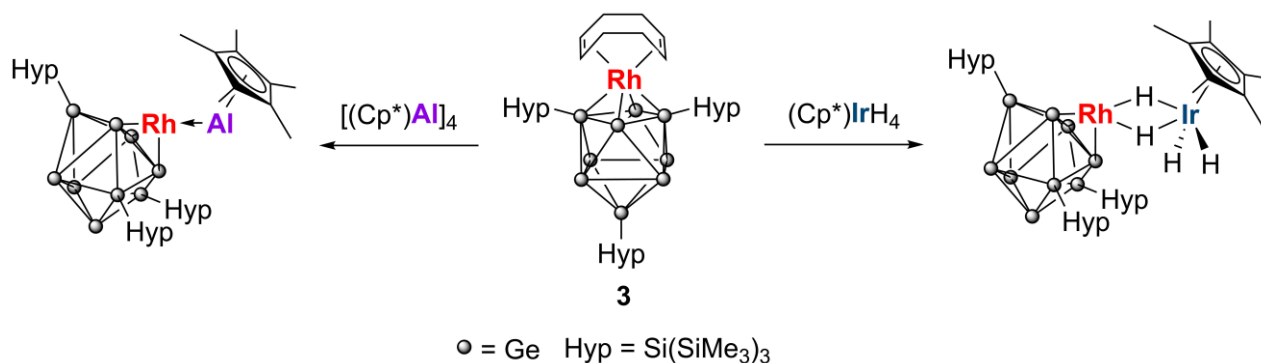
Compound **3** was then reacted with various L and L₂ type ligands (phosphines, carbenes, alkynes) to modify the rhodium coordination sphere, which resulted in an isomerisation towards new *closo*- and *hypercloso*-clusters, showing that the nonagermanide support can respond to the steric and electronic requirements of the transition metal centre. This strategy was then used to prepare a heterobimetallic complex with bridging hydrides, in which the two transition metal centres react cooperatively towards H₂ and D₂. These post-modified clusters

were protonated to produce their conjugate hydrides. They were also subjected to preliminary studies in catalysis, namely: H/D scrambling of H₂/D₂ mixtures, alkyne hydrogenation, and alkene isomerisation.

[KGe₉(Hyp)₃] and compound **3** were also investigated in cluster expansion chemistry, aiming to controllably vary the Rh:Ge ratio and prepare a range of novel homo- and hetero-multimetallic clusters where the transition metal centres retain their diene ligands. This demonstrated some unique capabilities of Zintl cluster-based complexes as a TMMGA model.

6.2. Future Work

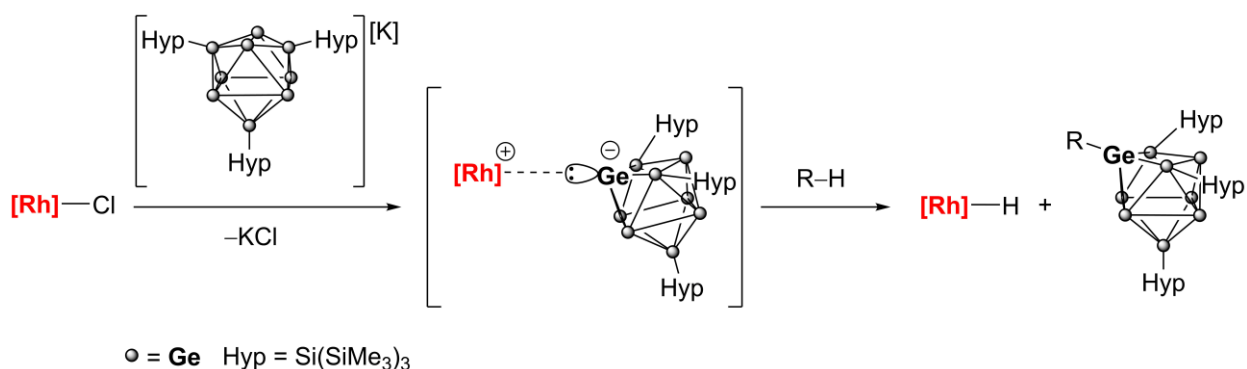
Preparation of alternative bridging hydride complexes using the methods in Chapter 4 would firstly be of great interest. For example, preparing complexes involving a [(Cp*)IrH_n] moiety may open up applications to aromatic C–H functionalisation, as Camp and co-workers have found with their iridium–tantalum systems.⁴ Alternatively, utilising nucleophilic, low oxidation state main group systems, such as [(Cp*)Al]₄, as non-innocent ligands may allow access to interesting cooperative reactivity, much like the interesting Rh–Al complexes prepared by Nakao (Scheme 6.1).^{5,6}



Scheme 6.1: Proposed future reactivity of **3** using the synthetic strategy developed in Chapter 4.

As discussed briefly at the end of Chapter 5, further work exploring the use of multimetallic clusters in organic transformations that require two or three transition metal diene fragments in close proximity is also of interest ($\{\text{Rh}(\text{L})\}\{\text{M}(\text{L})\}_n[\text{Ge}_9(\text{Hyp})_3\text{Cl}_n]$) ($\text{M} = \text{Rh}, \text{Ir}$; $\text{L} = \text{diene}$) (**13** – **15**). These transformations show that such systems support the fine tuning of transition metal–main group element ratios and therefore offer the ability to build closer molecular models to the intermetallic interfaces proposed for TMMGAs.⁷ In addition, since $\text{Rh}(\text{COD})$ and $\text{Ni}(\text{COD})$ containing complexes are well-established in catalysis, it would be interesting to explore the use of $[\{\text{Rh}(\text{COD})\}\{\text{Ni}(\text{COD})\}_2\{\text{Ge}_9(\text{Hyp})_3\}]$ (**16**), in transformations which make use of both centres.

Furthermore, evidence in the literature shows that $[\text{Ge}_9(\text{Hyp})_3]^-$ can act as a non-coordinating ion.⁸ The employment of a large bi- or tridentate ligand at a cationic rhodium centre, such as bis-1,2(di-*tert*-butylphosphino)ethane or a bis-(imino)pyridine to prevent coordination to the cluster may offer some frustrated Lewis pair (FLP) type reactivity,^{9,10} exploiting the nucleophilic nature of the six germanium lone pairs on the Zintl cluster counter anion. Pairing this concept with the Solid-State Molecular OrganoMetallic (SMOM) chemistry developed by the Weller group,^{11–13} which can be used to isolate cationic rhodium σ -alkane complexes in the solid-state,¹⁴ may lead to the cleavage of the aliphatic C–H bonds (Scheme 6.2).



Scheme 6.2: FLP type C–H activation by using $[\text{Ge}_9(\text{Hyp})_3]^-$ as a reactive counterion.

6.3. Publications

Some of the work in this thesis can be found in the following publications:

1. Townrow, O. P. E.; Chung, C.; Macgregor, S. A.; Weller, A. S.; Goicoechea, J. M. A Neutral Heteroatomic Zintl Cluster for the Catalytic Hydrogenation of Cyclic Alkenes. *J. Am. Chem. Soc.* **2020**, *142*, 18330–18335.
2. Townrow, O. P. E.; Weller, A. S.; Goicoechea, J. M. Cluster Expansion and Vertex Substitution Pathways in Nickel Germanide Zintl Clusters. *Chem. Commun.* **2021**, *57*, 7132–7135.

Two manuscripts, detailing the ligand substitution and cluster expansion results, are currently in preparation.

In addition, in collaboration with a colleague, we published the following article for which I performed the computational chemistry:

1. Abbenseth, J.; Townrow, O. P. E.; Goicoechea, J. M. Thermoneutral N–H Bond Activation of Ammonia by a Geometrically Constrained Phosphine. *Angew. Chem. Int. Ed.* **2021**, *60*, 23625–23629.

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- (8) Kysliak, O.; Schrenk, C.; Schnepf, A. Reactivity of $[\text{Ge}_9\{\text{Si}(\text{SiMe}_3)_3\}_3]^-$ Towards Transition-Metal M^{2+} Cations: Coordination and Redox Chemistry. *Chem. Eur. J.* **2016**, *22*, 18787–18793.
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7. Experimental

7.1. General Synthetic Considerations

All reactions and product manipulations were carried out under an inert atmosphere of argon or dinitrogen using standard Schlenk-line or glovebox techniques (MBraun UNILab glovebox maintained at < 0.1 ppm H_2O and < 0.1 ppm O_2). *n*-Pentane (pent; Sigma-Aldrich, HPLC grade, $\geq 99\%$), *n*-hexane (hex; Sigma-Aldrich, HPLC grade, $\geq 97\%$), benzene (Rathburn, HPLC grade, 99.8%), diethyl ether (Sigma-Aldrich, HPLC grade, 99.8%) and toluene (Sigma-Aldrich, HPLC grade, 99.8%), were purified using an MBraun SPS-800 solvent system. Tetrahydrofuran (THF; Sigma-Aldrich, HPLC grade, $\geq 99.9\%$) and cyclohexane (cy; HPLC grade, $\geq 99.9\%$) were distilled over sodium metal/benzophenone. 2-methyltetrahydrofuran (2-MeTHF; Sigma Aldrich, Anhydrous, $\geq 99\%$) was freeze-pump-thaw degassed and stored over activated 3 Å molecular sieves. 1-hexanol (Sigma-Aldrich, anhydrous, $\geq 99\%$), 2-propanol (Sigma-Aldrich, HPLC, 99%) and ethanol (Sigma-Aldrich, absolute) were used as received.

Benzene- d_6 (Sigma-Aldrich, 99.5%), toluene- d_8 (Sigma-Aldrich, 99.5%) and tetrahydrofuran- d_8 (Sigma-Aldrich, 99.5%) were distilled over sodium metal/benzophenone. All dry solvents were stored under argon in gas-tight ampoules over activated 3 Å molecular sieves.

K_4Ge_9 was synthesized according to literature procedures,¹ by heating a stoichiometric mixture of the elements (potassium, 99.95%, Alfa Aesar; germanium powder -100 mesh, 99.999%, Alfa Aesar) at 900 °C for 2 days in sealed niobium containers jacketed in evacuated fused-silica ampoules.

$[\text{Rh}(\text{COD})\text{Cl}]_2$,² $\text{Na}[\text{B}(\text{Ar}^{\text{F}})_4]$ ($\text{Ar}^{\text{F}} = 3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2$),³ and IMe_4 ($\text{IMe}_4 = 1,3,4,5\text{-tetramethylimidazol-2-ylidene}$),^{4,5} were prepared according to literature procedures.

$[\text{Rh}(\text{NBD})\text{Cl}]_2$,⁶ $[\text{Rh}(\text{COD})_2][\text{B}(\text{Ar}^{\text{F}})_4]$,⁷ $[\text{Rh}(\text{NBD})_2][\text{B}(\text{Ar}^{\text{F}})_4]$,⁷ and Brookhart's acid $([\text{H}(\text{OEt}_2)_2][\text{B}(\text{Ar}^{\text{F}})_4])^8$ (modified to use HCl, 2 M in diethyl ether, rather than HCl gas) were prepared according to literature procedures and stored at $-40\text{ }^\circ\text{C}$ in an inert atmosphere glovebox.

Table 7.1: Supplier and purification procedures for commercially available chemicals.

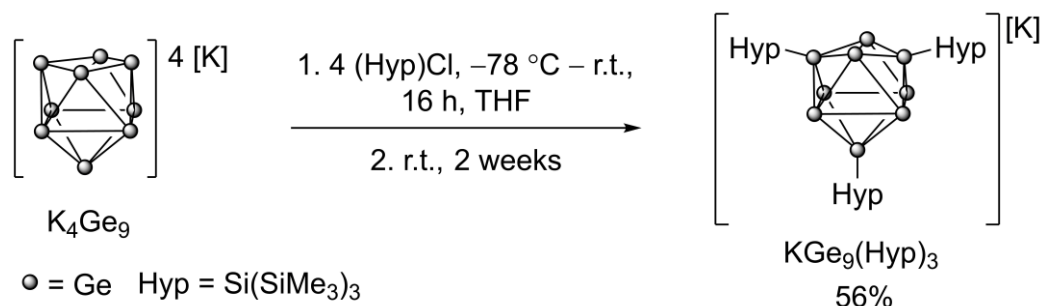
Reagent	Supplier	Purity	Purification
Potassium	Alfa Aesar	99.95%	Used as received
Germanium	Alfa Aesar	99.999%	Used as received
Sodium	Acros Organics	99.8%, oiled sticks	Washed with hexane, dried under vacuum
2.2.2-crypt	VWR	99%	Dried under vacuum
1,5-Cyclooctadiene	Sigma Aldrich	>99%	Distilled before use
<i>cis</i> -cyclooctene	Alfa Aesar	97%	Distilled before use, contains 3% cyclooctane
Bis(1,5-cyclooctadiene)nickel	Alfa Aesar	96%	Used as received, stored at $-40\text{ }^\circ\text{C}$ under N_2
Bis(cyclopentadienyl) nickel	Alfa Aesar	98%	Used as received
Bis(cyclopentadienyl)tungsten dihydride	Alfa Aesar	97%	Used as received
1,2-Bis(diphenylphosphino)ethane	Alfa Aesar	97%	Used as received
Bis(cyclopentadienyl)cobalt hexafluorophosphate	Sigma-Aldrich	98%	Used as received
Chloro(cyclopentadienyl) (triphenylphosphine)nickel	Santa Cruz Biotechnology	—	Used as received
Deuterium	Sigma Aldrich	99.96 atom % D	Used as received

<i>N,N'</i> -dimethylthiourea	Sigma-Aldrich	99%	Used as received
Ferrocene	Sigma-Aldrich	99%	Triply sublimed before use
1-hexene	Sigma-Aldrich	≥99%	Dried over CaH ₂
HCl (2 M in diethyl ether)	Sigma-Aldrich	–	Used as received
3-hydroxy-2-butanone	Sigma-Aldrich	–	Used as received
2,5-norbornadiene	Sigma-Aldrich	97%	Used as received
1-octyne	Sigma-Aldrich	97%	Degassed before use
Rhodium(III) chloride hydrate	Precious Metals Online	–	Used as received
Tetramethylsilane	Alfa Aesar	>99%	Dried over CaH ₂ , stored under N ₂ at –40 °C
Tetra(<i>n</i> -butylammonium) hexafluorophosphate	Sigma-Aldrich	98%	Recrystallised from ethanol
Trimethylphosphine	Sigma-Aldrich	97%	Used as received
Triphenylphosphine	Sigma-Aldrich	99%	Used as received
Methyldiphenylphosphine	Sigma-Aldrich	99%	Used as received
Tri(<i>p</i> -tolyl)phosphine	Sigma-Aldrich	98%	Used as received

7.2. Chapter 2

7.2.1. Improved Synthesis of [KGe₉(Hyp)₃]

The literature known syntheses of [KGe₉(Hyp)₃] from K₄Ge₉ and (Hyp)Cl are typically performed in either MeCN with a 10 fold excess of (Hyp)Cl to avoid the presence of [K₂Ge₉(Hyp)₂] in the product (yield not clearly reported).⁹ Alternatively, the reaction can be carried out in THF with an isolated yield of 28% (relative to K₄Ge₉).¹⁰ This prompted us to optimise the preparation to increase the yield of desolvated, non-sequestered, [KGe₉(Hyp)₃].



