

Direct Transformation of SiH₄ to a Molecular L(H)₂Co=Si=Co(H)₂L Silicide Complex

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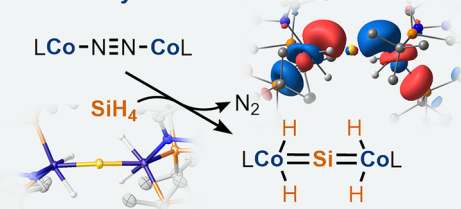
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ABSTRACT: The synthesis of bimetallic molecular silicide complexes is reported, based on the use of multiple Si–H bond activations in SiH₄ at the metal centers of 14-electron LCo^I fragments (L = Tp⁺, HB(3,5-diisopropylpyrazolyl)₃[−]; [BP₂^{tBu}Pz], PhB(CH₂P^{tBu}Bu)₂(pyrazolyl)). Upon exposure of (Tp⁺Co)₂(μ-N₂) (1) to SiH₄, a mixture of (Tp⁺Co)₂(μ-H) (2) and (Tp⁺Co)₂(μ-H)₂ (3) was formed and no evidence for Si–H oxidative addition products was observed. In contrast, [BP₂^{tBu}Pz]-supported Co complexes led to Si–H oxidative additions with the generation of silylene and silicide complexes as products. Notably, the reaction of ([BP₂^{tBu}Pz]Co)₂(μ-N₂) (5) with SiH₄ gave the dicobalt silicide complex [BP₂^{tBu}Pz](H)₂Co=Si=Co(H)₂[BP₂^{tBu}Pz] (8) in high yield, representing the first direct route to a symmetrical bimetallic silicide. The effect of the [BP₂^{tBu}Pz] ligand on Co–Si bonding in 7 and 8 was explored by analysis of solid-state molecular structures and density functional theory (DFT) investigations. Upon exposure to CO or DMAP (DMAP = 4-dimethylaminopyridine), 8 converted to the corresponding [BP₂^{tBu}Pz]Co(L)_x adducts (L = CO, *x* = 2; L = DMAP, *x* = 1) with concomitant loss of SiH₄, despite the lack of significant Si–H interactions in the starting complex. On heating to 60 °C, 8 underwent reaction with MeCl to produce small quantities of Me_xSiH_{4−x} (*x* = 1–3), demonstrating functionalization of the μ-silicon atom in a molecular silicide to form organosilanes.

Rational synthesis of a molecular silicide:



INTRODUCTION

Binary transition-metal silicide phases (M_xSi_y) are critical solid-state materials used in microelectronic technologies,^{1–3} and as catalysts that enable important industrial and technological transformations of silicon-containing materials.^{4–6} Most significantly, the Direct Process is practiced on an enormous, worldwide industrial scale to convert elemental silicon and MeCl to Me₂SiCl₂.⁷ This process involves Si–Cl and Si–C bond formations on the surface of a copper silicide and enables the silicones industry.^{7–10} Interestingly, various transition-metal silicide nanoparticles are used to grow silicon nanowires, created *via* decomposition of molecular silane species at the silicide surface.^{6,11,12} Thus, metal silicide catalysts exhibit surface chemistry that promotes useful bond-forming and bond-breaking reactions of silane derivatives.

Metal silicides may be more generally useful in silicon technology; however, the search for new chemical transformations is hindered by a lack of information relating to the reaction mechanisms that occur on a silicide surface, and the specific surface structures involved in this chemistry. In this regard, well-defined molecular models for metal silicide reactive sites should reveal atomic-level insights into the reactivity associated with strong metal-silicon bonding interactions.

Until very recently,^{13,14} molecular metal silicides were represented by a small range of metal-silicon carbonyl clusters generated in complex product mixtures by the reaction of a metal carbonyl with organosilanes or SiH₄. For example,

MacKay and Nicholson reported the *spiro*-silicon cluster [(OC)₈Fe₂]₂(μ₄-Si) from reaction of SiH₄ with Fe₂(CO)₉,¹⁵ whereas Si₂H₆ and Co₂(CO)₈ generate complex mixtures that include [(OC)₇Co₂]₂(μ₄-Si), [(OC)₄Co]₂(μ₄-Si)[Co₃(CO)₉], and [(OC)₄Co]₂(μ₅-Si)₂[Co₄(CO)₁₁].¹⁶ In 2018, Filippou *et al.* described a specialized route to a bimetallic silicide, by the reaction of (SIPr)SiBr₂ (SIPr = 1,3-*bis*-(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene) with two equivalents of [Tp⁺Mo(CO)₂(PMe₃)][−] (Tp⁺ = HB(3,5-dimethylpyrazolyl)₃[−]) to produce Tp⁺(OC)₂Mo≡Si–Mo(CO)₂(PMe₃)Tp⁺ (Figure 1a). This complex, referred to by the authors as a metallasilylidyne, was reduced to a dianionic {Mo=Si=Mo}^{2−} analogue.¹⁷ Despite these interesting examples, there remains a need for rational synthetic routes to well-defined molecular silicides and reactivity studies that characterize the chemical properties for isolated M_xSi_y units.

Our research group recently reported a route to bimetallic silicides involving cleavage of all bonds to silicon in the simple silanes SiH₄ and PhSiH₃.¹⁴ Specifically, a precursor to the 14-electron fragment [BP₃^{tPr}]Co^I ([BP₃^{tPr}] = [PhB(CH₂P^{tPr}Pr)₃][−])

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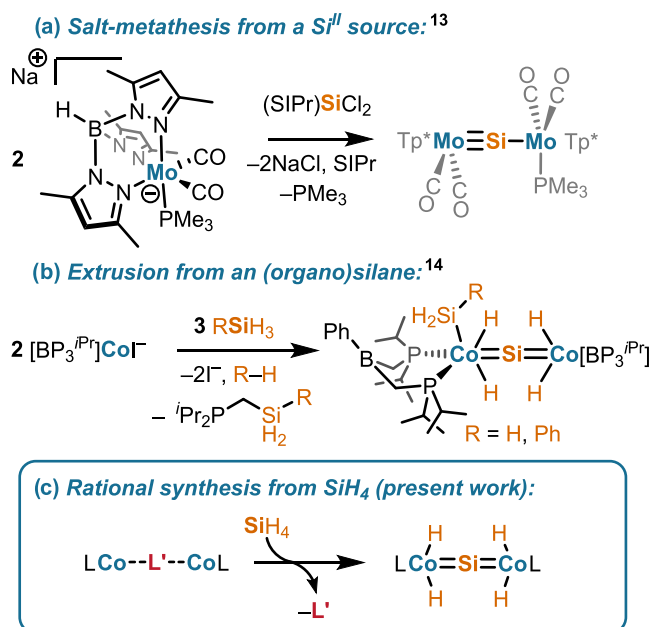


