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Efficient generation of stable adducts of Si(II) dihydride using a donor–acceptor approach†‡

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A stable Si(II) dihydride complex, IPr·SiH_2·BH_3 (IPr = [(HCNDipp)$_2$C:]; Dipp = 2,6-^{i}$Pr_2C_6H_3$), was synthesized and preliminary reactivity involving this source of encapsulated silylene is reported.

The ability to intercept reactive main group species in the presence of strong electron pair donors, such as N-heterocyclic carbenes (NHCs), has had a profound influence in advancing modern inorganic chemistry.[1] Motivated by these breakthroughs, our group has recently employed a related donor–acceptor strategy[2] to access stable adducts of :GeH_2 and :SnH_2,[3] and various inorganic congeners of ethylene, H_2SiEH_2 (E = Ge and Sn).[3] In this communication, we introduce an efficient route to a stable bis adduct of the highly sought-after parent silylene, :SiH_2,[4,5] and explore initial coordination chemistry involving this novel Group 14 dihydride.

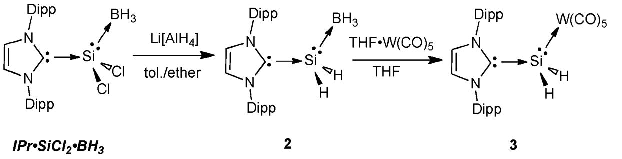
Interest in :SiH_2 stems from its postulated existence during the thermolytic synthesis of Si films from SiH_4,[6] while metallosilylenes (M═SiR_2) have been implicated as intermediates in hydrosilane polymerization and in the synthesis of halomethylsilanes.[7] Of particular relevance to the title work, Robinson and coworkers have synthesized a compound bearing a formal :SiH_2 unit, IPr·*SiH_2*·BH_2–SiH(B_3H_7)·IPr, *via* a complex borane-induced Si–Si cleavage reaction involving the disilene bis adduct IPr·Si═Si·IPr (IPr = [(HCNDipp)$_2$C:]; Dipp = 2,6-^{i}$Pr_2C_6H_3$).[8]

Previously we showed that the germylene donor–acceptor complex, IPr·GeH_2·BH_3 (**1**), could be prepared from the reaction of the germanium(II) halide precursor, IPr·$GeCl_2$, with 2 equiv. of Li[BH_4].[3a] However a later attempt by Roesky and coworkers to apply a similar strategy toward the synthesis of the Si(II) analogue IPr·SiH_2·BH_3 (**2**) was not successful. Specifically, treatment of IPr·$SiCl_2$[1g] with Li[BH_4] in THF resulted in an unusual LiH elimination reaction and the formation of the halosilylene adduct IPr·$SiCl_2$·BH_3 in high yield.[9] The reluctance of the Si–Cl bonds in IPr·$SiCl_2$·BH_3 to undergo hydride replacement chemistry with Li[BH_4] mirrored our observations with the silagermene adduct IPr·$Cl_2SiGeCl_2$·W(CO)$_5$, wherein Si–H bond formation required the use of Li[AlH_4] as a hydride source.[3d]

Our initial attempts to generate IPr·SiH_2·BH_3 (**2**) from the reaction of IPr·$SiCl_2$·BH_3 with Li[AlH_4] in ethereal solvents led to the formation of the known alane, IPr·AlH_3, as a major product,[10] with only trace amounts (<5%) of the desired silylene adduct **2** observed by NMR spectroscopy. In order to mitigate IPr·AlH_3 formation, we decided to repeat the hydride transfer reaction in a solvent mixture of lower polarity (toluene/ether mixture) while concurrently decreasing the reaction time to 1.5 h. Fortunately these alterations in the reaction parameters led to the clean formation of the desired Si(II) dihydride adduct IPr·SiH_2·BH_3 (**2**) as a colorless solid in a moderate isolated yield of 55% (Scheme 1).