Scheme 7.1: Preparation of $[\text{KGe}_9(\text{Hyp})_3]$.

In a typical synthesis, freshly ground K_4Ge_9 (2 g, 2.47 mmol) was dispersed in distilled THF (100 ml). This was cooled to -78°C and a solution of $(\text{Hyp})\text{Cl}$ (3 g, 10.6 mmol) in THF (25 ml) was added dropwise over 30 minutes.

The grey suspension was stirred with a glass coated stir bar, warming slowly to room temperature overnight. In the morning, the cooling bath was removed and the mixture was stirred for two weeks to produce a red-orange solution.

This was filtered through a glass fibre filter and the THF removed *in vacuo*, drying on a vacuum line overnight to remove all of the residual solvent. The orange solid was then extracted with toluene (100 ml) and passed through a glass fibre filter into a Schlenk flask to separate any KCl that had dissolved in the THF extract.

The Schlenk flask was tilted parallel to the worktop and the toluene was slowly evaporated *in vacuo* over the course of 5 hours to produce large red needle-like crystals of the previously reported solvate complex $[\text{K}(\text{tol})_3][\text{Ge}_9(\text{Hyp})_3] \cdot \text{tol}$,¹⁰ and a red oil (Figure 2.1). When dried further on a vacuum line overnight, the red oil hardened and the orange needles turned opaque, due to loss of the toluene.

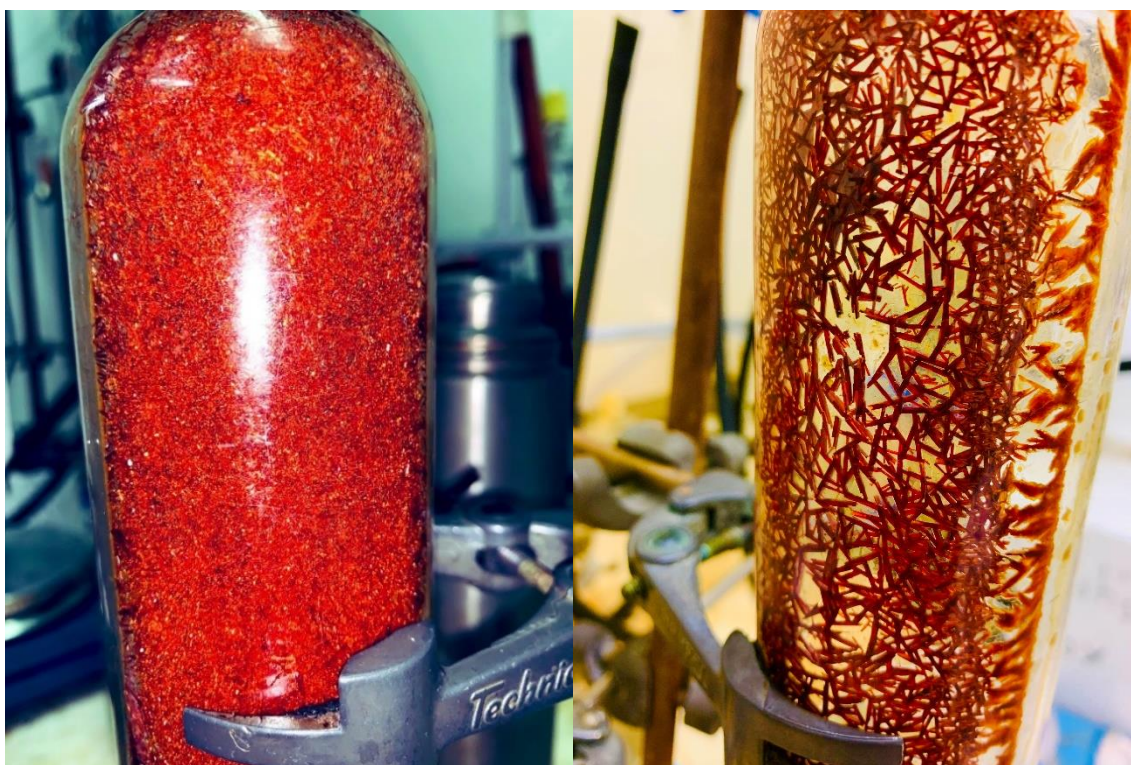
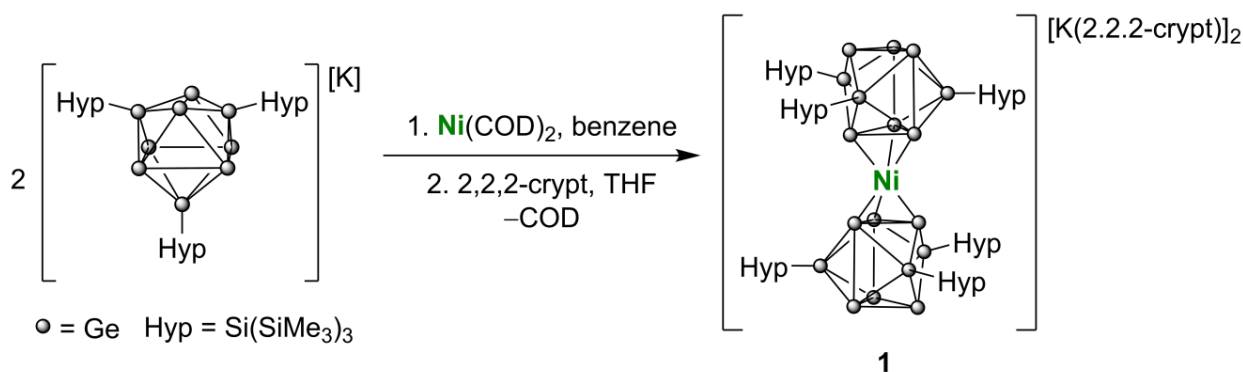


Figure 7.1: Crystals of $[\text{K}(\text{tol})_3][\text{Ge}_9(\text{Hyp})_3] \cdot \text{tol}$ grown from slow evaporation of toluene. Left: Before washing with *n*-hexane; Right: after washing with *n*-hexane.

This is important since solvation with THF or toluene causes a partial solubility in hexane and can lower yields in the subsequent step. The red oil, containing polysilane by-products, was removed by extraction with *n*-hexane (3×15 ml) using a glass fibre filter fitted to a PTFE cannula. Care must be taken when removing the filter cannula into air since even residual solids of $[\text{KGe}_9(\text{Hyp})_3]$ are highly pyrophoric and combust immediately on contact with air. *n*-Pentane is particularly advised against as an alternative to *n*-hexane for this reason. The yellow-orange microcrystalline solid was dried *in vacuo* to obtain pure, desolvated $[\text{KGe}_9(\text{Hyp})_3]$ (2.0 g, 1.39 mmol; 56%). The increased yield is most probably due to a combination of the main notable differences when compared to the literature reported syntheses: 1) the use of a THF solution of (Hyp)Cl in cooled addition (as opposed to the addition of molten (Hyp)Cl); 2) a longer reaction time (2 weeks) due to the insolubility of K_4Ge_9 in THF; and 3) a stepwise workup (Scheme 2.4). The NMR spectra are consistent with

the literature reported values.⁹ ^1H NMR (d_8 -THF, 298 K, 400.17 MHz): δ (ppm) 0.25 (s, 81H; CH_3), ^{29}Si NMR (d_8 -THF, 298 K, 79.5 MHz): δ (ppm) -108.47 , -10.09 .

7.2.2. Synthesis of $[\text{K}(2.2.2\text{-crypt})]_2[\text{Ni}\{\text{Ge}_9(\text{Hyp})_3\}_2]$ ($[\text{K}(2.2.2\text{-crypt})]_2\mathbf{1}$)



Scheme 7.2: Preparation of $[\text{K}(2.2.2\text{-crypt})]_2\mathbf{1}$.

$[\text{KGe}_9(\text{Hyp})_3]$ (100 mg, 0.07 mmol) and benzene (~ 3 ml) were added to an ampoule and stirred until an orange solution formed. $[\text{Ni}(\text{COD})_2]$ (10 mg, 0.07 mmol) was then added and the orange solution turned green within 30 minutes. The mixture was stirred for 14 hours with a glass coated stir bar to yield a dark green suspension. A light green-brown solution was filtered off and the black-green precipitate was washed with toluene (2 ml). NOTE: Washing with more toluene results in further dissolution of the product.

The solid was then dissolved in THF (5 ml) to form a dark blue-green solution and dried *in vacuo* at 0.1 mbar over the course of 20 minutes to produce a dark green pyrophoric powder $[\text{K}(\text{THF})_n]_2\mathbf{1}$. NOTE: if dried at a lower pressure, for longer, or with heating, the formation of an orange powder ($[\text{KGe}_9(\text{Hyp})_3]$) occurs. As can be seen from the NMR data, even after careful drying, there is $\sim 3\%$ $[\text{K}(\text{THF})_n][\text{Ge}_9(\text{Hyp})_3]$ present. Standing in THF also results in partial decomposition to $[\text{K}(\text{THF})_n][\text{Ge}_9(\text{Hyp})_3]$. For example, standing for 3 days results in a greener solution and black precipitate, analysed as a 70 : 30 ratio of $[\text{K}(\text{THF})_n]_2\mathbf{1}$: $[\text{K}(\text{THF})_n][\text{Ge}_9(\text{Hyp})_3]$ by ^1H -NMR spectroscopy.

^1H NMR (d_8 -THF, 298 K, 400.17 MHz): δ (ppm) 0.37 (s, 162H; CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (d_8 -THF, 298 K, 125.81 MHz): δ (ppm) 4.25 (CH_3). ^{29}Si NMR (d_8 -THF, 298 K, 79.5 MHz): δ (ppm) -107.10 , -10.48 .

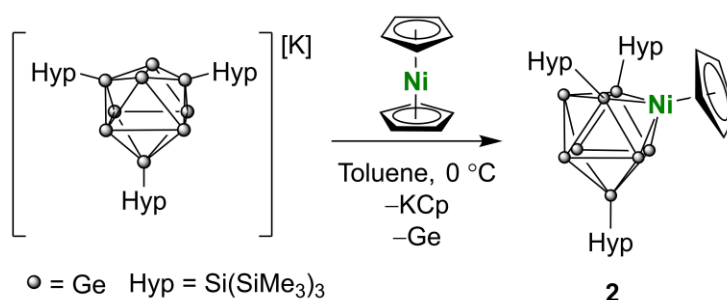
To obtain crystals suitable for single crystal X-ray crystallography, the powder was mixed with 2.2.2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane) (30 mg, 0.08 mmol), dissolved in a minimum amount of THF and left to stand at $-40\text{ }^\circ\text{C}$ for 1 week, producing green-blue crystals of $[\text{K}(2.2.2\text{-crypt})]_2\mathbf{1}$.

Elemental analysis calcd. for $\text{C}_{90}\text{H}_{234}\text{Ge}_{18}\text{K}_2\text{N}_4\text{Ni}_1\text{O}_{12}\text{Si}_{24}$ ($M = 3683.29\text{ g}\cdot\text{mol}^{-1}$): C 29.35, H 6.40, N 1.52. Found: C 28.61, H 5.96, N 1.78.

^1H NMR (d_8 -THF, 298 K, 400.17 MHz): δ (ppm) 0.38 (s, 162H; CH_3), 2.58 (t, 24H; CH_2), 3.57 (t, 24H; CH_2), 3.61 (s, 24H; CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (d_8 -THF, 298 K, 125.81 MHz): δ (ppm) 4.30 (CH_3), 54.96 (CH_2), 68.64 (CH_2), 71.47 (CH_2). ^{29}Si NMR (d_8 -THF, 298 K, 79.5 MHz): δ (ppm) -107.10 , -10.48 .

7.2.3. Synthesis of $[(\text{Cp})\text{Ni}\{\text{Ge}_8(\text{Hyp})_3\}]$ (**2**)

Method A:

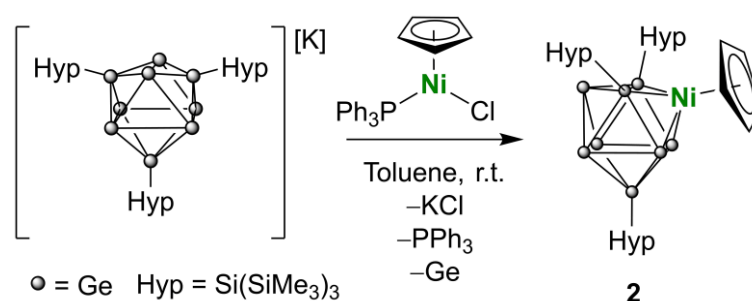


Scheme 7.3: Preparation of compound **2** via $[\text{Ni}(\text{Cp})_2]$ (Method A).

