

N-nacnac stabilized tetrylenes: access to silicon hydride systems *via* migration processes

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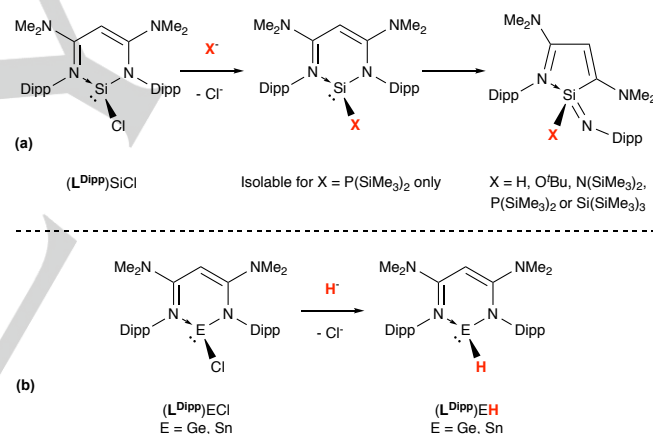
Dedicated to Hansgeorg Schnöckel on the occasion of his 80th birthday

Abstract: The use of an amino-functionalized β -diketiminate ('N-nacnac') ligand in low-valent silicon chemistry is investigated. In particular, the use of (L^{Dipp})SiCl (L^{Dipp} = HC{(Me₂N)CNDipp}₂) to generate silicon-containing products *via* metathesis chemistry is explored, in light of previously reported complications arising from heterocycle ring contraction. In the case of Na[C₅H₅], chloride metathesis is accompanied not by rearrangement of the N-nacnac ligand, but by a C-to-Si hydrogen migration process, generating the hydridosilicon(IV) species (L^{Dipp})Si(H)(C₅H₄), which features a silafulvene core. The potential intermediate arising from initial chloride/cyclopentadienide substitution can be modelled by the chemistry of the corresponding Ge(II) and Sn(II) systems, which generate (L^{Dipp})E(η^1 -C₅H₅) (E = Ge, Sn) *via* straightforward metathesis chemistry. A Si(II) hydride species can be generated from (L^{Dipp})SiCl *via* metathesis by making use of a d-block reagent which can act as both hydride source and coordinative trap for (L^{Dipp})SiH. Thus, the reaction of (L^{Dipp})SiCl with K[(η^5 -C₅H₄Me)Mn(CO)₂H] leads to the formation of (η^5 -C₅H₄Me)Mn(CO)₂{Si(H)(L^{Dipp})} - the first silylene complex containing this half-sandwich manganese fragment.

The synthetic versatility of metathesis chemistry underpins the value of sub-valent metal halides as precursors to a wide range of Main Group compounds in low oxidation states.^[1] Within group 14, E(II) halides are commercially available for the heavier elements of the group (E = Ge - Pb), but Si(II) halides have become available only more recently. The syntheses of IDipp·Si(hal)₂, (hal = Cl, Br; IDipp = 1,3-diisopropylphenyl-imidazolyldene), *via* either dehydrohalogenation or reduction approaches, represented a key breakthrough, providing readily-available sources of the [Si(hal)₂] fragment.^[2,3] Since this discovery, a range of other carbene-stabilized Si(II) systems featuring Si—hal bonds have been reported.^[4] In addition, related compounds featuring Si—Cl bonds supported by chelating mono-anionic LX donors such as amidinates or β -diketiminate have been developed, and their behaviour towards metathesis and reduction processes evaluated.^[5,6]

