

Activations of all Bonds to Silicon (Si–H, Si–C) in a Silane with Extrusion of [CoSiCo] Silicide Cores

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Supporting Information

ABSTRACT: The [BP3^{iPr}]Co(I) synthon Na- $(\text{THF})_{6}\{[BP_{3}^{iPr}]\text{CoI}\}(\mathbf{1}, [BP_{3}^{iPr}] = \kappa^{3} - PhB(CH_{2}P^{i}Pr_{2})_{3}^{-})$ reacts with PhSiH₃ or SiH₄ to form unusual {[BP₂ $(SiH_2R)CoH_2$ = $Si = \{H_2Co[BP_3^{iPr}]\}$ species (R = Ph, 2a; $\vec{R} = H$, 2b; $[BP_2^{iPr}] = \kappa^2 - PhB(CH_2P^iPr_2)_2$ that result from activation of all Si-H and Si-C bonds in the starting silanes. Solution-spectroscopic data (multinuclear NMR, IR) for 2a,b, and the solid-state structure of 2a, indicate substantial Co=Si=Co multiple bonding and minimal interaction of the core Si atom with nearby hydride ligands. In the presence of 4-dimethylaminopyridine (DMAP), 1 reacts with PhSiH₃ to give $[BP_3^{iPr}]^{-1}$ $(H)_2$ CoSiHPh(DMAP) (3). Complexes 2a,b eliminate RSiH₃ upon thermolysis in the presence of DMAP to generate { $[BP_2^{iPr}]Co(NC_5H_3NMe_2)$ }=Si={H₂Co- $[BP_3^{iPr}]\}$ (4).

C rystalline and amorphous transition-metal silicide (M_xSi_y) phases are of immense technological importance for their roles in electronic materials,¹⁻⁶ and in processes that form and break chemical bonds to silicon.⁷⁻⁹ Elemental silicon is a reactant in the Direct Process, which is practiced on a large industrial scale to convert silicon and MeCl to Me₂SiCl₂, via intermediate copper silicide phases such as Cu₃Si.^{7,8,10,11} In addition, silicide phases mediate the reverse type of reaction, in which silanes (e.g., SiH₄, PhSiH₃, and Ph₂SiH₂) are used as the silicon source for producing nanoscaled silicon structures such as nanowires and nanocrystals.¹²⁻¹⁵ The latter processes involve the controlled crystallization of elemental Si at elevated temperatures (>300 °C), from a metal silicide phase formed by activation of Si—H and/or Si—C bonds.

A few studies have provided mechanistic information on the Direct Process, which is thought to proceed through silylene intermediates that engage in Si—C and Si—Cl bond-forming steps.^{7–11,16–19} However, detailed studies of the reverse process, in which a silicide is produced by Si—element bond activations in a silane, have not been well described.²⁰ This report describes a molecular model system in which the generation of Co-silicide complexes results from activations of all bonds in PhSiH₃ or SiH₄ by reaction with a Co(I) complex, Na⁺(THF)₆{[BP₃^{iPr}]CoI}⁻ (1), to produce dicobalt species containing unusual Co=Si=Co silicide cores. Notably, discrete MSiM linkages are rare²⁰ and their direct formation from silane starting materials is unprecedented.

Complex 1, which serves as a source of $[BP_3^{iPr}]Co(I)$, was readily prepared in good yields by reduction of $[BP_3^{iPr}]CoI$

with Na/Hg in THF (eq 1).²¹ The Evans method measurement of the magnetic moment of 1 (3.0 $\mu_{\rm B}$) is consistent with an S = 1 configuration, and the structure of 1 was crystallographically established (see Supporting Information).



Treatment of a THF solution of 2 equiv of 1 with 3 equiv of RSiH₃ (R = Ph, H) resulted in a rapid color change from purple to deep red. Workup of the reaction mixtures gave deposition of a white powder, presumably NaI, and $2a_{,b}$ as analytically pure, dark-red solids (eq 2).