A toluene (20 ml) solution of $[\text{Ni}(\text{Cp})_2]$ (26 mg, 0.14 mmol) was added dropwise to a solution $[\text{KGe}_9(\text{Hyp})_3]$ (200 mg, 0.14 mmol) in toluene (20 ml) over the course of 25 minutes at $0\text{ }^\circ\text{C}$.

The orange solution was stirred overnight to yield a dark brown mixture. This was filtered, and the pyrophoric grey solid was washed with toluene (3×5 ml). Both toluene fractions were combined and the solvent was removed *in vacuo*. The product was extracted in *n*-hexane (3×10 ml) as a dark green-brown solution. This was reduced in volume to 2–3 ml and left to stand in a -80 °C freezer for 14 hours, producing needle-like emerald green crystals of **2** (60 mg, 30%). Emerald green crystals of **2** suitable for single crystal X-ray crystallography were grown from a concentrated solution of toluene, rather than *n*-hexane.

Method B:



Scheme 7.4: Preparation of compound **2** via [(Cp)Ni(PPh₃)Cl] (Method B).

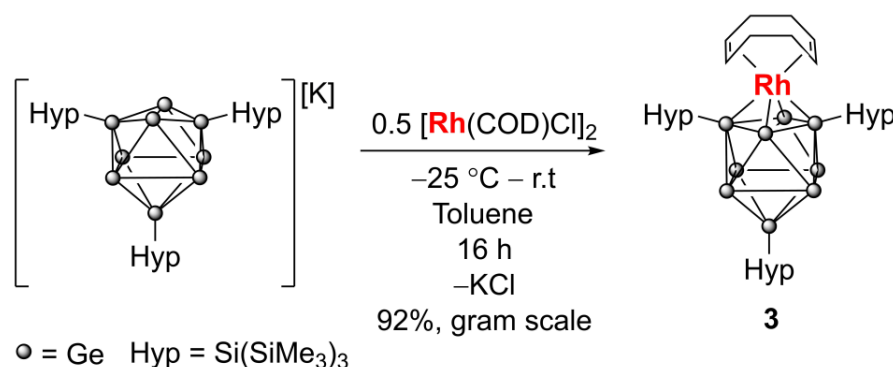
To a solid mixture of [(Cp)Ni(PPh₃)Cl] (30 mg, 0.07 mmol) and [KGe₉(Hyp)₃] (100 mg, 0.07 mmol), toluene (10 ml) was added at room temperature. The dark brown solution was stirred to a dark brown mixture overnight. The toluene was then removed *in vacuo* and the product was extracted in *n*-hexane (3×10 ml) as a dark green-brown solution. The *n*-hexane was then removed *in vacuo* and excess PPh₃ was removed by sublimation at 80 °C. The green-brown product was then re-dissolved in *n*-hexane (3 ml) and left to stand in a -80 °C freezer for 14 hours, producing emerald green crystals of **2** (35 mg, 35%).

Elemental analysis calcd. for C₃₂H₈₆Ge₈Ni₁Si₁₂ ($M = 1447.86 \text{ g} \cdot \text{mol}^{-1}$): C 26.55, H 5.99. Found: C 26.52, H 5.82.

^1H NMR (C_6D_6 , 298 K, 400.17 MHz): δ (ppm) 0.49 (s, 54H; CH_3), 0.60 (s, 27H; CH_3), 5.18 (s, 5H; CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 125.81 MHz): δ (ppm) 3.31 (CH_3), 4.24 (CH_3), 87.73 (CH). ^{29}Si NMR (C_6D_6 , 298 K, 79.5 MHz): δ (ppm) -101.1 , -76.1 , -8.4 .

7.3. Chapter 3

7.3.1. Synthesis of $[\text{Rh}(\text{COD})\{\text{Ge}_9(\text{Hyp})_3\}]$ (**3**)



Scheme 7.5: Preparation of compound **3**.

Half an equivalent of $[\text{Rh}(\text{COD})\text{Cl}]_2$ in toluene was added dropwise to a cooled ($-25\text{ }^\circ\text{C}$) toluene solution of $[\text{KGe}_9(\text{Hyp})_3]$ over the course of 30 minutes under argon. It was found that the use of more polar solvents, such as THF, or performing the reaction at room temperature significantly decreases the yield of the reaction. The use of lower temperatures also reduces the yield due to precipitation of the $[\text{Ge}_9(\text{Hyp})_3]^-$ precursor, effectively limiting the efficacy of dropwise addition.

This resulted in a red-orange to brown colour change. The brown solution was slowly warmed to room temperature overnight. The solvent was removed *in vacuo* and a red-brown solution of the neutrally charged, hydrocarbon soluble cluster $[\text{Rh}(\text{COD})\{\text{Ge}_9(\text{Hyp})_3\}]$ (**3**) was extracted with *n*-hexane. Upon concentrating and cooling to $-80\text{ }^\circ\text{C}$, red-brown crystals suitable for single crystal X-ray diffraction could be obtained in an 88% isolated yield after combining 3 crops. Since the hexane solution was pure enough for further synthesis, it was

found that the best isolated yields (>92%) on a preparative scale (>1 g) arose from dissolution of the dried hexane extract into benzene (~5 ml) and subsequent lyophilisation to produce a red-brown powder (Scheme 3.2). These finely divided powders can spontaneously ignite on contact with air, so care must be taken in the manipulation of compound **3**.

Elemental analysis calcd. for $C_{35}H_{93}Ge_9RhSi_{12}$ ($M = 1607.60 \text{ g}\cdot\text{mol}^{-1}$): C 26.15, H 5.83. Found: C 26.13, H 5.82.

Major component:

^1H NMR (C_6D_6 , 298 K, 400.17 MHz): δ (ppm) 0.29 (s, 54H; CH_3), 0.57 (s, 27H; CH_3), 1.93 (m, 4H; CH_2) 2.31 (m, 4H; CH_2), 5.48 (s, 4H; CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 125.81 MHz): δ (ppm) 3.55 (CH_3), 4.67 (CH_3), 31.35 (CH_2), 85.18 (d, $^1J_{C-Rh} = 8.0 \text{ Hz}$; CH). ^{29}Si NMR (C_6D_6 , 298 K, 79.5 MHz): δ (ppm) -95.1, -46.6, -9.6.

^1H NMR (C_7H_8 , 193 K, 400.17 MHz): δ (ppm) 0.33 (s, 54H; CH_3), 0.60 (s, 27H; CH_3), 1.84 (br. m, 4H; CH_2) 2.26 (br. m, 4H; CH_2), 5.44 (br. s, 4H; CH). ^{29}Si NMR (C_7H_8 , 193 K, 79.5 MHz): δ (ppm) -99.3, -49.2, -8.9.

^1H NMR (C_6D_6 , 333 K, 400.17 MHz): δ (ppm) 0.29 (s, 54H; CH_3), 0.56 (s, 27H; CH_3), 1.98 (m, 4H; CH_2) 2.35 (m, 4H; CH_2), 5.46 (s, 4H; CH). ^{29}Si NMR (C_6D_6 , 333 K, 79.5 MHz): δ (ppm) -93.6, -45.5, -9.2.

Minor component:

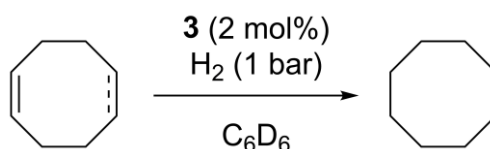
^1H NMR (C_6D_6 , 298 K, 400.17 MHz): δ (ppm) 0.47 (s, 54H; CH_3), 0.53 (s, 27H; CH_3), 2.06 (m, 4H; CH_2) 2.41 (m, 4H; CH_2), 4.31 (s, 4H; CH); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 125.81 MHz): δ (ppm) 3.46 (CH_3), 4.39 (CH_3), 33.00 (CH_2), 77.35 (d, $^1J_{C-Rh} = 9.3 \text{ Hz}$; CH). ^{29}Si NMR (C_6D_6 , 298 K, 79.5 MHz): δ (ppm) -88.8, -9.4.

^1H NMR (C_7D_8 , 193 K, 400.17 MHz): δ (ppm) 0.40 (br. s, $\sim 40\text{H}$; CH_3), 0.70 (br. s, $\sim 40\text{H}$; CH_3), 1.94 (br. m, 4H; CH_2), 2.35 (br. m, 4H; CH_2), 4.29 (s, $\sim 4\text{H}$; CH). ^{29}Si NMR (C_7D_8 , 193 K, 79.5 MHz): δ (ppm) -107.4 , -49.8 , -21.1 , -9.8 .

^1H NMR (C_6D_6 , 333 K, 400.17 MHz): δ (ppm) 0.48 (br. s, 81H; CH_3), 2.06 (br. m, 4H; CH_2), 2.45 (br. m, 4H; CH_2), 4.31 (br. s, 4H; CH). ^{29}Si NMR (C_6D_6 , 333 K, 79.5 MHz): δ (ppm) Could not resolve peaks.

7.3.2. Catalysis Procedures

7.3.2.1. Low Pressure

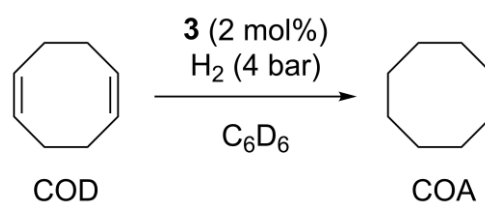


Scheme 7.6: Hydrogenation of COD or COE at 1 bar H_2 .

An ampoule with an internal volume of 50 ml was charged with a stock solution of **3** (0.0152 M in C_6D_6 , 500 μl) and a stock solution of COD and ferrocene (0.676 M and 0.0432 M, respectively, in C_6D_6 , 500 μl). The solution was degassed by the freeze-pump-thaw method three times before stirring for 5 minutes in a room-temperature water bath (22 ± 2 $^\circ\text{C}$ for all data points). A stopwatch was started and the ampoule was pressurised with H_2 (1 bar, 1.81 mmol) for 15 seconds before sealing. At the desired time-point, the timer was stopped and the solution was frozen in liquid nitrogen before it was degassed by the freeze-pump-thaw method three times. An aliquot was transferred to an NMR tube via a cannula and analysed for product formation.

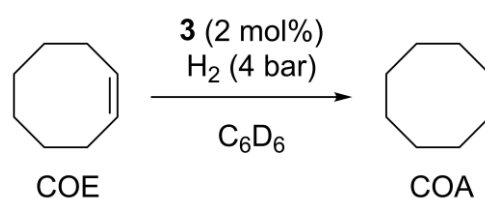
An identical setup was employed for the hydrogenation of COE, using the same catalyst stock solution and a stock solution of COE and ferrocene (0.662 M and 0.0432 M, respectively, in C_6D_6 , 500 μl).

7.3.2.2. High Pressure



Scheme 7.7: Hydrogenation of COD at 4 bar H_2 .

A high-pressure NMR tube with an internal volume of 1750 μl was charged with COD (10 μl , 0.082 mmol), tetramethylsilane (10 μl , 0.073 mmol), a stock solution of **3** (0.011 M in C_6D_6 , 152 μl) and C_6D_6 (228 μl), to a total volume of 380 μl , providing a headspace volume of 1350 μl . This was then degassed by the freeze-pump-thaw method three times. The entire tube was then cooled to 77 K before applying a 2 bar over pressure of H_2 for 12 seconds whilst submerged in liquid nitrogen. The tube was thawed at room temperature and three consecutive NMR measurements were performed. The tube was then removed from the spectrometer and shaken vigorously for 10 seconds before placing back in the spectrometer. This cycle was continued for the duration of the experiment, allowing a regular supply of dissolved H_2 to the reaction.



Scheme 7.8: Hydrogenation of COE at 4 bar H_2 .

An analogous procedure was used for COE (11 μl , 0.082 mmol). This reaction was found to be 16 times faster than the COD hydrogenation and was also found to use up H_2 much faster than diffusion at higher concentrations of catalyst. Due to this, kinetic profiles could not be

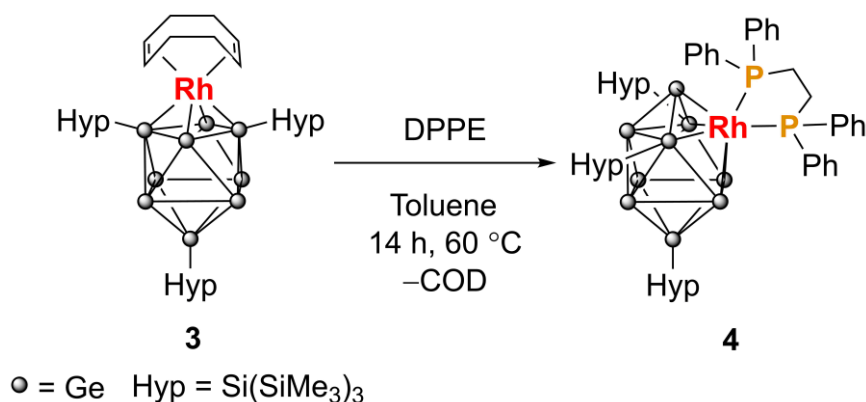
obtained. Interestingly, COE hydrogenation was found at very small catalyst loadings (0.0005 M).

7.3.2.3. Hg Drop Test

An ampoule with rotaflow stopcock and an internal volume of 20000 μl was charged with COD (210 μl , 1.722 mmol), tetramethylsilane (100 μl , 0.734 mmol), **3** (55.34 mg, 0.0344 mmol) and C_6D_6 (7690 μl), to a total volume of 8000 μl , providing a headspace volume of 12000 μl . This was then degassed by the freeze-pump-thaw method three times and thawed at room temperature before applying a 2 bar over pressure of H_2 . A stopwatch was started and reaction was stirred and the stopcock was left open, supplying a constant supply of H_2 for 600 minutes. For each measurement, the gas was replaced with argon, and the stopwatch was stopped, a 380 μl aliquot was transferred to an NMR tube via syringe and immediately measured. The solution was then freeze-pump-thaw degassed once and the headspace was again pressurised with H_2 before restarting the stopwatch. This allows for time corrections, approximately 15 mins per measurement. Hg (2.00 g, 1 mmol) was added at $t = 285$ min, and had no effect on the rate of reaction.