Figure 1. Methods to access bimetallic silicide complexes. (a) Synthesis of an unsymmetrical silicide by salt metathesis of a low-valent silicon source. (b) Synthesis of unsymmetrical silicides by μ -silicon atom extrusion from (organo)silanes. (c) Solid-State Molecular Structures of **2** (Left) and **3** (Right) with 50% Probability Thermal Ellipsoids Drawn^a

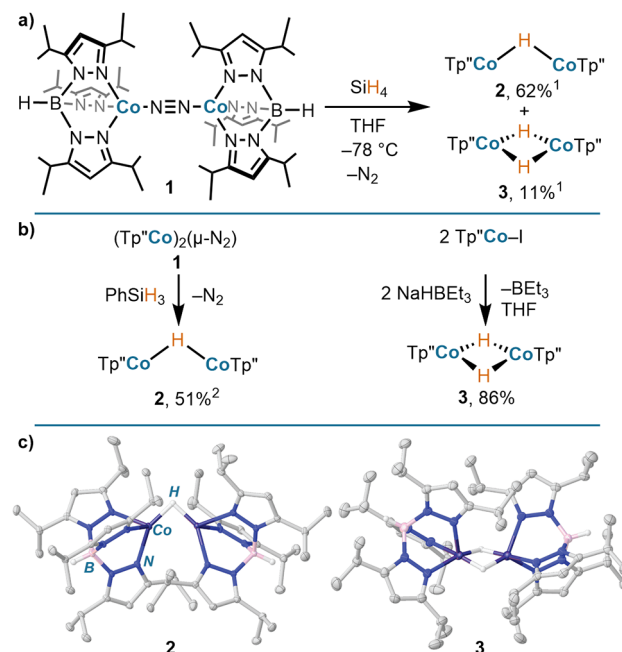
was observed to react with SiH_4 or PhSiH_3 to give unsymmetrical silicides $[\text{BP}_2^{\text{iPr}}](\text{RSiH}_2)(\text{H})_2\text{Co}=\text{Si}=\text{Co}-(\text{H})_2[\text{BP}_3^{\text{iPr}}]$ ($[\text{BP}_2^{\text{iPr}}] = \text{PhB}(\text{CH}_2\text{P}^{\text{iPr}}\text{Pr}_2)_2$; $\text{R} = \text{H}, \text{Ph}$), where the μ -silicon atom is derived from the parent silane (Figure 1b). These reactions represent the first examples of well-defined silicide “extrusion” from simple silanes. However, this synthetic route appeared to involve a complex process relying on fragmentation of the $[\text{BP}_3^{\text{iPr}}]$ ligand with concomitant formation of a cobalt-bound silyl ligand.

To date, there has been no general synthetic route to bimetallic molecular silicides *via* the direct conversion of a silane. However, known silane activations that involve “double $\text{Si}-\text{H}$ ” bond cleavage^{18–21} suggest that a straightforward method to achieve this aim could involve activation of all bonds to SiH_4 with two metal centers to generate $\text{L}(\text{H})_2\text{M}=\text{Si}=\text{M}(\text{H})_2\text{L}$ complexes (Figure 1c). The divergent assembly of such platforms would be well suited for the evaluation of electronic and chemical properties for simple silicides. This report describes the unexpected hydrogen-atom abstraction observed upon reaction of a $\text{Tp}^{\text{R}}\text{Co}^{\text{I}}$ synthon with SiH_4 or PhSiH_3 ($\text{Tp}^{\text{R}} = \text{HB}(3,5\text{-diisopropylpyrazolyl})_3^-$). Refinement of the ligand design identified a $[\text{PhB}(\text{CH}_2\text{P}^{\text{tBu}}\text{Pz})_2(\text{pyrazolyl})]^-$ ($[\text{BP}_2^{\text{tBu}}\text{Pz}]$)-ligated cobalt platform for $\text{Si}-\text{H}$ bond activation and silicide extrusion from SiH_4 . Prior work by Thomas and Peters demonstrated that the $[\text{BP}_2^{\text{tBu}}\text{Pz}]$ ligand functions as a stronger donor than related *tris*-phosphine borate ligands $[\text{PhB}(\text{CH}_2\text{PR}_2)_3]^-$, based on cyclic voltammetric studies of iron complexes.²² Thus, the $[\text{BP}_2^{\text{tBu}}\text{Pz}]$ ligand was expected to produce an electron-rich $[\text{BP}_2^{\text{tBu}}\text{Pz}]\text{M}$ fragment that more readily activates bonds in silane substrates. Additionally, the diminished steric demand of the $[\text{BP}_2^{\text{tBu}}\text{Pz}]$ ligand relative to $[\text{BP}_3^{\text{iPr}}]$ was expected to allow access to more reactive $\{\text{MSiM}\}$ cores.

