

# Structural snapshots of concerted double E–H bond activation at a transition metal center

Joseph A.B. Abdalla,<sup>1</sup> Alexa Caise,<sup>1</sup> Christian P. Sindlinger,<sup>1</sup> Rémi Tirfoin,<sup>1</sup> Amber L. Thompson,<sup>1</sup> Alison J. Edwards<sup>2</sup> and Simon Aldridge<sup>\*,1</sup>

<sup>1</sup> Inorganic Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford, OX1 3QR, UK.

<sup>2</sup> Australian Centre for Neutron Scattering, Australian Nuclear Science and Technology Organization, New Illawarra Road, Lucas Heights, NSW 2234, Australia.

simon.aldridge@chem.ox.ac.uk

## Abstract (153 words)

Bond activation at a transition metal center is a key fundamental step in numerous chemical transformations. The oxidative addition of element–hydrogen bonds, for example, represents a critical step in a range of widely applied catalytic processes. Despite this, experimental studies characterizing intermediates along the bond activation pathway are very rare. In this work, we report on fundamental studies defining a new oxidative activation pathway: combined experimental and computational approaches yield structural snapshots of the simultaneous activation of both bonds of a  $\beta$ -diketiminato-stabilized  $\text{GaH}_2$  unit at a single metal center. Systematic variation of the supporting phosphine ligands and single crystal X-ray/neutron diffraction are exploited in tandem to allow structural visualization of the activation process, from a  $\eta^2\text{-H}_2$   $\sigma$ -complex showing little Ga–H bond activation, through species of intermediate geometry featuring stretched Ga–H and compressed M–H/M–Ga bonds, to a fully activated metal dihydride featuring a neutral (carbene-type) N-heterocyclic Ga<sup>I</sup> ligand.

**Main text (3050 words – not including abstract, methods, captions; 6 display items – 5 figures and 1 table)**

Bond activation at transition metal centers is key to a wide range of societally important chemical reactions, being a fundamental step in catalytic processes underpinning synthetic, medicinal and materials science.<sup>1</sup> Bond cleavage can be achieved through a number of routes, with oxidative addition at late transition metal centers being among the most widely exploited and extensively studied (particularly for ‘noble’ metals such as ruthenium, rhodium and palladium).<sup>2-11</sup> Experimental and theoretical studies imply that E-H bond activation by such systems proceeds via initial formation of a  $\eta^2$ -E,H  $\sigma$ -complex, with transfer of electron density from the metal into the E-H  $\sigma^*$  orbital bringing about bond weakening, and ultimately cleavage to give the corresponding elementyl hydride (see Fig. 1(a)).<sup>2,9,11-18</sup> Despite its widespread relevance, however, studies describing sequentially intercepted intermediates along this reaction trajectory for a given (single) metal system are very rare.<sup>19,20</sup>

<Fig. 1>

Simultaneous activation of two E-H bonds via an analogous  $\eta^2$ -H,H  $\sigma$ -complex leading to the formation of a metal dihydride (Fig. 1(b)) has very little precedent (even for the more polar group 13 E-H bonds which are the focus of this study),<sup>22-26</sup> since it requires a metal precursor with a formal electron count of  $\leq 14$ , or an *in situ* source thereof. Processes for which experimental mechanistic evidence is available (e.g. the direct formation of Fischer carbene complexes  $[L_nM=C(OR)R']$  from the corresponding ether,  $H_2C(OR)R'$ ) are thought to proceed via a two-step C-H oxidative addition/ $\alpha$ -migration mechanism.<sup>27-34</sup> Nevertheless, such chemistry represents an attractive net transformation, given the widespread use of metal carbene and related complexes (for example in homogenous catalysis), and the importance of dehydrogenation reactions in chemical processes relevant to applications in energy, polymer synthesis, etc.<sup>35,36</sup>

In the current contribution we demonstrate the viability of a concerted single-step double E-H activation process. Systematic variation in the ancillary metal-bound ligands and single-crystal X-ray/neutron diffraction are exploited in tandem to demonstrate sequential steps in the activation process, from a  $\eta^2$ -H,H  $\sigma$ -complex showing little E-H bond activation, through species of intermediate geometry featuring stretched E-H and compressed M-H/M-E bonds, to a fully activated metal dihydride featuring a neutral (carbene-like) elementylidene ligand. Experimental geometric data have been analysed in the light of Atoms in Molecules and fragment orbital calculations to yield the first ‘snapshot’ visualization of a bond activation process of this type.

The  $EH_2$ -containing system chosen for the current study is the bulky  $\beta$ -diketiminato supported gallane  $(NacNac)^{Dipp}GaH_2$  [ $(NacNac)^{Dipp} = HC(MeCDippN)_2$ , where  $Dipp = C_6H_3^iPr_2-2,6$ ],<sup>37</sup> which has previously been shown to undergo dehydrogenation at metal carbonyl fragments to give complexes of the type  $M_x(CO)_y\{Ga(NacNac)^{Dipp}\}$  ( $M = Cr, Mo, W, Fe, Co$ ), containing the neutral two-electron (carbene analogue) gallylene ligand,  $:Ga(NacNac)^{Dipp}$ . Spontaneous reductive loss of  $H_2$  at  $M$  in these systems is driven by the presence of the strongly  $\pi$ -accepting carbonyl ligand set.<sup>24,25</sup> The use of ancillary phosphine donors was therefore targeted in order to stabilise higher oxidation state hydride-containing species, which might represent intermediate species in this double E-H activation. Moreover, since the sterics/electronics of

phosphine donors can readily be tuned, we perceived that this approach would allow systematic control over the extent of the E-H activation process.

## Results and Discussion

**(i) Syntheses and X-ray/neutron diffraction studies.** The reaction of  $(\text{NacNac})^{\text{Dipp}}\text{GaH}_2$  with  $[\text{Rh}(\text{dppp})(\text{COD})][\text{BAR}^f_4]$  ( $\text{dppp} = (\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_5)_2$ ;  $\text{COD} = 1,5\text{-cyclooctadiene}$ ;  $\text{Ar}^f = \text{C}_6\text{H}_3(\text{CF}_3)_2\text{-3,5}$ ) under a dihydrogen atmosphere leads to loss of the COD ligand (as *cyclooctane*) and to clean formation of  $[\text{Rh}(\text{dppp})\{\eta^2\text{-(H,H)-H}_2\text{Ga}(\text{NacNac})^{\text{Dipp}}\}][\text{BAR}^f_4]$  (**2-dppp**; Fig. 2). Spectroscopically, **2-dppp** gives rise to a doublet in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, with the magnitude of the coupling constant ( $^1J_{\text{RhP}} = 151.8$  Hz) supporting a description as a  $\text{Rh}^{\text{I}}$  complex (*cf.* 167 Hz for  $[\text{Rh}(\text{dppp})(\eta^2\text{-(H,H)-H}_3\text{B-NMe}_3)]^+$ ).<sup>38</sup> A single upfield resonance is observed in the  $^1\text{H}$  NMR spectrum integrating to two hydrogens ( $\delta_{\text{H}} -6.23$  ppm), thus confirming the presence of the  $\text{Rh}(\mu\text{-H})_2\text{Ga}$  unit in solution;<sup>25</sup> the Dipp  $^i\text{Pr}$  signals (one septet and two doublets), are also consistent with a system in which  $\text{C}_2$  symmetry is retained and *both* Ga-H bonds are bound to the metal center.