7.4. Chapter 4

7.4.1. Synthesis of $[\text{Rh}(\text{DPPE})\{\text{Ge}_9(\text{Hyp})_3\}]$ (**4**)



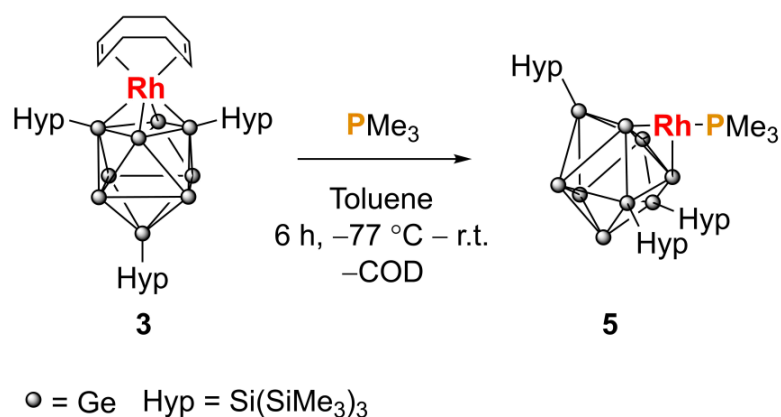
Scheme 7.9: Preparation of $[\text{Rh}(\text{DPPE})\{\text{Ge}_9(\text{Hyp})_3\}]$ (**4**).

A toluene (5 ml) solution of 1,2-bis(diphenylphosphino)ethane (26 mg, 0.065 mmol) was added dropwise to a toluene solution of compound **3** (100 mg, 0.062 mmol) in toluene (5 ml) over the course of 5 minutes at room temperature. The deep red-brown solution was then heated to 60 °C overnight, after which the solution appeared slightly redder. The toluene and COD was removed *in vacuo* and the resulting dark red product extracted with *n*-pentane (4 × 2 ml). Yield: 80 mg, 65% yield from three crops.

Elemental analysis calcd. for $C_{53}H_{105}Ge_9P_2RhSi_{12}$ ($M = 1897.81 \text{ g}\cdot\text{mol}^{-1}$): C 33.54, H 5.58. Found: C 34.05, H 5.27.

^1H NMR (C_6D_6 , 298 K, 400.17 MHz): δ (ppm) 0.46 (s, 81H; CH_3), 1.68 (d, $^2J_{H-P} = 20.55 \text{ Hz}$, 4H; CH_2), 7.12 (t, $^3J_{H-H} = 7.15 \text{ Hz}$, 4H; *p*-CH), 7.25 (m, 8H; *m*-CH), 7.65 (m, 8H; *o*-CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 100.64 MHz): δ (ppm) 3.96 (CH_3), 32.04 (t, $^1J_{C-P} = 22.1$; CH_2), 128.37 (*m*-CH), 129.82 (*p*-CH), 134.12 (t, $^2J_{C-P} = 5.1 \text{ Hz}$; *o*-CH), 139.08 (m; *ipso*-C). ^{29}Si NMR (C_6D_6 , 298 K, 79.5 MHz): δ (ppm) -84.38, -9.76. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 161.9 MHz): δ (ppm) 43.85 (d, $^1J_{P-Rh} = 160.4 \text{ Hz}$).

7.4.2. Synthesis of $[\text{Rh}(\text{PMe}_3)\{\text{Ge}_9(\text{Hyp})_3\}]$ (**5**)



Scheme 7.10: Preparation of $[\text{Rh}(\text{PMe}_3)\{\text{Ge}_9(\text{Hyp})_3\}]$ (**5**).

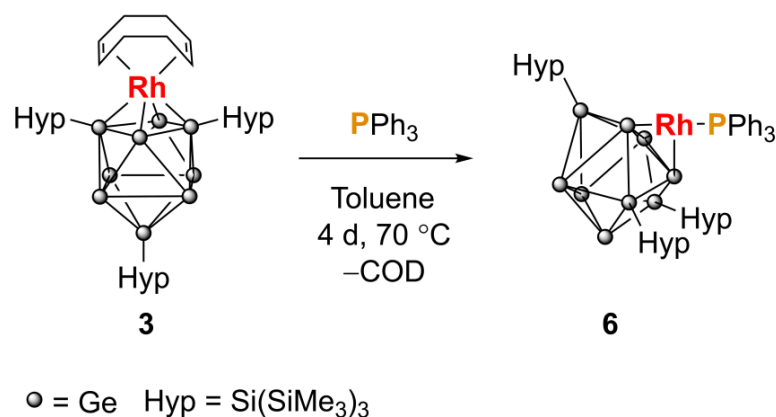
[Rh(COD){Ge₉(Hyp)₃}] (**3**) (100 mg, 0.062 mmol) was dissolved in toluene (20 ml) and cooled to −77 °C. PMe₃ in toluene (0.031 M, 2 ml, 0.062 mmol) was added dropwise over the course of 10 minutes. The brown solution was stirred for 90 minutes before warming to room temperature and stirring for 4 hours. The toluene was removed *in vacuo* and the product was extracted in *n*-hexane (10 ml) as a brown solution. The product was dried *in vacuo* and lyophilized from benzene (4 ml). Yield: 91 mg, 93%. CAUTION: fine dry powders of compound **5** ignite spontaneously in air.

Black-brown crystals suitable for X-ray crystallography were obtained by dissolving 50 mg in 0.5 ml *n*-hexane and cooling to −40 °C.

Elemental analysis calcd. for C₃₀H₉₀Ge₉PRhSi₁₂ (*M* = 1575.62 g·mol^{−1}): C 22.87, H 5.76. Found: C 23.98, H 5.84.

¹H NMR (C₆D₆, 298 K, 400.2 MHz): δ (ppm) 0.50 (s, 81H; CH₃), 1.13 (d, ²*J*_{H-P} = 9.3 Hz, 9H; CH₃). ¹³C{¹H} NMR (C₆D₆, 298 K, 100.64 MHz): δ (ppm) 3.13 (CH₃), 26.78 (d, ¹*J*_{C-P} = 28.2 Hz; CP). ²⁹Si NMR (C₆D₆, 298 K, 99.32 MHz): δ (ppm) −95.2, −9.7. ³¹P{¹H} NMR (C₆D₆, 298 K, 202.39 MHz): δ (ppm) −13.47 (d, ¹*J*_{P-Rh} = 210.3 Hz).

7.4.3. Synthesis of [Rh(PPh₃){Ge₉(Hyp)₃}] (**6**)



Scheme 7.11: Preparation of [Rh(PPh₃){Ge₉(Hyp)₃}] (**6**).

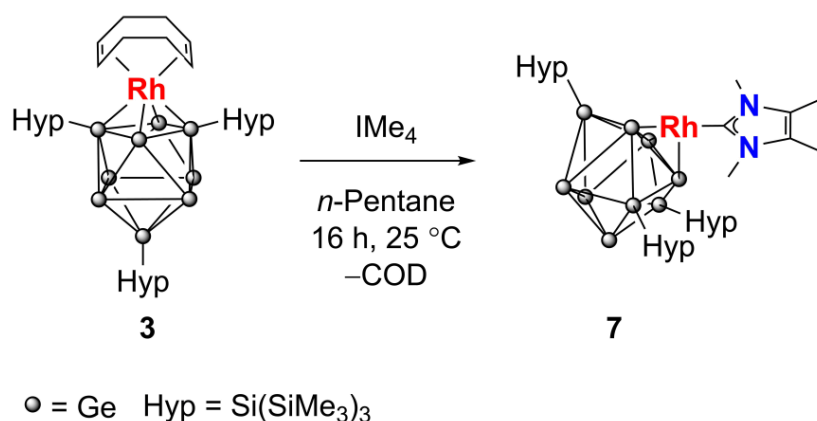
Toluene (20 ml) was added to a mixture of **3** (250 mg, 0.16 mmol) and PPh₃ (41 mg, 0.16 mmol) at room temperature. The brown solution was stirred for 3 hours before heating to 70 °C for 4 days. The toluene was removed *in vacuo* and the product was extracted in *n*-pentane (10 ml) as a brown solution. The product was dried *in vacuo* and lyophilized from benzene (3 ml). The resulting fine brown powder was purified by sublimation of any excess (typically ~5%) PPh₃ at 85 °C over 12 hours. This was then again extracted with *n*-pentane (5 ml) and lyophilized from benzene (3 ml) to yield **6** as a brown powder (240 mg, 84%). CAUTION: fine dry powders of compound **6** ignite spontaneously in air.

Black-brown crystals suitable for X-ray crystallography were obtained by dissolving 200 mg in 0.5 ml *n*-hexane and cooling to –40 °C.

Elemental analysis calcd. for C₄₅H₉₆Ge₉PRhSi₁₂ (*M* = 1761.83 g·mol^{–1}): C 30.68, H 5.49. Found: C 30.71, H 5.77.

¹H NMR (C₆D₆, 298 K, 499.93 MHz): δ (ppm) 0.46 (s, 81H; CH₃), 6.99 (m, 3H; CH), 7.04 (m, 6H; CH), 7.66 (m, 6H; CH). ¹³C{¹H} NMR (C₆D₆, 298 K, 125.72 MHz): δ (ppm) 3.04 (CH₃), 128.57 (CH), 128.65 (CH), 130.19 (CH), 134.75 (CH), 134.86 (CH) 136.10 (d, ¹J_{C–P} = 41.4 Hz; CP). ²⁹Si NMR (C₆D₆, 298 K, 99.32 MHz): δ (ppm) –94.2, –9.6. ³¹P{¹H} NMR (C₆D₆, 298 K, 202.39 MHz): δ (ppm) 49.28 (d, ¹J_{P–Rh} = 214.0 Hz).

7.4.4. Synthesis of $[\text{Rh}(\text{IME}_4)\{\text{Ge}_9(\text{Hyp})_3\}]$ (**7**)



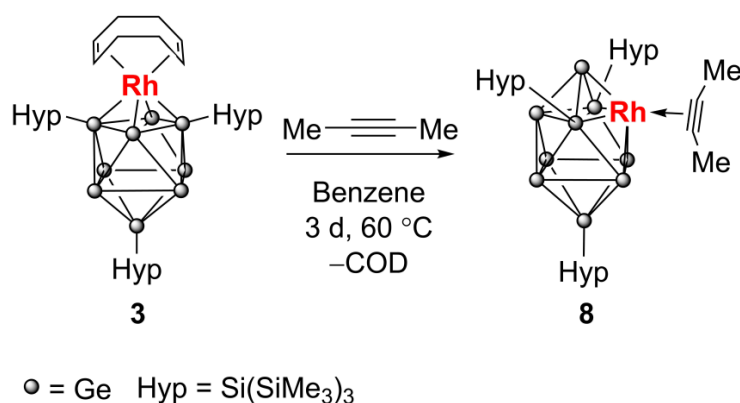
Scheme 7.12: Preparation of $[\text{Rh}(\text{IME}_4)\{\text{Ge}_9(\text{Hyp})_3\}]$ (**7**).

3 (100 mg, 0.062 mmol) was dissolved in *n*-pentane (5 ml) and added to a suspension of IME_4 (8 mg, 0.062 mmol) in *n*-pentane (5 ml) at room temperature. The brown suspension was stirred for 16 hours before filtering. The solution was concentrated to ~1 ml and cooled to $-40\text{ }^\circ\text{C}$ producing black crystals of compound **7** (60 mg, 58%) which were suitable for crystallography.

Elemental analysis calcd. for $\text{C}_{34}\text{H}_{93}\text{Ge}_9\text{N}_2\text{RhSi}_{12}(\text{C}_5\text{H}_{12})$ ($M = 1623.73 + 72.15\text{ g}\cdot\text{mol}^{-1}$): C 27.64, H 6.19, N 1.65. Found: C 27.19, H 6.02, N 1.77.

^1H NMR (C_6D_6 , 298 K, 499.93 MHz): δ (ppm) 0.55 (s, 81H; CH_3), 1.16 (s, 6H; CH_3), 3.38 (s, 6H; CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 125.72 MHz): δ (ppm) 3.28 (CH_3), 9.00 (CH_3), 40.38 (CH_3), 171.4 (d, $^1J_{\text{C-Rh}} = 76.0\text{ Hz}$; $\text{C}=\text{Rh}$). ^{29}Si NMR (C_6D_6 , 298 K, 99.32 MHz): δ (ppm) -97.7 , -9.7 .

7.4.5. Synthesis of $[\text{Rh}(\text{C}_2\text{Me}_2)\{\text{Ge}_9(\text{Hyp})_3\}]$ (**8**)



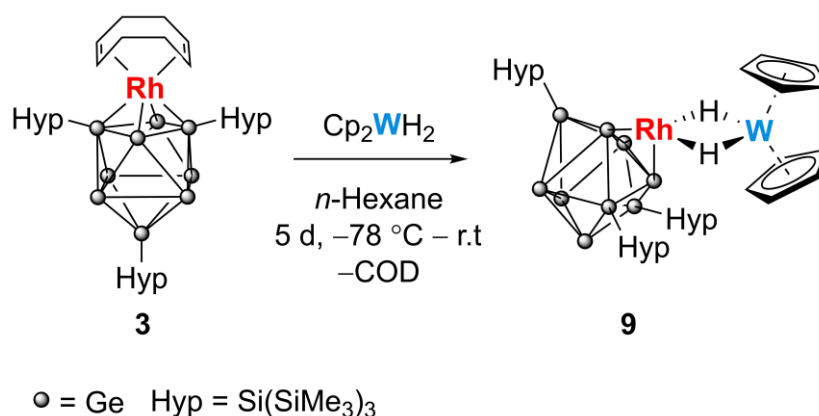
Scheme 7.13: Preparation of $[\text{Rh}(\text{C}_2\text{Me}_2)\{\text{Ge}_9(\text{Hyp})_3\}]$ (**8**).