RESULTS AND DISCUSSION

Reactions of $(\text{Tp}^{\text{R}}\text{Co})_2(\mu\text{-N}_2)$ (1**) with Silanes.** Low-valent cobalt complexes supported by a scorpionate ligand were selected for the initial evaluation of silicide extrusion from SiH_4 . Such ligands have been demonstrated to support closely related 3d-metal dinitrogen complexes $(\text{Tp}^{\text{R,R'}}\text{M})_2(\mu\text{-N}_2)$,²³ which have the possibility to react with SiH_4 to furnish $\text{Tp}^{\text{R,R'}}(\text{H})_2\text{M}=\text{Si}=\text{M}(\text{H})_2\text{Tp}^{\text{R,R'}}$ silicides. The desired starting material $(\text{Tp}^{\text{R}}\text{Co})_2(\mu\text{-N}_2)$ (**1**) was obtained in good yield (84%) by KC_8 reduction of $\text{Tp}^{\text{R}}\text{Co}^{\text{I}}$.²⁴

Scheme 1. (a) Reaction of **1** with SiH_4 , Producing a Mixture of **2** and **3**. (b) Independent Syntheses of **2** and **3**. (c) Solid-State Molecular Structures of **2** (Left) and **3** (Right) with 50% Probability Thermal Ellipsoids Drawn^a



^aMost hydrogen atoms are omitted for clarity. ¹Yields determined *via* ¹H NMR spectroscopy by integration against an internal standard of $(\text{Me}_3\text{Si})_2\text{O}$. ²Product mixture contains 11% of **3**, *via* ¹H NMR spectroscopy by integration against an internal standard of $(\text{Me}_3\text{Si})_2\text{O}$.

Surprisingly, treatment of **1** with one equiv of SiH_4 resulted in conversion to two paramagnetic species (Scheme 1a) according to ¹H NMR spectroscopic analysis of the reaction mixture, and this observation suggests that the desired silicide $\text{Tp}^{\text{R}}(\text{H})_2\text{Co}=\text{Si}=\text{Co}(\text{H})_2\text{Tp}^{\text{R}}$ was not generated. The major product of the reaction was isolated from cold (-35°C) ether and identified crystallographically as the mixed-valent $\text{Co}^{\text{I}}/\text{Co}^{\text{II}}$ monohydride $(\text{Tp}^{\text{R}}\text{Co})_2(\mu\text{-H})$ (**2**); the hydride ligand was explicitly located in the difference map and refined isotropically in the X-ray solid-state molecular structure. Identification of the second (minor) product $(\text{Tp}^{\text{R}}\text{Co})_2(\mu\text{-H})_2$ (**3**) was facilitated by an independent synthesis (*vide infra*). Complex **2** was reliably produced in modest yields by treatment of **1** with one equiv of PhSiH_3 (Scheme 1b) in a reaction that generates trace quantities of the dehydrocoupling product $(\text{PhSiH}_2)_2$ and small quantities of **3** (11%; see Supporting Information page S2). The outcome of this reaction was

unchanged when one equiv of 4-dimethylaminopyridine (DMAP) was added to **1** prior to the addition of PhSiH_3 , indicating that a prototypical base-stabilized silylene^{14,25} of the form $\text{Tp}''(\text{H})_2\text{CoSiHPh}(\text{DMAP})$ was also not accessible for this system and that the reaction pathway involves hydrogen-atom abstraction.

Believing the minor species (**3**) formed upon treatment of **1** with RSiH_3 ($\text{R} = \text{H}, \text{Ph}$) to be the dihydride complex $(\text{Tp}''\text{Co})_2(\mu\text{-H})_2$, an independent synthesis was sought. Treatment of $\text{Tp}''\text{CoI}$ with NaHBET_3 and subsequent workup afforded plates of the $\text{Co}^{\text{II}}/\text{Co}^{\text{II}}$ dimer **3** (Scheme 1b), the identity of which was confirmed by single-crystal X-ray diffraction analysis. The ^1H NMR spectroscopic features of **3** are identical to those of the minor species formed upon the reaction of **1** with SiH_4 or PhSiH_3 . Evans method measurements of the magnetic susceptibility of **3** indicate that it is an $S = 2$ species with $\mu_{\text{eff}} = 5.5 \mu_{\text{B}}$ ($\mu_{\text{S.O.}}(4e) = 4.9 \mu_{\text{B}}$).

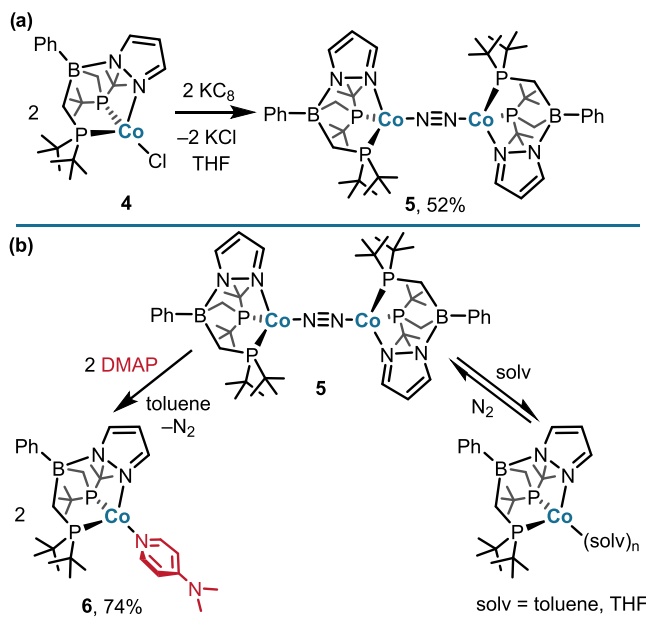
As complex **2** is a rare instance of a mixed-valent $\text{Co}^{\text{I}}/\text{Co}^{\text{II}}$ hydride,^{26,27} its electronic structure was briefly interrogated. The magnetic susceptibility of **2** ($\mu_{\text{eff}} = 6.0 \mu_{\text{B}}$), measured by the Evans method, suggests an $S = 5/2$ system. However, as samples of **2** are invariably contaminated with small ($\sim 10\%$) quantities of **3**, this value serves only as a rough estimate of the magnetic susceptibility. The perpendicular mode X-band EPR spectrum (Figure S22) of a frozen 2-methyltetrahydrofuran glass of **2** at 10 K displays a broad axial resonance at $g_{\parallel} = 2.300$, and $g_{\perp} = 2.170$. The signal at 96 mT supports the assignment of an $S = 5/2$ system since the effective g value ($g_{\text{eff}} \cong 6.99$) exceeds possible theoretical effective g values for $S = 3/2$ systems ($g_{\text{max}} \cong 6$).²⁸ It is noted also that a non-Kramers system (*i.e.*, a system possessing an integer value of S) such as **3** will not resonate under the conditions of perpendicular mode EPR, indicating that mixed-valent **2** is responsible for the observed spectrum. In the solid-state, **2** is essentially isostructural to the closely related $S = 1/2$ $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ monohydride $(\text{Tp}''\text{Cu})_2(\mu\text{-H})$ ($g_{\parallel} = 2.250$, and $g_{\perp} = 2.060$), reported by Warren *et al.*²⁹