<Fig. 2>

The molecular structure of **2-dppp** determined by X-ray and neutron diffraction (Fig. 3 and Supplementary Fig. 5), reveals an approximately square planar geometry at rhodium, in accordance with its formulation as a 16-electron  $\text{Rh}^{\text{I}}$  complex. The bridging hydrides were initially located using the X-ray difference Fourier map and refined with displacement and same distance restraints to  $\text{Rh}(1)$ .<sup>39</sup> The non-hydrogen framework was then used to phase the neutron diffraction data, prior to examination of the difference Fourier maps, which clearly showed the presence of the bridging hydrogen atoms (Supplementary Fig. 5) with Rh-H and Ga-H distances of 1.81(1)/1.81(1) Å and 1.87(1)/1.87(1) Å, respectively. The Rh-Ga separation [2.538(1) Å (X-ray diffraction)] falls within the sum of the respective covalent radii (2.64 Å),<sup>40</sup> but is longer than any reported Rh-Ga single bond [current longest: 2.441(1) Å],<sup>41-43</sup> suggesting that there is little direct Rh-Ga interaction in this case. Additionally, the P-Rh-P bite angle [ $\angle\text{P}(1)\text{-Rh}(1)\text{-P}(2) = 90.3(1)^\circ$ ] is relatively narrow, and the formulation of **2-dppp** as a  $\eta^2\text{-H,H}$   $\sigma$ -gallane complex of  $\text{Rh}^{\text{I}}$  is therefore in line with previous reports that the  $\text{Rh}^{\text{I}}$  oxidation state is favoured with small-bite angle chelating phosphines.<sup>44-46</sup>

<Fig. 3>

By contrast, the reaction of  $[\text{Rh}(\text{PCy}_3)_2][\text{Al}(\text{pftb})_4]$  (generated *in situ*) with  $(\text{NacNac})^{\text{Dipp}}\text{GaH}_2$  leads to the formation of the  $\text{Rh}^{\text{III}}$  gallylene dihydride complex  $[\text{Rh}(\text{PCy}_3)_2(\text{H})_2\{\text{Ga}(\text{NacNac})^{\text{Dipp}}\}][\text{Al}(\text{pftb})_4]$  [**2-PCy<sub>3</sub>**, Fig. 2;  $\text{Cy} = \text{cyclo-C}_6\text{H}_{11}$ ;  $\text{pftb} = \text{OC}(\text{CF}_3)_3$ ]. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum features a doublet with a smaller  $^1J_{\text{RhP}}$  coupling constant (121.9 Hz) than that observed for **2-dppp**, and the much higher field  $^1\text{H}$  hydride resonance ( $\delta_{\text{H}} = -17.72$  ppm,  $^1J_{\text{RhH}} = 21.0$  Hz) is as expected for terminal hydride ligands attached to a  $\text{Rh}^{\text{III}}$  center (*cf.*  $[\text{Rh}(\text{PCy}_3)_2(\text{H})_2(\eta^2\text{-(H,H)-H}_3\text{B-NMe}_3)]^+$ :  $\delta_{\text{H}} = -19.62$  ppm,  $^1J_{\text{RhH}} = 22.1$  Hz).<sup>47</sup> The molecular structure of **2-PCy<sub>3</sub>** determined by X-ray and neutron crystallography (Fig. 3 and Supplementary Fig. 6) reveals an approximately octahedral coordination geometry at  $\text{Rh}(1)$ , resulting from coordination of two  $\text{PCy}_3$  ligands, a neutral  $:\text{Ga}(\text{NacNac})^{\text{Dipp}}$  donor and two terminal hydrides. The gallylene unit and the two  $\text{PCy}_3$  ligands are found in a meridional arrangement, and the sixth coordination site is occupied by an agostic interaction involving one of the P-bound *cyclohexyl* groups [ $d\{\text{Rh}(1)\text{-H}(461)\} = 2.06(2)$  Å from neutron diffraction].<sup>48</sup> The use of the non-

chelating PCy<sub>3</sub> ligand permits a wider P-Rh-P angle [ $\angle P(1)-Rh(1)-P(2) = 104.9(1)^\circ$ ], consistent with previous studies which suggest that the Rh<sup>III</sup> oxidation state is more accessible in conjunction with a larger bite angle.<sup>44-46</sup> In addition, the Rh-Ga distance [2.368(1) Å] is substantially shorter than that found in **2-dppp** [2.537(1) Å], being within the range expected for unsupported Rh-Ga covalent bonds [2.282(1) – 2.441(1) Å],<sup>40-42</sup> and therefore consistent with the presence of a direct Rh-Ga interaction. The two terminal hydride ligands, H(1) and H(2) are located *cis* to the gallylene ligand, and the very long Ga-H separations [mean 2.39(3) Å, compared to Rh-H distances of 1.60(2) Å (both neutron diffraction)] argue against any structurally significant Ga-H interaction.<sup>40</sup> Thus, in contrast to **2-dppp**, the structural and spectroscopic data for **2-PCy<sub>3</sub>** are consistent with complete activation of the (NacNac)<sup>Dipp</sup>GaH<sub>2</sub> entity, leading to cleavage of both Ga-H bonds, with accompanying formation of two Rh-H bonds and a Rh<sup>III</sup>←Ga<sup>I</sup> donor/acceptor interaction.