We have recently been interested in the chemistry of amino-functionalized β -diketiminate (N-nacnac) ligands,^[7,8] as electron-rich variants of the widely used donor family that are resistant to the deprotonation chemistry seen for systems featuring methyl groups in the backbone β -position.^[9] With this in mind, we have developed routes to E(II) chloride species of the type (L^{Dipp})ECl (E = Si, Ge, Sn; L^{Dipp} = HC{(Me₂N)CNDipp}₂), and have begun to explore the potential of these systems as precursors in silicon,

germanium and tin chemistry.^[7] In the case of the silicon system, we have found that (L^{Dipp})SiCl is a viable precursor to systems of the type (L^{Dipp})Si(O)X *via* an oxidation/substitution methodology (e.g. for X = H, OR), but that simple metathesis chemistry at Si(II) can be complicated by rearrangement of the ligand backbone.^[7c,7e] Thus, in the presence of strongly donating nucleophiles, heterocycle contraction to give imidosilicon(IV) products is facile (Scheme 1(a)). In particular, this has restricted access to the corresponding Si(II) hydride species (L^{Dipp})SiH,^[10] which has been shown to undergo facile rearrangement to its thermodynamically more stable Si(IV) counterpart. Such chemistry offers marked contrast to the corresponding Ge(II) and Sn(II) hydrides which can be accessed *via* straightforward metathesis processes, and characterized as monomeric systems featuring terminal E—H bonds (Scheme 1(b)).^[7a,7b]



Scheme 1. Previously reported reactions of (a) N-nacnac stabilized chlorosilylene, and (b) -germylenes/stannylenes with nucleophiles: substitution and rearrangement chemistry (Dipp = 2,6-Pr₂C₅H₃).

We were keen to investigate further the metathesis chemistry of systems of the type (L^{Dipp})ECl (E = Si, Ge, Sn), and in the current manuscript report on their contrasting reactivity towards Na[C₅H₅]. While rearrangement of the N-nacnac ligand is not an issue in this chemistry, the contrasting stabilities of the E(II) oxidation states are ultimately key in facilitating the observed reaction pathways. In addition, while the 'free' Si(II) hydride species (L^{Dipp})SiH has previously been shown to be unstable with respect to ring contraction, we present an alternative hydride transfer strategy utilising (L^{Dipp})SiCl which allows for trapping of the (non-rearranged) hydrido-silylene within the coordination sphere of a transition metal.^[11]

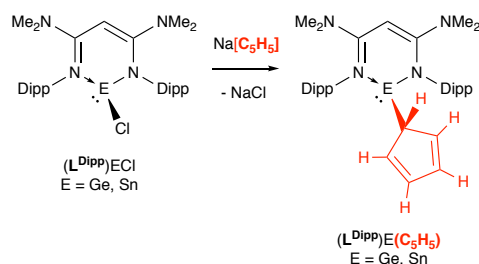
The reactions of N-nacnac stabilized chlorogermylene (L^{Dipp})GeCl and -stannylene (L^{Dipp})SnCl with Na[C₅H₅] in toluene proceed in reasonable yield to generate the corresponding

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Ge(II) and Sn(II) cyclopentadienyl complexes (Scheme 2). Both products have been characterized by multinuclear NMR and elemental microanalysis, and their structures in the solid state determined by X-ray crystallography. In the ^1H NMR spectrum, each compound is characterized by a pair of doublets and a septet for the Dipp ^iPr groups, consistent with ready rotation about the N-C_{ipso} bonds on the NMR timescale, and by a single resonance (integrating to 5H) for the cyclopentadienyl ligand (at $\delta_{\text{H}} = 5.53$ and 5.62 ppm, respectively).

The solid-state structures of each compound determined crystallographically (Figure 1), are consistent with lower molecular symmetry, with the C₅H₅ ligand being bound in η^1 -fashion, and the E—C bond being projected essentially orthogonal to the EN₂ plane (with N—E—C angles of 96.3(1)/98.6(1) $^\circ$ (E = Ge) and 94.7(1)/95.0(1) $^\circ$ (E = Sn)). In each case, the geometry of the (L^{Dipp})E fragment remains largely unperturbed from the chloride precursor and the E—C bond lengths (2.167(1) and 2.368(3) Å, respectively) are in line with previously reported examples of cyclopentadienyl complexes of Ge(II) and Sn(II).^[12]



Scheme 2. Syntheses of η^1 -bound cyclopentadienylgermylene and -stannylene complexes (L^{Dipp})ECl (E = Ge, Sn).