A potential explanation for the lack of Co-Si bond formation in **1** is that the comparatively weak ligand field enforced by the Tp'' ligand, relative to $[\text{BP}_3^{\text{R}}]$ ($\text{R} = \text{Ph}, \text{Pr}$),^{14,30} promotes odd-electron processes (*e.g.*, hydrogen-atom transfer) as opposed to Si-H oxidative addition, and favors products with high-spin ground states.^{23,31} Another factor may be that the Tp'' ligand provides insufficient steric protection to support $\{\text{MSiM}\}$ units in dicobalt systems. The limited steric demand of the Tp'' ligand is manifested in the solid-state molecular structures of **2** (Scheme 1c, left) and **3** (Scheme 1c, right), which display relatively close $\text{Co}\cdots\text{Co}$ contacts of 2.3771(6) Å and 2.4106(8) Å, respectively. The analogous distance in $[\text{BP}_2^{\text{tBuPr}}](\text{PhSiH}_2)(\text{H})_2\text{Co}=\text{Si}=\text{Co}(\text{H})_2[\text{BP}_3^{\text{tPr}}]$ is 4.1202(5) Å.¹⁴ These observations suggest that the Tp'' ligand accommodates much closer packing of metal centers in bimetallic complexes than was observed in $[\text{BP}_3^{\text{tPr}}]$ -based systems.¹⁴

Phenylsilane Activation by $[\text{BP}_2^{\text{tBuPz}}]\text{Co}(\text{DMAP})$. Attention turned to the $[\text{BP}_2^{\text{tBuPz}}]$ ligand, as it was expected to provide a stronger ligand field and steric repulsion to enforce a greater metal-metal separation to favor the formation of $\{\text{MSiM}\}$ units. Incorporation of the $[\text{BP}_2^{\text{tBuPz}}]$ ligand at cobalt was achieved by treatment of CoCl_2 with $(\text{Et}_2\text{O})\text{Li}[\text{BP}_2^{\text{tBuPz}}]$ in THF solution. Following workup, $[\text{BP}_2^{\text{tBuPz}}]\text{CoCl}$ (**4**) was isolated as an analytically pure turquoise solid in good (74%) yield. Reduction of **4** with one equiv of KC_8 in THF resulted in

a rapid color change to dark brown, and workup produced a dark brown solid identified by X-ray crystallography as the dinitrogen complex $([\text{BP}_2^{\text{tBuPz}}]\text{Co})_2(\mu\text{-N}_2)$ (**5**; Scheme 2).

Scheme 2. (a) KC_8 Reduction of **4** to Form **5**. (b) Displacement of N_2 from **5** by DMAP and Reversible Dissociation of N_2 by Solvent

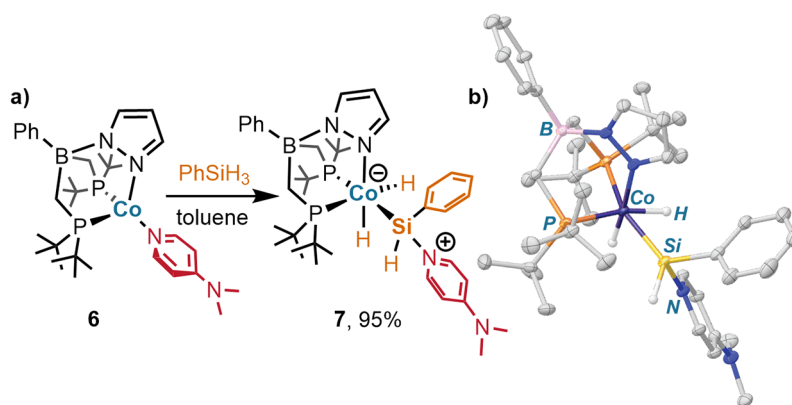


Surprisingly, effervescence was observed upon dissolution of **5** in arene solvents or THF. Presumably, this results from the loss of coordinated N_2 , as evidenced by changes in the ^1H NMR spectra obtained for **5** under ambient conditions, after five freeze-pump-thaw cycles, or under four atm of N_2 (Scheme 2b; see Supporting Information page S5, Figures S33–S40). In contrast, no evidence for related processes was observed for dinitrogen complex **2**.

To develop a less labile system, a DMAP complex was prepared by treatment of **5** with two equivalents of DMAP to give $[\text{BP}_2^{\text{tBuPz}}]\text{Co}(\text{DMAP})$ (**6**; Scheme 2b). This complex was then explored as a synthon or precursor to the 14-electron Co^{I} fragment $[\text{BP}_2^{\text{tBuPz}}]\text{Co}$, which was of interest as a potential reaction center for double Si-H bond activations of silanes (*cf.* Figure 1c). The reaction of **6** with PhSiH_3 resulted in a rapid color change from dark brown to orange, and ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra are consistent with the near-quantitative formation of a diamagnetic C_1 symmetrical product, assigned as the base-stabilized silylene complex $[\text{BP}_2^{\text{tBuPz}}](\text{H})_2\text{CoSiHPh}(\text{DMAP})$ (**7**; Scheme 3). Crystals of **7** were obtained by diffusion of $(\text{Me}_3\text{Si})_2\text{O}$ into a saturated THF solution. The solid-state molecular structure of **7**, determined by single-crystal X-ray diffraction, consists of *pseudo*-octahedral complexes of cobalt (Scheme 3b). The hydrogen atoms bonded to cobalt and silicon were located in the difference map and refined isotropically. The silicon atom of the $\text{SiHPh}(\text{DMAP})$ ligand lies in the P-Co-P plane and is associated with a Co-Si bond length of 2.1428(5) Å. This distance is modestly contracted relative to the Co-Si bond length of 2.1524(8) Å in $[\text{BP}_3^{\text{tPr}}](\text{H})_2\text{CoSiHPh}(\text{DMAP})$ (**A**), a closely related analogue.¹⁴