The use of the *bis*(phosphine) donor set in **2-PCy<sub>3</sub>** that is (i) more strongly  $\sigma$ -donating, and (ii) non-chelating, promotes the formation of the higher rhodium oxidation state (*cf.* **2-dppp**).<sup>46</sup> With a view to probing intermediate cases of bond activation we therefore targeted analogous systems featuring the *chelating* trialkylphosphines dcype and dcyp [Cy<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PCy<sub>2</sub> and Cy<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PCy<sub>2</sub>; Fig. 2]. Accordingly, hydrogenation of a mixture of (NacNac)<sup>Dipp</sup>GaH<sub>2</sub> and either [Rh(dcype)(COD)][Al(pftb)<sub>4</sub>] or [Rh(dcyp)(COD)][Al(pftb)<sub>4</sub>] in 1,2-difluorobenzene at room temperature leads to the formation of a single major product in each case (**2-dcype** and **2-dcyp** respectively), the identities of which could be established via mass spectrometry and elemental microanalysis. In solution at least, these systems are characterized by similar spectroscopic data to **2-dppp**, with each giving rise to a doublet in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum with a <sup>1</sup>J<sub>RhP</sub> coupling constant of *ca.* 150 Hz [<sup>1</sup>J<sub>RhP</sub> = 149.4 Hz (**2-dcype**), 146.7 Hz (**2-dcyp**), *cf.* 151.8 Hz for **2-dppp**]. At first inspection, these values suggest that **2-dcype/2-dcyp** might be viewed as Rh<sup>I</sup> complexes, similar to **2-dppp**. However, we are cautious in interpreting these data in terms of the metal oxidation state, in particular given the unusual coordination geometries observed for the metal center in each case (*vide infra*). Thus, the unambiguous Rh<sup>III</sup> complex [Rh(PCy<sub>3</sub>)(H)<sub>2</sub>{Ga(NacNac)<sup>Dipp</sup>]<sub>2</sub>]<sup>+</sup> (**3**; Supplementary Fig. 9), which has been isolated as a side product in the synthesis of **2-PCy<sub>3</sub>**: (i) has been shown crystallographically to possess a highly unusual planar 5-coordinate rhodium geometry similar to those of **2-dcype/2-dcyp**; and (ii) is characterized in solution by <sup>1</sup>H and <sup>31</sup>P NMR data ( $\delta_H = -8.00$  ppm; <sup>1</sup>J<sub>RhH</sub> = 16.0 Hz and <sup>1</sup>J<sub>RhP</sub> = 146.8 Hz) which are similar to **2-dcype/2-dcyp**. Given the clear influence of metal coordination geometry (as well as oxidation state) on <sup>1</sup>J<sub>RhP</sub> we therefore hesitate to use these data to discriminate between Rh<sup>I</sup> and Rh<sup>III</sup> formalisms for **2-dcype** and **2-dcyp**.

Both **2-dcype** and **2-dcyp** can be obtained as large, orange-red single crystals by layering a concentrated fluorobenzene solution with heptane, thereby allowing each to be studied by both X-ray and neutron diffraction (Fig. 3 and Supplementary Figs. 7 and 8). The rhodium center in both complexes is found to be in a close-to-planar environment, defined by the two phosphorus atoms and the two hydrides, with the gallium center also lying in the same plane. The P–Rh–P bite angle in **2-dcype** [84.3(1)<sup>o</sup> from X-ray diffraction] is narrower than that measured for **2-dcyp** [95.2(1)<sup>o</sup>, 94.5(1)<sup>o</sup> for the two near-identical molecules in the asymmetric unit], as expected given the shorter tether between the two phosphorus atoms, but other features of the two structures are remarkably similar. Most strikingly, the Rh-Ga distances [2.339(1) Å for **2-**

**dcype**; 2.350(1) Å for both components of **2-dcypp**] are very much shorter than that found for Rh<sup>I</sup>  $\sigma$ -complex **2-dppp** [2.538(1) Å], and are much more in line with that found in the Rh<sup>III</sup> system **2-PCy<sub>3</sub>** [2.368(1) Å]. The distances measured for **2-dcype/2-dcypp** are in fact among the shortest Rh-Ga bonds yet reported (2-coordinate gallium: [Rh(GaCp\*)<sub>4</sub>(GaMe)]<sup>+</sup>, 2.2815(6) Å; 3-coordinate gallium: Rh(GaCp\*)<sub>4</sub>{GaCp\*(OSO<sub>2</sub>CF<sub>3</sub>)}, 2.3326(4) Å),<sup>42,43</sup> and consequently suggest that there is a significant degree of direct Rh-Ga bonding (in marked contrast to **2-dppp**). As such, both complexes might readily be described in terms of an unprecedented planar five-coordinate metal coordination environment.

Of key importance structurally is the use of single-crystal neutron diffraction to establish unequivocally the position of the metal-bound hydrides in **2-dcype** and **2-dcypp**, as has recently been demonstrated, for example, to elegant effect in assessing Si-H bond activation in silanes.<sup>49,50</sup> In our case we exploited the greater neutron flux inherent in the Laue method to enable measurements to be carried out on relatively small single crystals of **2-dcype/2-dcypp**.<sup>51</sup> Close similarities between the two metal coordination environments are revealed, with the hydrides being located close to the RhP<sub>2</sub> plane in both cases. The Rh-H distances are relatively short [*e.g.* 1.64(2) for **2-dcype**, *cf.* 1.60(2) Å for the terminal Rh-H bonds in **2-PCy<sub>3</sub>**], and the Ga-H contacts [*e.g.* 1.93(2) and 1.94(2) Å for **2-dcype**] are significantly elongated compared to the parent gallane [1.53(2), 1.54(2) Å],<sup>37</sup> even with allowance made for the shortening of the latter by X-ray diffraction measurements.<sup>52,53</sup> In addition, it is significant that the alignment of the NacNac heterocycle with respect to the RhP<sub>2</sub> coordination plane differs markedly between **2-dcype/2-dcypp** and **2-dppp**. In the Rh<sup>I</sup> system **2-dppp** the Nacnac plane lies almost orthogonal to that of the RhP<sub>2</sub> unit (angle between least-squares planes determined from X-ray data = 77.2°), consistent with a near-tetrahedral gallium center, and with retention of significant Ga-H interactions. In **2-dcype** and **2-dcypp**, by contrast, these planes are a long way from being perpendicular (torsion angles: 33.2 and 33.9/38.0°, respectively), while the P<sub>2</sub>Rh(H)<sub>2</sub> unit itself remains planar. This ligand alignment therefore implies a N<sub>2</sub>GaH<sub>2</sub> gallium coordination geometry which is far from tetrahedral. This observation, taken together with the long Ga-H and short Rh-H/Rh-Ga distances, suggests a much greater degree of Ga-H bond activation in **2-dcype** and **2-dcypp** than in **2-dppp**. On the other hand, consideration of the planar five-coordinate coordination sphere of Rh(1) for both **2-dcype** and **2-dcypp** (and the differences in the Ga-H/Rh-H lengths compared to **2-PCy<sub>3</sub>**), suggests that this process falls short of the complete Ga-to-Rh hydrogen transfer postulated for the six-coordinate Rh<sup>III</sup> system **2-PCy<sub>3</sub>**. As such, **2-dcype** and **2-dcypp** might be viewed as structural ‘snapshots’ on the pathway to double Ga-H bond activation.

