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Low-Coordinate NHC-Cobalt(0)-Olefin Complexes: Synthesis, Structure, and Their Reactions with Hydrosilanes

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S Supporting Information

ABSTRACT: The one-pot reaction of CoCl₂ with 1 or 2 equiv of Nheterocyclic carbene (NHC) ligands, vinyltrimethylsilane (vtms), and 2 equiv of reducing reagents (KC8 or Na(Hg)) proved an effective protocol for the synthesis of three-coordinate NHC-cobalt(0)-olefin complexes, and by which the new low-coordinate cobalt(0) complexes $[(NHC)Co(vtms)_2]$ (NHC = 1,3-di(2',6'-diethylphenyl)-4,5-(CH₂)₄imidazol-2-ylidene (cyIDep), 6; 1,3-diadamantylimidazol-2-ylidene (IAd), 7) and $[(NHC)_2Co(vtms)]$ (NHC = 1-(2',4',6'-trimethy)phenyl)-3-cyclohexylimidazol-2-ylidene (IMesCy), 8; 1,3-dicyclohexylimidazol-2-ylidene (ICy), 9) were prepared in moderate yields and further characterized by spectroscopic methods. The NHC-cobalt(0)vtms complexes can serve as low-coordinate NHC-cobalt(0)



precursors to react with hydrosilanes. From the reactions of Ph₂SiH₂ with the corresponding NHC-cobalt(0)-vtms complexes, the cobalt silvl complexes $[(cyIDep)(H)Co(\mu-\eta^2:\eta^2-H_2SiPh_2)(\mu-\eta^2-HSiPh_2)_2Co(H)(cyIDep)]$ (10), $[(NHC)Co(\mu-\eta^2-SiHPh_2)_2-V_2(\mu-\eta^2-HSiPh_2)_2Co(H)(cyIDep)]$ Co(NHC)] (NHC = IPr, 13; IAd, 14), and [(IMesCy)₂Co(H)(SiHPh₂)] (15) were synthesized. Further reactivity studies established the thermal decomposition of 10 to give $[(cyIDep)Co(\mu-\eta^2-HSiPh_2)_2Co(cyIDep)]$ (11), H₂, and Ph₂SiH₂, the reaction of 11 with Bu^tNC (4.5 equiv) to afford [(cyIDep)(Bu^tNC)Co(μ - η ²-HSiPh₂)₂Co(CNBu^t)₃] (12) and cyIDep, as well as the conversion of 15 to a silyl-functionalized NHC-cobalt(II) complex 16 upon eliminating H₂. These cobalt silyl complexes have been characterized by single-crystal X-ray diffraction studies, NMR, absorption, and infrared spectroscopies, as well as elemental analyses. The diversified reaction outcomes demonstrate the rich reaction chemistry of low-coordinate NHC-cobalt(0) complexes.

■ INTRODUCTION

Cobalt(0) complexes are an important class of low-valent cobalt species, and their capability of performing oxidative addition with versatile covalent bonds forms the basis of many cobalt-mediated or catalyzed reactions.^{1,2} The most wellstudied cobalt(0) complex is probably the dinuclear complex $Co_2(CO)_8$ that can function as an equivalent of two molecules of the $17e^{-}$ species $Co(CO)_4$ to react with substrates, giving cobalt(I) complexes as the products of oxidative addition reactions.^{1,2} While the four-coordinate species $Co(CO)_4$ could only exist transiently, analogue phosphine complexes, e.g., $Co(PMe_3)_4$ and $Co(dppf)_2$ (dppf = 1,1'-bis-(diphenylphosphino)ferrocene), are isolable and their oxidative addition reactions with organic substrates have been extensively studied.³⁻⁹ As a notable recent example, Li showed that $Co(PMe_3)_4$ reacts with perfluorinated toluene to give the cobalt(II) benzyne complex $[Co(PMe_3)_3(\eta^2-C_6F_3(4-CF_3))]^9$ In addition to phosphine ligands, isocyanides are also known to stabilize four-coordinate cobalt(0) species. Using the bulky isocyanide ligand CNAr^{Mes2}, Figueroa achieved the synthesis of $[Co(CNAr^{Mes2})_4]$ (Ar^{Mes2} = 2,6-di(2',4',6'-trimethylphenyl)phenyl).¹⁰

While the known cobalt(0) complexes are dominated in numbers by the ones with the coordination numbers of five and four, there are a few low-coordinate cobalt(0) complexes scattering in the literature. In his seminal study on $Co(PMe_3)_{4}$ Klein briefly noted the preparation of the three-coordinate cobalt complex (PMe₃)₂Co(η^2 -PhNNPh) from the reaction of $Co(PMe_3)_4$ with PhNNPh.³ The structure of this threecoordinate complex has not been unambiguously established. More recently, Peters reported the first example of twocoordinate formal cobalt(0) complex [Co(Et₂-cAAC)₂] utilizing cyclic alkylaminocarbene ligand Et₂-cAAC (3,3-diethyl-5,5dimethyl-1-(2',6'-diisopropylphenyl)pyrrolidine-2-ylidene) as ligands.¹¹ We found that the combination of N-aryl-substituted NHCs with vinylsilane presents an effective ligand environment for the stabilization of three-coordinate cobalt(0) complexes [(IMes)Co(dvtms)] (1 in Chart 1, dvtms = divinyltetramethyldisiloxane) and $[(NHC)Co(vtms)_2]$ (2–5 in Chart 1, NHC = IMes, IPr, sIPr, cyIPr; vtms = vinyltrimethylsilane).¹²⁻¹⁴ Preliminary reactivity study revealed the reactions of these three-coordinate cobalt(0) complexes with organic

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Chart 1. Schematic Representations of the NHC-Cobalt(0)-Olefin Complexes and the Designations for NHCs



azides to furnish mononuclear cobalt(II) and cobalt(IV) imido complexes in the forms of (NHC)Co(NAr) and (NHC)Co-(NAr)₂, respectively. The results hint at the synthetic utility of this type of low-coordinate cobalt(0) complexes and prompt further exploration on their reactivities. In this regard, we report herein a systematic synthetic study on three-coordinate NHCcobalt(0)-vtms complexes featuring different NHCs, and, more intriguingly, the diversified reactivity of these low-coordinate cobalt(0) complexes toward hydrosilanes as shown below.

RESULTS AND DISCUSSION

Preparation of NHC-Cobalt(0)-vtms. In the previous study, we found that the vtms complex 2 exhibits higher reactivity over 1 toward bulky organic azide, which might arise from the ease of vtms in 2 to dissociate from the metal's coordination sphere than the chelate ligand dvtms in 1.¹³ Noted this, we targeted on cobalt(0)-vtms complexes bearing different NHCs. Employing the synthetic protocol used for 1–5, four new NHC-cobalt(0)-vtms complexes **6–9** (Chart 1) were prepared from the one-pot reactions of CoCl₂ with vtms, reducing-agents (KC₈ or Na(Hg)) and the corresponding NHC ligands in THF at room temperature. The reactions can be described by the stoichiometries shown in eqs 1 and 2 in Scheme 1. In practice, vtms was used in excess amounts to

Scheme 1. Stoichiometries of the Reaction for the Preparations of the NHC-Co(0)-vtms Complexes

C_0Cl_2 + NHC + 2 vtms + 2 M \longrightarrow (NHC) C_0 (vtms) ₂ + 2 MCl	(eq. 1)				
M = Na or K					
$C_0Cl_2 + 2 \text{ NHC} + vtms + 2 \text{ M} \longrightarrow (NHC)_2C_0(vtms) + 2 \text{ MCl}$	(eq. 2)				
M = Na or K					

ensure the moderate isolated yields (34-53%) of the cobalt(0) complexes. The ratio of NHC-to-vtms in **2**–**9** (1:2 or 2:1) seems to be determined by the steric property of the NHCs as the attempts to prepare $(cyIDep)_2Co(vtms)$ with bulky ligand on the stoichiometry of eq 2 furnished **6** as the sole isolable cobalt(0) product (Figure S40), and the reaction to prepare (IMesCy)Co(vtms)₂ according to the stoichiometry of eq 1 formed complex **8** (Figure S41). The relatively low isolated yields should be due to the formation of insoluble species, presumably cobalt black, in these reactions. It should also be mentioned that the use of olefin as coligand is important for the

stabilization of low-coordinate NHC-cobalt(0) complexes since the reduction of $(IMes)_2CoCl_2$ with 2 equiv of sodium amalgam in the absence of olefins resulted in the formation of the cobalt(II) cyclometalated NHC complex [Co-(IMes')₂].¹⁵