Comparison of the steric maps of the $[\text{BP}_2^{\text{tBuPz}}]$ and $[\text{BP}_3^{\text{tPr}}]$ ligands in the analogous complexes **7** and **A**, calculated

Scheme 3. (a) Activation of PhSiH_3 by **6** to Form Base-Stabilized Silylene **7**. (b) Solid-State Molecular Structure of **7** with 50% Probability Thermal Ellipsoids Drawn^a



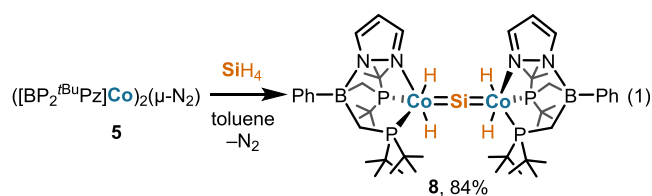
^aMost hydrogen atoms are omitted for clarity.

using SambVca 2.1,³² shows that the buried volume of $[\text{BP}_2^{\text{tBuPz}}]$ ($\%V_{\text{bur}} = 75.0$)³³ is significantly less than that of $[\text{BP}_3^{\text{iPr}}]$ ($\%V_{\text{bur}} = 86.8$).³⁴ Thus, the shortened Co–Si bond length of **7** relative to that in **A** may be a manifestation of the diminished steric demand of the ancillary ligand. These features are reflected in the Co–Si Wiberg bond indices (WBIs)³⁵ for **7** (1.31) and **A** (1.28) based on density functional theory (DFT) calculations at the $\omega\text{B97X-D3/def2-TZVP//CPCM}(\text{benzene})$ level of theory. The steric demands of both $[\text{BP}_2^{\text{tBuPz}}]$ and $[\text{BP}_3^{\text{iPr}}]$ are significantly greater than that of Tp^* ($\%V_{\text{bur}} = 59.3$).³⁶

The multinuclear NMR spectra of **7** and **A** provide further insight into the effect of the ancillary ligands. At 292 K, complex **7** displays resonances consistent with a C_1 -symmetrical structure, with two distinct 1:1 Co–H resonances in the ^1H NMR spectrum at $\delta -28.27$ and -11.66 ppm. These resonances correspond to the hydride ligands oriented *trans*- and *cis*- to the N donor atom, respectively, based on multiplet analysis. An analogous trend in δ_{H} has been observed for the hydride ligands in $[(\text{Pr}_2\text{PCH}_2\text{CH}_2)_2\text{NH}]\text{CoH}_3$.³⁷ Accordingly, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **7** displays two resonances of approximately equal areas (δ 72.0, 81.3 ppm). By comparison, the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of complex **A** at 292 K are consistent with a *pseudo*- C_3 structure. The ^{29}Si – ^1H HMBC NMR spectrum of **7** displays a cross-peak at 34 ppm, which correlates to the Si–H proton with $^1J_{\text{HSi}} = 154$ Hz. The chemical shift of the ^{29}Si nucleus in **7** is more upfield than that observed for **A** (δ_{Si} 61 ppm),¹⁴ but remains consistent with a base-stabilized silylene complex.^{25,38}

Direct Silane Activation to Form a Dicobalt Silicide.

The synthesis of **7** indicated that the 14-electron $[\text{BP}_2^{\text{tBuPz}}]\text{Co}^{\text{I}}$ fragment might be effective for the generation of the silicide $[\text{BP}_2^{\text{tBuPz}}](\text{H})_2\text{Co}=\text{Si}=\text{Co}(\text{H})_2[\text{BP}_2^{\text{tBuPz}}]$ (**8**). Indeed, exposure of a toluene solution of **5** to one equiv of SiH_4 (15% in N_2) resulted in an instantaneous color change from dark red to deep greenish-blue. Following removal of the solvent, crystallization by diffusion of pentane into a saturated THF solution at -35 °C allowed for the isolation of **8** as an analytically pure crystalline solid in good (84%) yield (eq 1). Notably, this is the first instance of a reaction that produces a symmetrical bimetallic silicide from the activation of SiH_4 .



The solid-state molecular structure of **8** (Figure 2a) possesses idealized C_2 symmetry; the pyrazole substituents of the two $[\text{BP}_2^{\text{tBuPz}}]$ ligands are oriented in a staggered *syn* fashion, creating a relatively open pocket that exposes the central silicon atom (Figure 2b). The μ_2 -silicon atom displays essentially linear coordination ($\angle(\text{Co}=\text{Si}=\text{Co}) = 169.07(6)^\circ$) and very short Co–Si bond distances ($d(\text{Co}=\text{Si})_{\text{ave}} = 2.058(1)$ Å). The hydride ligands, located in the Fourier difference map and refined isotropically, are arranged to produce *pseudo*-octahedral coordination about each cobalt center in a manner analogous to that observed for **7**. Notably, the hydride ligands do not form a tetrahedral array about the μ -silicon atom (Figure 2c), indicating minimal “ SiH_4 ” character in the silicide core.¹⁴ The solid-state structure of **8** is superficially similar to that of the previously reported complex $[\text{BP}_2^{\text{iPr}}](\text{PhSiH}_2)(\text{H})_2\text{Co}=\text{Si}=\text{Co}(\text{H})_2[\text{BP}_3^{\text{iPr}}]$ (**B**), although the latter complex possesses longer central Co–Si bonds ($d(\text{Co}=\text{Si})_{\text{ave}} = 2.074(1)$ Å).

In the ^1H NMR spectrum of **8** at 292 K, the hydride ligand resonances appear as very broad, featureless singlets centered at -24.43 and -8.66 ppm. Variable-temperature NMR studies with toluene- d_8 solutions of **8** show that these resonances are readily sharpened at sub-ambient temperatures, although fine structure, such as coupling to ^{31}P and ^{29}Si , was not observed due to interaction with the nearby quadrupolar ^{59}Co nucleus ($I = 7/2$).³⁹ At 203 K, the two Co–H resonances give rise to integrations of 2:2 relative to the $[\text{BP}_2^{\text{tBuPz}}]$ ligand in the ^1H NMR spectrum; decoalescence of the phosphorus resonances is also observed, with the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum displaying two broad singlets of approximately equal areas (Figure S52).