<Table 1>

(ii) **Probes of electronic structure.** With a view to probing further the differences in Ga-H bond activation between the  $\sigma$ -complex **2-dppp** and partially activated **2-dcypp**, Atoms in Molecules (AIM) analyses were undertaken on both systems (Supplementary Fig. 3).<sup>54</sup> In the case of **2-dppp** this approach returns bond critical points (BCPs) between gallium and the bridging hydrogen atoms, as well as between rhodium and the hydrides, with the electron density at the BCPs being slightly higher between Rh and H ( $\rho$  = 0.0989, 0.1029 e bohr<sup>-3</sup>) than between Ga and H ( $\rho$  = 0.0577, 0.0618 e bohr<sup>-3</sup>). Two ring critical points (RCPs) are also found, one for each Rh-H-Ga interaction ( $\rho$  = 0.0570, 0.0587 e bohr<sup>-3</sup>), consistent with a formulation as a  $\eta^2$ -H<sub>2</sub>  $\sigma$ -

complex which features a pair of Ga( $\mu$ -H)Rh three-center interactions. In the case of **2-dcypp**, by contrast, no BCPs are found between Ga(2) and H(1)/H(2), while critical points are found between Rh(1) and H(1)/H(2) (with relatively high electron densities:  $\rho = 0.1206, 0.1207 \text{ e bohr}^{-3}$ ). A BCP is also located between Rh(1) and Ga(2) ( $\rho = 0.0655 \text{ e bohr}^{-3}$ ), indicative of a direct Rh-Ga bonding interaction. These calculated data are therefore also consistent with a description of the structure of **2-dcypp** in the solid state that is further along the pathway to Ga-H bond activation than **2-dppp**.

The electronic factors underpinning the sequentially increased bond activation on going from **2-dppp** to **2-dcype**/**2-dcypp** (and ultimately **2-PCy<sub>3</sub>**) have been probed by examination of the relevant molecular orbitals using Density Functional Theory (DFT). To this end we sought (i) to identify the major bonding interactions between the [(phosphine)<sub>2</sub>Rh]<sup>+</sup> and (NacNac)<sup>Dipp</sup>GaH<sub>2</sub> fragments in the least activated system, **2-dppp**, and (ii) to probe the effects of the changing character of the [(phosphine)<sub>2</sub>Rh]<sup>+</sup> fragment orbitals as a function of the ancillary phosphine ligands. In the case of **2-dppp**, an ETS-NOCV (combined Extended Transition State / Natural Orbitals for Chemical Valence) analysis<sup>55</sup> shows that the two major contributions to the interaction between the [(dppp)Rh]<sup>+</sup> and (NacNac)<sup>Dipp</sup>GaH<sub>2</sub> fragments (Fig. 4) involve (i) donation from the highest occupied molecular orbital (HOMO) of the gallane (a Ga-H bonding orbital of approximate local *b<sub>2</sub>* symmetry) to the lowest unoccupied molecular orbital (LUMO) of the cationic rhodium fragment (accounting for 55.8 kcal mol<sup>-1</sup> of the instantaneous interaction energy); and (ii) back-bonding from the HOMO-3 of the metal fragment (predominantly composed of Rh 4*d<sub>yz</sub>* character) to the LUMO+1 of the gallane (contributing 24.3 kcal mol<sup>-1</sup>). The nature of the fragment orbitals involved in the latter (back-bonding) interaction (Fig. 4(b)) is such that in-phase overlap is established (i) between the central lobe of the metal-based HOMO-3 and the Ga 4s component of the (NacNac)<sup>Dipp</sup>GaH<sub>2</sub> LUMO+1; and (ii) between the outer lobes of the metal-centered orbital and the two hydrogen 1s orbitals. Thus, in addition to populating an orbital of Ga-H  $\sigma^*$  character (i.e. weakening the Ga-H bonds), bonding interactions are established between Rh and the two bridging hydrogens and between Rh and Ga. In the case of [(dppp)Rh]<sup>+</sup> the HOMO-3 lies relatively low in energy (-8.79 eV or -202.7 kcal mol<sup>-1</sup>), but as the ancillary ligands are changed sequentially to **2-dcype**, **2-dcypp** and ultimately (PCy<sub>3</sub>)<sub>2</sub>, this fragment orbital is destabilized (-8.69, -8.41, -8.12 eV, respectively) leading to enhanced possibilities for back-bonding, with attendant Ga-H bond weakening and Rh-H/Rh-Ga strengthening (as is observed experimentally).

<Fig. 4>

In the case of **2-PCy<sub>3</sub>**, geometric considerations imply that hydrogen transfer from gallium to rhodium is essentially complete and that an alternative fragmentation analysis based on the Rh<sup>III</sup> cation [(Cy<sub>3</sub>P)<sub>2</sub>(H)<sub>2</sub>Rh]<sup>+</sup> and the carbene-type ligand (NacNac)<sup>Dipp</sup>Ga: is more appropriate. In the intermediate cases **2-dcype** and **2-dcypp**, both limiting descriptions might be considered, and with this in mind the interaction energies associated with fragmentation into either [(phosphine)<sub>2</sub>Rh]<sup>+</sup>/(NacNac)<sup>Dipp</sup>GaH<sub>2</sub> or [(phosphine)<sub>2</sub>Rh(H)<sub>2</sub>]<sup>+</sup>/(NacNac)<sup>Dipp</sup>Ga units were evaluated computationally. In both cases, this analysis clearly shows that fragmentation according to a Rh<sup>III</sup>/Ga<sup>I</sup> formalism is the lower energy process (e.g. 68.2 kcal mol<sup>-1</sup> for **2-dcype** vs 122.1 kcal mol<sup>-1</sup> for the alternative Rh<sup>I</sup>/Ga<sup>III</sup> fragments). Thus, if anything, a description of electronic structure closer to the [(phosphine)<sub>2</sub>Rh(H)<sub>2</sub>]<sup>+</sup>/(NacNac)<sup>Dipp</sup>Ga limit would appear to be most appropriate for **2-dcype** and

**2-dcypp**, consistent with the significant degree of Ga-H bond activation and short Rh-Ga contacts observed in the solid state structures of these compounds. ETS-NOCV analyses for both of these systems show that the major contribution to the bonding between [(phosphine)<sub>2</sub>Rh(H)<sub>2</sub>]<sup>+</sup> and (NacNac)<sup>Dipp</sup>Ga fragments (e.g. 84% of the instantaneous interaction energy for **2-dcype**) comes from gallylene-to-metal  $\sigma$ -donation (Supplementary Fig. 2) consistent with a predominant description of both complexes in terms of a Rh←Ga donor/acceptor bond (as shown in Fig. 1).