3 (100 mg, 0.062 mmol) was dissolved in benzene (10 ml). 2-butyne (50 μl , 0.64 mmol) was added and the red-brown solution was heated to 60 $^\circ\text{C}$ for 4 days. The solution was lyophilized and redissolved in *n*-pentane (2 ml). This was then reduced in volume to *ca.* 0.5 ml and cooled to -40 $^\circ\text{C}$ for 2 days, yielding large black-red crystals of compound **8** suitable for X-ray crystallography (80 mg, 83%).

Elemental analysis calcd. for $\text{C}_{31}\text{H}_{87}\text{Ge}_9\text{RhSi}_{12}$ ($M = 1553.63 \text{ g}\cdot\text{mol}^{-1}$): C 23.97, H 5.64. Found: C 24.15, H 5.76.

^1H NMR (C_6D_6 , 298 K, 400.2 MHz): δ (ppm) 0.48 (s, 81H; CH_3), 2.27 (d, $^3J_{\text{H-Rh}} = 2.23 \text{ Hz}$, 6H; CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 150.99 MHz): δ (ppm) 2.89 (CH_3), 17.15 (d, $^2J_{\text{C-Rh}} = 1.6 \text{ Hz}$; CH_3), 103.36 (d, $^1J_{\text{C-Rh}} = 18.5 \text{ Hz}$; CC). ^{29}Si NMR (C_6D_6 , 298 K, 99.32 MHz): δ (ppm) -94.22 , -9.7 .

7.4.6. Synthesis of $[\text{Rh}(\mu\text{-H})_2\text{W}(\text{Cp})_2\{\eta^3\text{-Ge}_9(\text{Hyp})_3\}]$ (**9**)



Scheme 7.14: Preparation of $\text{Rh}(\mu\text{-H})_2\text{W}(\text{Cp})_2[\eta^3\text{-Ge}_9(\text{Hyp})_3]$ (**9**).

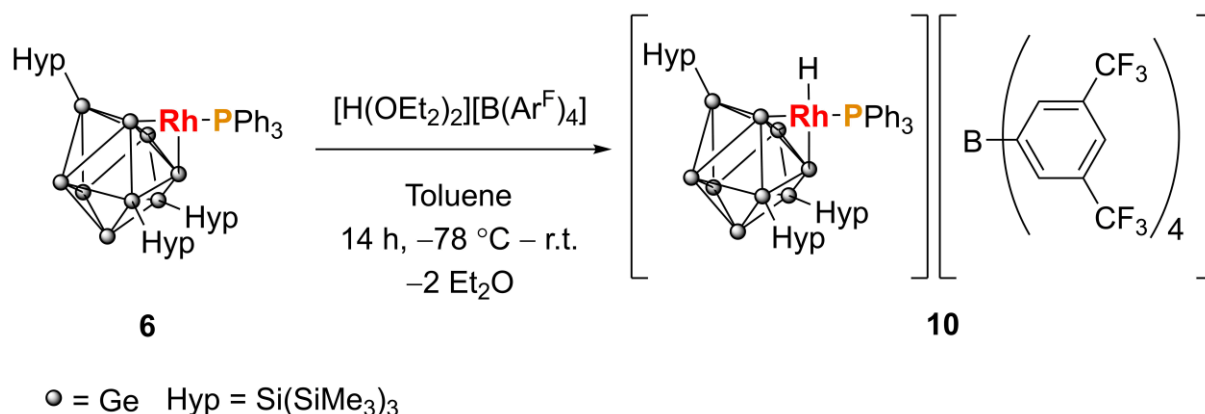
Compound **3** (300 mg, 0.19 mmol) was dissolved in *n*-hexane (20 ml) and cooled to $-78\text{ }^\circ\text{C}$. $(\text{Cp})_2\text{WH}_2$ (60 mg, 0.19 mmol) was dispersed in *n*-hexane (10 ml). The stirring $(\text{Cp})_2\text{WH}_2$ mixture was then added dropwise to the solution of **3** over the course of 20 minutes. This was allowed to stir and warm to room temperature for 18 hours. The solution was then reduced in volume to $\sim 10\text{ ml}$ *in vacuo* and stirred at room temperature under a static vacuum for 4 days, producing a brown suspension. Upon standing for 3 hours, the mixture was filtered, affording compound **9** as a brown powder. The product was dried *in vacuo* and lyophilized from benzene (5 ml) to yield a fine brown powder of compound **9** (240 mg, 71%). CAUTION: compound **9** is highly pyrophoric. Black crystals suitable of X-ray crystallography were obtained by dissolving 30 mg in a 1:10 mixture of toluene and *n*-pentane ($\sim 0.5\text{ ml}$ total volume) and cooling to $-40\text{ }^\circ\text{C}$.

Attempts to heat the reaction to above $45\text{ }^\circ\text{C}$ or stir the reaction longer ($\sim 1\text{ week}$) resulted in the formation of decomposition products.

Elemental analysis calcd. for $\text{C}_{37}\text{H}_{93}\text{Ge}_9\text{RhSi}_{12}\text{W}$ ($M = 1815.59\text{ g}\cdot\text{mol}^{-1}$): C 24.48, H 5.16. Found: C 23.62, H 4.24.

^1H NMR (C_6D_6 , 298 K, 400.16 MHz): δ (ppm) -16.15 (d, $^1J_{\text{Rh-H}} = 26.2$ Hz $^1J_{\text{W-H}} = 76.0$ Hz, 2H; RhH_2W), 0.59 (s, 81H; CH_3), 4.26 (s, 10H; CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 125.72 MHz): δ (ppm) 3.26 (CH_3), 77.55 (CH). ^{29}Si NMR (C_6D_6 , 298 K, 99.32 MHz): δ (ppm) -95.21 , -9.55 .

7.4.7. Synthesis of $[\text{RhH}(\text{PPh}_3)\{\text{Ge}_9(\text{Hyp})_3\}][\text{B}(\text{Ar}^{\text{F}})_4]$ (**10**)



Scheme 7.15: Preparation of $[\text{RhH}(\text{PPh}_3)\{\text{Ge}_9(\text{Hyp})_3\}][\text{B}(\text{Ar}^{\text{F}})_4]$ (**10**).

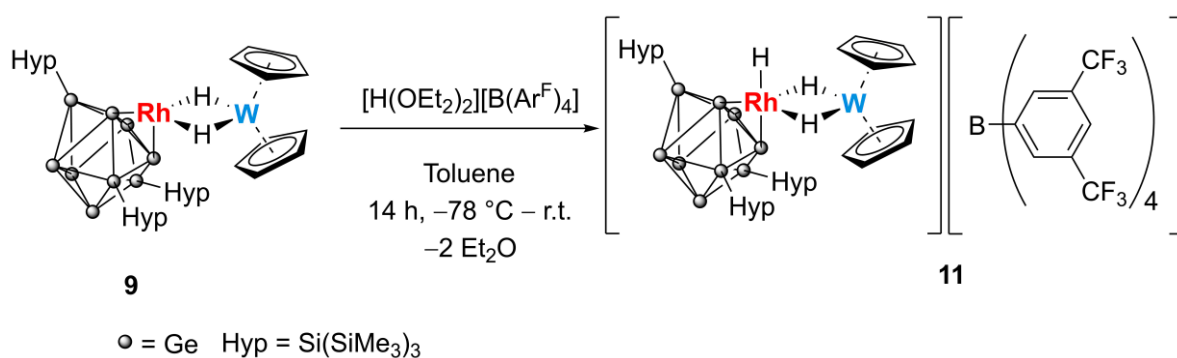
Compound **6** (100 mg, 0.057 mmol) and $[\text{H}(\text{OEt}_2)_2][\text{B}(\text{Ar}^{\text{F}})_4]$ (60 mg, 0.059 mmol) were added to an ampoule, which was quickly cooled to -78 °C. The solids were stirred and cold toluene (-78 °C, 10 ml) was added. The reaction was stirred at -78 °C for 30 minutes before warming slowly to room temperature overnight to produce a reddish-brown solution and brown oil. This was filtered to a Schlenk flask and washed with toluene (3×10 ml) until the extracts were almost colourless. The red-brown solution was dried *in vacuo* to produce a red oil. *n*-hexane (30 ml) was then added and the flask and shaken to disperse the oil as a dark red mixture, this was then allowed to stand overnight, producing black-red crystals of **10**.

N.B. Due to the insolubility of **10** in C_6D_6 , **10** can also be prepared in Et_2O *in situ* and monitored by ^{31}P NMR spectroscopy, however, attempts to form solids from this reaction were unsuccessful.

Elemental analysis calcd. for $C_{53}H_{105}Ge_9P_2RhSi_{12}$ ($M = 2626.06 \text{ g}\cdot\text{mol}^{-1}$): C 35.22, H 4.18.
Found: C 31.92, H 3.63.

^1H NMR (C_6D_6 , 298 K, 400.17 MHz): δ (ppm) -1.48 (dd, $^2J_{H-P} = 3.4 \text{ Hz}$, $^1J_{H-Rh} = 12.6 \text{ Hz}$ 1H; RhH), 0.07 (s br., 27H; CH_3), 0.33 (s br., 54H; CH_3), 7.01 (m, 9H; CH), 7.37 (m, 6H; *o*-CH), 7.70 (s, 4H; *p*-CH), 8.46 (s, 8H; *o*-CH). $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 128.40 MHz) δ (ppm): -5.84 (s, 1B; $B(\text{Ar}^F)_4$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 151 MHz): δ (ppm) 2.32 (CH_3), 3.19 (CH_3), 118.06 (m; CH), 125.30 (q (one signal hidden under C_6D_6), $^1J_{C-F} = 272.2 \text{ Hz}$; CF_3), 129.25 (d, $^3J_{C-P} = 10.4 \text{ Hz}$ CP), 129.95 (qq, $^2J_{C-F} = 30.6 \text{ Hz}$, $^3J_{C-B} = 2.8 \text{ Hz}$; CCF_3), 131.50 (d, $^1J_{C-P} = 45.1 \text{ Hz}$; CH), 131.84 (d, $^4J_{C-P} = 2.2 \text{ Hz}$; CH), 134.43 (d, $^2J_{C-P} = 13.2 \text{ Hz}$ CP) 135.50 (br. s; CH), 162.90 (q, $^1J_{C-B} = 50.58 \text{ Hz}$; CB. $^{19}\text{F}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 376.53 MHz): δ (ppm) -61.67 (s, 24F; CF_3). ^{29}Si NMR (C_6D_6 , 298 K, 79.5 MHz): δ (ppm) -83.87 , -8.38 . $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 162 MHz): δ (ppm) 41.39 (d, $^1J_{P-Rh} = 188.9 \text{ Hz}$).

7.4.8. Synthesis of $[\text{RhH}((\mu\text{-H})_2\text{W}(\text{Cp})_2)\{\text{Ge}_9(\text{Hyp})_3\}][\text{B}(\text{Ar}^F)_4]$ (**11**)



Scheme 7.16: Preparation of $[\text{RhH}((\mu\text{-H})_2\text{W}(\text{Cp})_2)\{\text{Ge}_9(\text{Hyp})_3\}][\text{B}(\text{Ar}^F)_4]$ (**11**).

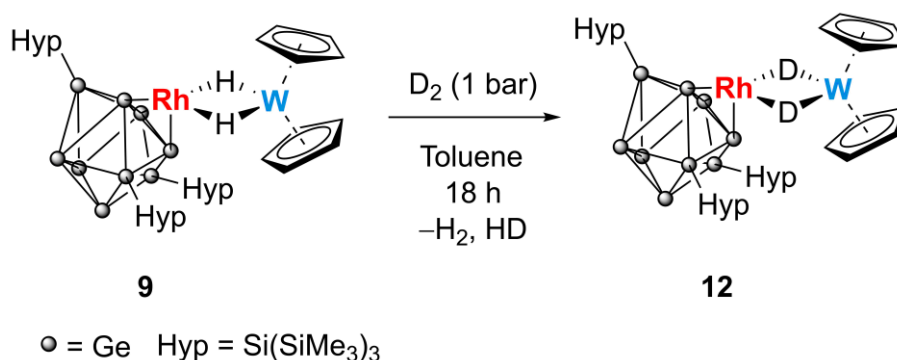
A mixture of **9** (50 mg, 0.027 mmol) and $[\text{H}(\text{OEt}_2)_2][\text{B}(\text{Ar}^F)_4]$ (28 mg, 0.027 mmol) were added to an ampoule, which was quickly cooled to -78°C . The solids were stirred and cold toluene (-78°C , 15 ml) was added. The reaction was stirred at -78°C for 30 minutes before warming slowly to room temperature overnight to produce a reddish-brown solution and brown oil. This was filtered to a Schlenk flask and washed with toluene ($3 \times 10 \text{ ml}$) until the

extracts were almost colourless. The red-brown solution was dried *in vacuo* to produce a red-brown oil. This was then dissolved in Et₂O (3 ml) and slowly evaporated to ~1 ml before cooling to –40 °C, producing dark red crystals of **11** (70 mg, 64%).

Elemental analysis calcd. for C₆₉H₁₀₆BF₂₄Ge₉RhSi₁₂W (*M* = 2679.81 g·mol^{–1}): C 30.93, H 3.99. Found: C 29.58, H 3.81.