Complexes 6-9 are air- and moisture-sensitive. As isolated, 6 presents as a green crystalline solid resembling 1-5, the IAd complex 7 as blue crystals, and the bis(NHC) complexes 8 and 9 as red solids. They are soluble in low-polarity solvents, e.g., benzene, toluene, Et₂O, and THF. The measured solution magnetic susceptibilities of 6–9 (around 2.9 $\mu_{\rm B}$) are close to those of 1-5. The moments are larger than the spin-only value of 1.73 $\mu_{\rm B}$ for an S = 1/2 system, which might be due to strong spin-orbit coupling and/or the presence of trace paramagnetic impurities in the samples. The ¹H NMR spectra of these cobalt(0) complexes all exhibit broad paramagnetically shifted resonances (Figures S12–S14 and S17). The spectra of 6 and 7 in C_6D_6 show 13 and 8 sets of peaks, respectively, indicating their idealized C₂ molecular symmetry. There are 35 and 22 signals appearing on the corresponding ¹H NMR spectra of 8 and 9, consistent with their C_s molecular symmetry revealed by X-ray crystallographic studies (vide infra).

Figures 1, 2, and S1 depict the molecular structures of 7-9 established by single-crystal X-ray diffraction studies. The



Figure 1. Molecular structure of 7 showing 30% probability ellipsoids and a partial atom-numbering scheme. Hydrogens were omitted for clarity. Selected bond lengths (Å) and angles (deg): Co1-C1 1.929(4), Co1-C2 2.023(3), Co1-C3 2.050(3), C2-C3 1.429(4), C1-Co1-C2 90.45(8), C2-Co1-C2A 179.11(15), C2-Co1-C3A 138.03(11), C1-Co1-C3 131.52(8), C2-Co1-C3 41.08(10), C3A-Co1-C3 96.95(15).

trigonal planar core in the structure of 7 resembles those of reported NHC-cobalt(0)-olefin complexes 1 and 2 and also their analogue nickel, palladium, and platinum complexes (NHC)M(dvtms) (M = Ni, Pd, Pt).^{16–18} Characteristic structure data of 7 include a short Co–C(carbene) distance of 1.929(4) Å, a long C(olefin)–C(olefin) separation of 1.429(4) Å that is longer than the C=C bond in vinylsilane (1.32 Å),^{19,20} and the near perpendicular alignment of the C2–C3–C01–C2A–C3A plane toward the imidazole plane (dihedral angle of 88 deg). The bis(NHC) complexes 8 and 9 also feature trigonal planar cores with the Co–C(carbene)–C(carbene)–C(olefin)–C(olefin) atoms being coplanar. The distances of the two Co–C(carbene) bonds in 8 and 9 are comparable to each other (1.923(2) and 1.929(2) Å in average, respectively) and also close to those in 1, 2, and 7. The



Figure 2. Molecular structure of 8 showing 30% probability ellipsoids and a partial atom-numbering scheme. Hydrogens were omitted for clarity. Selected bond lengths (Å) and angles (deg): Co1-C1 1.922(2), Co1-C2 1.924(2), Co1-C3 1.979(2), Co1-C4 2.038(2), C3-C4 1.441(3), C1-Co1-C2 107.43(9), C1-Co1-C3 98.16(9), C1-Co1-C4 140.09(9), C2-Co1-C3 153.58(10), C2-Co1-C4 111.93(9), C3-Co1-C4 42.02(9).

C(olefin)–C(olefin) distances (1.441(3) and 1.443(2) Å for 8 and 9, respectively) are marginally longer than that in 7 (1.429(4) Å). The Co–C(olefin) distances (1.979(2) and 2.038(2) Å in 8; and 1.986(2) and 2.013(2) Å in 9) are slightly shorter than those in 7 (2.023(3) and 2.050(3) Å). These data hint at the enhanced 3d(Co)-to- π^* (olefin) back-donation in the (NHC)₂Co(vtms) complexes as compared that in (NHC)-Co(vtms)₂.

The Reactions of (NHC)Co(vtms)₂ with Hydrosilanes. With the series of three-coordinate cobalt(0) complexes in hands, we further investigated their reactions with hydrosilanes. These cobalt(0) complexes could react with the primary hydrosilane PhSiH₃ to give diamagnetic species featuring high-field ¹H NMR signals attributable to cobalt-bound hydride. However, the attempts to isolate the resulting cobalt-containing products were generally unsuccessful. The exploration on the reactions with tertiary hydrosilanes indicated the inertness of these NHC-cobalt(0)-vtms complexes toward Ph₃SiH, Et₃SiH, and (EtO)₃SiH at ambient temperature, probably due to steric reason. On the other hand, the study on the reactions of NHC-cobalt(0)-vtms with the secondary hydrosilane Ph₂SiH₂ is fruitful, leading to the isolation of diverse cobalt silyl complexes.

The reaction of $[(cyIDep)Co(vtms)_2]$ (6) with an excess amount of Ph₂SiH₂ (3.4 equiv) in diethyl ether at room temperature gave the dinuclear complex $[(cyIDep)(H)Co(\mu-\eta^2:\eta^2-H_2SiPh_2)(\mu-\eta^2-HSiPh_2)_2Co(H)(cyIDep)]$ (10) in 87% isolated yield as a yellow solid (Scheme 2). Complex 10 has been fully characterized by ¹H, ¹³C, and ²⁹Si NMR spectroscopies, infrared spectroscopy, and elemental analysis (C, H, and N). In addition to the dinuclear cobalt complex 10, the hydrosilylation product Me₃SiCH₂CH₂SiHPh₂ was also detected by GC-MS as the byproduct. However, neither 6 nor 10 proved efficient catalyst for the hydrosilylation of vtms with Ph₂SiH₂.

Figure 3 shows the core structure of 10. At a glance, the dinuclear complex shows an idealized C_2 molecular symmetry with each cobalt center being coordinating with a cyIDep ligand and three bridging Ph₂SiH₂ moieties. The long Si…Si separations (3.19, 3.12, and 3.60 Å for Si1–Si2, Si1–Si3, and Si2–Si3, respectively) indicate the absence of Si–Si bond between the silane moieties.^{21–23} The Co–Co distance

Scheme 2. Reactions of $(NHC)Co(vtms)_2$ with Ph_2SiH_2 and the Further Conversions of the Resulting Silyl Complexes



Figure 3. Core molecular structure of 10 showing 30% probability ellipsoids and a partial atom-numbering scheme. Except the carbon atoms connecting with silicon and cobalt atoms, the phenyl groups and the NHC moieties are omitted for clarity. Selected bond lengths (Å): Co1-Co2 2.578(1), Co1-Si1 2.325(1), Co1-Si2 2.362(1), Co1-Si3 2.255(1), Co1-C1 1.932(3), Co2-Si1 2.340(1), Co2-Si2 2.246(1), Co2-Si3 2.366(1), Co2-C2 1.929(3), Co1-H1B 1.53(3), Co1-H3A 1.42(3), Co1-H2 1.55(3), Co2-H3B 1.57(3), Co2-H1A 1.53(3), Co2-H 1.38(3), Si1-H1A 1.60(3), Si1-H1B 1.62(3), Si2-H2 1.55(3), Si3-H3B 1.64(3).

