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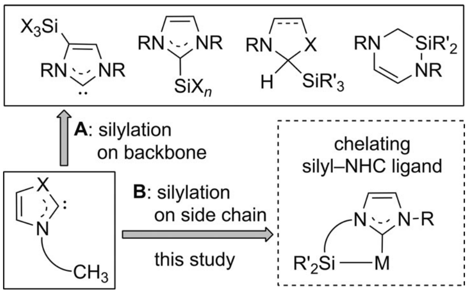
Carbene Complexes

Anchoring of Silyl Donors on a N-Heterocyclic Carbene through the Cobalt-Mediated Silylation of Benzylic C–H Bonds**

*Zhenbo Mo, Yang Liu, and Liang Deng**

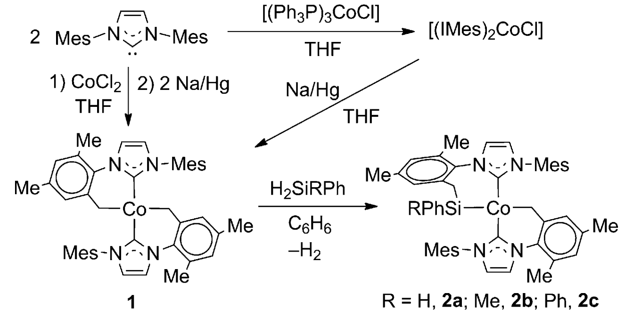
Silyl ligands stand out as particularly versatile ligands owing to their exceptionally strong σ-donating ability and *trans* effect.[1] These properties should make silyl-containing ligands capable of generating coordinatively unsaturated metal species, directing the coordination and dissociation of other ligands, and therefore conferring enhanced reactivity or accelerated catalytic turnover to their complexes.[2] N-Heterocyclic carbenes (NHCs) are another type of strongly σ-donating ligand with a strong *trans* effect and have joined the cyclopentadienyl anions and phosphine ligands as particularly useful widely applied ligands.[3] Accompanying the emergence of versatile monodentate NHCs,[4] numerous functionalized NHC ligands featuring tethered substitutents or binding sites, such as borate, alkoxide, enolate, amine, amide, imine, heterocycle, thioether, and phosphine groups, have been developed and applied in transition-metal chemistry.[5,6] In contrast, functionalized NHC ligands featuring silyl donors have remained elusive, although some NHCs with silyl substitutents on the imidazole ring are known (Scheme 1).[7] The absence of this type of potentially useful ligand might result from the inherent challenge of combining a nucleophilic carbene with a Lewis acidic silane moiety in the same ligand scaffold, as there have been reports of silanes reacting with NHCs to afford Lewis acid–base adducts,[8] Si–H insertion products,[9] or even ring expansion of the NHC (Scheme 1).[10]



Scheme 1. Silylation of N-heterocyclic carbenes.

With this knowledge in mind, we envisioned that instead of the direct synthesis of a silyl-donor-functionalized NHC ligand, a postsilylation method involving the reaction of hydrosilanes with a cyclometalated transition-metal–NHC complex might be a more feasible route. This idea was inspired by our previous finding that the cyclometalated NHC complex [Co(IMes′)$_2$] (**1**) can react with CO, isocyanides, and diazo compounds to furnish novel donor-group-functionalized NHC complexes.[11] Herein, we report the preparation of the first silyl-donor-functionalized NHC complexes by a sequential cobalt-mediated C–H activation and silylation protocal, their reactivity toward H_2 and BH_3·thf, and more interestingly, their remarkable catalytic performance in the catalytic hydrosilylation of 1-octene with $PhSiH_3$. In this transformation, the very fast initial rate and the high turnover number and selectivity of these catalysts were superior to those observed for [$Co_2(CO)_8$] and [$(IPr_2Me_2)_2CoPh_2$] (IPr_2Me_2: 2,5-diisopropyl-3,4-dimethylimidazol-1-ylidene).