In conclusion, we report on experimental/computational studies offering structural snapshots of the simultaneous activation of both bonds of an EH<sub>2</sub> unit at a transition metal center. The extent of E-H bond activation can be systematically controlled by variation in the nature of the ancillary phosphine ligands, with less strongly donating and narrower bite-angle chelating phosphines favoring the formation of an essentially unstretched  $\eta^2$ -H<sub>2</sub>  $\sigma$ -complex, and stronger non-chelating donors giving rise to a fully activated metal dihydride featuring a heterocyclic Ga<sup>I</sup> ligand. The use of a donor set (such as dcype or dcypp) offering intermediate characteristics generates a species featuring stretched E-H and compressed M-H/M-E bonds. The availability of these experimentally determined molecular structures has allowed us to evaluate computationally a possible pathway which links a weakly bound (square planar)  $\eta^2$ -H<sub>2</sub>  $\sigma$ -complex to a fully activated six-coordinate (agostically supported) Rh<sup>III</sup> dihydride (Fig. 5). In the case of the PCy<sub>3</sub> system, a process proceeding via initial Ga-H bond lengthening and Rh-H/Rh-Ga contraction to give a planar five-coordinate species, akin to **2-dcype**/**2-dcypp** is calculated to be exergonic (in agreement with experiment). Rotation of the Rh-Ga vector out of the coordination plane further lowers the energy of the system (by ca. 5 kcal mol<sup>-1</sup> for a 28° distortion). From this point, rotation of one of the Rh-H bonds into an apical position (with accompanying evolution of the Rh<sup>III</sup>-H-C agostic interaction in the *trans* apical site) can be shown to proceed via a very low energetic barrier (transition state at +2.3 kcal mol<sup>-1</sup> above the preceding intermediate, +12.2 kcal mol<sup>-1</sup> above the global minimum) to generate the experimentally observed geometry of the Rh<sup>III</sup> product.

<Fig. 5>

## Methods (474 words)

Manipulations were carried out under a dry, oxygen-free argon atmosphere, with reagents dissolved or suspended in dry aprotic solvents, and combined or isolated using cannula and glove box techniques. Compounds **2-dppp**, **2-dcype** and **2-dcypp** were synthesized from  $[\text{Rh}(\text{dppp})(\text{COD})][\text{BAR}^f_4]$ ,  $[\text{Rh}(\text{dcype})(\text{COD})][\text{Al}(\text{pftb})_4]$  and  $[\text{Rh}(\text{dcypp})(\text{COD})][\text{Al}(\text{pftb})_4]$ , in yields of 52%, 74% and 68% respectively, via the respective reactions with  $(\text{NacNac})^{\text{Dipp}}\text{GaH}_2$  in 1,2-difluorobenzene under 4 atm. pressure of dihydrogen. **2-PCy<sub>3</sub>** was obtained (in 65% yield) from the reaction of  $[\text{Rh}(\text{PCy}_3)_2(\mu\text{-Cl})_2]$  with  $\text{Li}[\text{Al}(\text{pftb})_4]$  and  $(\text{NacNac})^{\text{Dipp}}\text{GaH}_2$  in 1,2-difluorobenzene. This reaction also generates  $[\text{Rh}(\text{PCy}_3)(\text{H})_2\{\text{Ga}(\text{NacNac})^{\text{Dipp}}\}_2][\text{Al}(\text{pftb})_4]$  (**3**) in 5-10% yield, with **2-PCy<sub>3</sub>** being separated by recrystallization from a fluorobenzene/hexane mixture. Single crystals of all compounds suitable for X-ray/neutron diffraction studies were obtained by layering concentrated fluorobenzene solutions of the respective complexes with hexane or heptane. New compounds were characterized by elemental analysis, mass spectrometry and multinuclear NMR spectroscopy; the structures of **2-dppp**, **2-dcype**, **2-dcypp**, **2-PCy<sub>3</sub>** and **3** were determined by both X-ray and neutron crystallography. Low temperature single-crystal X-ray diffraction data were collected using a (Rigaku) Oxford Diffraction SuperNova instrument, and the structures were solved using SuperFlip within the refinement software CRYSTALS. In general, all non-hydrogen atoms were refined with anisotropic displacement parameters; where displacement ellipsoids were found to be prolate, efforts were made to model the disorder, using same distance, displacement similarity and vibrational restraints as per the CIF. Hydrogen atoms were generally visible in the difference map, so they were positioned geometrically and then refined separately with restraints prior to inclusion in the final refinement using a riding model. Metal-bound hydrogen atoms were positioned using the difference Fourier map and refined as part of the final model using same distance restraints and restrained isotropic displacement parameters. The Laue single-crystal neutron diffraction studies were carried out using the KOALA instrument at the OPAL reactor at the Australian Nuclear Science and Technology Organization.<sup>50</sup> In each case, the coordinates from the X-ray refinement were used as a starting model for refinement against the neutron intensities, after the minor component of any disorder had been removed. All atoms, including hydrogen atoms were refined using anisotropic displacement ellipsoids with restraints as necessary. Difference maps showing the hydrides and selected hydrogen atoms, as well as images displaying the displacement ellipsoids of key core atoms are given in the Supplementary Figs. 5-9; key final refinement statistics are also included in the Supporting Information. Density Functional Theory (DFT), as implemented in the Amsterdam Density Functional code, has been employed to calculate molecular geometries, orbital energies and compositions, and to carry out Atoms in Molecules calculations. The ETS-NOCV approach was used to analyse complex formation from metal/ligand fragments. The potential energy surface along a potential activation pathway was carried out using the Gaussian09.D01 program. [dppp =  $(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_5)_2$ ; dcype =  $\text{Cy}_2\text{P}(\text{CH}_2)_2\text{PCy}_2$ ; dcypp =  $\text{Cy}_2\text{P}(\text{CH}_2)_3\text{PCy}_2$ , Cy = *cyclo*- $\text{C}_6\text{H}_{11}$ ; COD = 1,5-*cyclooctadiene*;  $\text{Ar}^f = \text{C}_6\text{H}_3(\text{CF}_3)_2\text{-3,5}$ ; pftb =  $\text{OC}(\text{CF}_3)_3$ ;  $(\text{NacNac})^{\text{Dipp}} = \text{HC}(\text{MeCDippN})_2$ ; Dipp =  $\text{C}_6\text{H}_3/\text{Pr}_2\text{-2,6}$ ]. X-ray and neutron crystallographic data for compounds **2-dppp**, **2-dcype**, **2-dcypp**, **2-PCy<sub>3</sub>** and **3** are freely available from the Cambridge Crystallographic Data Centre (CCDC 1504637-1504646). Other data has been deposited



with the Oxford University Research Archive (ORA). Alternatively, requests for materials can be addressed to S.A. ([simon.aldridge@chem.ox.ac.uk](mailto:simon.aldridge@chem.ox.ac.uk)).