Multinuclear NMR analyses of the crude reaction mixtures containing **2a**,**b** reveal the formation of 1 equiv of ${}^{i}Pr_{2}PCH_{2}SiH_{2}R$ (R = Ph, H, respectively, by ${}^{1}H$ NMR spectroscopy), thereby accounting for the loss of a $[BP_{3}^{iPr}]$ ligand side arm from **1**, as well as the requirement for 3 equiv RSiH₃ in affecting the complete consumption of **1**. The crude reaction mixture from **2a** also contains 1 equiv of benzene, apparently evolved from the Ph substituent of 1 equiv of PhSiH₃. Similarly, the crude reaction mixture for **2b** also contains ${}^{i}Pr_{2}PCH_{2}SiH_{3}$ and H₂ (see Supporting Information).

The solid-state molecular structure of **2a** (Figure 1a) exhibits relatively long Si—H ($d_{ave} = 1.77$ Å) and extremely short Co=Si distances (d(Co1-Si1) = 2.0737(7) Å; d(Co2-Si1) = 2.0750(7) Å), indicating multiple bonding in the central Co=Si=Co unit. The Co-H distances ($d_{ave} = 1.44$ Å) are similar to those of other crystallographically characterized terminal Co-H bond lengths ($d_{ave} = 1.42$ Å).²² The hydride positions, which were located in the difference map and refined isotropically, indicate that the silicon and hydrides do not form a tetrahedral SiH₄ unit (Figure 1b,c),

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Figure 1. (a) Solid-state molecular structure 2a; the isopropyl CH₃ groups, non *ipso*-C atoms of the Ph rings, and most H atoms have been omitted for clarity. (b) View of the core atoms of 2a along the Co—Si—Co axis. (c) Newman projection of the core atoms of 2a, viewed along the same axis as in panel b.

which would be expected in the case of limited Si—H activation, as in $[({}^{i}Pr_{3}P)_{2}(H)_{2}Ru]_{2}(\mu$ -SiH₄).²³ These solidstate data for **2a** are consistent with its assignment as possessing a Co=Si=Co core with minimal Si—H bonding.

The ¹H NMR spectrum of 2a exhibits hydride resonances at -13.0 and -10.5 ppm as featureless singlets, which belong to the $[BP_3^{iPr}]Co$ and $[BP_2^{iPr}]Co$ fragments, respectively (assignments by ${}^{31}P-{}^{1}H$ HMBC NMR). The ${}^{29}Si-{}^{1}H$ HMBC NMR spectrum of 2a reveals an extremely downfield-shifted Si nucleus at 350 ppm, which couples only to the hydride resonance at -13.0 ppm with a very small coupling constant of ${}^{1}J_{\text{SiH}} = 8$ Hz. The lack of strong Si—H coupling suggests little direct Si-H bonding character. The IR spectrum of 2a contains bands at 1812 and 1720 cm⁻¹, resulting from Co-H stretches of the $[BP_2^{iPr}](SiH_2Ph)CoH_2$ and $H_2Co[BP_3^{iPr}]$ fragments, respectively. The decreased energy of the 1720 cm⁻¹ band results from a weak bridging interaction with the central Si atom, consistent with the NMR data. The spectroscopic properties of 2b are very similar to those of 2a, though the ²⁹Si-¹H HMBC NMR spectrum exhibits very weak coupling constants for both sets of hydride ligands to the central Si (δ_{Si} = 354 ppm; ¹ J_{SiH} = 5, 7 Hz).

The Co=Si=Co cores of 2a and 2b result from exhaustive Si—H and Si—C bond activations in PhSiH₃ and SiH₄, and analysis of THF- d_8 solutions of the crude reaction mixtures reveal no detectable quantities of silane redistribution products, indicating that the formation of 2a,b is mechanistically distinct from the pathway giving rise to $[({}^{i}Pr_{3}P)_{2}(H)_{2}Ru]_{2}(\mu$ -SiH₄).^{23,24} Complexes 2a,b are the first silicide complexes to be prepared directly from silane precursors; a related species, $[Tp'(CO)_{2}Mo]\equiv$ Si—[Mo-(PMe₃)(CO)₂Tp'] (Tp' = HB(3,5-Me₂C₃N₂)₃⁻), was generated by a salt-metathesis reaction between Na[Tp'Mo-(CO)₂(PMe₃)] and 0.5 equiv of Br₂Si(SIPr) (SIPr = $C[N(2,6-iPr_{2}C_{6}H_{3})CH_{2}]_{2})$. The corresponding symmetrical silicide, { $[Tp'(CO)_{2}Mo]=$ Si= $[Mo(CO)_{2}Tp']$ ²⁻, was prepared by KC₈ reduction of the Mo≡Si—Mo starting material.²⁰