Our previous study showed that the reduction of [$(IMes)_2CoCl$], prepared from [$(Ph_3P)_3CoCl$] and IMes (IMes: 1,3-dimesitylimidazol-2-ylide), with sodium amalgam results in the formation of the cyclometalated cobalt(II)–NHC complex [Co(IMes′)$_2$] (**1**; Scheme 2).[11] Upon further investigation, we found that **1** can be prepared more conveniently by the one-pot reaction of $CoCl_2$ with IMes (2 equiv) and sodium amalgam (2 equiv; Scheme 2). The addition of $PhSiH_3$ (1 equiv) to a suspension of **1** in benzene at room temperature resulted in the slow dissolution of the complex and a concomitant color change from reddish-brown to green over several hours. The silyl-donor-functionalized NHC complex **2a** was isolated from the green solution after workup as yellowish-green crystals in 63 % yield (Scheme 2).



Scheme 2. Synthetic routes to silyl-donor-functionalized NHC–cobalt(II) complexes. Mes = mesityl (2,4,6-trimethylphenyl).

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[*] Z. Mo, Y. Liu, Prof. Dr. L. Deng
State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences
345 Lingling Road, Shanghai, 200032 (P. R. China)
E-mail: deng@sioc.ac.cn
Homepage: http://dengliang.sioc.ac.cn/

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The reactions of **1** with $PhMeSiH_2$ and Ph_2SiH_2 in benzene proceeded very slowly at ambient temperature. However, full consumption of **1** was observed in 4 h when the reaction mixtures were heated to 70 °C, and yellowish-green crystals of **2b** and **2c** were isolated from the resulting green solutions in 60 and 46 % yield, respectively. No reaction occurred when **1** was treated with $(EtO)_3SiH$ or Ph_3SiH at room temperature. Further heating to 70 °C led to the formation of a pale-yellow suspension, and attempts to isolate products by recrystallization were unsuccessful. Notably, when an excess amount of the silane was used to prepare the silyl-functionalized NHC–cobalt complexes, **2a–c** were also obtained in moderate yield along with small amounts of polysilanes.

Complexes **2a–c** are air- and moisture-sensitive. They are soluble in *n*-hexane, benzene, and THF and have been characterized by ^1H NMR spectroscopy, UV/Vis/NIR spectroscopy, IR spectroscopy, elemental analysis, and single-crystal X-ray diffraction studies.[12] The ^1H NMR spectra of these complexes in C_6D_6 feature paramagnetically shifted signals in the range from +40 to −41 ppm. Whereas the signals in the region between +10 and 0 ppm are clustered, signals outside of this region are well-separated and characteristic. No discernible ^{29}Si NMR resonance between +300 and −300 ppm (as referenced to $SiMe_4$) was observed. Solution magnetic data indicate an $S = 1/2$ spin state for these complexes (2.6(1), 2.6(1), and 2.7(1) μB for **2a–c**, respectively). The absorption spectra of **2a–c** in benzene (see Figure S1 in the Supporting Information) are consistent with these results and exhibit d–d transition bands around 1110 ($\varepsilon = 57\ dm^3 mol^{-1} cm^{-1}$), 1070 ($\varepsilon = 108\ dm^3 mol^{-1} cm^{-1}$), and 1103 nm ($\varepsilon = 83\ dm^3 mol^{-1} cm^{-1}$), respectively, which are in line with that of **1** (1050 nm, $\varepsilon = 68\ dm^3 mol^{-1} cm^{-1}$), and typical of square-planar cobalt(II) compounds.[13]

Single-crystal X-ray diffraction studies[14] revealed that all the complexes have a distorted square-planar cobalt(II) center bearing two anionic bidentate ligands: a silyl-donor-functionalized NHC ligand $[IMesSi]^-$ and an $[IMes']^-$ ligand (Figure 1). The chelation of the $[IMesSi]^-$ ligand to the cobalt center in **2a–c** leads to the formation of a boat-shaped seven-membered chelating ring with a bite angle close to 90° (88.5(1), 91.5(1), and 88.5(1)°, respectively) and a Co–C(carbene) distance (2.048(5), 2.067(2), and 2.070(2) Å) and Co–Si bond length (2.300(2), 2.309(1), and 2.327(2) Å) comparable to those of previously reported low-spin cobalt–silyl[15] and four-coordinate cobalt(II)–NHC complexes.[11,16] The Co–C(benzyl) bonds in the [(IMes')Co] fragments of **2a–c** have distances of 2.048(5), 2.067(2), and 2.070(2) Å, which are longer than those in **1** (2.025(2) Å).[11] This difference suggests a strong *trans* effect of the silyl moieties.