## References

1. Hartwig, J. F. *Organotransition metal chemistry: from bonding to catalysis*. University Science Books, Sausalito, CA, 2010.
2. Kubas, G. J. *Metal Dihydrogen and  $\sigma$ -Bond Complexes: Structure, Theory and Reactivity*. Kluwer Academic/Plenum Publishers, New York, NY, 2001.
3. Crabtree, R. H. The organometallic chemistry of alkanes. *Chem. Rev.* **85**, 245-269 (1985).
4. Arndtsen, B. A., Bergman, R. G., Mobley, T. A. & Peterson, T. H. Selective intermolecular carbon-hydrogen bond activation by synthetic metal complexes in homogeneous solution. *Acc. Chem. Res.* **28**, 154-162 (1995).
5. Shilov, A. E. & Shul'pin, G. B. Activation of C-H bonds by metal complexes. *Chem. Rev.* **97**, 2879-2932 (1997).
6. Jones, W. D. Isotope effects in C-H bond activation reactions by transition metals. *Acc. Chem. Res.* **36**, 140-146 (2003).
7. Labinger, J. A. & Bercaw, J. E. Understanding and exploiting C-H activation. *Nature* **417**, 507-514 (2002).
8. Crabtree, R. H. Organometallic C-H activation. *J. Organomet. Chem.* **689**, 4083-4091 (2004).
9. Schubert, U. Coordination of Si-H  $\sigma$  bonds to transition metals. *Adv. Organomet. Chem.* **30**, 151-187 (1990).
10. Alcaraz, G. & Sabo-Etienne, S. Coordination and dehydrogenation of amine-boranes at metal centers. *Angew. Chem. Int. Ed.* **49**, 7170-7179 (2010).
11. Riddlestone, I. M., Abdalla, J. A. B. & Aldridge, S. Coordination and activation of E-H bonds (E = B, Al, Ga). *Adv. Organomet. Chem.* **63**, 1-38 (2015).
12. Kubas, G. J., Ryan, R. R., Swanson, B. I., Vergamini, P. J. & Wasserman, H. J. Characterization of the first examples of isolable molecular hydrogen complexes,  $M(CO)_3(PR_3)_2(H_2)$  (M = molybdenum or tungsten; R = Cy or isopropyl). Evidence for a side-on bonded dihydrogen ligand. *J. Am. Chem. Soc.* **106**, 451-452 (1984).
13. Hall, C. & Perutz, R. N. Transition metal alkane complexes. *Chem. Rev.* **96**, 3125-3146 (1996).
14. Cowan, A. J. & George, M. W. Formation and reactivity of organometallic alkane complexes. *Coord. Chem. Rev.* **252**, 2504-2511 (2008).
15. Bernskoetter, W. H., Schauer, C. K., Goldberg, K. I. & Brookhart, M. Characterization of a rhodium(I)  $\sigma$ -methane complex in solution. *Science* **326**, 553-556 (2009).
16. Pike, S. D. *et al.* Synthesis and characterization of a rhodium(I)  $\sigma$ -alkane complex in the solid state. *Science* **337**, 1648-1651 (2012).
17. Pandey, K. K. Transition metal  $\sigma$ -borane complexes. *Coord. Chem. Rev.* **253**, 37-55 (2009).
18. Lin, Z. Transition metal  $\sigma$ -borane complexes. *Struct. Bonding (Berlin)* **130**, 123-148 (2008).
19. Crabtree, R. H., Holt, E. M., Lavin, M. & Morehouse, S. M. Inter- vs. intramolecular carbon-hydrogen activation: a carbon-hydrogen-iridium bridge in  $[IrH_2(8\text{-methylquinoline})_2]BF_4$  and a  $CH + M \rightarrow CMH$  reaction trajectory. *Inorg. Chem.* **24**, 1986-1992 (1985).

20. See also Ekkert, O., White, A. J. P. & Crimmin, M. Trajectory of approach of a zinc-hydrogen bond to transition metals. *Angew. Chem. Int. Ed.* **55**, 16031-16034 (2016).
21. Green, J. C., Green, M. L. H. & Parkin, G. The occurrence and representation of three-centre two-electron bonds in covalent inorganic compounds. *Chem. Commun.* **48**, 11481–11503 (2012).
22. Alcaraz, G., Helmstedt, U., Clot, E., Vendier, L. & Sabo-Etienne, S. A terminal borylene ruthenium complex: from B–H activation to reversible hydrogen release. *J. Am. Chem. Soc.* **130**, 12878-12879 (2008).
23. Alcaraz, G., Grellier, M. & Sabo-Etienne, S. Bis  $\sigma$ -bond dihydrogen and borane ruthenium complexes: bonding nature, catalytic applications, and reversible hydrogen release. *Acc. Chem. Res.* **42**, 1640-1649 (2009).
24. Turner, J. *et al.* Formation of sub-valent carbenoid ligands by metal-mediated dehydrogenation chemistry: coordination and activation of  $\text{H}_2\text{Ga}\{\{\text{NDippCMe}\}_2\text{CH}\}$ . *Chem. Sci.* **4**, 4245-4250 (2013).
25. Abdalla, J. A. B. *et al.* Coordination and activation of Al–H and Ga–H bonds. *Chem.-Eur. J.* **20**, 17624–17634 (2014).
26. O'Neill, M. *et al.* Borane to boryl hydride to borylene dihydride: explicit demonstration of boron-to-metal  $\alpha$ -hydride migration in aminoborane activation. *J. Am. Chem. Soc.* **133**, 11500-11503 (2012).
27. Empsall, H. D. *et al.* Synthesis and X-ray structure of an unusual iridium ylide or carbene complex. *J. Chem. Soc., Chem. Commun.* 589–590 (1977).
28. Boutry, O. *et al.* Double C–H activation at the  $\alpha$ -carbon of cyclic ethers by  $\text{Tp}^*\text{Ir}(\text{C}_2\text{H}_4)_2$ . *J. Am. Chem. Soc.* **114**, 7288–7290 (1992).
29. Li, Z.-W. & Taube, H. Dihydrogen complexes of tetraammineosmium(II) with carbene as co-ligand: facile hydrogen transfer from cyclic ethers to the metal center. *J. Am. Chem. Soc.* **116**, 11584–11585 (1994).
30. Luecke, H. F., Arndtsen, B. A., Burger, P. & Bergman, R. G. Synthesis of Fischer carbene complexes of iridium by C–H bond activation of methyl and cyclic ethers: evidence for reversible  $\alpha$ -hydrogen migration. *J. Am. Chem. Soc.* **118**, 2517–2518 (1996).
31. Holtcamp, M. W., Labinger, J. A. & Bercaw, J. E. C–H activation at cationic platinum(II) centers. *J. Am. Chem. Soc.* **119**, 848–849 (1997).
32. Coalter, J. N., Ferrando, G. & Caulton, K. G. Geminal dehydrogenation of a  $\text{C}(\text{sp}^3)\text{CH}_2$  group by unsaturated Ru(II) or Os(II). *New J. Chem.* **24**, 835–836 (2000).
33. Lee, D.-H., Chen, J., Faller, J. W. & Crabtree, R. H. Reversible  $\alpha$ -elimination in the conversion of  $\text{N-CH}_3$  to  $\text{N-CH=Ir}$  by double C–H activation. *J. Chem. Soc., Chem. Commun.* 213–214 (2001).
34. Whited, M. T. & Grubbs, R. H. Late metal carbene complexes generated by multiple C–H activations: examining the continuum of  $\text{M=C}$  bond reactivity. *Acc. Chem. Res.* **42**, 1607-1616 (2009).
35. Bourissou, D., Guerret, O., Gabbai, F. P. & Bertrand, G. Stable carbenes. *Chem. Rev.* **100**, 39-92 (2000).
36. Staubitz, A., Robertson, A. P. M. & Manners, I. Ammonia-borane and related compounds as dihydrogen sources. *Chem. Rev.* **110**, 4079-4124 (2010).
37. Singh, S. *et al.* Syntheses, characterization, and X-ray crystal structures of  $\beta$ -diketiminato group 13 hydrides, chlorides, and fluorides. *Inorg. Chem.* **45**, 1853-1860 (2006).