(2.578(1) Å) is longer than the separation found in dinuclear cobalt complexes (2.47-2.52 Å)²⁴ and suggests the weak Co-Co interaction in the molecule. A close examination on the interactions of the silane moieties with the cobalt centers then revealed that one of the silane bridges could be viewed as a μ - η^2 : η^2 -H₂SiPh₂ ligand (Si1 in Figure 3), and that the other two (Si2 and Si3 in Figure 3) are best described as silvl ligands [μ - η^2 -SiHPh₂]⁻. The μ - η^2 : η^2 -H₂SiPh₂ ligand has the comparable Si1-Co1 and Si1-Co2 distances of 2.325(1) and 2.340(1) Å, the equal H1B-Co1 and H1A-Co2 distances of 1.53(3) Å, and the Si1-H1A and Si1-H1B distances of 1.60(3) and 1.62(3) Å. These Si-H separations locate on the short end of typical η^2 -(Si-H)-transition-metal complexes (1.6–1.9 Å).² The Co-Si distances are apparently longer than those of the reported cobalt silvl complexes, e.g., 2.246(3) Å in $[(\eta^5 - C_5H_4CH_2CH_2PBu_2^t)(H)CoSiHPhMe]$,²⁶ 2.256–2.261 Å in $[Cp*Co(SiHPh_2)_2(H)_2]^{27}$ and 2.228(1) Å in [(NHC-silyl-NHC)Co (N_2)].²⁸ Different from the bridging hydrosilane ligand, each of the two silvl ligands $[\mu - \eta^2 - \text{SiHPh}_2]^-$ has

nonequivalent Si–Co separations toward the two cobalt center (2.362(1) and 2.246(1) Å for Si2; 2.255(1) and 2.366(1) Å for Si3). The shorter Co–Si distances are consistent with those of the aforementioned cobalt silyl complexes, whereas the longer ones are comparable to those of the reported complexes having η^2 -(Si–H)-Co interactions. In addition, the H…Co distances of these η^2 -(Si–H)-Co interactions (1.55(3) and 1.57(3) Å) are also consistent with those of the reported ones.²⁵ In contrast to these H…Co separations, the distances of Co1–H3A and Co2–H of the hydride ligands in **10** (1.42(3) and 1.38(3) Å) are shorter and typical of Co–H bonds (1.40–1.50 Å).^{26,27,29–31} In accord with this, the infrared spectrum of **10** in solid state exhibits resonances at 1944 cm⁻¹, assignable to the Co–H stretching resonances.

While the crystal structure data suggest the identity of 10 as a dinuclear cobalt(II) silyl hydride (B in Chart 2), its solution

Chart 2. Canonical Forms of 10



NMR data indicate the presence of fluxional process in solution phases. Complex 10 is diamagnetic in nature. Its C₆D₆ solution exhibits a characteristic high-field ¹H NMR peak at -8.97 ppm, assignable to cobalt-bound hydride. Peak integrations suggest a cyIDep/hydride ratio of 1:3. The high-field signal does not show decoalescence even when the toluene- d_8 solution of 10 was cooled to -60 °C (Figure S30), hinting at fast conversion between the Co···(η^2 -H-Si) and H–Co–Si forms. There is only one ${}^{29}Si{}^{1}H$ NMR signal at 64.5 ppm in the spectrum of 10. This signal is slightly broaden in the ${}^{29}Si$ NMR spectrum, and a small J_{Si-H} value of 18 Hz could be estimated by the hydride signal on the ¹H NMR spectrum. The chemical shift of the ²⁹Si NMR signal is much different from those of the reported diamagnetic bridging diarylsilylene complexes and bridging diarylhydrosilyl complexes, e.g., $[Cp*Ru(\mu-H)_2(\mu_2-SiPh_2)_2]$ RuCp*] (110 ppm),³² [(Me₃P)₃Pt₃(μ_2 -SiPh₂)₃] (279 ppm), $[(Cy_3P)Pt(\mu-SiPh_2)(\mu-SiH_2Et_2)Pt(PCy_3)] (230 \text{ ppm}),^{34}$ $[(dppm)Ru_2(CO)_6(\mu_2-Si(p-tolyl)_2)]$ (173 ppm),³⁵ [(dppm)- $\operatorname{Ru}_{2}(\operatorname{CO})_{5}(\mu_{2}-\operatorname{Si}(p-\operatorname{tolyl})_{2})(\operatorname{H})(\operatorname{SiH}(p-\operatorname{tolyl})_{2})]$ (150 ppm), $\left[(dppm)Ru_2(CO)_4(\mu_2-Si(p-tolyl)_2)(H)_2(SiH(p-tolyl)_2)_2\right] (155)$ ppm),³⁵ [(Cy₃P)Pt(μ -SiHPh₂)(μ -SiHEt₂)Pt(PCy₃)] (196 ppm),³⁴ and [(IPr₂H₂)Ni(μ -HSiPh₂)₂Ni(IPr₂H₂)] (118 ppm, $IPr_2H_2 = 1,3$ -diisopropylimidazol-2-ylidene).³⁶ On the basis of these NMR data, we speculate that the fluxional process of 10 in solution might operate between the structures of A and B with little contribution C and D that contain silylene bridges (Chart 2).

The formation of **10** in the reaction of $[(cyIDep)Co(vtms)_2]$ (6) with Ph₂SiH₂ differs from that of the reaction of the nickel(0) complex $[(IPr_2H_2)Ni(COD)Ni(IPr_2H_2)]$ with Ph₂SiH₂.³⁶ In the latter case, the silyl-bridged dinickel complex $[(IPr_2H_2)Ni(\mu-HSiPh_2)_2Ni(IPr_2H_2)]$ was formed. Noting this, we further examined the thermal decomposition reaction of **10** with the aim to achieve the synthesis of analogue cobalt(I) silyl complex. Indeed, heating the solid of **10** at 120 °C under a vacuum could result in the production of the dinuclear cobalt(I) silyl complex $[(cyIDep)Co(\mu-\eta^2-HSiPh_2)_2Co-(cyIDep)]$ (**11**) (Scheme 2). In this decomposition reaction, Ph₂SiH₂ and H₂ are the probable byproducts as heating a solution of **10** with styrene led to the formation of ethylbenzene and the Ph₂HSiCH₂CH₂Ph (Figure S39) along with **11**. The two organic products should come from cobalt-mediated hydrogenation and hydrosilylation of styrene.

The molecular structure of 11 (Figure 4) resembles those of the group 10 complexes $[(L)M(\mu-SiHR_2)M(L)]$ (M = Ni, Pd,



Figure 4. Molecular structure of 11 showing 30% probability ellipsoids and a partial atom-numbering scheme. Besides the hydrogen atoms on silicon, all other hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): Co1–Co1A 2.599(1), Co1–C1 1.931(2), Co1–Si1 2.246(1), Co1–Si1A 2.336(1), Co1–H 1.58(3), Si1–H 1.66(3), Si1A–Co1–Co1A 53.829(16), Si1–Co1–Si1A 110.926(19), C1–Co1–Si1 111.00(6), C1–Co1–Si1A 137.94(6).

Pt; L = PCy₃, IPr₂H₂; R = alkyl and aryl).^{34,36-38} It contains a Co_2Si_2 diamond core with a Co-Co distance of 2.599(1) Å, a Si-Si distance of 3.78 Å, and nonequivalent Co-Si distances of 2.246(1) and 2.336(1) Å. The Co-Si distances, in addition with the distances of Co1-H and Si1A-H (1.58(3) and 1.66(3) Å, respectively), suggest the 3c-2e bond nature of the Co-(η^2 -H-Si) interactions. The paramagnetic nature of 11 (μ_{eff} = 2.7 $\mu_{\rm B}$ in C₆D₆ at room temperature) made the assignment of the Co-H-Si signal in its ¹H NMR spectrum difficult. Fortunately, the further reaction of 11 with Bu^tNC (4.5 equiv) could furnish the diamagnetic complex [(cyIDep)- $(Bu^tNC)Co(\mu-HSiPh_2)_2Co(CNBu^t)_3$ (12) (Scheme 2), whose ¹H NMR spectrum shows a hydride signal at -5.3ppm. Comparing the molecular structures of 12 (Figure 5) and 11 indicated that the reaction has rendered in the dissociation of a cyIDep ligand, which was also detected by ¹H NMR experiment. The two hydrosilyl bridges in 12 are coordinating with one cobalt center (Co2) via Co–Si σ -bond and the other cobalt center (Co1) via 3c-2e Co-(η^2 -H-Si) interactions. The Co-H and Co-Si distances of the 3c-2e bonds are similar to those in 11. Being consistent with the solid state structure, the 29 Si NMR spectrum of 12 measured on its C₆D₆ solution exhibits a peak at 101 ppm with a large Si–H coupling constant of $J_{Si-H} = 80$ Hz. The ²⁹Si NMR data are comparable to that of $[(IPr_2H_2)Ni(\mu-HSiPh_2)_2Ni(IPr_2H_2)]$ (118 ppm and 63 Hz) reported by Radius.³⁶ According to these data, we tentatively