The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **8** at 292 K displays a single low-intensity resonance at 274 ppm. This resonance appears at a notably higher field than those of previously characterized silicides, including **B** (δ 350 ppm)¹⁴ and $\text{Tp}^*(\text{OC})_2\text{Mo}=\text{Si}=\text{Mo}(\text{CO})_2(\text{PMe}_3)\text{Tp}^*$ (δ 438.9 ppm).¹³ The value of J_{HSi} could not be determined from the ^1H NMR spectra of **8** at any temperature across the measured range due to broadening

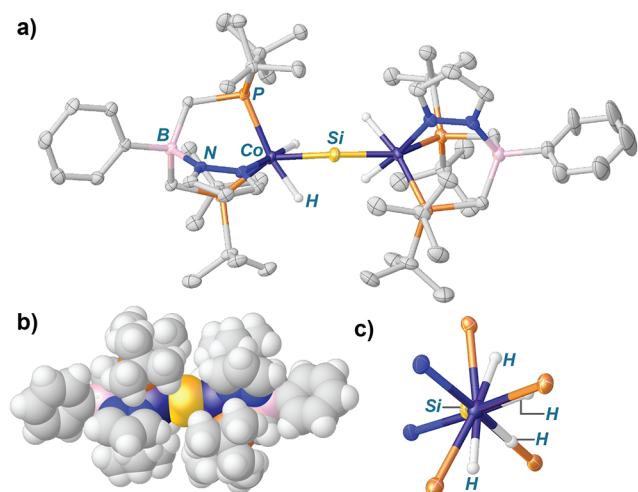


Figure 2. (a) Solid-state molecular structure of **8** with 50% probability thermal ellipsoids drawn. Most hydrogen atoms are omitted for clarity. (b) Space-filling model of **8**. (c) View of **8** along the Co...Co axis, illustrating the nontetrahedral array of hydride ligands about the μ -Si atom.

of the hydride resonances, while attempts to determine J_{HSi} via ^{29}Si – ^1H HMBC NMR experiments were frustrated by the lack of cross-peaks in the spectrum. Similarly, efforts to record a CP-MAS solid-state ^{29}Si NMR spectrum of **8** were unsuccessful, although this likely arises from the large anisotropy expected for the silicon nucleus,^{40–42} as well as the presence of many nearby spin-active (and quadrupolar) nuclei (i.e., ^1H , ^{31}P , ^{59}Co).³⁹

Computational investigations shed light on the degree of interaction between silicon and the flanking hydride ligands. The DFT-optimized (nontruncated) geometries of **8** and **B** reproduce the solid-state molecular structures with good accuracy, capturing the Co–Si bond lengths ($\Delta d(\text{Co}–\text{Si}) < 0.03 \text{ \AA}$) and Co–Si–Co angles ($\Delta \angle(\text{Co}–\text{Si}–\text{Co}) < 3^\circ$). The Si...H WBI values for **8** range from 0.42 to 0.45, while those for **B** range from 0.39 to 0.42. These values are significantly diminished compared to those of the Si–H bonds within the SiHPh(DMAP) substituents in **7** (WBI 0.82) and **A** (WBI 0.82), which serve as useful internal standards for a WBI value associated with a Si–H single bond. This analysis is consistent with minimal Si...H interactions in **8** and **B**; in other words, these silicides are best described as $\text{L}(\text{H})_2\text{Co}=\text{Si}=\text{Co}(\text{H})_2\text{L}$ structures, rather than as $\text{LCo}(\mu\text{-SiH}_4)\text{CoL}$.⁴³ An atoms in molecules (AIM) analysis⁴⁴ of **8** locates two bond paths connecting the μ -silicon atom to the two hydride ligands that are oriented *cis* relative to the N donor atom of each $[\text{BP}_2^{\text{tBu}}\text{Pz}]$ ligand, potentially indicating a weak residual Si...H interaction (see Supporting Information Figure S19). Such interactions, which are well documented for 3d-metal silylene complexes,^{14,30,45–47} are also present to a minor extent in **B**, as shown in the original report of this compound,¹⁴ which described a minimal $^1J_{\text{Si-H}}$ coupling constant of 8 Hz.⁴⁸

The Co–Si WBIs for the $\{\text{CoSiCo}\}$ core of **8** (1.47, 1.47) are slightly greater than those of **B** (1.45, 1.44), reflecting the trend established for **7** and **A** of strengthened Co–Si bonding in $[\text{BP}_2^{\text{tBu}}\text{Pz}]$ systems. Also, these bond indices are substantially greater than the Co–Si WBI for the PhSiH_2 substituent in **B** (1.07). A scan of the potential energy surface for rotation of the $[\text{BP}_2^{\text{tBu}}\text{Pz}](\text{H})_2\text{Co}$ units about the Co–Co

axis in **8** was conducted. The energy profile (Figure S13) shows that the molecular geometry found in the solid state corresponds to the energetic minimum in solution ($\Delta E_{\text{rot}} = 9.0 \text{ kcal mol}^{-1}$) and provides support for the hydride ligand positions determined by crystallography.