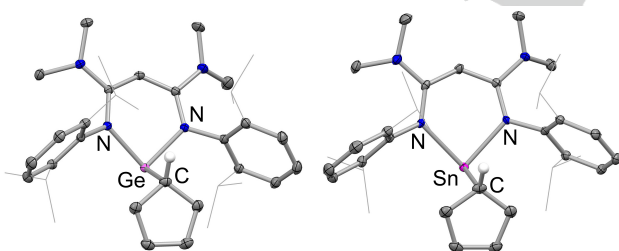
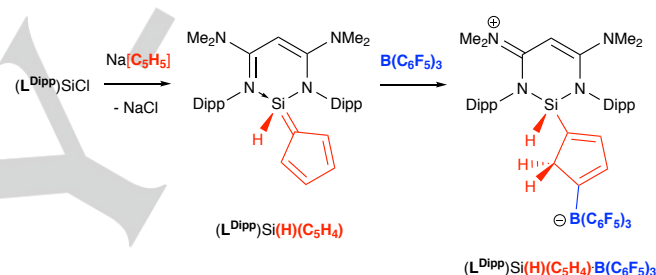


Figure 1. Molecular structures of (L^{Dipp})Ge(η^1 -C₅H₅) (left) and (L^{Dipp})Sn(η^1 -C₅H₅) (right) in the solid state as determined by X-ray crystallography. Thermal ellipsoids have been set at 35 % probability, with ^iPr substituents represented in the wireframe format, and most hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): (for (L^{Dipp})Ge(η^1 -C₅H₅)) Ge—C 2.167(1), Ge—N 2.050(1), 2.036(1), N—Ge—N 91.0(1); (for (L^{Dipp})Sn(η^1 -C₅H₅)) Sn—C 2.368(3), Sn—N 2.214(2), 2.257(2), N—Sn—N 86.5(1).

In the case of (L^{Dipp})SiCl, however, the course of the reaction with Na[C₅H₅] is implied by *in situ* NMR measurements to proceed *via* a different pathway (Scheme 3). In the ^1H spectrum a SiH signal grows in at $\delta_{\text{H}} = 5.69$ ppm ($^1J_{\text{SiH}} = 232$ Hz) and two multiplets each integrating to 2H (at $\delta_{\text{H}} = 6.45$ and 6.83 ppm) appear in the region characteristic of alkenic C—H bonds.

However, the pattern of signals associated with the N-nacnac ligand backbone is retained (i.e. the γ -CH signal at 4.18 ppm and the NMe₂ signal integrating to 12H at $\delta_{\text{H}} = 2.10$ ppm), implying that heterocycle contraction of the type seen in conjunction with simple chloride-for-hydride substitution (Scheme 1) has not occurred. The ^{29}Si NMR signal associated with the product ($\delta_{\text{Si}} = -25.0$ ppm) is shifted significantly upfield compared to that of the precursor (+1.8 ppm), and an infrared band at 2213 cm⁻¹ is consistent with the generation of a Si—H bond.^[10] The identification of the product of this reaction as the Si(IV) cyclopentadienyldiene hydride, (L^{Dipp})Si(H)(C₅H₄) could be established by X-ray crystallography (Figure 2). The migration of one of the CH hydrogens of the [C₅H₅] group from carbon to silicon, with accompanying formation of a formal Si=C double bond, is associated with a marked change in the orientation of the C₅ ring. As such, while the C₅ ring in the cases of (L^{Dipp})ECl (E = Ge, Sn) lies approximately parallel to the (N-nacnac)E plane (interplane angles of 13.5 and 20.9 $^\circ$, respectively), that in (L^{Dipp})Si(H)(C₅H₄) is projected nearly perpendicular to it (75.4 $^\circ$; Figures 1 and 2).



Scheme 3. Sequential reactions of (L^{Dipp})SiCl with Na[C₅H₅] and B(C₆F₅)₃, involving hydrogen migration steps.