The structure of IPr·SiH_2·BH_3 (**2**) is presented in Fig. 1,[11] and bears geometric features that closely resemble those found within the germanium congener IPr·GeH_2·BH_3 (**1**).[3a] The dative C_{Ipr}–Si bond length in **2** [1.9284(15) Å] is slightly shorter than the related C_{Ipr}–Si interactions found within the SiH_2 adduct, IPr·SiH_2·BH_2–SiH(B_2H_7)·IPr [1.934(4) and 1.944(4) Å], and in IPr·$SiCl_2$·BH_3 [1.937(2) Å].[8,9] The adjacent Si–B distance in **2** [1.992(2) Å] lies in the range reported for previously known BH_3 adducts involving formal Si(II) donor sites [1.965(2) to 1.996(4) Å].[4b,8,9] Each of the hydrogen atoms bound to Si and B in **2** were located in the electron difference map and refined isotropically to expected Si–H and B–H distances.

Consistent with the abovementioned crystallographic data, the IR spectrum of IPr·SiH_2·BH_3 (**2**) exhibited a sharp band at 2096 cm^{-1} due to coincident ν_{sym} and ν_{asym} Si–H stretching modes, along with diagnostic ν($^{10/11}$B–H) stretching vibrations



Scheme 1 Synthesis of the Si(II) dihydride adducts **2** and **3**.

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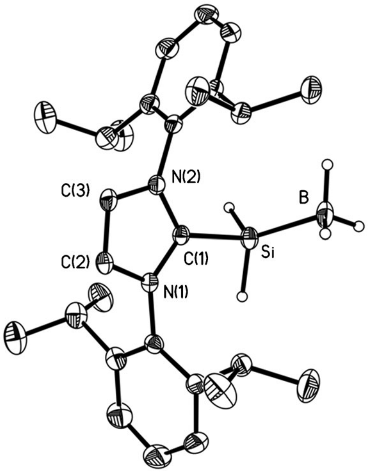


Fig. 1 Thermal ellipsoid plot (30% probability) of IPr·SiH_2·BH_3 (**2**). IPr-bound hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–Si 1.9284(15), Si–B 1.992(2), Si–H 1.409(18) and 1.439(18), B–H 1.02(2), 1.02(3) and 1.12(2); C(1)–Si–B 112.11(8), H–Si–H 102.0(10).

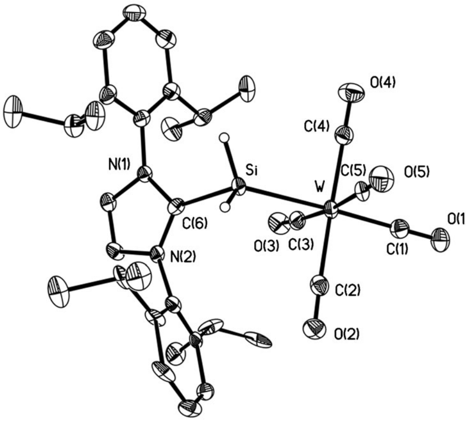


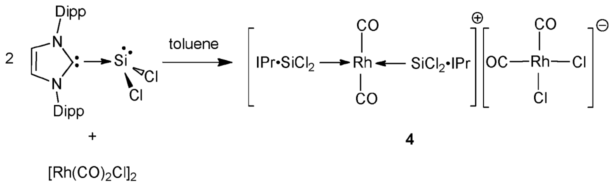
Fig. 2 Thermal ellipsoid plot (30% probability) of IPr·SiH_2·W$(CO)_5$ (**3**). IPr-bound hydrogen atoms and hexane solvent are omitted for clarity; Si–H distances were constrained to equal values during the refinement. Selected bond lengths [Å] and angles [°]: C(6)–Si 1.928(13), Si–W 2.573(4), W–C(1) 1.966(15), W–C(2–5) 1.997(16) to 2.059(17), Si–H 1.32(9); C(6)–Si–W 121.4(4), Si–W–C(1) 176.2(4), Si–W–C(2–5) 85.0(4) to 91.6(4).