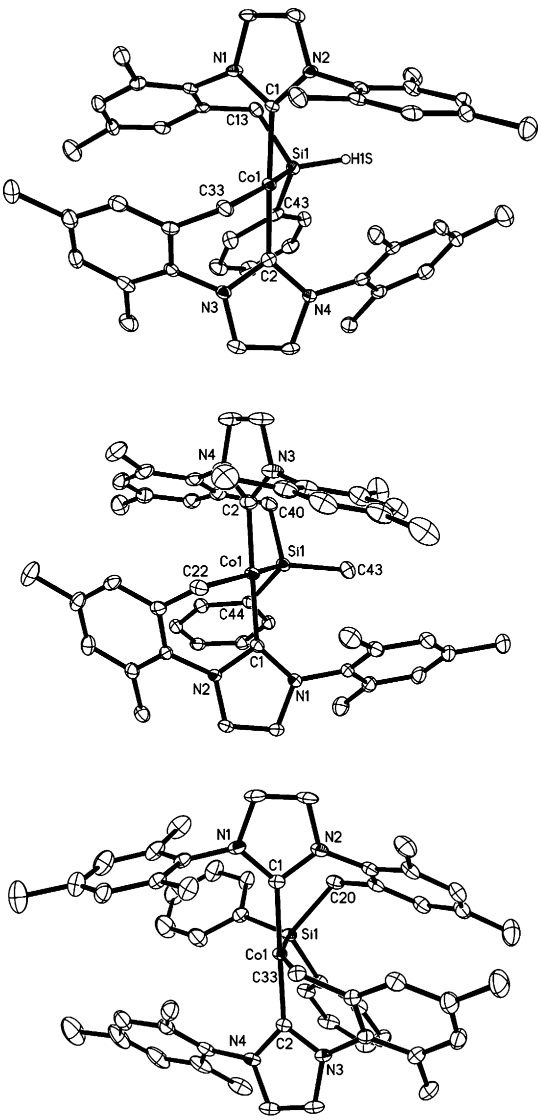
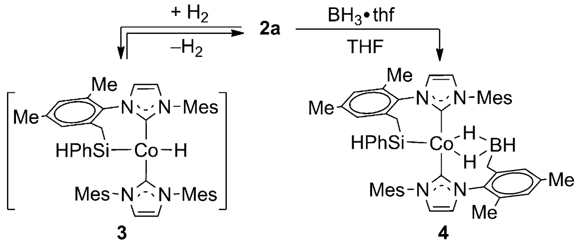


Figure 1. Molecular structures of **2a** (top), **2b** (middle), and **2c** (bottom) showing 30% probability ellipsoids. Key bond distances [Å] and angles [°] for **2a**: Co1–Si1 2.300(2), Co1–C33 2.048(5), Co1–C1 2.048(5), Co1–C2 1.891(5), Si1-Co1-C33 164.4(2), C1-Co1-C2 178.3(2); for **2b**: Co1–Si1 2.309(1), Co1–C22 2.067(2), Co1–C1 1.931(2), Co1–C2 1.912(2), Si1-Co1-C22 160.6(1), C1-Co1-C2 174.3(1); for **2c**: Co1–Si1 2.327(1), Co1–C33 2.070(2), Co1–C1 1.900(2), Co1–C2 1.907(2), Si1-Co1-C33 161.7(1), C1-Co1-C2 176.3(1).