Figure 5. Molecular structure of 12 showing 30% probability ellipsoids and a partial atom-labeling scheme. Besides of the hydrogen atom connecting with Si, all the other hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): Co1-Co2 2.657(1), Co1-Si1 2.303(2), Co1-Si2 2.283(2), Co1-C1 1.934(4), Co1-C2 1.761(4), Co1-H2 1.60(6), Co1-H1 1.62(4), Co2-Si1 2.288(2), Co2-Si2 2.286(2), Co2-C3 1.827(4), Co2-C4 1.802(4), Co2-C5 1.830(4), Si2-Co1-Si1 89.31(4), C1-Co1-Si1 131.15(12), C1-Co1-Si2 126.44(11), C2-Co1-C1 95.93(16), C3-Co2-Co1 115.64(12), C4-Co2-Co1 135.38(15), C5-Co2-Co1 115.35(13).

assigned **12** as a silyl-bridged Co(0)-Co(II) complex (cyIDep)(Bu^tNC)Co⁰(μ -HSiPh₂)₂Co^{II}(Bu^tNC)₃.

The cobalt(0) complexes containing more steric demanding NHCs $[(IPr)Co(vtms)_2]$ (3) and $[(IAd)Co(vtms)_2]$ (7) are also reactive toward Ph₂SiH₂. The reactions of 3 and 7 with Ph₂SiH₂ (2 equiv) occurred readily at room temperature, and from which the brown crystalline solids of $[(NHC)Co(\mu HSiPh_2)_2Co(NHC)$ (NHC = IPr, 13; IAd, 14) were isolated in 26% and 47% yields, respectively (Scheme 2). Complexes 13 and 14 were characterized by infrared spectroscopy and elemental analysis. The molecular structure of 13 was further confirmed by X-ray crystallographic study (Figure S2). As listed in Table 1, the Co₂Si₂ diamond core in 13 has the corresponding Co-Si distances comparable to those of 11. Interestingly, the Co–Co distance in 13 (2.497(1) Å) is shorter than that those in 11 by ca. 0.10 Å. The origin of the short Co-Co distance in 13 is unclear. A plausible cause might be the pronounced intramolecular London dispersion force in 13 due

Table 1. Selected Bond Distances (Å) of the Dinuclear Cobalt Complexes 10–13

	10	11	12	13
Co-Co	2.578(1)	2.599(1)	2.657(1)	2.497(1)
Si-Si	3.19, 3.12, 3.60	3.78	3.22	3.80
Co-SiA ^a	2.325(1), 2.362(1)	2.336(1)	2.303(2), 2.283(2)	2.317(1)
	2.340(1), 2.366(1)			
Co-SiB ^b	2.255(1), 2.246(1)	2.246(1)	2.288(2), 2.286(2)	2.228(1)
Co-C(carbene)	1.932(3), 1.929(3)	1.931(2)	1.934(4)	1.927(2)

"Co-Si distances of the 3c-2e Co-H-Si interactions. ^bCo-Si distances of Co-SiPh₂H.

to the presence of the isopropyl groups on the NHC ligands.³⁹ Being supportive to this speculation, **13** exhibits poor solubility in common low-polarity solvents (benzene, Et_2O , and THF), which prevented further characterization by solution NMR spectroscopies. Complex **14** shows improved solubility over **13**, and its ¹H NMR spectrum (Figure S27) resembles that of **11** with broad paramagnetically signals in the range 12 to -9 ppm. In addition, the absorption spectra of **11** and **14** (Figures S8 and S10) are also similar.

The Reactions of $(NHC)_2Co(vtms)$ with Ph_2SiH_2 . Being different from the aforementioned reactions affording dinuclear cobalt complexes, the interactions of $(NHC)_2Co(vtms)$ with Ph_2SiH_2 gave mononuclear cobalt complexes. Treatment of $[(IMesCy)_2Co(vtms)]$ (8) with Ph_2SiH_2 (2 equiv) in Et₂O at -20 °C resulted in a reddish brown solution, and from which yellow crystals of the cobalt(II) complex $[(IMesCy)_2Co(H)-(SiHPh_2)]$ (15) were isolated in 21% yields when performing recrystallization at low temperature (-30 to -20 °C) (Scheme 3). As shown in Figure 6, 15 displays a square planar





Figure 6. Molecular structure of 15 showing 30% probability ellipsoids and a partial atom-labeling scheme. Except the hydrides on cobalt and silicon atoms, all other hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): Co1-H 1.47(4), Co1-Si1 2.249(1), Co1-C1 1.937(4), Co1-C2 1.909(4), C1-Co1-Si1 157.9(1), C2-Co1-Si1 97.2(1), C2-Co1-C1 104.9(2).

coordination geometry with the cobalt center coordinating with one terminal hydride ligand, one hydrosilyl ligand [SiHPh₂]⁻, and two IMesCy ligands in a *cis*-form. The short Co–H and Co–Si distances (1.47(4) and 2.249(1) Å, respectively) and long Si–H separation (2.17 Å) suggest the cobalt(II) silyl hydride nature of **15** that is analogous to the group 10 complexes *cis*-[L₂M(H)(SiHPh₂)] (M = Pt, L = Cy₃P, Ph₃P; M = Ni, L = IPr₂H₂; M = Ni, L₂ = 1,2-bis(di(*tert*-butyl)phosphino)ethane).^{40–42} A NMR scale reaction of [(ICy)₂Co-(vtms)] (**9**) with Ph₂SiH₂ indicated the formation of similar paramagnetic species as 15 (Figures S31 and S32). But, the attempts to isolate the species via preparative scale reactions were unsuccessful. The distinct outcome of the reactions of $(NHC)Co(vtms)_2$ and $(NHC)_2Co(vtms)$ with Ph_2SiH_2 should associate with the different steric nature of the NHC-cobalt fragments (NHC)Co versus $(NHC)_2Co$. The latter fragment might be more sterically shielding, preventing the dimerization of the mononuclear cobalt silyl species $(NHC)_2Co(H)$ - $(SiHPh_2)$.

Complex 15 is unstable at room temperature. In $C_6D_{6^j}$ its decomposition could give rise to the cobalt(II) complex [(cyCSi)Co(IMesCy')] (16) that features a silyl-functionalized NHC chelate (cyCSi) and a cyclometalated IMesCy ligand (IMesCy') (Scheme 3 and Figure S33). Alternatively, 16 could be synthesized directly from the reaction of 8 with Ph_2SiH_2 (Scheme 3). As shown in Figure 7, the two carbene moieties in



Figure 7. Molecular structure of 16 showing 30% probability ellipsoids and a partial atom-labeling scheme. Hydrogen atoms were omitted for clarity. Selected bond length (Å) and angles (deg): Co1–Si1 2.292(1), Co1–C1 1.906(2), Co1–C2 1.902(2), Co1–C3 2.051(2), C1–Co1–Si1 96.28(7), C1–Co1–C3 82.33(10), C2–Co1–Si1 89.60(7), C2–Co1–C1 172.21(10), C2–Co1–C3 93.44(10), C3–Co1–Si1 163.82(7).

16 are in *trans*-configuration. The silyl side arm has the Co–Si distance of 2.2918(7) Å and the Si–Co–C(benzyl) angle of 163.82(7) deg, which are in analogy to the reported complexes $[(MesCSi)M(IMes')]^{15,43}$ (M = Fe, Co; IMes' denoted for the cyclometalated IMes ligand) prepared from the reactions of the bis-cyclometalated IMes complexes $[M(IMes')_2]$ with hydrosilanes. The mechanism for the conversion of 15 to 16 should be complicated. As the processes of C–H bond activation and Si–C bond formation must be involved in the conversion, we speculate that cobalt silylene $(IMesCy)_2Co(SiPh_2)$ (E in Scheme S1) or cyclometalated NHC cobalt silyl (IMesCy)Co-(IMesCy')(SiHPh_2) (F in Scheme S1) are the probable intermediate. The validation of these routes needs further study.