from 2238 to 2345 cm^{-1}. The ^{29}Si{^{1}H} NMR spectrum featured a well-resolved quartet pattern centered at −55.6 ppm [$^1J_{\text{Si–B}}$ = 46 Hz], while the –BH$_3$ acceptor unit in **2** appeared as a quartet in the ^{11}B NMR spectrum [δ = −46.2; $^1J_{\text{BH}}$ = 93 Hz]. The isotopomer IPr·SiD_2·BH_3 (**2D**) was also synthesized and yielded a ν(Si–D) IR band at 1522 cm^{-1}, congruent with the expected change in Si–H/D harmonic oscillator strength on going from **2** to **2D**. Theoretical calculations on the silylene–borane $ImMe_2$·SiH_2·BH_3 {$ImMe_2$ = [$(HCNMe)_2$C:]}[11] gave optimized structural and IR spectroscopic parameters that closely matched those of **2**. Moreover, NBO analysis indicated the presence of a polar dative C_{IPr}–Si interaction [77% bonding density on C] and a relatively non-polar Si–B single bond [Wiberg Bond Index (WBI) = 0.989].

The SiH_2 complex **2** appears to be significantly more stable than its Ge analogue IPr·GeH_2·BH_3 (**1**). For example, IPr·SiH_2·BH_3 (**2**) is stable up to *ca.* 230 °C in the solid state and remains unaltered in hot toluene (100 °C, 12 h). By comparison, complex **1** has a much lower T_{dec} of 130 °C in the solid state, while decomposition to Ge metal, H_2 and IPr·BH_3 is rapid at *ca.* 100 °C in toluene.[3a] Moreover, IPr·SiH_2·BH_3 is unreactive towards Cy_3P at room temperature, whereas the GeH_2 adduct **1** reacts with Cy_3P to give the known phosphine–borane adduct Cy_3P·BH_3, IPr·BH_3 and the imidazole aminal [$(HCNDipp)_2CH_2$] as soluble products (*ca.* 25% conversion after 24 h).[11] These observations are in line with the expected increase in both the electron donating and accepting abilities of the SiH_2 unit relative to GeH_2,[5b] leading to a higher degree of stability for IPr·SiH_2·BH_3.

An interesting silylene group transfer reaction was noted when IPr·SiH_2·BH_3 (**2**) was combined with THF·W$(CO)_5$. In this process the IPr·SiH_2 unit remained intact to give a thermally stable tungsten complex IPr·SiH_2·W$(CO)_5$ (**3**) in a 66% yield with concomitant loss of THF·BH_3 (Scheme 1). The NMR spectroscopic and X-ray crystallographic data[11] (Fig. 2) for **3** were in accordance with the formation of a tungsten-bound silylene. The IR spectrum of **3** afforded sharp bands at 2086 and 2107 cm^{-1} that were assigned as symmetric and asymmetric Si–H stretching modes, respectively, on the basis of DFT studies involving the model complex, $ImMe_2$·SiH_2·W$(CO)_5$.[11] The frequencies of the Si–H IR vibrations in **3** were of similar value as in the Si(II) hydride adduct, [^{t}BuNC(Ph)N^{t}Bu]SiH·BH_3 [2107 cm^{-1}].[4b] The *trans* disposed carbonyl ligand in **3** (relative to the Si donor) gave a characteristic A_1 vibration at 2044 cm^{-1}; this value is slightly lower than the related stretching frequencies in the heavier element analogues IPr·EH_2·W$(CO)_5$ (E = Ge and Sn; $\nu(\text{CO})_{\text{trans}}$ = 2047 cm^{-1} in both cases).[3b] These data suggest that the IPr·SiH_2 group is a marginally stronger electron donor than either of the Ge and Sn derivatives. Of further note, West's N-heterocyclic silylene [$(HCN^tBu)_2$Si:] does not form an adduct with BH_3, thus implying that the IPr·SiH_2 unit is a stronger Lewis base than this classic Si(II) heterocyclic donor.[5c,12] DFT studies on $ImMe_2$·SiH_2·W$(CO)_5$ identified a similar dative $C_{\text{IPr}}{}^{\delta-}$–$Si^{\delta+}$ bond [WBI = 0.725] as in $ImMe_2$·SiH_2·BH_3; moreover the SiH_2 groups in both adducts have considerable hydridic character (H^{δ}–). Lastly, the Si–W bonding electron density in $ImMe_2$·SiH_2·W$(CO)_5$ was moderately polarized towards Si (61%; WBI = 0.791).[11]