In the context of silicides as intermediates in bond-forming and -cleaving reactions of silanes, complexes 2a,b represent interesting molecular models for further investigation. Though solid-phase catalysts for these reactions require more forcing conditions to "decompose" the silane precursors,^{9,12,13} and presumably involve reactions of surface and bulk silicide species,⁹ the formation of **2a,b** shows that this process can occur under mild conditions via metal-mediated reactions.

To gain further insight into the mechanism leading to the formation of **2a**, THF solutions of complex **1** were treated with PhSiH₃, followed rapidly by addition of 4-dimethylaminopyridine (DMAP) as a trapping reagent. This led to isolation of the base-stabilized silylene complex $[BP_3^{,Pr}](H)_2CoSiHPh-(DMAP)$ (**3**, eq 3).



Figure 2. Solid-state molecular structure of 3; the isopropyl CH_3 groups, non *ipso*-C atoms of the Ph rings, and most H atoms have been omitted for clarity.

The solid-state molecular structure of 3 (Figure 2) reveals a distorted octahedral coordination environment about the Co atom with a Co—Si distance of 2.1524(8) Å, which is significantly longer than that observed in 2a. Complex 3 bears close structural similarities to $[BP_3^{Ph}]Ru(\mu-H)(\eta^3-H_2SiMePh-$ (DMAP)), though the coordination environments about Si are different in each case.^{25,26} The formation of 3 suggests that the unstabilized silylene dihydride, [BP3^{iPr}]Co(H)2=SiHPh, may be an intermediate in the mechanistic pathway resulting in 2a. This assumption is consistent with a possible mechanism involving condensation of $[BP_3^{iPr}]Co(H)_2$ SiHR (R = H, Ph) with a hydride species, e.g. $[BP_2^{iPr}]Co(H)(THF)_{x}$ to form a bimetallic species with a bridging silvne ligand, $\{[BP_2^{iPr}]\}$ CoH_2 - Si(R) = { $H_2Co[BP_3^{iPr}]$ }. This species would then react further to provide 2a,b (Scheme S1). Interestingly, treatment of toluene solutions of 1 with PhSiH₃ resulted in formation of $[BP_2^{iPr}]Co(H)_2(\kappa^2-Si,P-^iPr_2PCH_2SiHPh)$ (see Supporting Information) rather than 2a, suggesting that THF is important in stabilizing an intermediate that leads to the silicide product.

To examine further the bonding in the Co=Si=Co cores of **2a** and **2b**, density functional theory (DFT) computations (ω B97X-D3; def2-TSVP (Co, Si, P, hydride), def2-SVP (C,H) basis sets) were carried out using a model complex, {[BP₂^{Me}](SiH₂Ph)CoH₂}=Si={H₂Co[BP₃^{Me}]} (**2***;

в

 $[BP_x^{Me}] = PhB(CH_2PMe_2)_{xi}$, x = 2, 3). The computed Mulliken charges for the two Co atoms, as well as their respective hydride ligands, are essentially neutral, while the central Si atom bears a partial negative charge of -0.80. This is in contrast to monometallic silylene complexes, which possess substantial silylium (R_3Si^+) character.^{25,27,28} The computed Co—Si distances of 2.0252 and 2.0280 Å are somewhat shorter than those measured experimentally for **2a**, likely resulting from the diminished steric demands of the $[BP_x^{Me}]$ ligands. The Si—H and Co—H distances in the core of **2*** average 1.82 and 1.56 Å respectively, in agreement with the X-ray data for **2a** which indicate that the H atoms are closer to Co than to Si.