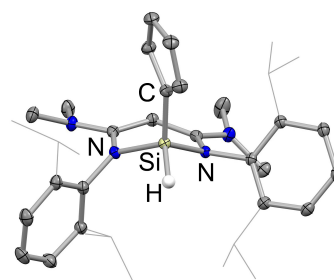


Figure 2. Molecular structure of (L^{Dipp})Si(H)(C₅H₄) in the solid state as determined by X-ray crystallography. Thermal ellipsoids have been set at 35 % probability, with ^iPr substituents represented in the wireframe format, and most hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Si—C 1.784(1), Si—N 1.768(1), 1.800(1), N—Si—N 98.5(1).

A similar C-to-Si migration process has been reported very recently by P. Roesky and co-workers, in the reaction of the amidinate-supported chlorosilylene {PhC(N^{*i*}Bu)₂}SiCl with K[C₅Me₄H], although in this case the 1,2-hydride shift process to yield {PhC(N^{*i*}Bu)₂}Si(H)(C₅Me₄) requires the addition of an external Lewis acid, (Y{N(SiMe₃)₂})₃.^[13] Nonetheless, from a structural perspective the two systems are similar, being

characterized by short SiC distances (1.784(1) and 1.761(2) Å), consistent with the presence of Si=C double bond character.^[14,15] A description of $(\text{L}^{\text{Dipp}})\text{Si}(\text{H})(\text{C}_5\text{H}_4)$ as a silafulvene is also consistent with alternating long/short CC distances within the C_5 ring (successively 1.429(3)/1.423(2), 1.388(2)/1.389(2) and 1.406(2) Å). Although the position of the silicon-bound hydrogen atom in $(\text{L}^{\text{Dipp}})\text{Si}(\text{H})(\text{C}_5\text{H}_4)$ must be assessed with the usual caveats relating to the use of X-ray diffraction, its presence is supported by both the ^1H NMR spectrum in benzene- d_6 solution and IR data in the solid state.

The contrasting formation of Si(IV) and E(II) products ($\text{E} = \text{Ge}, \text{Sn}$) in this chemistry is in line with well-documented trends in the stability of the +2 oxidation state on descending group 14. Indeed, quantum chemical calculations carried out on the E(IV) systems $(\text{L}^{\text{Dipp}})\text{E}(\text{H})(\text{C}_5\text{H}_4)$ and their E(II) counterparts $(\text{L}^{\text{Dipp}})\text{E}(\eta^1\text{-C}_5\text{H}_5)$ show that the relative energies of the E(IV) compounds are -61.4, +55.1 and +170.9 kJ mol $^{-1}$, for $\text{E} = \text{Si}, \text{Ge}, \text{Sn}$, respectively (see ESI). Interestingly, the formation of $(\text{L}^{\text{Dipp}})\text{Si}(\text{H})(\text{C}_5\text{H}_4)$ via formal 1,2-hydrogen migration, contrasts with the ring-contracted products observed in the reactions of $(\text{L}^{\text{Dipp}})\text{SiCl}$ with other anionic nucleophiles, and which are thought to result from intramolecular nucleophilic attack by the silicon-centred lone pair at the ligand backbone β -position.^[7c,7f] In the case of $(\text{L}^{\text{Dipp}})\text{Si}(\text{H})(\text{C}_5\text{H}_4)$, the initial step of the reaction is thought to involve chloride metathesis, generating a Si(II) species akin to its heavier congeners $(\text{L}^{\text{Dipp}})\text{E}(\eta^1\text{-C}_5\text{H}_5)$ ($\text{E} = \text{Ge}, \text{Sn}$). Hydride migration is then presumably facilitated by the presence of a strongly nucleophilic lone pair at silicon and a proximal hydrogen attached to the α -carbon of the cyclopentadienyl ring.