CONCLUSIONS

In this study, we showed that the one-pot reaction of $CoCl_2$ with NHC, vtms, and alkali metals is a useful protocol for the preparation of three-coordinate NHC-cobalt(0)-olefin complexes. Depending on the steric property of NHC ligands, either (NHC)Co(vtms)₂ (NHC = IPr, sIPr, cyIPr, cyIDep, IMes, IAd) or (NHC)₂Co(vtms) (NHC = IMesCy, ICy) can be obtained from the reaction using one or two equiv of NHCs (relative to $CoCl_2$). These paramagnetic NHC-cobalt(0) complexes are characterized by ¹H NMR and UV–vis

spectroscopies, single-crystal X-ray diffraction studies, as well as elemental analyses. They represent the rare examples of lowcoordinate cobalt(0) complexes.

Examining the reactions of these NHC-cobalt(0)-olefin complexes with Ph₂SiH₂ revealed their capability of serving as NHC-cobalt(0) precursors to perform oxidative addition reactions with Si-H bonds. The reactions of [(cyIDep)Co- $(vtms)_2$, $[(IPr)Co(vtms)_2]$, $[(IAd)Co(vtms)_2]$, and $[(IMesCy)_2Co(vtms)]$ with excess amounts of Ph₂SiH₂ give $[(cyIDep)(H)Co(\mu-H_2SiPh_2)(\mu-HSiPh_2)_2Co(H)(cyIDep)]$ (10), $[(IPr)Co(\mu-SiHPh_2)_2Co(IPr)]$ (13), $[(IAd)Co(\mu SiHPh_2_2Co(IAd)$ (14), and [(IMesCy)_2Co(H)(SiHPh_2)] (15), respectively. Complex 10 is the adduct of three molecules of Ph₂SiH₂ with two (cyIDep)Co fragments. NMR characterization on the solutions of 10 suggest the presence of the fluxional process between the Co... $(\eta^2$ -H-Si) and H–Co–Si forms. Complexes 13 and 14 are dinuclear cobalt(I) silvl complexes with Co...(η^2 -H-Si) interactions, and might result from the reductive elimination of H₂ from their dinuclear cobalt(II) hydride silvl precursors (NHC)(H)Co(μ -SiHPh₂)₂-Co(H)(NHC). Complex 15 is a cobalt(II) silvl hydride and can be viewed as the oxidative addition of $(IMesCy)_2Co(0)$ with Ph₂SiH₂. The diversified reaction outcomes demonstrate the effect of the steric property of the NHC ligands on the reactivity of the NHC-cobalt(0)-olefin complexes. With these understandings, we are now exploring the catalytic applications of these NHC-cobalt(0)-olefin complexes in hydrosilylation reactions.

EXPERIMENTAL SECTION

General Procedures. All experiments were performed under an atmosphere of dry dinitrogen or argon with the rigid exclusion of air and moisture using standard Schlenk techniques, or in a glovebox. All organic solvents were dried with a solvent purification system (Innovative Technology) and bubbled with dry N₂ gas prior to use. Ph_2SiH_2 was further dried by 4 Å molecular sieves. 1,3-Bis(2',6'diethylphenyl)imidazol-2-ylidene) (cyIDep),⁴⁴ 1,3-bis-adamantyl-imidazol-2-ylidene) (IAd),⁴⁵ [HIMesCy]Cl,⁴⁶ 1,3-bis-cyclohexyl-imidazol-2-ylidene (ICy),⁴⁷ KC₈,⁴⁸ and 3¹³ were prepared according to previous literatures. All other chemicals were purchased from either Strem or J&K Chemical Co. and used as received unless otherwise noted. ¹H, ¹³C and ²⁹Si NMR spectra were recorded on Agilent 400 MHz or Agilent 600 MHz spectrometer. Chemical shifts were reported in units with references to the residual protons of the deuterated solvents for proton chemical shifts, the ¹³C of deuterated solvents for carbon chemical shifts, and the ²⁹Si of SiMe₄ for silicon chemical shifts. The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra required the inverse gated $^1\text{H-decoupling}$ techniques. Elemental analyses were performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS). Magnetic moments were measured by the method originally described by Evans with stock and experimental solutions containing a known amount of a (CH₃)₃SiOSi(CH₃)₃ standard.^{49,50} Absorption spectra were recorded with a Shimadzu UV-3600 UV-vis-NIR spectrophotometer. IR spectra were recorded with a NICOLET AVATAR 330 FT-IR spectrophotometer.

X-ray Structure Determination. Diffraction-quality crystals were obtained as $7-9,10\cdot 2C_7H_8$, **11**, **12**, **13**· C_6H_6 , **15**· Et_2O , and **16** from recrystallizations in Et₂O, Et₂O, Et₂O, toluene/*n*-hexane, THF/ toluene, *n*-pentane, benzene, Et₂O, and Et₂O respectively, at room temperature or -20 °C (**12** and **15**). Crystals were coated with Paratone-N oil and mounted on a Bruker APEX CCD-based diffractometer equipped with an Oxford low-temperature apparatus. Data were collected at 140(2) K. Cell parameters were retrieved with SMART software and refined using SAINT software on all reflections. Data integration was performed with SAINT, which corrects for Lorentz polarization and decay. Absorption corrections were applied

using SADABS.⁵¹ Space groups were assigned unambiguously by analysis of symmetry and systematic absences determined by XPREP. All structures were solved and refined using SHELXTL.⁵² Metal and first coordination sphere atoms were located from direct-methods Emaps. Non-hydrogen atoms were found in alternating difference Fourier synthesis and least-squares refinement cycles and during final cycles were refined anisotropically. Hydrogen atoms on the coordination sphere of cobalt were located from the difference maps and refined. Other hydrogen atoms were placed in calculated positions employing a riding model. CCDC 1560269–1560277 contain the supplementary crystallographic data for these complexes. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Preparation of IMesCy. To the suspension of [HIMesCy]Cl (3.00 g, 9.84 mmol) in THF (50 mL) was added KOBu^{*t*} (1.44 g, 12.8 mmol). After stirring at room temperature for 14 h, the reaction was subjected to a vacuum to remove the volatiles. The residue was extracted by a mixture of *n*-hexane and toluene (50/50, 100 mL), and filtered. The filtrate was then subjected to vacuum to remove the volatiles, affording the free NHC ligand IMesCy as a white solid (2.00 g, 76%). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ (ppm) 6.79 (s, 2H), 6.68 (s, 1H), 6.47 (s, 1H), 4.25–4.05 (m, 1H), 2.21–2.03 (m, 11H), 1.76–1.56 (m, 4H), 1.52–1.40 (m, 1H), 1.26–1.10 (m, 2H), 1.10–0.95 (m, 1H). ¹³C NMR (101 MHz, C₆D₆, 25 °C): δ (ppm) 216.18 (br, C_{carbene}), 139.70, 136.97, 135.51, 129.05, 119.90, 116.49, 59.96, 35.28, 25.95, 25.85, 21.04, 18.17.

Preparation of [(cylDep)Co(vtms)₂] (6). To a mixture of cylDep (1.60 g, 4.14 mmol) and CoCl_2 (0.54 g, 4.11 mmol) was added THF (30 mL). After stirring at room temperature for 3 h, vinyltrimethylsilane (1.30 g, 13.0 mmol) and KC₈ (1.30 g, 9.62 mmol) were added to the resulting blue solution. After further stirring at room temperature for 21 h, the mixture turned into to a dark green suspension. After filtration, the filtrate was subjected to a vacuum to remove the solvent. The green residue was then extracted by *n*-hexane (20 mL), and filtered. The filtrate was standing at room temperature to evaporate the solvent, by which green crystals of 6 were obtained (0.92 g, 35%). ¹H NMR (400 MHz, C_6D_{67} 20 °C): δ (ppm) 70.64 ($v_{1/2}$ = 1679 Hz), 52.54 ($v_{1/2}$ = 1234 Hz), 44.51 ($v_{1/2}$ = 1709 Hz)), 12.31 ($v_{1/2}$ = 138 Hz), 5.47 ($v_{1/2}$ = 15 Hz), 5.09 ($v_{1/2}$ = 34 Hz), 4.26($v_{1/2}$ = 34 Hz), 3.68 ($v_{1/2}$ = 18 Hz), -0.66 ($v_{1/2}$ = 22 Hz), -1.95 ($v_{1/2}$ = 25 Hz), $-3.40 (v_{1/2} = 84 \text{ Hz}), -3.64 (v_{1/2} = 24 \text{ Hz}), -5.52 (v_{1/2} = 22 \text{ Hz}).$ Magnetic susceptibility (C₆D₆, 20 °C): $\mu_{\text{eff}} = 2.8(1) \mu_{\text{B}}$. Anal. Calcd for $C_{37}H_{58}CoN_2Si_2$: C, 68.79; H, 9.05; N, 4.34; Found: C, 68.86; H, 9.24; N, 4.60. Absorption spectrum (THF): λ_{max} (ε , M⁻¹ cm⁻¹) = 254 (17970), 646 (70), 829 (30) nm.