In an attempt to better gauge the electron donating ability of the IPr·SiH_2 unit, and gain access to novel late metal silylene chemistry,[7] we attempted to prepare the Rh carbonyl complex [IPr·SiH_2·Rh$(CO)_2$Cl]. Complexes of the general form [L·Rh$(CO)_2$Cl] (L = 2e$^-$ donor) are used to benchmark relative ligand donor strengths by monitoring changes in the ν(CO) stretching frequencies.[13] We initially investigated the chemistry between IPr·SiH_2·BH_3 and [Rh$(CO)_2$Cl]$_2$, and in each case observed the rapid formation of Rh metal and the generation of a large number of inseparable carbene-containing products. A stable Rh–silylene complex was obtained when IPr·$SiCl_2$ was reacted with [Rh$(CO)_2$Cl]$_2$. In place of forming the target monometallic complex, [IPr·$SiCl_2$·Rh$(CO)_2$Cl], its coordination isomer *trans*-[(IPr·$SiCl_2$)$_2$Rh$(CO)_2$]*cis*-[Rh$(CO)_2Cl_2$] (**4**) was obtained as an orange crystalline solid (eqn (1)); a higher isolated yield of **4** (87%) was obtained with an excess of $[Rh(CO)_2Cl]_2$.[11]



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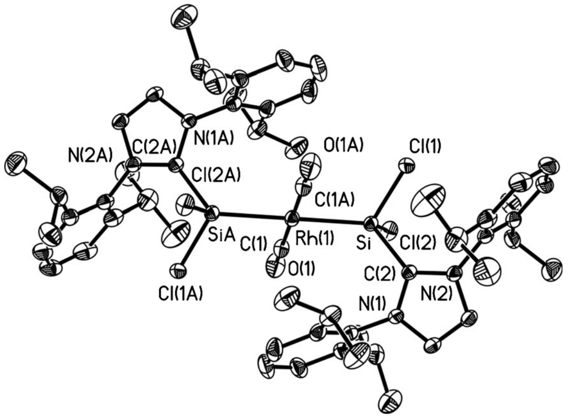

Fig. 3 Thermal ellipsoid plot (30% probability) of the *trans*-$[(IPr{\cdot}SiCl_2)_2Rh(CO)_2]^+$ cation in **4**. IPr-bound hydrogen atoms and CH_2Cl_2 solvent are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh(1)–Si 2.3605(8), Rh(1)–C(1) 1.901(4), C(2)–Si 1.939(3); C(2)–Si–Rh(1) 123.41(10), Cl(1)–Si–Cl(2) 102.56(5), Si–Rh(1)–C(1) 90.94(11), Si–Rh(1)–Si(A) 180.0.

The structure of **4** was verified by single-crystal X-ray crystallography (Fig. 3),[11] while $^{13}C\{^1H\}$ NMR spectroscopic studies revealed the retention of two distinct carbonyl environments in solution.[14] The ligation of two $IPr{\cdot}SiCl_2$ units to a sole Rh center in **4** is a likely consequence of the reduced proximal bulk at the donor site of this $2e^-$ ligand relative to NHCs (which readily give the monosubstituted complexes, $[(NHC)Rh(CO)_2Cl]$).[13] Unfortunately our attempts to generate a Rh-bound silylene complex featuring reactive Si–H groups *via* the reaction of **4** with various hydride sources exclusively led to the formation of metallic Rh and complicated product mixtures. The synthesis of a complex with stable Si(II)–Rh interactions represents a new addition to the growing family of metallosilylenes,[7,15] and future work will focus on investigating other methods to deliver SiH_2 functionality onto metal centers.

In summary, we have uncovered an efficient synthetic pathway for the preparation of stable donor–acceptor adducts of SiH_2. Future work will involve an in-depth study of the reactivity of the $IPr{\cdot}SiH_2$ array including the exploration of potential Si–H bond activation processes. These studies could add valuable insight into the nature of metal-assisted catalysis involving silanes.[4c,7]

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