38. Dallanegra, R., Robertson, A. P. M., Chaplin, A. B., Manners, I. & Weller, A. S. Tuning the  $[L_2Rh \cdots H_3B-NR_3]^+$  interaction using phosphine bite angle. Demonstration by the catalytic formation of polyaminoboranes. *Chem. Comm.* **47**, 3763-3765 (2011).
39. Cooper, R. I., Thompson, A. L. & Watkin, D. J. CRYSTALS enhancements: dealing with hydrogen atoms in refinement. *J. Appl. Cryst.* **43**, 1100-1107 (2010).
40. Cordero, B. *et al.* Covalent radii revisited. *Dalton. Trans.* 2832-2838 (2008).
41. Cadenbach, T. *et al.* Molecular alloys, linking organometallics with intermetallic Hume-Rothery phases: the highly coordinated transition metal compounds  $[M(ZnR)_n]$  ( $n \geq 8$ ) containing organo-zinc ligands. *J. Am. Chem. Soc.* **131**, 16063-16077 (2009).
42. Cadenbach, T., Gemel, C., Zacher, D. & Fischer, R. A. Methylgallium as a terminal ligand in  $[(Cp^*Ga)_4Rh(GaCH_3)]^+$ . *Angew. Chem. Int. Ed.* **47**, 3438-3441 (2008).
43. Bollermann, T. *et al.* Homoleptic hexa and penta gallylene coordinated complexes of molybdenum and rhodium. *Inorg. Chem.* **50**, 5808-5815 (2011).
44. Freixa, Z. & van Leeuwen, P. Bite angle effects in diphosphine metal catalysts: steric or electronic? *Dalton. Trans.* 1890-1901 (2003).
45. DuBois, D. L. *et al.* Hydride transfer from rhodium complexes to triethylborane. *Organometallics* **25**, 4414-4419 (2006).
46. Wilson, A. D., Miller, A. J. M., DuBois, D. L., Labinger, J. A. & Bercaw, J. E. Thermodynamic studies of  $[H_2Rh(diphosphine)_2]^+$  and  $[HRh(diphosphine)_2(CH_3CN)]^{2+}$  complexes in acetonitrile. *Inorg. Chem.* **49**, 3918-3926 (2010).
47. Sewell, L. J., Lloyd-Jones, G. C. & Weller, A. S. Development of a generic mechanism for the dehydrocoupling of amine-boranes: a stoichiometric, catalytic, and kinetic study of  $H_3B-NMe_2H$  using the  $[Rh(PCy_3)_2]^+$  fragment. *J. Am. Chem. Soc.* **134**, 3598-3610 (2012).
48. Brookhart, M., Green, M. L. H. & Parkin, G. Agostic interactions in transition metal compounds. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 6908-6914.
49. Smart, K. A. *et al.* Step by step introduction of silazane moieties at ruthenium: different extents of Ru-H-Si bond activation. *Inorg. Chem.* **52**, 2654-2661 (2013).
50. Smart, K. A. *et al.* Nature of Si-H interactions in a series of ruthenium silazane complexes using multinuclear solid-state NMR and neutron diffraction. *Inorg. Chem.* **53**, 1156-1165 (2014).
51. Edwards, A. J. Neutron diffraction – recent applications to chemical structure determination. *Aus. J. Chem.* **64**, 869-872 (2011).
52. Aldridge, S. & Downs, A. J. Hydrides of the main group metals; new variations on an old theme. *Chem. Rev.* **101**, 3305-3365 (2001).
53. Bau, R. & Drabnis, M. H. Structures of transition metal hydrides determined by neutron diffraction. *Inorg. Chim. Acta* **259**, 27-50 (1997).
54. Bader, R. F. W. A quantum theory of molecular structure and its applications. *Chem. Rev.* **91**, 893-928 (1991).

55. Mitoraj, M. P., Michalak, A., Ziegler, T. A Combined Charge and Energy Decomposition Scheme for Bond Analysis. *J. Chem. Theory Comput.* **5**, 962-975 (2009).

**Supplementary Information** is linked to the online version of the paper at [www.nature.com/nature](http://www.nature.com/nature).

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**Author Information** X-ray and neutron crystallographic data for compounds **2-dppp**, **2-dcype**, **2-dcypp**, **2-PCy<sub>3</sub>** and **3** are freely available from the Cambridge Crystallographic Data Centre (CCDC 1504637-1504646). Reprints and permissions information is available at [www.nature.com/reprints](http://www.nature.com/reprints). Correspondence and requests for materials should be addressed to S.A. ([simon.aldridge@chem.ox.ac.uk](mailto:simon.aldridge@chem.ox.ac.uk)).

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## Affiliations

<sup>1</sup> **Inorganic Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford, OX1 3QR, UK.**

Joseph A.B. Abdalla, Alexa Caise, Christian P. Sindlinger, Rémi Tirfoin, Amber L. Thompson and Simon Aldridge<sup>\*</sup>

<sup>\*</sup> To whom correspondence should be addressed. E-mail: [simon.aldridge@chem.ox.ac.uk](mailto:simon.aldridge@chem.ox.ac.uk) (SA)

<sup>2</sup> **Australian Centre for Neutron Scattering, Australian Nuclear Science and Technology Organisation, New Illawarra Road, Lucas Heights, NSW 2234, Australia.**

Alison J. Edwards

**Supplementary Information**

General considerations and starting material preparations; synthetic, spectroscopic and analytical data for new compounds; X-ray crystallographic studies; computational details; CIFs for all crystal structures (CCDC reference numbers: 1504637-1504646).