Preparation of [(IAd)Co(vtms)₂] (7). To a mixture of IAd (0.50 g, 1.47 mmol) and $CoCl_2$ (0.19 g, 1.49 mmol) was added THF (15 mL). After stirring at room temperature for 4 h, vinyltrimethylsilane (0.45 g, 4.49 mmol) and KC_8 (0.40 g, 2.96 mmol) were added. The mixture gradually changed to blue suspension after stirring at room temperature for 20 h. After filtration, the filtrate was subjected to vacuum to remove the solvent. The green residue was then extracted by Et₂O (10 mL), and filtered. The filtrate was standing at room temperature to evaporate the solvent, by which blue crystals of 7 were obtained (0.34 g, 38%). ¹H NMR (400 MHz, THF- d_{8} , 19 °C): δ (ppm) 13.84 ($v_{1/2}$ = 484 Hz), 11.69 ($v_{1/2}$ = 156 Hz), 2.28 ($v_{1/2}$ = 76 Hz), $-1.06 (v_{1/2} = 187 \text{ Hz}), -4.06 (v_{1/2} = 172 \text{ Hz}), -5.51 (v_{1/2} = 157 \text{ Hz})$ Hz), -16.74 ($v_{1/2}$ = 1908 Hz), -31.10 (very br). Magnetic susceptibility (C₆D₆): $\mu_{\text{eff}} = 2.9(1) \mu_{\text{B}}$. Anal. Calcd for C₃₃H₅₆CoN₂Si₂: C, 66.51; H, 9.47; N, 4.70; Found: C, 66.57; H, 9.94; N, 4.78. Absorption spectrum (THF): λ_{max} (ε , M⁻¹ cm⁻¹) = 252 (15450), 592 (40), 672 (40) nm.

Preparation of [(IMesCy)₂Co(vtms)] (8). To the solution of IMesCy (1.09 g, 4.00 mmol) in THF was added CoCl₂ (0.25 g, 1.92 mmol). After stirring at room temperature for 7 h, vinyltrimethylsilane (0.32 g, 3.19 mmol) and KC₈ (0.54 g, 4.03 mmol) were added. The mixture changed to reddish brown gradually after further stirring at room temperature for 24 h. The mixture was then filtered to afford a reddish brown solution. Removal of the solvent by vacuum gave a reddish brown residue that was further washed by *n*-hexane (3 × 10

mL) and dried under vacuum to give 8 as reddish brown solid (0.77 g, 53%). Single-crystals of 8 were obtained by standing its Et_2O solution at room temperature after evaporation of solvent. ¹H NMR (400 MHz, $C_6 D_{6\prime}$ 19 °C): δ (ppm) 87.17 ($v_{1/2}$ = 1447 Hz), 72.49 ($v_{1/2}$ = 1673 Hz), 54.29 (($v_{1/2}$ = 1016 Hz), 27.23 ($v_{1/2}$ = 40 Hz), 21.05 ($v_{1/2}$ = 39 Hz), 19.86 ($v_{1/2}$ = 64 Hz), 16.39 ($v_{1/2}$ = 99 Hz), 15.58, 15.52, 13.54 $(v_{1/2} = 220 \text{ Hz}), 11.87 (v_{1/2} = 46 \text{ Hz}), 10.28 (v_{1/2} = 64 \text{ Hz}), 6.30 (v_{1/2})$ = 78 Hz), 4.64 ($v_{1/2}$ = 73 Hz), -2.38 ($v_{1/2}$ = 24 Hz), -2.71, -2.77, $-3.12 (v_{1/2} = 27 \text{ Hz}), -3.34 (v_{1/2} = 16 \text{ Hz}), -3.86, -4.02 (v_{1/2} = 51 \text{ Hz})$ Hz), -4.35 ($v_{1/2} = 15$ Hz), -4.98 ($v_{1/2} = 29$ Hz), -5.55 ($v_{1/2} = 27$ Hz), -6.26 ($v_{1/2}$ = 29 Hz), -8.99 ($v_{1/2}$ = 26 Hz), -10.02 ($v_{1/2}$ = 26 Hz), $-15.18 (v_{1/2} = 85 \text{ Hz})$, $-17.35 (v_{1/2} = 68 \text{ Hz})$, $-17.76 (v_{1/2} = 64 \text{ Hz})$ Hz), -19.65 ($v_{1/2}$ = 130 Hz), -22.33 ($v_{1/2}$ = 50 Hz), -25.10 ($v_{1/2}$ = 53 Hz), -134.46 (very br), -139.03 (very br). Because of peak overlap, the half-peak widths of some signals were not listed. Magnetic susceptibility (C₆D₆, 20 °C): $\mu_{\text{eff}} = 3.2(1) \mu_{\text{B}}$. Anal. Calcd for C41H60CoN4Si: C, 70.76; H, 8.69; N, 8.05. Found: C, 71.46; H, 8.46; N, 7.87. Absorption spectrum (THF): λ_{max} (ϵ , M⁻¹ cm⁻¹) = 264 (11340), 368 (6030), 664 (70) nm.

Preparation of [(ICy)₂Co(vtms)] (9). To the solution of ICy (1.04 g, 4.48 mmol) in THF was added CoCl₂ (0.29 g, 2.23 mmol) at room temperature. After stirring for 1.5 h, vinyltrimethylsilane (0.67 g, 6.68 mmol) was added, and then after 10 min, KC_8 (0.60 g, 4.44 mmol) was added. After stirring at room temperature for 17 h, the mixture was filtered to give a reddish brown solution. Removal of the solvent by a vacuum gave a reddish brown residue that was further washed by *n*-hexane (5 mL) and dried under a vacuum to give 9 as reddish brown solid (0.964 g, 34%). Single-crystals of 9 were obtained by standing its Et₂O solution at room temperature after evaporation of solvent. ¹H NMR (400 MHz, C_6D_6 , 25° C) δ (ppm) 117.22 ($v_{1/2}$ = 483 Hz), 113.20, 25.66 ($v_{1/2}$ = 730 Hz), 20.67 ($v_{1/2}$ = 138 Hz), 17.26 ($v_{1/2}$ = 94 Hz), 14.09 ($v_{1/2}$ = 109 Hz), 12.14 (br), 5.41 (very br), 0.92, -1.93 (very br), $-2.91 (v_{1/2} = 167 \text{ Hz})$, $-4.35 (v_{1/2} = 134 \text{ Hz})$, -4.90, -5.76 $(v_{1/2} = 35 \text{ Hz}), -11.11 (v_{1/2} = 92 \text{ Hz}), -15.40 \text{ (very br)}, -21.84 \text{ (very br)}$ br), $-24.38 (v_{1/2} = 93 \text{ Hz}), -26.09 (v_{1/2} = 144 \text{ Hz}), -35.03 (very br),$ -48.15 (very br), -127.63 (very br). Due to peak overlap, the halfpeak widths of some signals were not listed. Magnetic susceptibility (C_6D_6) : $\mu_{eff} = 2.8(2) \mu_B$. Anal. Calcd for $C_{35}H_{60}CoN_4Si$: C, 67.38; H, 9.69; N, 8.98.; Found: C, 67.07; H, 10.07; N, 9.26. Absorption spectrum (THF): $\lambda_{max} (\varepsilon, M^{-1} \text{ cm}^{-1}) = 241 (14090), 358 (8670), 489$ (3620), 659 (60) nm.