Reactions of Silicide 8. Complex **8** is a good candidate for the investigation of silicide reactivity, given its symmetrical structure and the apparent accessibility of the μ -silicon center. Inspection of the Kohn–Sham orbitals obtained from the DFT-optimized structure of **8** shows that the frontier orbitals (Figure 3) possess significant μ -silicon character. The highest-

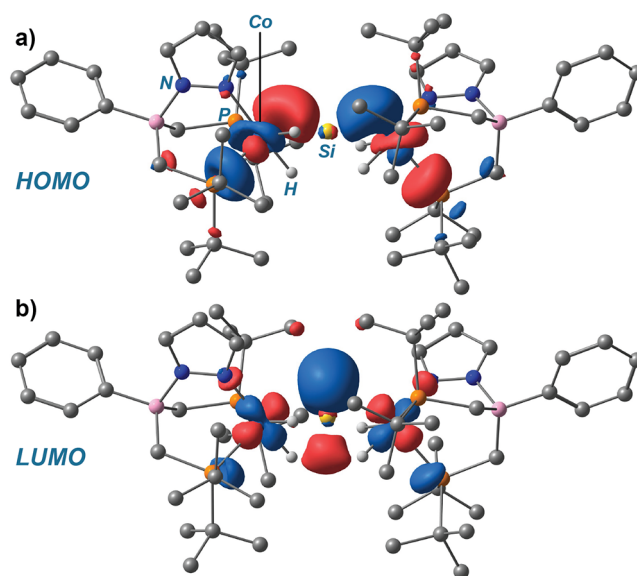
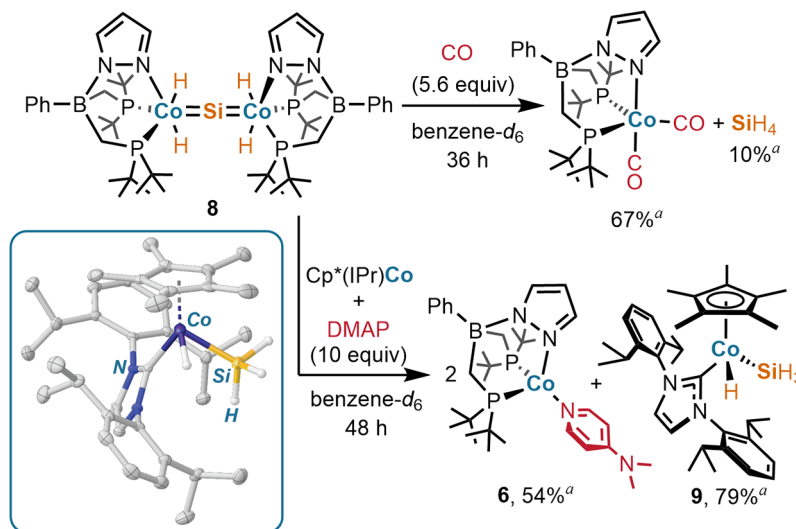


Figure 3. DFT-calculated molecular orbitals of **8** rendered at an isovalue of 0.04. Most hydrogen atoms are omitted for clarity. (a) HOMO, (b) LUMO.

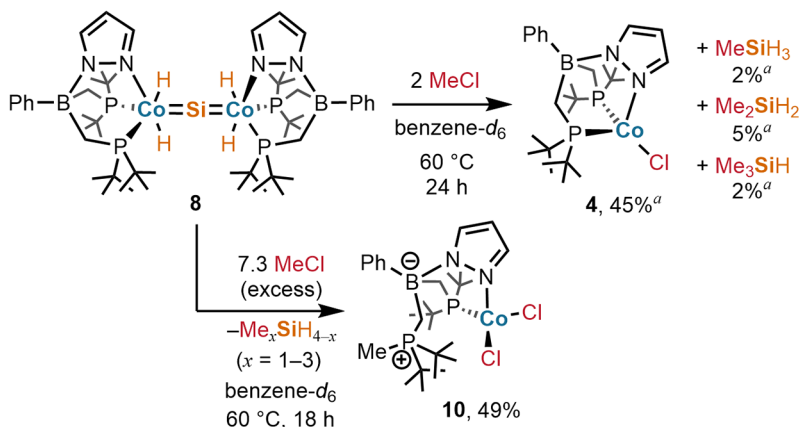
occupied molecular orbital (HOMO) of **8** (Figure 3a) is predominantly $\sigma(\text{Co}–\text{Si}–\text{Co})$ in character, while the lowest-unoccupied molecular orbital (LUMO) of **8** (Figure 3b) is dominated by $\pi^*(\text{Co}–\text{Si}–\text{Co})$ character. The composition of these frontier orbitals indicates that redox and Lewis acid/base transformations are likely to involve the silicide core of **8**.

Treatment of **8** with excess CO resulted in gradual conversion to a new diamagnetic product, identified crystallographically and by independent synthesis as $[\text{BP}_2^{\text{tBu}}\text{Pz}]\text{Co}(\text{CO})_2$ (Scheme 4), in 67% yield (based on integration against an internal standard of $(\text{Me}_3\text{Si})_2\text{O}$). Monitoring the reaction progress by ^1H NMR spectroscopy with use of an internal standard indicated that SiH_4 was evolved in low yield (10%). The yield of SiH_4 in this reaction is likely underestimated due to its low solubility in benzene.⁴⁹

The yield of SiH_4 released by treatment of **8** with a Lewis base was more accurately measured by “trapping” SiH_4 using an added complex that activates Si–H bonds. Thus, treatment of **8** with DMAP (10 equiv) in the presence of an unsaturated scavenger complex, $\text{Cp}^*(\text{IPr})\text{Co}$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$; IPr = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene),⁵⁰ resulted in conversion over 48 h to **6** (54% yield vs internal standard) and $\text{Cp}^*(\text{IPr})\text{Co}(\text{H})(\text{SiH}_3)$ (**9**; 79% yield vs internal standard; Scheme 4).⁵¹ This reaction is notable in that it demonstrates an unusual SiH_4 transfer between metal centers, despite a lack of “ SiH_4 character” in the ground state of the starting silicide.

Scheme 4. Displacement of SiH_4 from **8** by Excess CO or by Treatment with Excess DMAP in the Presence of $\text{Cp}^*(\text{IPr})\text{Co}^a$ 

^aYields determined via ^1H NMR spectroscopy by integration against an internal standard of $(\text{Me}_3\text{Si})_2\text{O}$. Inset: Solid-state molecular structure of **9** with 50% probability thermal ellipsoids drawn. Most hydrogen atoms are omitted for clarity.

Scheme 5. Reaction of **8** with Two Equivalents of MeCl, Generating **4** and Methylhydrosilanes (top)^a

^aYields determined via ^1H NMR spectroscopy by integration against an internal standard of $(\text{Me}_3\text{Si})_2\text{O}$. Reaction of **8** with an excess (7.3 equiv) of MeCl, generating **10** (bottom).