The relatively short Si=C bond in $(\text{L}^{\text{Dipp}})\text{Si}(\text{H})(\text{C}_5\text{H}_4)$ suggests a description as a base-stabilized silene,^[14-16] and with a view to accessing a related (cationic) system via abstraction of the silicon-bound hydride, we investigated its reactivity towards the potent Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$. Unexpectedly, the addition of $\text{B}(\text{C}_6\text{F}_5)_3$ does not lead to hydride abstraction, but to assimilation of the Lewis acid at the 3-position of the carbocycle, and to the formation of a zwitterionic product featuring cationic $[(\text{N-nacnac})\text{Si}]^+$ and an anionic borate fragment (Scheme 3 and Figure 3). Retention of the silicon-bound hydrogen is indicated by a signal at $\delta_{\text{H}} = 5.34$ ppm in the ^1H NMR spectrum of the product, and the hydride migration/rearrangement within the C_5

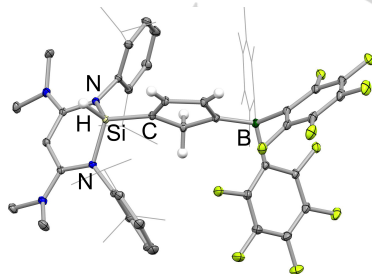
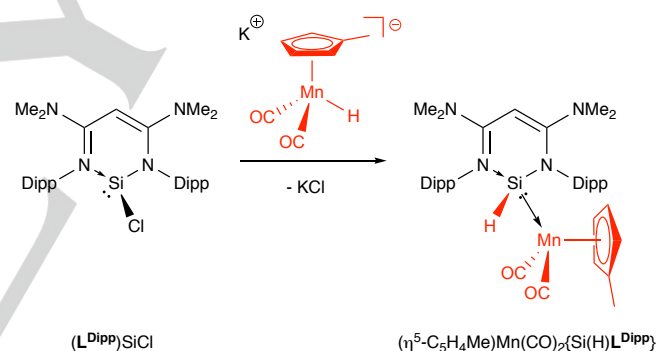


Figure 3. Molecular structure of $(\text{L}^{\text{Dipp}})\text{Si}(\text{H})(\text{C}_5\text{H}_4\{\text{B}(\text{C}_6\text{F}_5)_3\})$ in the solid state as determined by X-ray crystallography. Thermal ellipsoids have been set at 35 % probability, with 'Pr substituents (and one C_6F_5 group) represented in the wireframe format, and most hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Si—C 1.808(2), Si—N 1.767(2), 1.774(2), C—B 1.620(3), N—Si—N 103.9(1).

carbocycle accompanying the attack of $\text{B}(\text{C}_6\text{F}_5)_3$ at the 3-position is evidenced by the retention of only two (^1H) alkenic signals (at 6.48 and 6.72 ppm), together with the formation of a higher field ^2H signal associated with the methylene function (at 2.72 ppm). This form of rearrangement of a system containing a $\text{C}_5\text{H}_4=\text{E}$ unit following coordination of a strongly Lewis acidic borane finds precedent, for example, in the reactivity of the phosphonium ylid $\text{Ph}_3\text{PC}_5\text{H}_4$ towards boron-centred cations.^[17]

While the reactivity of $(\text{L}^{\text{Dipp}})\text{SiCl}$ towards hydride-containing reagents such as $\text{K}[\text{Et}_3\text{BH}]$ has been shown to result in heterocycle ring contraction in addition to H-for-Cl metathesis (Scheme 1),^[7c,7f] we wondered if it might be possible to trap the target $(\text{L}^{\text{Dipp}})\text{SiH}$ molecule by the use of alternative transition-metal hydride sources. We hypothesized that a (d-block) metal-to-silicon hydride transfer process would not only enable the formation of the desired Si—H bond, but also allow for trapping of the resulting hydridosilylene via coordination at the unsaturated metal centre generated by hydride loss. Accordingly, we examined the reactivity of $(\text{L}^{\text{Dipp}})\text{SiCl}$ towards the half-sandwich manganese carbonylate hydride $\text{K}[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2\text{H}]$. The product so generated can be isolated as a yellow crystalline solid which has been characterized by spectroscopic and analytical means, and by X-ray crystallography (Scheme 4 and Figure 4).



Scheme 4. Generation and trapping of a N-nacnac stabilized hydridosilylene via reaction of $(\text{L}^{\text{Dipp}})\text{SiCl}$ with $\text{K}[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2\text{H}]$.