¹H NMR (C₆D₆, 298 K, 400.17 MHz): δ (ppm) –15.41 (d, ¹J_{Rh-H} = 27.8 Hz ¹J_{W-H} = 83.3 Hz, 2H; RhH₂W), –0.03 (d, ¹J_{Rh-H} = 12.2 Hz, 1H; RhH), 0.21 (s, 27H; CH₃), 0.42 (s, 54H; CH₃), 4.31 (s, 10H; CH). ¹¹B{¹H} NMR (C₆D₆, 298 K, 128.40 MHz): δ (ppm) –5.96 (s, 1B; B(ArF)₄). ¹³C{¹H} NMR (C₆D₆, 298 K, 151 MHz): δ (ppm) 2.45 (CH₃), 2.71 (CH₃), 79.71 (s; CH), 118.12 (m; CH), 125.20 (q (one signal hidden under C₆D₆), ¹J_{C-F} = 272.2 Hz; CF₃), 129.94 (qq, ²J_{C-F} = 31.6 Hz, ³J_{C-B} = 3.0 Hz; CCF₃), 135.44 (br. s; CH), 162.80 (q, ¹J_{C-B} = 50.58 Hz; CB). ¹⁹F{¹H} NMR (C₆D₆, 298 K, 376.53 MHz): δ (ppm) –61.89 (s, 24F; CF₃). ²⁹Si NMR (C₆D₆, 298 K, 79.5 MHz): δ (ppm) –85.83, –84.26, –8.57, –7.98.

7.4.9. Synthesis of [Rh(μ-D)₂W(Cp)₂{Ge₉(Hyp)₃}] (**12**)



Scheme 7.17: Preparation of [Rh(μ-D)₂W(Cp)₂{Ge₉(Hyp)₃}] (**12**).

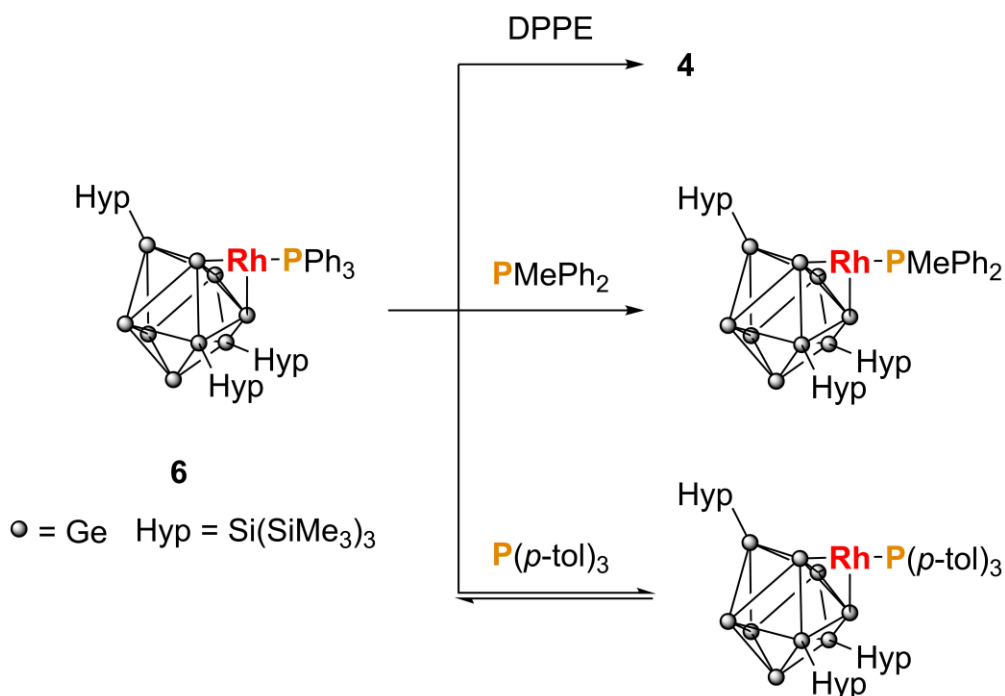
Compound **9** (15 mg, 0.01 mmol) was dissolved in toluene (0.4 ml) in a J. Young NMR tube. This was degassed by three freeze-pump-thaw cycles and pressurized with D₂ (1 bar). The

reaction mixture was stirred by tumbling the NMR tube overnight producing compound **12**, H₂ and HD.

Degassing the sample and replacing the atmosphere with H₂ (1 bar), regenerates **9** quantitatively by NMR.

²H NMR (C₇H₈, 298 K, 76.74 MHz) δ (ppm): -16.06 (d, ¹J_{Rh-D} = 4.1 Hz; ¹J_{W-D} 12 Hz, 2D; RhD₂W)

7.4.10. Ligand Exchange Experiments



Scheme 7.18: NMR scale ligand exchange reactions by reacting **6** with phosphines.

Compound **6** (10 mg, 0.006 mmol) was added to an NMR tube with a J. Young stopcock and dissolved in C₆D₆. DPPE (~2.5 mg, ~0.003 mmol), PMePh₂ (~1.5 mg, ~0.006 mmol) or P(*p*-tol)₃ (~2 mg, ~0.006 mmol) was added in a glovebox and the tube shaken.

DPPE and PMePh₂ displaced PPh₃, forming **4** and Rh(PMePh₂)[Ge₉(Hyp)₃] respectively.

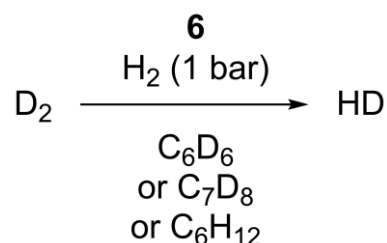
Rh(PMePh₂)[Ge₉(Hyp)₃]. ¹H NMR (C₆D₆, 298 K, 400.17 MHz): δ (ppm) 0.48 (s, 81H; CH₃), 1.89 (dd, ²J_{H-P} = 8.3 Hz, ³J_{H-Rh} = 1.8 Hz, 3H; CH₃). ²⁹Si NMR (C₆D₆, 298 K, 79.5 MHz): δ (ppm) -94.22, -9.73. ³¹P{¹H} NMR (C₆D₆, 298 K, 161.9 MHz): δ (ppm) 22.72 (d, ¹J_{P-Rh} = 208.0 Hz).

P(*p*-tol)₃ formed a mixture of **6**, Rh(P(*p*-tol)₃)[Ge₉(Hyp)₃], P(*p*-tol)₃ and PPh₃.

Rh(P(*p*-tol)₃)[Ge₉(Hyp)₃]. ¹H NMR (C₆D₆, 298 K, 400.17 MHz): δ (ppm) 0.48 (s, 81H; CH₃). ²⁹Si NMR (C₆D₆, 298 K, 79.5 MHz): δ (ppm) -94.43, -9.74. ³¹P{¹H} NMR (C₆D₆, 298 K, 161.9 MHz): δ (ppm) 45.94 (d, ¹J_{P-Rh} = 212.7 Hz).

7.4.11. Catalysis Procedures

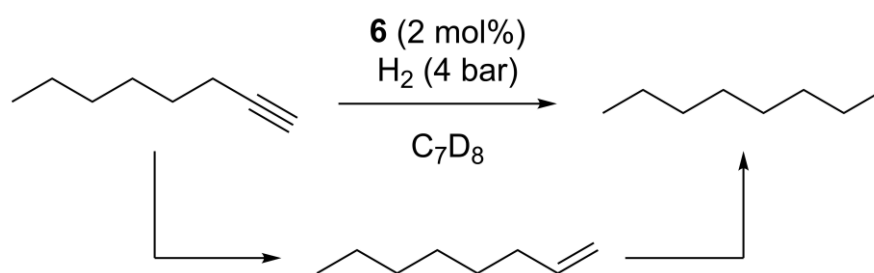
7.4.11.1. H/D Scrambling



Scheme 7.19: H/D scrambling of a H₂/D₂ mixture in the presence of **6**.

Compound **6** (6 mg, 0.0034 mmol) was added to an NMR tube with a J. Young stopcock and dissolved in either C₆D₆ or C₇D₈. This was freeze-pump-thaw degassed three times before charging with D₂ (0.5 bar) and stirring overnight to saturate the solution. The solution was then frozen, and partially degassed (~10² mbar) before charging with H₂ (1 bar). HD formation was observed within 5 minutes of the H₂ addition by ¹H NMR spectroscopy.

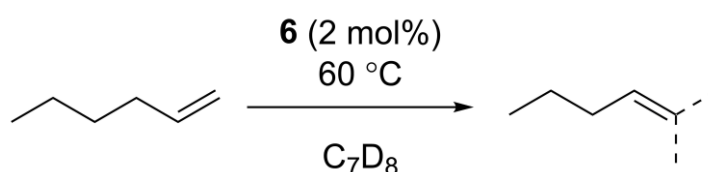
7.4.11.2. Alkyne hydrogenation



Scheme 7.20: Hydrogenation of 1-octyne.

A high-pressure NMR tube with an internal volume of 1750 μl was charged with 1-octyne (10 μl , 0.063 mmol), tetramethylsilane (10 μl , 0.073 mmol), **6** (2 mg, 0.0011 mmol) and C_7D_8 (360 μl), to a total volume of 380 μl , providing a headspace volume of 1350 μl . This was then degassed by the freeze-pump-thaw method three times. The entire tube was then cooled to 77 K before applying a 2 bar over pressure of H_2 for 12 seconds whilst submerged in liquid nitrogen. The tube was thawed at room temperature and three consecutive NMR measurements were performed. The tube was then removed from the spectrometer and continuously tumbled before placing back in the spectrometer. This cycle was continued for the duration of the experiment, allowing a regular supply of dissolved H_2 to the reaction.

7.4.11.3. Alkene Isomerisation



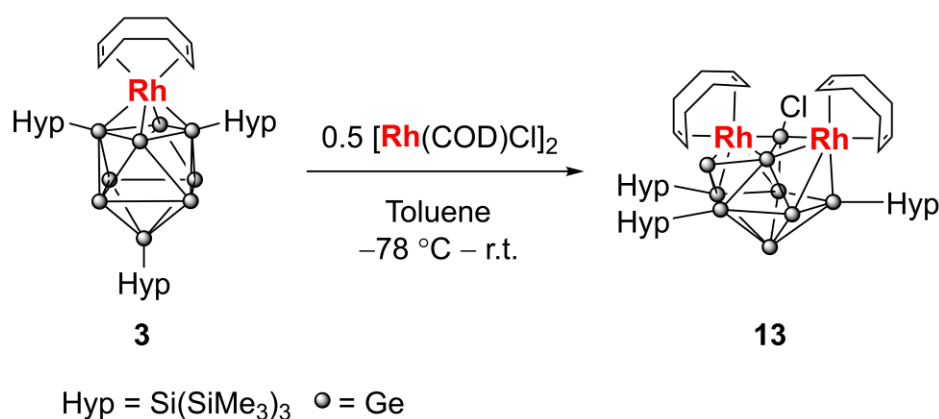
Scheme 7.21: Isomerisation of 1-hexene.

Compound **6** (3 mg, 0.0017 mmol) and ferrocene (2 mg, 0.011 mmol) in C_7D_8 (400 μl) was added to an NMR tube. 1-hexene (10 μl , 0.08 mmol) was added using a microsyringe and the solution immediately frozen in a liquid nitrogen bath. The NMR probe was pre-heated to 80

°C, the sample added and a stopwatch started. Isomerisation was monitored by ^1H NMR spectroscopy for 12 hours before adding to an oil bath for further measurements. The stopwatch was stopped when taken out to measure a data point and restarted when the reaction mixture was returned to the bath.

7.5. Chapter 5

7.5.1. Synthesis of $[\{\text{Rh}(\text{COD})\}_2\{\text{Ge}_9(\text{Hyp})_3\text{Cl}\}]$ (**13**)



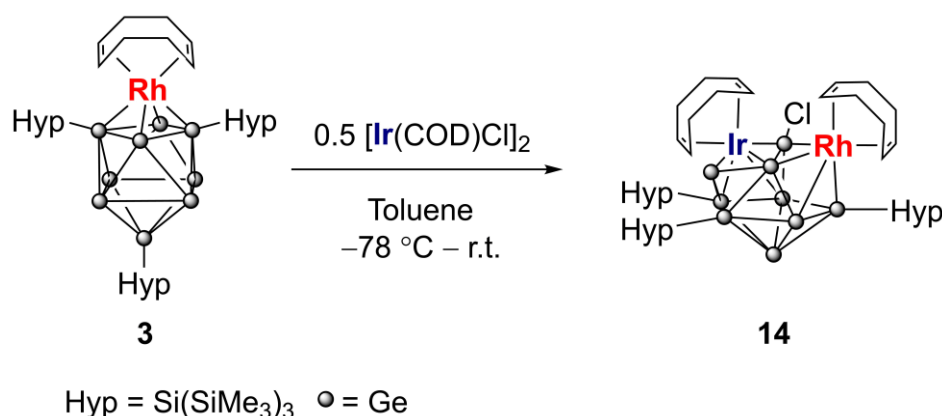
Scheme 7.22: Preparation of $[\{\text{Rh}(\text{COD})\}_2\{\text{Ge}_9(\text{Hyp})_3\text{Cl}\}]$ (**13**).

A toluene (5 ml) solution of $[\text{Rh}(\text{COD})\{\text{Ge}_9(\text{Hyp})_3\}]$ (**3**) (50 mg, 0.03 mmol) cooled to -78 °C was added to a toluene (5 ml) solution of $[\text{Rh}(\text{COD})\text{Cl}]_2$ (10 mg, 0.02 mmol) at -78 °C. This was allowed to stir, warming to room temperature over the course of an hour and stirred for a further three hours at room temperature. The brown solution was then dried *in vacuo*, extracted in hexane (*ca.* 3 ml) and filtered using a glass fibre plug to remove a small amount of black solid. The solution was slowly evaporated until precipitate started forming (*ca.* 0.5 ml) and then cooled to -40 °C overnight producing dark brown crystals of **13** (50 mg, 88%) suitable for X-ray crystallography.

Elemental analysis calcd. $\text{C}_{43}\text{H}_{104}\text{ClGe}_9\text{Rh}_2\text{Si}_{12}$ (+ C_6H_{14}) ($M = 1853.26 + 86.18 \text{ g}\cdot\text{mol}^{-1}$): C 30.36, H 6.08. Found: C 29.49, H 5.91.