Preparation of $[(cylDep)(H)Co(\mu-\eta^2:\eta^2-H_2SiPh_2)(\mu-\eta^2-\eta^2)]$ HSiPh₂)₂Co(H)(cylDep)] (10). To a green solution of complex $[(cyIDep)Co(vtms)_2]$ (0.85 g, 1.31 mmol) in Et₂O (15 mL) was added Ph_2SiH_2 (0.83 g, 4.51 mmol) dropwisely. The solution changed to a yellowish brown suspension with the precipitation of a yellowish brown solid. After stirring at room temperature for 0.5 h, the mixture was filtrated to leave a yellow residue. The solid was washed by Et₂O (20 mL) and dried under a vacuum to afford 10 as a yellowish solid (0.82 g, 87%). Yellowish crystals of 10.2C7H8 were obtained by slow diffusion of *n*-hexane into the toluene solution of **10**. ¹H NMR (400 MHz, C₆D₆, 20 °C): δ (ppm) 7.12–7.03 (m, 18H), 7.02–6.95 (t, J = 7.6 Hz, 5H), 6.91 (t, J = 7.4 Hz, 12H), 6.85 (d, J = 7.6 Hz, 7H), 2.60-2.45 (m, 8H), 2.45-2.30 (m, 8H), 1.58 (s, 8H), 1.12 (s, 8H), 0.96 (t, J = 7.5 Hz, 24H, $-CH_3$, -8.97 (s, 6H). ¹³C NMR (101 MHz, C₆D₆, 19 °C): δ (ppm) 189.08 (C_{carbene}), 144.85, 140.77, 138.12, 137.64, 129.76, 128.51, 126.23, 126.19, 125.76, 24.48, 22.69, 22.49, 12.67. ²⁹Si{¹H} NMR (119.2 MHz, C₆D₆, 25 °C): δ (ppm) 64.46. ²⁹Si NMR (119.2 MHz, C_6D_{62} 25 °C): δ (ppm) 64.50 (m). Anal. Calcd for C90H104C02N4Si3: C, 74.86; H, 7.26; N, 3.88. Found: C, 74.88; H, 7.46; N, 3.71. Absorption spectrum (THF): λ_{max} (ϵ , M⁻¹ cm⁻¹) = 266 (25800), 318 (16190), 470 (1770) nm. IR spectrum (KBr, cm⁻¹): ν = 3038 (s), 2965 (s), 2935 (s), 2874 (s), 2851 (s), 1944 (m), 1684 (m), 1426 (s), 1384 (m), 1351 (s), 1275 (s), 1234 (m), 1187 (m), 1145 (m), 1093 (m), 1061 (m), 1038 (m), 987 (m), 807 (m), 732 (s), 699 (s), 486 (s), 459 (m), 438 (s).

Preparation of $[(cylDep)Co(\mu-HSiPh_2)_2Co(cylDep)]$ (11). To a 10 mL flask was added 10 (0.12 g, 0.083 mmol). Under vacuum, the solid was heated at 120 °C for 4 h, during which the solid changed to dark brown. After being cooled to room temperature, the solid was

extracted with by n-hexane (5 mL) to afford a dark brown solution. Single-crystals of 11 were obtained by standing its THF/toluene solution at room temperature after evaporation of solvent (0.050 g, 48%). ¹H NMR (400 MHz, C₆D₆, 20 °C): δ (ppm) 8.34 ($v_{1/2}$ = 20 Hz), 5.60 ($v_{1/2}$ = 19 Hz), 4.58, 4.39, 2.44 ($v_{1/2}$ = 19 Hz), 2.04 ($v_{1/2}$ = 26 Hz), 1.93 ($v_{1/2}$ = 17 Hz), 1.74 ($v_{1/2}$ = 17 Hz), 1.29 ($v_{1/2}$ = 19 Hz). Because of peak overlap, the half-peak widths of some signals were not listed. Magnetic susceptibility (C₆D₆, 20 °C): $\mu_{eff} = 2.7(2) \mu_{B}$. Anal. Calcd for C78H90C02N4Si2: C, 74.49; H, 7.21; N, 4.46. Found: C, 74.21; H, 7.01; N, 4.66. Absorption spectrum (THF): λ_{max} (ϵ , M⁻¹ cm^{-1}) = 261 (16960), 384 (6980), 578 (1400), 1297 (80) nm. IR spectrum (KBr, cm⁻¹): $\nu = 3037$ (m), 2964 (s), 2933 (s), 2875 (m), 2852 (m), 1703 (s), 1670 (m), 1589 (w), 1564 (m), 1461 (s), 1425 (m), 1384 (m), 1352 (m), 1327 (m), 1277 (m), 1232 (m), 1188 (m), 1170 (m), 1144 (m), 1111 (m), 1091 (m), 1039 (m), 1023 (m), 998 (m), 906 (m), 863 (m), 808 (m), 767 (m), 733 (s), 700(s), 487 (s), 442 (m), 430 (m).

Preparation of [(cyIDep)(Bu^tNC)Co(µ-HSiPh₂)₂Co(CNBu^t)₃] (12). To a solution of 11 (0.10 g, 0.08 mmol) in toluene (5 mL) was added Bu^tNC (0.030 g, 0.36 mmol). After stirring for 8 h at room temperature, the color of the solution changed to dark brown. After removal of the solvent under vacuum, the brown residue was extracted by n-pentane (5 mL) and filtered. Dark brown crystals of 12 were obtained by standing its *n*-pentane solution at -20 °C for days (0.028 g, 28%). The low yield is due to the high solubility of 12 in *n*-pentane. ¹H NMR (400 MHz, C₆D₆, 21 °C): δ (ppm) 7.75 (dd, J = 6.4, 3.0 Hz, 4H), 7.51 (dd, J = 7.2, 1.5 Hz, 4H), 7.22-7.17 (m, 12H), 7.01 (dd, J = 8.2, 6.9 Hz, 2H), 6.93 (d, J = 7.6 Hz, 4H), 2.92 (dq, J = 15.5, 7.6 Hz, 4H), 2.60 (dq, J = 15.3, 7.5 Hz, 4H), 1.80 (s, 4H), 1.53 (s, 9H), 1.24 (s, 4H), 1.14 (t, J = 7.6 Hz, 12H), 0.95 (s, 27H), -5.29 (s, 2H). ¹³C NMR (101 MHz, C₆D₆, 21 °C): δ (ppm) 195.58 (C_{carbene}), 173.22, 172.74, 151.61, 147.44, 140.77, 138.60, 137.42, 137.28, 129.41, 125.94, 125.93, 125.80, 125.78, 125.36, 54.85, 54.26, 31.28, 30.82, 24.52, 22.91, 22.35, 13.21. ²⁹Si{¹H} NMR (119.2 MHz, C₆D₆, 25 °C): δ (ppm) 101.24. ²⁹Si NMR (119.2 MHz, C₆D₆, 25 °C): δ (ppm) 101.24 (d, J = 80 Hz). Anal. Calcd for $C_{71}H_{92}Co_2N_6Si_2$: C, 70.85; H, 7.70; N, 6.98. Found: C, 71.05; H, 8.01; N, 6.88. Absorption spectrum (THF): $\lambda_{\text{max}} (\varepsilon, \text{M}^{-1} \text{ cm}^{-1}) = 287 (37110), 560 (6320) \text{ nm. IR spectrum (KBr,}$ cm^{-1} : $\nu = 3044$ (m), 2971 (s), 2933 (s), 2874 (s), 2104 (s), 2033 (s), 1580 (w), 1460 (m), 1424 (m), 1385 (m), 1363 (m), 1352 (m), 1275 (m), 1212 (m), 1188 (m), 1145 (w), 1088 (m), 1059 (w), 1036 (w), 1026 (w), 987 (w), 808 (m), 770 (m), 734 (m), 696 (s), 679 (m), 502 (s), 483 (s), 441 (m).