NMR data for the product are consistent with retention of the 6-membered N-nacnac heterocycle (e.g. a single signal for the NMe_2 groups at $\delta_{\text{H}} = 2.33$ ppm, integrating to 12H),^[7] and with the formation of a Si—H bond (singlet at $\delta_{\text{H}} = 6.26$ ppm, $^1J_{\text{SiH}} = 166$ Hz). The implied trapping of the hydridosilylene $(\text{L}^{\text{Dipp}})\text{SiH}$ by coordination at the 16-electron $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2]$ fragment could subsequently be confirmed crystallographically (Figure 4). $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2\{\text{Si}(\text{H})\text{L}^{\text{Dipp}}\}$ represents the first structurally characterized silylene complex containing this half-sandwich manganese dicarbonyl fragment. Its formulation as such is supported by a Mn—Si distance (2.2826(7) Å), which is similar to those of related complexes featuring the $[\text{Mn}(\text{CO})_4]$ unit (e.g. 2.2816(8) and 2.2789(8) Å for $\{[(\text{PhC}(\text{N}^i\text{Bu})_2)\text{SiCl}]_2\text{Mn}(\text{CO})_4\}^+$).^[18] Moreover, notwithstanding the difficulties in locating hydrogen atoms by X-ray methods, a description as a silylene complex (rather than a compound featuring a coordinated Si—H bond) is supported by (i) a $^1J_{\text{SiH}}$

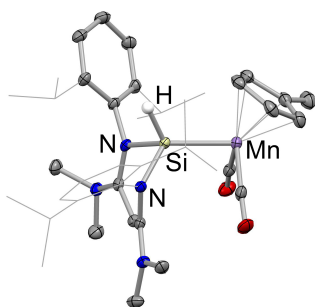


Figure 4. Molecular structure of $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2\{\text{Si}(\text{H})\text{L}^{\text{Dipp}}\}$ in the solid state as determined by X-ray crystallography. Thermal ellipsoids have been set at 30 % probability, with ^iPr substituents represented in the wireframe format, and most hydrogen atoms and solvent molecule omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Mn—Si 2.2826(7), Si—H 1.42(3), Mn \cdots H 3.20(3), Si—N 1.817(2), 1.848(2), N—Si—Si 94.7(1).

coupling constant measured in benzene- d_6 solution of 166 Hz,^[19] and (ii) stretching frequencies for the carbonyl ancillary ligands (1891, 1825 cm^{-1}) which are similar to those for related carbene complexes (e.g. 1914, 1849 cm^{-1} for $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2$ (IETMe), where IETMe = 1,3-diethyl-4,5-dimethyl-imidazolyli-dene),^[20] but significantly lower than those measured for silane σ -complexes of the $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2]$ fragment (e.g. 2004, 1947 cm^{-1} for $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2(\text{HSiPh}_2\text{F})$).^[21] At a broader level, the carbonyl stretching frequencies measured for $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2\{\text{Si}(\text{H})\text{L}^{\text{Dipp}}\}$ suggest that the $(\text{L}^{\text{Dipp}})\text{SiH}$ ligand is a very strong σ -donor indeed, with electron-releasing capabilities that rival or exceed those of NHC donors.^[22]

In conclusion, we present two examples of metathesis chemistry for the N-nacnac supported Si(II) complex $(\text{L}^{\text{Dipp}})\text{SiCl}$ which proceed without complication from heterocycle ring contraction. In the case of $\text{Na}[\text{C}_5\text{H}_5]$, the product is a hydrido-Si(IV) species formed *via* a C-to-Si hydrogen migration process which accompanies the $\text{Cl}/[\text{C}_5\text{H}_5]$ metathesis step. As potential models for this initial metathesis process, the corresponding products isolated for the heavier congeners $(\text{L}^{\text{Dipp}})\text{ECl}$ (E = Ge, Sn) are the simple η^1 -cyclopentadienyl complexes $(\text{L}^{\text{Dipp}})\text{E}(\eta^1\text{-C}_5\text{H}_5)$. The isolation of $(\text{L}^{\text{Dipp}})\text{Si}(\text{H})(\text{C}_5\text{H}_4)$ in the silicon case suggests that a subsequent α -hydrogen migration step is more facile than nucleophilic attack at the backbone β -carbon, which has been previously shown to lead to ring contraction. An alternative strategy for maintaining the integrity of the N-nacnac ligand backbone has been developed in the case of the hydrido-silylene $(\text{L}^{\text{Dipp}})\text{SiH}$, which can be trapped in the coordination sphere of a transition metal by employing a d-block reagent that can also act as the hydride source. Thus $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2\{\text{Si}(\text{H})\text{L}^{\text{Dipp}}\}$ can be isolated from the reaction of $(\text{L}^{\text{Dipp}})\text{SiCl}$ with the anionic manganese carbonylate hydride complex $\text{K}[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2\text{H}]$.