^1H NMR (C_6D_6 , 298 K, 400.19 MHz): δ (ppm) 0.50 (s, 27H; CH_3), 0.54 (s, 27H; CH_3), 0.69 (s, 27H; CH_3), 1.40 (m, 1H; CH_2), 1.71 (m, 1H; CH_2), 1.79 (m, 1H; CH_2), 2.08 (m, 1H; CH_2), 2.27 (m, 5H; CH_2), 2.46 (m, 5H; CH_2), 2.78 (m, 1H; CH_2), 2.88 (m, 1H; CH_2), 3.03 (t, $J_{\text{H-H}} = 7.5$ Hz, 1H, CH), 3.26 (t, $J_{\text{H-H}} = 7.3$ Hz, 1H, CH), 3.66 (q, $J_{\text{H-H}} = 7.1$ Hz, 1H, CH), 4.74 (t, $J_{\text{H-H}} = 8.1$ Hz, 1H, CH), 4.94 (br. s, 2H; CH), 5.66 (br. s, 2H; CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 150.99 MHz): δ (ppm) 4.24 (CH_3), 4.30 (CH_3), 5.08 (CH_3), 23.52 (CH_2), 28.40 (CH_2), 28.42 (CH_2), 29.97 (CH_2), 30.66 (CH_2), 31.59 (CH_2), 32.05 (CH_2), 32.97 (CH_2), 35.57 (CH_2), 77.34 (d, $^1J_{\text{C-Rh}} = 8.5$ Hz; CH), 80.49 (d, $^1J_{\text{C-Rh}} = 9.7$ Hz; CH), 82.04 (br m.; CH), 84.52 (d, $^1J_{\text{C-Rh}} = 5.8$ Hz; CH) 90.45 (br m.; CH) 98.19 (d, $^1J_{\text{C-Rh}} = 5.6$ Hz; CH). ^{29}Si NMR (C_6D_6 , 298 K, 79.51 MHz): δ (ppm) -79.74 , -74.85 , -62.92 , -8.55 – -8.16 .

7.5.2. Synthesis of $[\{\text{Rh}(\text{COD})\}\{\text{Ir}(\text{COD})\}\{\text{Ge}_9(\text{Hyp})_3\text{Cl}\}]$ (**14**)



Scheme 7.23: Preparation of $[\{\text{Rh}(\text{COD})\}\{\text{Ir}(\text{COD})\}\{\text{Ge}_9(\text{Hyp})_3\text{Cl}\}]$ (**14**).

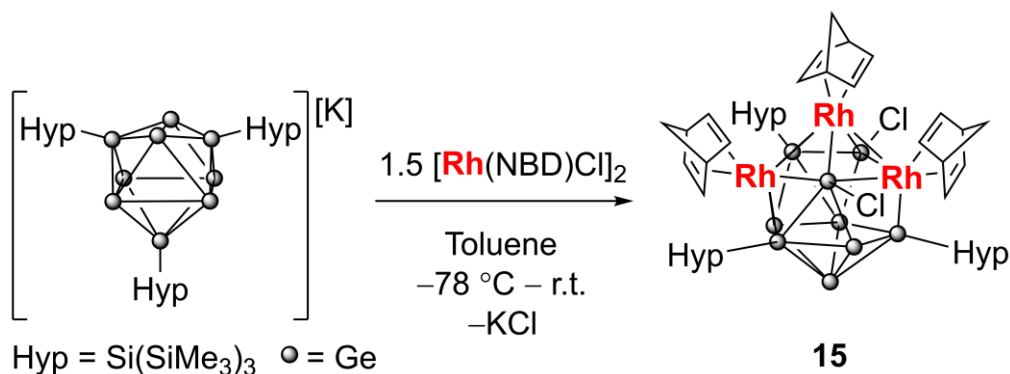
A toluene (10 ml) suspension of $[\text{Ir}(\text{COD})\text{Cl}]_2$ (90 mg, 0.13 mmol) cooled to -78 °C was added to a toluene (15 ml) solution of $[\text{Rh}(\text{COD})\{\text{Ge}_9(\text{Hyp})_3\}]$ (**3**) (250 mg, 0.15 mmol) at -78 °C in the dark. This was allowed to stir for 1 hour then slowly warmed to room temperature before stirring for a further three hours. The brown solution was then dried *in vacuo*, extracted in pentane (*ca.* 15 ml), and filtered to remove a small amount of black solid. The solution was removed *in vacuo* and the resultant brown solid lyophilised from benzene (*ca.* 4 ml),

producing 200 mg (69 %) of brown powder. This was then dissolved in hexane (*ca.* 2 ml) and cooled to $-40\text{ }^{\circ}\text{C}$ producing dark red crystals of **14**. **14** ignites spontaneously in air. It was found that performing the reaction and workup in the dark improved yields and decreased the formation of black insoluble solids.

Elemental analysis calcd. For $\text{C}_{43}\text{H}_{104}\text{ClGe}_9\text{IrRhSi}_{12}$ ($M = 1942.57\text{ g}\cdot\text{mol}^{-1}$): C 26.59, H 5.40. Found: C 26.19, H 3.17.

^1H NMR (C_6D_6 , 298 K, 400.19 MHz): δ (ppm) 0.48 (s, 27H; CH_3), 0.55 (s, 27H; CH_3), 0.70 (s, 27H; CH_3), 1.10 (m, 1H; CH_2), 1.62 (m, 1H; CH_2), 1.93 (m, 1H; CH_2), 2.12 (m, 2H; CH_2), 2.24 (m, 1H; CH_2), 2.36 (m, 4H; CH_2), 2.43 (m, 4H; CH_2), 2.67 (m, 1H; CH_2), 2.85 (m, 1H; CH_2), 2.96 (t, $J_{\text{H-H}} = 7.0\text{ Hz}$, 1H, CH), 3.19 (td, $J_{\text{H-H}} = 8.5, 4.1\text{ Hz}$, 1H, CH), 3.26 (td, $J_{\text{H-H}} = 8.5, 2.8\text{ Hz}$, 1H, CH), 4.42 (t, $J_{\text{H-H}} = 7.0\text{ Hz}$, 1H, CH), 4.83 (br. s, 2H; CH), 5.69 (br. s, 2H; CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 150.99 MHz): δ (ppm) 4.22 (CH_3), 4.32 (CH_3), 5.10 (CH_3), 23.52 (CH_2), 28.42 (CH_2), 30.73 (CH_2), 31.09 (CH_2), 31.79 (CH_2), 32.89 (CH_2), 34.50 (CH_2), 37.64 (CH), 65.75 (d, $^1J_{\text{C-Rh}} = 22.5\text{ Hz}$; CH), 70.36 (CH) 80.79 (CH), 80.86 (br. m; CH). ^{29}Si NMR (C_6D_6 , 298 K, 79.51 MHz): δ (ppm) $-78.36, -74.64, -64.28, -8.34 - 8.33$.

7.5.3. Synthesis of $[\{\text{Rh}(\text{NBD})\}_3\{\text{Ge}_9(\text{Hyp})_3\text{Cl}_2\}]$ (**15**)



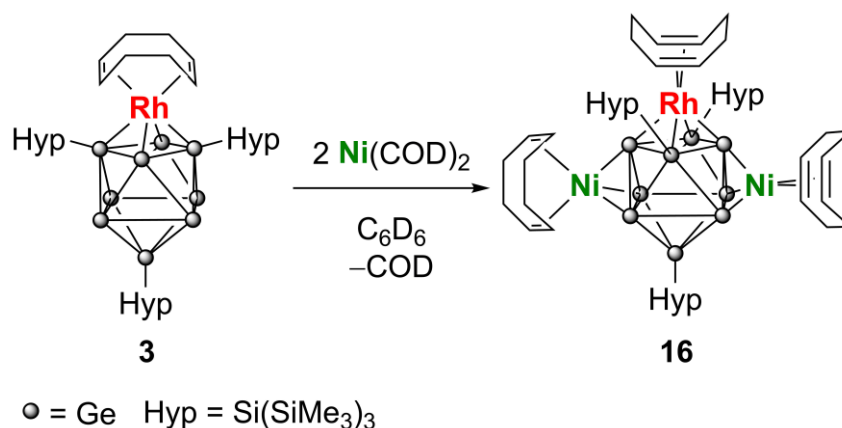
Scheme 7.24: Preparation of $[\{\text{Rh}(\text{NBD})\}_3\{\text{Ge}_9(\text{Hyp})_3\text{Cl}_2\}]$ (**15**).

A toluene (20 ml) solution of $[\text{Rh}(\text{NBD})\text{Cl}]_2$ (140 mg, 0.30 mmol) was added dropwise to a solution $\text{K}[\text{Ge}_9(\text{Hyp})_3]$ (280 mg, 0.19 mmol) in toluene (20 ml) over the course of 25 minutes at room temperature. The intense red-brown solution was stirred using a glass coated stir bar overnight. The toluene was removed *in vacuo* and the product was extracted in *n*-pentane (30 ml) as a red-brown solution. This was reduced to 10 ml and left to stand in a $-80\text{ }^\circ\text{C}$ freezer for 16 hours, producing dark red crystals of **15** (310 mg, 80%).

Elemental analysis calcd. for $\text{C}_{48}\text{H}_{102}\text{Cl}_2\text{Ge}_9\text{Rh}_3\text{Si}_{12}$ ($M = 2049.65\text{ g}\cdot\text{mol}^{-1}$): C 28.13, H 5.02. Found: C 28.20, H 4.68.

^1H NMR (C_6D_6 , 298 K, 400.19 MHz): δ (ppm) 0.59 (s, 27H; CH_3), 0.60 (s, 27H; CH_3), 0.64 (s, 27H; CH_3), 1.14 (br. s, 2H; CH_2), 1.21 (br. s, 4H; CH_2), 3.35 (br. s, 2H; CH), 3.53 (br. s, 2H; CH), 3.58 (br. s, 2H; CH), 3.85 (br. s, 2H; CH), 4.31 (br. s, 2H; CH), 4.35 (br. s, 2H; CH), 4.40 (br. s, 2H; CH), 4.66 (br. s, 2H; CH), 4.84 (br. s, 2H; CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 150.99 MHz): δ (ppm) 4.44 (CH_3), 4.95 (CH_3), 5.78 (CH_3), 47.48 (CH_2), 47.82 (CH_2), 48.04 (CH_2), 48.40 (d, $^1J_{\text{C-Rh}} = 6.2\text{ Hz}$; CH), 51.12 (d, $^1J_{\text{C-Rh}} = 6.7\text{ Hz}$; CH), 51.32 (d, $^1J_{\text{C-Rh}} = 6.7\text{ Hz}$; CH), 51.62 (d, $^1J_{\text{C-Rh}} = 6.5\text{ Hz}$; CH), 52.96 (d, $^1J_{\text{C-Rh}} = 6.5\text{ Hz}$; CH), 56.64 (d, $^1J_{\text{C-Rh}} = 6.1\text{ Hz}$; CH), 60.44 (d, $^2J_{\text{C-Rh}} = 4.4\text{ Hz}$; CH), 61.16 (d, $^2J_{\text{C-Rh}} = 4.3\text{ Hz}$; CH), 62.34 (d, $^2J_{\text{C-Rh}} = 4.2\text{ Hz}$; CH). ^{29}Si NMR (C_6D_6 , 298 K, 79.51 MHz): δ (ppm) -81.31 , -65.47 , -62.73 , -7.97 , -6.99 .

7.5.4. Synthesis of [$\{\text{Rh}(\text{COD})\}\{\text{Ni}(\text{COD})\}_2\{\text{Ge}_9(\text{Hyp})_3\}$] (**16**)



Scheme 7.25: Preparation of [$\{\text{Rh}(\text{COD})\}\{\text{Ni}(\text{COD})\}_2\{\text{Ge}_9(\text{Hyp})_3\}$] (**16**).

[$\text{Rh}(\text{COD})\{\text{Ge}_9(\text{Hyp})_3\}$] (**3**) (50 mg, 0.0311 mmol) and [$\text{Ni}(\text{COD})_2$] (17 mg, 0.0618 mmol) were mixed in a vial in a glovebox. C_6D_6 (2 ml) was added and the blood-red solution was stirred overnight. Following analysis, the solvent and COD were removed under a dynamic vacuum and the resulting dark red solid was redissolved in *n*-pentane (2 ml). This was slowly evaporated to ca. 1 ml and cooled to -40°C . Red-black crystals suitable for X-ray crystallography were produced after 3 days (40 mg, 66% yield).

Elemental analysis calcd. for $\text{C}_{51}\text{H}_{117}\text{Ge}_9\text{Ni}_2\text{RhSi}_{12}$ ($M = 1941.55 \text{ g}\cdot\text{mol}^{-1}$): C 31.55, H 6.07. Found: C 27.82, H 4.36.

^1H NMR (C_6D_6 , 298 K, 499.93 MHz): δ (ppm) 0.51 (s, 54H; CH_3), 0.73 (s, 27H; CH_3), 1.77 (m, 8H; CH_2), 2.16 (m, 4H; CH_2), 2.40 (m, 8H; CH_2), 2.67 (m, 4H; CH_2), 4.90 (s, 4H; CH), 5.58 (s, 8H; CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 125.72 MHz): δ (ppm) 4.03 (CH_3), 4.71 (CH_3), 29.92 (CH_2), 32.24 (CH_2), 80.55 (d, $^1J_{\text{C-Rh}} = 8.3 \text{ Hz}$; CH), 95.19 (CH). ^{29}Si NMR (C_6D_6 , 298 K, 99.32 MHz): δ (ppm) -101.45 , -63.37 , -9.67 , -9.28 .

7.6. Characterisation Techniques

7.6.1. Single Crystal X-ray Diffraction

Crystals were selected under Paratone-N oil, mounted on micromount loops and quench-cooled using an Oxford Cryosystems open flow N₂ cooling device. Single-crystal X-ray diffraction data were collected using an Oxford Diffraction Supernova dual-source diffractometer equipped with a 135 mm Atlas CCD area detector. Data were collected at 150 K using monochromated Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) or Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) and processed using the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro). Equivalent reflections were merged and diffraction patterns processed with the CrysAlisPro suite. Structures were subsequently solved using SHELXT and refined on F^2 using the ShelXL 2018/1 package and ShelXL. In each case, the locations of the largest peaks in the final difference Fourier map calculations, as well as the magnitude of the residual electron densities, were of no chemical significance.