## Figure captions

**Fig. 1:** Single-step oxidative activation of one or two E-H bonds at a single metal center (shown for E = a group 13 element).<sup>21</sup> Panel (a) shows the sequential activation of a single E-H bond proceeding via a  $\eta^2$ -E,H  $\sigma$ -complex and leading to the formation of an elementyl hydride via E-H bond cleavage. Panel (b) shows a related process involving simultaneous activation of two E-H bonds, and proceeding via a  $\eta^2$ -H,H  $\sigma$ -complex to yield the corresponding element-ylidene dihydride.

**Fig. 2:** Syntheses of **2-dppp**, **2-dcype**, **2-dcypp** and **2-PCy<sub>3</sub>** from the corresponding [(phosphine)<sub>2</sub>Rh]<sup>+</sup> containing precursors (counter-anions omitted for clarity). (a) The synthetic routes to **2-dppp**, **2-dcype**, **2-dcypp** proceed via the hydrogenation of the chelating alkene ligand in the [L<sub>2</sub>Rh(COD)]<sup>+</sup> precursor (to give *cyclooctane*) in the presence of the  $\beta$ -diketiminate stabilized gallane; (b) the corresponding bis(tricyclohexylphosphine) system **2-PCy<sub>3</sub>**, by contrast is best accessed by using *in situ* chloride abstraction to generate the [L<sub>2</sub>Rh]<sup>+</sup> fragment.

**Fig. 3:** Molecular structures of the cationic components of (a) **2-dppp**, (b) **2-PCy<sub>3</sub>**, (c) **2-dcype** and (d) **2-dcypp** (lower right; one component of the asymmetric unit) as determined by X-ray diffraction. Most hydrogen atoms and counter-anions have been omitted for clarity. Key bond lengths (Å) and angles (°): (for **2-dppp**) Rh(1)-Ga(1) 2.538(1), P(1)-Rh(1)-P(2) 90.3(1), [from neutron diffraction: Rh(1)-H(1/2) 1.81(1), Ga(1)-H(1/2) 1.87(1)]; (for **2-PCy<sub>3</sub>**) Rh(1)-Ga(1) 2.368(1), Rh(1)-C(36) 2.791(5), P(1)-Rh(1)-P(2) 104.9(1), [from neutron diffraction: Rh(1)-H(1/2) 1.60(2), Rh(1)-H(461) 2.06(2), Ga(1)-H(1/2) 2.21(2), 2.57(3)]. Key bond lengths and angles for **2-dcype** and **2-dcypp** are given in Table 1.

**Fig. 4:** Key orbital interactions between the [(dppp)Rh]<sup>+</sup> and (NacNac)<sup>Dipp</sup>GaH<sub>2</sub> fragments in **2-dppp** calculated using an ETS-NOCV analysis:<sup>54</sup> (a) gallane-to-metal donation utilizing the HOMO of the gallane and the LUMO of the metal fragment; and (b) metal-to-gallane backbonding from the metal-based HOMO-3 to the gallane LUMO+1. For the fragment orbitals (shown center) the brown/pale blue color scheme describes the phases of the respective wavefunctions, while for the deformation densities (shown right) depletion/gain of electron density on combination of the respective fragment orbitals are represented by red/blue, respectively.

**Fig. 5:** A possible energetic pathway for the [(Cy<sub>3</sub>P)<sub>2</sub>Rh]<sup>+</sup> system linking a  $\eta^2$ -H,H  $\sigma$ -complex to a six-coordinate (agostically supported) Rh<sup>III</sup> dihydride. The systems at relative energies of +35.8, +14.8 and 0 kcal mol<sup>-1</sup> are modelled on the structures of **2-dppp**, **2-dcypp** and **2-PCy<sub>3</sub>** determined by crystallographic methods. ( $\theta$  is defined as the angle between the least-squares planes of the Ga(NacNac) ring and the RhP<sub>2</sub> fragment). From a model  $\eta^2$ -H,H  $\sigma$ -complex, Ga-H bond lengthening and Rh-H/Rh-Ga contraction to give a planar five-coordinate gallylene complex, akin to **2-dcype/2-dcypp** is calculated to be exergonic by >20 kcal mol<sup>-1</sup>. Projection of the Rh-Ga vector out of the coordination plane further lowers the energy, and subsequent rotation of one of the Rh-H bonds up into an apical position (with accompanying evolution of the *trans* Rh<sup>III</sup>-H-C agostic interaction) generates the experimentally observed geometry of the Rh<sup>III</sup> product via a very low energy transition state (+2.3 kcal mol<sup>-1</sup>).

**Table 1:** Key bond lengths (Å) and angles (°) for **2-dcype** and **2-dcypp** as determined by X-ray and neutron diffraction. The figure in parentheses represents the estimated standard deviation (ESD) associated with each measurement.

Table 1

	2-dcype		2-dcyp <sup>a</sup>	
	X-ray	Neutron	X-ray	Neutron
$d(\text{Rh-Ga})/\text{\AA}$	2.339(1)	2.34(2)	2.350(1) 2.350(1)	2.351(8) 2.342(8)
$d(\text{Rh-P})/\text{\AA}$	2.291(1) 2.304(1)	2.27(2) 2.33(2)	2.318(1) 2.320(1) 2.309(1) 2.326(1)	2.36(1) 2.29(1) 2.32(1) 2.37(1)
$d(\text{Rh-H})/\text{\AA}$	1.57(3) 1.58(3)	1.64(2) 1.64(2)	1.39(1) 1.40(1) 1.40(1) 1.40(1)	1.65(1) 1.65(1) 1.65(1) 1.65(1)
$d(\text{Ga-H})/\text{\AA}$	1.91(3) 2.04(3)	1.94(2) 1.93(2)	1.75(1) 1.75(1) 1.74(1) 1.74(1)	1.96(1) 1.96(1) 1.96(1) 1.96(1)
$\angle(\text{P-Rh-P})/^\circ$	84.3(1)	84.3(7)	95.2(1) 94.5(1)	94.7(4) 92.5(4)
Torsion, <sup>b</sup> $\theta/^\circ$	33.2	34.2	38.0 33.9	38.4 34.6

<sup>a</sup> Two molecules in the asymmetric unit. <sup>b</sup> Defined as the angle between the least-squares planes of the Ga(NacNac) ring and the RhP<sub>2</sub> fragment.

**Table of contents text**

X-ray and neutron diffraction studies, in conjunction with quantum chemical techniques, have been used to define a new oxidative bond activation pathway that involves simultaneous activation of both bonds of a  $\beta$ -diketiminato-stabilized  $\text{GaH}_2$  unit at a single metal center.