Experimental Section

Included here are experimental procedures and characterizing data for $(\text{L}^{\text{Dipp}})\text{Si}(\text{H})(\text{C}_5\text{H}_4)$ and $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2\{\text{Si}(\text{H})\text{L}^{\text{Dipp}}\}$. General details, other procedures/characterizing data and representative spectra are available in the ESI. X-ray

crystallographic structure data have been deposited with the CCDC: 2078870-2078874.

Synthesis of $(\text{L}^{\text{Dipp}})\text{Si}(\text{H})(\text{C}_5\text{H}_4)$: A toluene solution of $(\text{L}^{\text{Dipp}})\text{SiCl}$ (108 mg, 0.20 mmol) was slowly added to a suspension of $\text{Na}[\text{C}_5\text{H}_5]$ (23 mg, 0.26 mmol) in toluene at -78°C , and the reaction mixture allowed to warm to room temperature. After stirring for 12 h, the colour of the solution changed from light yellow to dark red. Removal of volatiles *in vacuo*, extraction into toluene, filtration and storage at -26°C afforded the product as orange crystals suitable for X-ray crystallography (47 mg, 41 % yield). ^1H NMR (C_6D_6 , 500 MHz): δ_{H} 1.04 (d, 6H, $(\text{CH}_3)_2\text{CH}$, $^3J_{\text{HH}} = 6.7$ Hz), 1.05 (d, 6H, $(\text{CH}_3)_2\text{CH}$, $^3J_{\text{HH}} = 6.6$ Hz), 1.16 (d, 6H, $(\text{CH}_3)_2\text{CH}$, $^3J_{\text{HH}} = 6.7$ Hz), 1.22 (d, 6H, $(\text{CH}_3)_2\text{CH}$, $^3J_{\text{HH}} = 6.5$ Hz), 2.10 (s, 12H, $(\text{CH}_3)_2\text{N}$), 3.17 (sept, 2H, $(\text{CH}_3)_2\text{CH}$, $^3J_{\text{HH}} = 6.7$ Hz), 3.51 (sept, 2H, $(\text{CH}_3)_2\text{CH}$, $^3J_{\text{HH}} = 6.6$ Hz), 4.18 (s, 1H, backbone CH proton), 5.69 (s, 1H, SiH, $^1J_{\text{SiH}} = 232$ Hz), 6.45 (overlapping doublets, 2H, endocyclic C_5H_4 protons), 6.83 (overlapping doublets, 2H, endocyclic C_5H_4 protons), 6.96–7.09 (aromatic protons, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 101 MHz): δ_{C} 24.2, 24.3, 25.4, 25.6 ($(\text{CH}_3)_2\text{CH}$), 29.2, 29.7 ($(\text{CH}_3)_2\text{CH}$), 41.0 ($(\text{CH}_3)_2\text{N}$), 77.1 (backbone methine C), 91.3 (Si=C), 112.1 (C_5H_4 3-CH), 116.7 (C_5H_4 2-CH), 124.8, 125.7, 137.4, 145.4, 147.2 (Ar), 164.6 (imine quaternary C). $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6 , 99.4 MHz): δ_{Si} -25.0. IR (ATR, $\nu_{\text{SiH}}/\text{cm}^{-1}$): 2213. Elemental analysis: calc. for $\text{C}_{36}\text{H}_{52}\text{N}_4\text{Si}$: C 76.00 %, H 9.21 %, N 9.85 %; meas. C 75.77 %, H 9.00 %, N 10.03 %.