The formation of these silyl-donor-functionalized NHC complexes can be viewed as the insertion of the silylene moieties into the Co–C(benzyl) bond of **1**,[17] but the genuine route is probably quite complicated. In an effort to probe the mechanism, we monitored the reaction of **1** with $PhSiH_3$ (1 equiv) in C_6D_6 by ^1H NMR spectroscopy in a sealed NMR tube. This experiment revealed that a paramagnetic intermediate, **3**, is involved en route to **2a** (see Figure S2).[12] Intermediate **3** can form an equilibrium with **2a** and H_2, as degassing of the mixture resulted in the conversion of **3** into **2a**, and reexposure of the degassed solution to a H_2 atmosphere (1 atm) induced the formation of **3** (see Figures S2 and S3).[12] We attempted to characterize **3** by ESIMS and IR spectroscopy and to isolate **3** by recrystallization under a H_2 atmosphere. However, the ease with which this species eliminated H_2 made these attempts unsuccessful. Recognizing that the reversible conversion is reminiscent of the reaction of **1** with H_2[11] and that of cyclometalated bis(imino)pyridine–cobalt(II) complexes with H_2 as described by Chirik and coworkers,[18] we reason that **3** is probably a cobalt(II) hydride species [(IMesSi)CoH(IMes)] resulting from hydrogenolysis of the Co–C(benzyl) bond in **2a** (Scheme 3).[19] This ascription is supported, to some degree, by the isolation of product **4**,



Scheme 3. Reactivity of **2a** toward H_2 and BH_3·thf.

which results from borylation of the Co–C(benzyl) bond, from the reaction of **2a** with BH_3·thf (Scheme 3). The structure of **4** was established unequivocally by an X-ray diffraction study.[14] The borylation reaction is akin to that observed by Aldridge and co-workers, who found that the reaction of the iridium(III) complex [(IMes)(IMes′)IrHCl] with $LiBH_4$ led to borylation of the metallocycle.[20]

Complex **4** has a distorted tetragonal-pyramidal cobalt center coordinated to one intact bidentate silyl–NHC ligand and one newly formed chelating borane–NHC ligand (Figure 2). The η^2-bound benzylborane anion in **4** has a Co–B separation of 2.169(4) Å comparable to that observed for its congeners *trans*-[$(Cy_3P)_2CoH(\eta^2\text{-}BH_4)$] (2.14(1) Å; Cy = cyclohexyl)[21] and [(terpyridine)Co(η^2-BH_4)] (2.16(1) Å).[22] Replacement of the [IMes′]$^-$ anion with the borane–NHC anion in the coordination sphere of the metal led to shorter Co–C(carbene) and Co–Si bonds (1.928(3) and 2.274(1) Å, respectively) in the [(IMesSi)Co] fragment as compared to those of **2a** (2.048(5) and 2.300(2), respectively). The shortening of these bond distances could be ascribed to the weak electron-donating ability of the borate anion, which makes the cobalt center less electron-rich and thus strengthens the Co–C and Co–Si interaction.

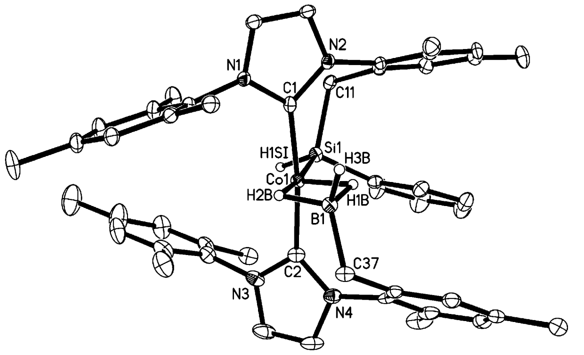
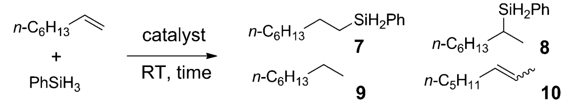


Figure 2. Molecular structure of **4** showing 30% probability ellipsoids. Key bond distances [Å] and angles [°]: Co1–Si1 2.274(1), Co1–B1 2.169(4), Co1–C1 1.928(3), Co1–C2 1.948(3), Co1–H2B 1.64(3), Co1–H1B 1.68(3), B1–H2B 1.26(3), B1–H1B 1.17(3), B1–H3B 1.20(3), Si1-Co1-B1 147.9(1), C1-Co1-C2 173.2(2).