The MOs of **2*** include two Co—Si—Co σ -bonding orbitals derived from Si 3*s* and 3*p*_z orbitals, which interact with two Co $3d_z^2$ group orbitals to form two 3c–2e bonding levels (Figure 3, 1 σ and 2 σ). Two π -bonding orbitals result from



Figure 3. Simplified depiction of the bonding molecular orbitals of 2* (left), and visualization of the corresponding computed molecular orbitals of 2* (right).

interaction of Si $3p_x$ and $3p_y$ orbitals with sets of Co $3d_{xz}$ and $3d_{yz}$ orbitals, respectively (Figure 3, 1π and 2π). A Mulliken population analysis indicates that only the 2σ and 1π MOs include partial hydride 1s orbital character. These features are consistent with the structural and spectroscopic features of **2a,b**, which also indicate weak silicide Si—H interactions and substantial Co=Si=Co bonding.

The electrophilic Si centers of silylene complexes readily coordinate Lewis bases (L) at Si to form base-stabilized $M = SiR_2(L)$ adducts.^{27–29} In light of the calculated charge of the Si atom in 2*, it was anticipated that 2a,b may exhibit substantially divergent reactivity. Heating of benzene solutions

of **2a,b** in the presence of DMAP (for 65 °C for 4 and 10 h, respectively) affected their conversion to $\{[BP_2^{i^{p_r}}]Co-(NC_5H_3NMe_2)\}$ =Si= $\{H_2Co[BP_3^{i^{p_r}}]\}$ (4; eq 5). Crystals of

$$\begin{array}{c} \begin{array}{c} \begin{array}{c} R \\ H_{2}Si \\ BP_{2}{}^{P} \end{array} \\ H \\ H \\ 2a/b \end{array} \\ \begin{array}{c} B \\ H \\ 2a/b \end{array} \\ \begin{array}{c} DMAP \\ benzene, 65 \\ B \\ B \\ B \\ H; 10 \\ -RSiH_{3}, H_{2} \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ Ph \\ B \\ B \\ B \\ B \\ B \\ H; 10 \\ H \\ \end{array} \\ \begin{array}{c} N \\ H \\ B \\ B \\ B \\ B \\ B \\ B \\ H; 71\% \end{array}$$

4 suitable for X-ray diffraction analysis were grown from a saturated THF solution layered with $(Me_3Si)_2O$ and maintained at -30 °C, and its solid-state molecular structure is shown in Figure 4. Due to disorder of the central Si atom, the remaining hydride ligands could not be located in the difference map. Complex 4 results from the C—H activation of DMAP and eliminations of RSiH₃ and H₂ from the $[BP_2^{iPr}](RSiH_2)CoH_2$ units of 2a,2b.



Figure 4. Solid-state molecular structure of 4; the isopropyl CH_3 groups, non *ipso*-C atoms of the Ph rings and most H atoms, have been omitted for clarity.

The Co=Si bond lengths of 4 are similar to analogous distances in 2a, and the ²⁹Si-¹H HMBC NMR spectrum reveals a Si resonance at 294 ppm, with evidence of weak coupling to the remaining Co-H hydrogens of the H₂Co-[BP₃^{iPr}] unit (¹J_{SiH} = 5 Hz).

In conclusion, complex 1 facilitates extreme degrees of Si-H and Si-C bond activations in PhSiH₃ and SiH₄ to generate species (2a,b) bearing rare MSiM cores, and demonstrates a new reactivity mode for such silanes. Though the full mechanism for the formation of 2a,b remains unclear, trapping studies have resulted in the isolation of 3, which suggests that a silylene dihydride intermediate is involved. With respect to related processes that generate silicon nanowires from silane precursors, the facile formation of silicides 2a,b implies a greater role of the metal catalyst than simply seeding nanowire growth. Current efforts are focused toward developing novel MSiM silicide complexes bearing more reactive Si cores with chemically innocent and less sterically demanding supporting ligands. Such systems should be amenable to the systematic exploration of the reactivity and behavior of the core Si atom with small molecules and elements.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b04265.

Experimental and computational methods, synthesis of $[BP_3^{i^{p_r}}]Co(DMAP)$ and $[BP_2^{i^{p_r}}]Co(H)_2(\kappa^2-Si,-P^{-i}Pr_2PCH_2SiHPh)$; characterization data; and details of X-ray crystallography (PDF)

X-ray crystallography structure data (CIF) Structure model of **2*** (XYZ)

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Notes

The authors declare no competing financial interest.

CCDC 1910274–1910279 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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