Synthesis of $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2\{\text{Si}(\text{H})\text{L}^{\text{Dipp}}\}$. Toluene (10 mL) was added to a solid mixture of $(\text{L}^{\text{Dipp}})\text{SiCl}$ (50 mg, 0.09 mmol) and $\text{K}[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2\text{H}]$ (27 mg, 0.12 mmol, 1.3 equiv.), and the reaction vessel heated at 80°C with stirring for 12 h. Filtration, followed by concentration to the point of incipient crystallisation and storage for several days at ambient conditions yielded yellow crystals of the product (42 mg, 65 % yield). ^1H NMR (C_6D_6 , 400 MHz): δ_{H} 0.95 (d, 6H, $(\text{CH}_3)_2\text{CH}$, $^3J_{\text{HH}} = 6.6$ Hz), 1.07 (d, 6H, $(\text{CH}_3)_2\text{CH}$, $^3J_{\text{HH}} = 6.6$ Hz), 1.33 (d, 6H, $(\text{CH}_3)_2\text{CH}$, $^3J_{\text{HH}} = 6.5$ Hz), 1.45 (d, 6H, $(\text{CH}_3)_2\text{CH}$, $^3J_{\text{HH}} = 6.7$ Hz), 2.05 (s, 3H, Cp'-bound CH_3), 2.33 (s, 12H, $(\text{CH}_3)_2\text{N}$), 3.06 (sept, 2H, $(\text{CH}_3)_2\text{CH}$, $^3J_{\text{HH}} = 6.6$ Hz), 4.12 (sept, 2H, $(\text{CH}_3)_2\text{CH}$, $^3J_{\text{HH}} = 6.6$ Hz), 4.23 (s, 2H, Cp' protons), 4.39 (s, 2H, Cp' protons), 4.64 (s, 1H, backbone CH proton), 6.26 (s, 1H, SiH, $^1J_{\text{SiH}} = 166$ Hz), 6.99–7.14 (aromatic protons, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 101 MHz): δ_{C} 25.3, 25.4, 25.8, 26.5 ($(\text{CH}_3)_2\text{CH}$), 27.6, 30.3 ($(\text{CH}_3)_2\text{CH}$), 40.7 ($(\text{CH}_3)_2\text{N}$), 79.6, 80.5 (Cp carbons), 80.8 (backbone methine C), 125.3, 125.6, 126.0, 140.8, 143.8, 145.6 (aromatic carbons), 165.2 (imine quaternary C), CO carbons not observed. $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6 , 99.4 MHz): 38.8. IR (ATR, $\nu_{\text{CO}}/\text{cm}^{-1}$): 1891, 1825.

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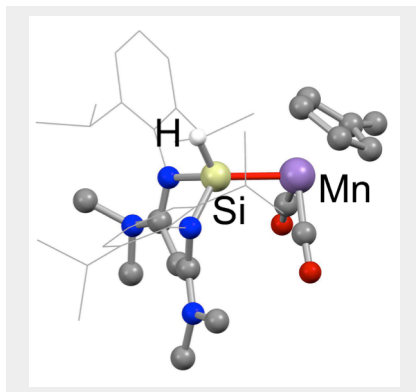
Keywords: silicon • β -diketiminate ligands • silylene • hydrogen migration • germanium • tin

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Metathesis between the 'N-nacnac' stabilised chlorosilylene ($(L^{Dipp})SiCl$ ($L^{Dipp} = HC\{(Me_2N)CDippN\}_2$) and $Na[C_5H_5]$ is accompanied by C-to-Si hydrogen migration, generating the hydrosilicon(IV) species $(L^{Dipp})Si(H)(C_5H_4)$. By contrast a Si(II) hydride species is generated from $(L^{Dipp})SiCl$ via reaction with $K[Cp^*Mn(CO)_2H]$, which acts as both hydride source and coordinative trap for $(L^{Dipp})SiH$, through the silylene complex $Cp^*Mn(CO)_2\{Si(H)L^{Dipp}\}$.



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access to silicon hydride systems via
migration processes**