The silyl hydride complex **9** was prepared independently by treatment of $\text{Cp}^*(\text{IPr})\text{Co}$ in pentane solution with one equiv of SiH_4 . The solid-state molecular structure of **9** (Scheme 4, inset) displays a Co–Si bond ($d(\text{Co}–\text{Si}) = 2.2074(7)$ Å) that is longer than those in **7** and **A**, and does not appear to possess secondary $\text{Si}\cdots\text{H}–\text{Co}$ interactions ($d(\text{Si}–\text{H}) = 2.14(3)$ Å). The $^{29}\text{Si}–^1\text{H}$ HMBC NMR spectrum of **9** displays a cross-peak with $\delta_{\text{Si}} -41$ ppm and coupling to the silicon-bound protons ($\delta_{\text{H}} 3.65$ ppm, $^1J_{\text{SiH}} = 162.2$ Hz). These structural and spectroscopic features are consistent with the assignment of **9** as a classical silyl hydride complex.

Since silicides are of great significance as catalysts in the Direct Process for the synthesis of Me_2SiCl_2 from MeCl, related reactivity for silicide **8** was explored (Scheme 5, top). Upon introduction of two equivalents of MeCl to a benzene- d_6 solution of **8**, no reaction was evident under ambient conditions. However, heating at 60 °C for 24 h resulted in complete consumption of **8** to produce **4** (45% yield vs internal standard) and trace quantities of MeSiH_3 (2%),

Me_2SiH_2 (5%), and Me_3SiH (2%; all yields with respect to an internal standard), according to ^1H and $^{29}\text{Si}–^1\text{H}$ HMBC NMR spectroscopy. Trace amounts of methane and ethane were also evident in the product mixture, consistent with one-electron processes. Following thermolysis, a dark gray powder was deposited in the reaction vessel. An inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis of the solids following aqueous KOH digestion shows the presence of cobalt and silicon, suggesting that the material is a solid-state cobalt silicide. It is unlikely that the material is metallic cobalt, as trace contamination of reaction solutions by solid Co^0 renders solution NMR spectroscopy virtually impossible. Notably, no solids are deposited upon thermolysis of benzene- d_6 solutions containing **8** exclusively.

Control reactions were conducted to determine the identity of the active species responsible for generating methylhydrosilanes. Heating of a J. Young NMR tube containing SiH_4 , MeCl, and benzene- d_6 at 60 °C for 24 h did not result in the formation of any methylsilanes according to the ^1H NMR

spectrum of the product mixture. Also, complex **4** was treated with MeCl (one equiv) and SiH₄ (0.5 equiv) in benzene-*d*₆ solution. While no reaction was evident under ambient conditions, heating to 60 °C for 24 h generated traces of MeSiH₃ (2% yield vs internal standard), while most of **4** remained unreacted (39% consumed). Under these conditions, no evolution of methane or ethane was observed by ¹H NMR spectroscopy (benzene-*d*₆). The consumption of **4** under these conditions appeared to be related to the deposition of a crystalline blue solid in the reaction vessel, which was identified crystallographically as the zwitterion [κ^2 -(P,N)-PhB(CH₂P⁺Bu₂)(CH₂P⁺Bu₂Me)Pz]CoCl₂ (**10**). Complex **10** was independently prepared in good yield (82%) by thermolysis of a toluene solution containing **4** and 1 atm of MeCl. Notably, the addition of excess MeCl (7.3 equivalents) to **8** in benzene-*d*₆ also led to the formation of **10**, albeit in reduced yield (49%; Scheme 5, bottom).

These experiments point to a complex mechanism involving one-electron redox steps and the presence of at least two active species. However, the cobalt complexes appear to be essential for the formation of functionalized silane products, as thermolysis of a SiH₄/MeCl mixture alone did not result in any conversion of the starting materials (*vide supra*). The selectivity of the reaction between **8** and MeCl for methylhydrosilanes is another unusual feature, as silicide phases typically react with MeCl to produce Me_xSiCl_{4-x} (*x* = 1–4).^{7,8,52} The presence of nearby hydride ligands in **8** likely plays a role in driving the formation of Si–H as opposed to Si–Cl bonds. Additionally, the favorable formation of Co–Cl bonds in complexes **4** and **10** over the course of the reaction may be partly responsible for the observed product distribution.

CONCLUSIONS

A synthon for the 14-electron [BP₂^{tBu}Pz]Co^I fragment has allowed observations of double Si–H bond activations in molecular hydrosilanes. This was shown in the synthesis of base-stabilized silylene complex **7**, which introduces two hydride ligands at Co. Most significantly, this fragment provides a rational and direct synthetic route to a bimetallic silicide complex *via* a fourfold Si–H bond activation process. The product of this reaction, silicide complex **8**, possesses close Co–Si contacts and minimal interactions between the μ -silicon center and flanking hydride ligands. Coupled with spectroscopic and computational investigations, these features indicate a distinct lack of “SiH₄ character” in **8**. These investigations indicate that the [BP₂^{tBu}Pz] ligand has a marked influence on the properties of the Co–Si linkages, promoting a greater extent of bonding compared to related [BP₃^{iPr}] systems; the diminished steric demand of the [BP₂^{tBu}Pz] ligand is likely a critical factor in this regard.

The reaction to produce **8** demonstrates for the first time that SiH₄ can be directly converted to silicide structures without triggering additional rearrangement/decomposition processes in the ancillary ligand. This proof-of-concept reaction opens the door to transformations of SiH₄ to molecular silicides with a broad range of low-valent, unsaturated transition-metal complexes. The subsequent transformations of **8** with small-molecule substrates highlight the non-innocence of the hydride ligands, which readily migrate to form Si–H bonds. This feature, which is not immediately apparent from inspection of the spectroscopic and structural properties of **8**, is potentially exploitable for

producing functionalized hydrosilanes. Future efforts are geared toward learning how to control this reactivity for the {CoSiCo} unit.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.2c11569>.

Experimental methods, detailed syntheses, details of crystallography, details of calculations, EPR spectroscopy, NMR spectra, computed atomic coordinates (PDF)

Accession Codes

CCDC 2210561–2210572 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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