Preparation of [(IPr)Co(µ-HSiPh₂)₂Co(IPr)] (13). To a solution of $[(IPr)Co(vtms)_2]$ (3, 0.36 g, 0.56 mmol) in toluene (15 mL) was afford added diphenylsilane (0.21 g, 1.12 mmol) dropwisely. During the course, the color of the mixture changed to brown. The mixture was then allowed to stand at room temperature without stirring for overnight, and a brown crystalline solid of 13 then precipitated out. After filtration, washed by hexane, and dried under vacuum, brown solid of 13 was obtained (0.18 g, 26%). The single-crystals of $13 \cdot C_6 H_6$ were obtained by the same method using benzene as solvent. Anal. Calcd for C₇₈H₉₄Co₂N₄Si₂•C₆H₆: C, 75.30; H, 7.52; N, 4.18; Found: C, 75.46; H, 7.84; N, 3.91. IR spectrum (KBr, cm⁻¹): $\nu = 3136$ (w), 3058 (m), 3044 (m), 2962 (s), 2927 (s), 2867 (s), 1698 (m), 1646 (w), 1588 (w), 1534 (w), 1459 (m), 1426 (w), 1403 (m), 1382 (m), 1362 (m), 1327 (m), 1287 (m), 1257 (m), 1180 (w), 1149 (w), 1115 (m), 1058 (m), 1041 (m), 1023 (m), 957 (m), 932 (m), 800 (m), 752 (m), 736 (m), 699 (m), 678 (m), 546 (m), 491 (m), 464 (m), 454 (m), 410 (m). The poor solubility of 13 prevented further detailed characterization.

Preparation of [(IAd)Co(μ-HSiPh₂)₂Co(IAd)] (14). To a blue solution of [(IAd)Co(vtms)₂] (7, 0.13 g, 0.22 mmol) in Et₂O (6 mL) was added Ph₂SiH₂ (0.10 g, 0.54 mmol) dropwisely. The color of the solution gradually changed to light green and then yellowish brown gradually. After stirring at room temperature for 10 min, the mixture was filtrated to leave a brown filtrate. Slow evaporation of solvent by standing the solution at room temperature afforded 14 as yellowish brown crystals (0.060 g, 47%). ¹H NMR (400 MHz, THF-*d*₈, 21 °C): δ (ppm) 11.07 (very br), 9.70 ($v_{1/2}$ = 12 Hz), 7.89 ($v_{1/2}$ = 14 Hz), 6.86

 $(v_{1/2} = 15 \text{ Hz}), 0.35 (v_{1/2} = 16 \text{ Hz}), -1.74 (v_{1/2} = 25 \text{ Hz}), -2.25 (v_{1/2} = 19 \text{ Hz}), -4.01 (v_{1/2} = 188 \text{ Hz}), -5.88 (very br). Anal. Calcd for C₇₀H₈₆Co₂N₄Si₂: C, 72.64; H, 7.49; N, 4.84. Found: C, 72.38; H, 7.50; N, 4.84. Absorption spectrum (THF): <math>\lambda_{max}$ (ε , M⁻¹cm⁻¹) = 266 (29600), 317 (20480), 380 (14690), 547(840), 1080 (180). Because of the poor solubility of 14 even in C₆H₆, THF or 1,2-difluorobenzene, the solution magnetic susceptibility was not measured. IR spectrum (KBr, cm⁻¹): ν = 3125 (w), 3042 (m), 2907 (s), 2850 (s), 2678 (w), 2044 (w), 1948 (w), 1948 (w), 1874 (w), 1810 (w), 1651 (w), 1578 (w), 1537 (w), 1474 (w), 1451 (m), 1424 (m), 1388 (m), 1375 (m), 1349 (m), 1305 (m), 1278 (m), 1261 (m), 1244 (m), 1227 (m), 1193 (m), 1160 (m), 1102 (s), 1077 (m), 1077 (m), 1042 (m), 999 (m), 980 (m), 953 (m), 901 (m), 840 (m), 816 (m), 773 (m), 730 (m), 701 (s), 680 (m), 667 (m), 499 (s), 463 (m), 432 (m), 409 (m).

Preparation of [(IMesCy)₂Co(H)(SiHPh₂)] (15). [(IMesCy)₂Co-(vtms)] (8, 0.21 g, 0.30 mmol) was dissolved in Et₂O (20 mL) to afford a reddish brown solution. After filtration and cooling at -20 °C, diphenylsilane (0.13 g, 0.71 mmol) was added. The mixture was kept at -20 °C for days without stirring, which led to the precipitation of **15**·Et₂O as yellowish crystals (0.050 g, ca. 21%). ¹H NMR characterization (Figures S28 and S31) indicated the coexistence of unknown impurity in the sample. Attempts to get pure sample of **15** by recrystallization were unsuccessful. The existence of the impurity prevented the further characterization.

Preparation of [(cyCSi)Co(IMesCy')] (16). To a suspension of [(IMesCy)₂Co(vtms)] (8, 0.27 g, 0.39 mmol) in Et₂O (10 mL) was added diphenylsilane (0.14 g, 0.78 mmol). After stirring at room temperature for 12 h, the solvent was removed by vacuum to afford a reddish-brown residue. Toluene (10 mL) was added to redissolve the residue. The resulting mixture was further heated at 70 °C for 4 h. After removal of the solvent, the residue was extracted by Et₂O (5 mL) and filtered. Green crystals of 16 were obtained by standing its Et₂O solution at room temperature after evaporation of solvent (0.08 g, 26%). ¹H NMR (400 MHz, C₆D₆, 19 °C) δ (ppm) 30.31 ($v_{1/2}$ = 705 Hz), 27.74 ($v_{1/2}$ = 151 Hz), 26.56 ($v_{1/2}$ = 239 Hz), 23.78, 23.43, 22.19 ($v_{1/2}$ = 140 Hz), 20.65 (($v_{1/2}$ = 117 Hz), 18.00, 17.64 ($v_{1/2}$ = 170 Hz), 14.55 ($v_{1/2}$ = 153 Hz), 14.02 ($v_{1/2}$ = 170 Hz), 12.88 ($v_{1/2}$ = 170 Hz), 10.94 ($v_{1/2}$ = 110 Hz), 10.04 ($v_{1/2}$ = 16 Hz), 7.71 ($v_{1/2}$ = 17 Hz), 6.82 $(v_{1/2} = 15 \text{ Hz}), 6.16 (v_{1/2} = 35 \text{ Hz}), 4.02 (v_{1/2} = 38 \text{ Hz}), 3.43, 2.62$ $(v_{1/2} = 31 \text{ Hz}), 0.37, -0.82 (v_{1/2} = 59 \text{ Hz}), -0.98 (v_{1/2} = 59 \text{ Hz}),$ $-1.12 (v_{1/2} = 11 \text{ Hz}), -1.26 (v_{1/2} = 33 \text{ Hz}), -1.41, -1.47, -2.87,$ -2.97 ($v_{1/2}$ = 15 Hz), -3.25 ($v_{1/2}$ = 51 Hz), -3.50 ($v_{1/2}$ = 53 Hz), -4.39 ($v_{1/2}$ = 36 Hz), -5.16 ($v_{1/2}$ = 85 Hz), -5.90, -6.14 ($v_{1/2}$ = 72 Hz), -7.28 ($v_{1/2} = 22$ Hz), -7.99 ($v_{1/2} = 31$ Hz), -8.34 ($v_{1/2} = 54$ Hz), $-8.86 (v_{1/2} = 74 \text{ Hz})$, $-9.11 (v_{1/2} = 10 \text{ Hz})$, -9.74, -9.95, $-11.51 (v_{1/2} = 139 \text{ Hz}), -12.65 (v_{1/2} = 94 \text{ Hz}), -15.11 (v_{1/2} = 121$ Hz), $-16.39 (v_{1/2} = 138 \text{ Hz})$, $-20.20 (v_{1/2} = 189 \text{ Hz})$, -21.86, -22.65, $-28.98 (v_{1/2} = 370 \text{ Hz}), -30.73$. Because of peak overlap, the halfpeak widths of some signals were not listed. Anal. Calcd for: C₄₈H₅₆CoN₄Si: C, 74.29; H, 7.22; N, 7.27. Found: C, 74.00; H, 7.10; N, 7.40. Absorption spectrum (THF): λ_{max} (ϵ , M⁻¹ cm⁻¹) = 297 (9260), 327 (7300), 620 (270), 1169 (40) nm.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01763.

Tables for crystal data, molecular structures, absorption spectra, NMR, IR, and GC-MS spectra (PDF)

Accession Codes

CCDC 1560269–1560277 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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The authors declare no competing financial interest.

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