7.6.2. NMR Spectroscopy

NMR samples were prepared inside an inert atmosphere glovebox in NMR tubes fitted with a gas-tight valve. ¹H NMR spectra were recorded at either 499.9 MHz or 400.1 MHz on a Bruker AVIII 500 or a Bruker AVIII 400 NMR spectrometer, respectively. ¹³C{¹H} NMR spectra were recorded at either 151 MHz, 125.8 MHz or 100.6 MHz on a Bruker NEO 600 with broadband helium cryoprobe, Bruker AVII 500 fitted with a cryoprobe or a Bruker AVIII 400 NMR spectrometer, respectively. ¹H and ¹³C{¹H} NMR spectra are reported relative to TMS and referenced to the most downfield residual solvent resonance.

¹¹B{¹H} NMR spectra were recorded at 128.4 MHz on a Bruker AVIII 400 NMR spectrometer. ¹⁹F NMR spectra were recorded at 376.5 MHz on a Bruker AVIII 400 NMR spectrometer. ²⁹Si/¹H HMBC NMR spectra were recorded at 79.5 MHz on a Bruker AVIII

400 NMR spectrometer. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded at 162.0 MHz on a Bruker AVIII 400 NMR spectrometer.

7.6.3. EPR Spectroscopy

EPR spectroscopy was performed by Dr Will Myers. X-band CW-EPR was acquired on a Bruker BioSpin EleXSys I E680 spectrometer with an XPB bridge, 1.5 T electromagnet, a Bruker BioSpin ER4122-SHQE-W resonator coupled to an Oxford Instruments ESR900 cryostat, controlled with an Oxford Instruments ITC-503S temperature controller. Liquid helium was used as a cryogen.

7.6.4. Elemental Analysis

Elemental analyses were carried out by Elemental Microanalyses Ltd. (Devon, U. K.). Samples (approx. 10 mg), submitted in sealed Pyrex ampoules.

7.6.5. Computational Details

The geometry optimizations, PCM solvent corrections and frequency calculations were run with Gaussian 16 Revision C.01.¹¹ Initially, benchmarking was done using a range of functionals^{12–19} and basis sets,^{20–29} detailed in Chapter 3.

After that, all calculations were performed using the BP86 functional.^{27,30} Rh, Ge and Si centres were described with Stuttgart RECPs and associated basis sets, with added f-orbital polarization on Rh ($\zeta = 1.35$),¹⁷ and d-orbital polarization on Ge ($\zeta = 0.230$) and Si ($\zeta = 0.284$).¹⁶ 6-31G** basis sets were used for C and H (called BS1).^{18,19} Single point energy calculations were performed on the optimised geometries, at the BP86/Def2-TZVP level of theory with added pseudopotential on Rh.³¹ Stationary points were fully characterized via analytical frequency calculations as either minima (all positive eigenvalues) or transition states (one negative eigenvalue). IRC calculations and subsequent geometry optimizations were used to confirm the minima linked by the transition states. Energies reported in the text

are based on the gas-phase free energies and incorporate a correction for dispersion effects using Grimme's D3 parameter set (i.e. BP86-D3) as well as solvation (PCM approach) in benzene.³²

7.6.6. Cyclic Voltammetry

Cyclic voltammetry was performed in a custom four-necked, flat-bottom pear shaped flask (30 ml) using a glassy carbon working electrode, platinum counter electrode and silver reference electrode, connected to a PalmSens Emstat3 Blue potentiostat. Typically, THF was used as a solvent, [NBu₄][PF₆] (0.2 M) was used as an electrolyte and the sample concentration was 0.001 M.

7.6.7. COPASI Kinetics Modelling

The experimental data, which included COD, COE, COE and the concentration of complexes compound **3** and "RhCOE" were modelled using the microkinetic simulation program COPASI. The model was stress tested by starting from for either COD or COE starting points, and was iterated on the observed concentrations of substrates, intermediates, products, organo- metallic speciation. A slow decomposition with a constant excess of H₂ was required to obtain a satisfactory fit. The COE hydrogenation cycle was first modelled, and specific rate constants were fixed, after which the model was used for the COD analysis. The resulting simulation recreates the multiple temporal profiles satisfactorily, giving confidence that it captures the essential elements of the catalytic manifold.

Briefly described, slow hydrogenation of compound **3** results in an intermediate species, Rh(COE), which we propose is the species observed in low concentrations during COE hydrogenation. Rh(COE) then undergoes either further (endergonic) reaction with H₂ to eventually form INT, or simple substitution by COD to return compound **3** and give free COE (observed). Under COD hydrogenation conditions, reaction of INT with COD again returns

compound **3**. With COE, Rh(COE) is formed. Both cycles produce COA. While the observed induction period in COE hydrogenation is explained by slow Rh(COE) build-up, for both substrates compound **3** is the principal resting state. The deceleration at longer reaction times in both COE and COD hydrogenations and the reduction in [**3**] are captured by the inclusion of a slow decomposition process with H₂ that reduces [Rh]_{total}, as observed experimentally in the absence of COD.

Table S1. Selected X-ray data collection and refinement parameters for **1–5**.

	[K(2.2.2-crypt)] ₂ [1]·2THF	2 ·1.5tol	3	4	5
Formula	C ₉₈ H ₂₅₀ Ge ₁₈ K ₂ N ₄ NiO ₁₄ Si ₂₄	C _{42.5} H ₉₈ Ge ₈ NiSi ₁₂	C ₃₅ H ₉₃ Ge ₉ RhSi ₁₂	C ₅₃ H ₁₀₅ Ge ₉ P ₂ RhSi ₁₂	C ₃₀ H ₉₀ Ge ₉ PRhSi ₁₂
CCDC	2087498	2087499	2030896	2030897	N.A.
Fw (g mol ⁻¹)	3826.69	1585.71	1607.39	1897.60	1575.28
Crystal system	triclinic	triclinic	orthorhombic	monoclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>Pca</i> 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	15.6461(3)	9.5585(4)	31.7600(5)	15.87130(10)	14.44110(10)
<i>b</i> (Å)	16.2709(4)	14.6574(6)	9.4393(2)	24.7754(2)	25.5519(2)
<i>c</i> (Å)	18.7924(3)	27.0969(12)	45.2314(8)	21.8346(2)	18.90460(10)
α (°)	85.101(2)	97.455(4)	90	90	90
β (°)	69.035(2)	97.365(4)	90	102.9130(10)	101.7710(10)
γ (°)	82.861(2)	102.627(3)	90	90	90
<i>V</i> (Å ³)	4428.43(17)	3524.8(3)	13560.0(4)	8368.62(12)	6829.06(8)
<i>Z</i>	1	2	8	4	4
Radiation, λ (Å)	Cu K α , 1.54184	Cu K α , 1.54184	Mo K α , 0.71073	Cu K α , 1.54184	Cu K α , 1.54184
Temp (K)	150(2)	150(2)	150(2)	150(2)	150(2)
ρ_{calc} (g cm ⁻³)	1.435	1.453	1.575	1.506	1.532
μ (mm ⁻¹)	5.785	6.059	4.401	7.372	8.686
Reflections collected	55057	27423	66312	61465	132946
Independent reflections	18293	12793	32553	17361	14310
Parameters	754	604	1081	721	569
R(int)	0.0366	0.0770	0.0563	0.0541	0.0521
R1/wR2, ^[a] I $\geq$ 2 σ I (%)	3.17/7.53	5.32/11.11	5.69/9.79	4.01/10.11	0.0393/ 0.0972
R1/wR2, ^[a] all data (%)	4.35/8.37	9.24/13.28	8.78/10.91	5.06/10.95	0.0456/ 0.1017
GOF	1.055	0.931	1.039	1.008	1.019

R1 = $[\Sigma||F_o| - |F_c||]/\Sigma|F_o|$; wR2 = $\{[\Sigma w[(F_o)^2 - (F_c)^2]^2]/[\Sigma w(F_o)^2]\}^{1/2}$; $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.0345 and 1.61 for **1**, 0.370 and 0.00 for **2**, 0.0408 and 0.00 for **3**, 0.669 and 0.0 for **4** and 0.0437 and 15.5828 for **5**.

Table S2. Selected X-ray data collection and refinement parameters for **7–12**.

	7 ·1hexane	8	9	10	11 ·1Et ₂ O
Formula	C ₄₀ H ₁₀₇ Ge ₉ N ₂ RhSi ₁₂	C ₃₁ H ₈₇ Si ₁₂ Ge ₉ Rh	C ₃₇ H ₉₃ Ge ₉ RhSi ₁₂ W	C ₈₆ H ₁₃₀ BF ₂₄ Si ₁₂ PGe ₉ Rh	C ₇₃ H ₁₁₆ BF ₂₄ Si ₁₂ Ge ₉ RhWO
CCDC	N.A.	N.A.	N.A.	N.A.	N.A.
Fw (g mol ⁻¹)	1709.57	1553.30	1815.26	2754.97	2753.61
Crystal system	triclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	16.3622(3)	14.41290(10)	14.27830(10)	15.0839(2)	17.9023(5)
<i>b</i> (Å)	19.8996(3)	25.1261(2)	25.64300(10)	19.3502(3)	13.8042(5)
<i>c</i> (Å)	25.9438(4)	18.79570(10)	19.84610(10)	21.6497(4)	44.4206(12)
α (°)	68.5600(10)	90	90	106.3130(10)	90
β (°)	79.8560(10)	100.8180(10)	101.5750(10)	96.7570(10)	96.969(3)
γ (°)	82.1130(10)	90	90	92.7710(10)	90
<i>V</i> (Å ³)	7715.4(2)	6685.71(8)	7118.64(7)	6000.51(17)	10896.4(6)
<i>Z</i>	4	4	4	2	4
Radiation, λ (Å)	Cu K α , 1.54184	Cu K α , 1.54184	Cu K α , 1.54184	Cu K α , 1.54184	Cu K α , 1.54184
Temp (K)	150(2)	150(2)	150(2)	150(2)	150(2)
ρ_{calc} (g cm ⁻³)	1.472	1.543	1.694	1.525	1.679
μ (mm ⁻¹)	7.552	8.645	11.032	5.511	7.778
Reflections collected	141405	148444	196405	89656	101192
Independent reflections	32320	13669	14899	24711	19207
Parameters	1332	507	839	1332	1312
R(int)	0.0488	0.0344	0.0545	0.0439	0.1242
R1/wR2, ^[a] I $\geq$ 2 σ I (%)	0.0544/ 0.1641	0.0197/0.0485	0.0219/0.0561	0.0346/ 0.0900	0.0647/ 0.1656
R1/wR2, ^[a] all data (%)	0.0593/ 0.1728	0.0202/0.0487	0.0227/0.0566	0.0404/ 0.0942	0.0910/ 0.1838
GOF	1.048	1.195	1.065	1.031	1.058

R1 = $[\sum||F_o| - |F_c||]/\sum|F_o|$; wR2 = $\{[\sum w[(F_o)^2 - (F_c)^2]^2]/[\sum w(F_o)^2]\}^{1/2}$; $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.1167 and 1.0887 for **7**, 0.0206 and 3.9088 for **8**, 0.0313 and 4.5415 for **9**, 0.0519 and 1.9069 for **10**, and 0.0908 and 0.00 for **11**.

Table S3. Selected X-ray data collection and refinement parameters for **13–16**.

	13 ·0.5hexane	14 ·0.5hexane	15 ·1.5pentane	16 ·1pentane
Formula	C ₄₆ H ₁₁₂ Si ₁₂ Ge ₉ Rh ₂ Cl	C ₄₆ H ₁₁₂ ClGe ₉ IrRhSi ₁₂	C _{55.5} H ₁₂₃ Si ₁₂ Cl ₂ Ge ₉ Rh ₃	C ₆₁ H ₁₄₁ Ge ₉ Ni ₂ RhSi ₁₂
CCDC	N.A.	N.A.	N.A.	2030898
Fw (g mol ⁻¹)	1897.01	1986.30	2160.55	2085.45
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	20.1442(3)	20.1858(4)	14.6325(5)	15.4949(2)
<i>b</i> (Å)	17.3827(3)	17.3370(5)	15.4931(5)	16.2265(2)
<i>c</i> (Å)	22.3853(4)	22.3872(5)	24.2350(4)	20.1839(3)
α (°)	90	90	72.799(2)	93.6950(10)
β (°)	93.5170(10)	93.414(2)	86.693(2)	110.9240(10)
γ (°)	90	90	62.919(3)	93.0250(10)
<i>V</i> (Å ³)	7823.7(2)	7820.7(3)	4653.8(3)	4714.62(11)
<i>Z</i>	4	4	2	2
Radiation, λ (Å)	Cu K α , 1.54184	Cu K α , 1.54184	Cu K α , 1.54184	Cu K α , 1.54184
Temp (K)	150(2)	150(2)	150(2)	150(2)
ρ_{calc} (g cm ⁻³)	1.611	1.687	1.542	1.469
μ (mm ⁻¹)	9.428	10.971	9.618	6.649
Reflections collected	35917	80579	51714	83908
Independent reflections	16340	16247	19217	19705
Parameters	770	734	802	834
R(int)	0.0554	0.0751	0.0394	0.0258
R1/wR2, ^[a] I $\geq$ 2 σ I (%)	0.0458/0.0985	0.0371/0.0799	0.0381/0.1015	2.83/7.38
R1/wR2, ^[a] all data (%)	0.0717/0.1121	0.0604/0.0906	0.0442/0.1079	3.14/7.62
GOF	1.008	1.006	1.034	1.039

R1 = $[\sum||F_o| - |F_c||]/\sum|F_o|$; wR2 = $\{[\sum w[(F_o)^2 - (F_c)^2]^2]/[\sum w(F_o)^2]\}^{1/2}$; $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.0407 and 0.00 for **13**, 0.0338 and 8.9577 for **14**, 0.0678 and 0.7717 for **15**, and 0.0377 and 6.6141 for **16**.

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