The successful synthesis of these silyl-donor-functionalized NHC complexes afforded the opportunity to examine the aforementioned assumption that the strongly electron donating ligand scaffold could endow complexes with unique catalytic performance. Although some cobalt–carbonyl,[23] cobalt–phosphine,[24] and cobalt–cyclopentadienyl complexes[25] have long been known to facilitate the hydrosilylation of alkenes, the reactions generally proceed with low catalytic activity under harsh reaction conditions, and alkene isomerization and dehydrogenative hydrosilylation tend to occur as side reactions.[23,24a,b] In contrast, the silyl-donor-functionalized cobalt complexes **2a–c** effectively catalyzed the hydrosilation of 1-octene with $PhSiH_3$ with remarkable initial rates and high selectivity.

The reaction of 1-octene with $PhSiH_3$ in the presence of **2a** (0.1 mol%) produced the hydrosilylation products n-$C_8H_{17}SiPhH_2$ (**7**) and n-$C_6H_{13}CHMeSiPhH_2$ (**8**) in 5 min in a ratio of 14:1 and 89% combined yield (Table 1, entry 1). Meanwhile, only trace amounts of n-C_8H_{18} (**9**) and 2-C_8H_{16} (**10**) arising from alkene hydrogenation and isomerization and no dehydrogenative hydrosilylation product were observed.[26] The decreased rate in the later stages of the reaction was not due to the decomposition of catalytic species, since the further addition of 1-octene and $PhSiH_3$ to the mixture triggered the catalytic hydrosilylation reaction, albeit with slightly decreased rates.[12] Moreover, another experiment with **2a** (0.005 mol%) led to the formation of the products in 75% yield in 24 h, which corresponds to a turnover number of 15000 (Table 1, entry 4). Under parallel conditions, reactions with catalysts **2b** and **2c** for 5 min gave the hydrosilylation products in 83 and 53% yield, respectively (Table 1, entries 2 and 3). The differing activity of catalysts **2a–c** is attributed to a substituent effect of the silyl moiety.

Table 1: Hydrosilylation of 1-octene with $PhSiH_3$ in the presence of different cobalt catalysts.[a]



Entry	Catalyst	t	Yield [%][b]			
			7	8	9	10
1	**2a** (0.1 mol%)	5 min	83	6	3	2
2	**2b** (0.1 mol%)	5 min	77	6	3	1
3	**2c** (0.1 mol%)	5 min	50	3	1	1
4	**2a** (0.005 mol%)	24 h	70	5	3	1
5	**5** (1.0 mol%)[c]	24 h	26	0	0	16
6	**6** (1.0 mol%)[d]	24 h	0	0	0	0

[a] Reaction conditions: 1-octene (5.0 mmol), $PhSiH_3$ (7.5 mmol), neat, room temperature. [b] The yields were determined by GC on the basis of 1-octene. [c] Complex **5**: [$Co_2(CO)_8$]. The reaction was carried out with 1-octene (4 equiv), and the yields given are based on $PhSiH_3$. [d] Complex **6**: *trans*-[$(IPr_2Me_2)_2CoPh_2$].

The high activity of the silyl-donor-functionalized NHC–cobalt(II) catalysts prompted comparison with other potential cobalt catalysts. A reaction carried out with the traditional cobalt carbonyl catalyst [$Co_2(CO)_8$] (**5**) with a 10-fold catalyst loading and much extended reaction time (24 h) only afforded the hydrosilylation product in 26% yield along with a significant amount of product **10** derived from isomerization of the olefin (16%; Table 1, entry 5). In sharp contrast, the monodentate NHC-coordinated cobalt(II) complex *trans*-[$(IPr_2Me_2)_2CoPh_2$] (**6**)[14,27] was ineffective in promoting the hydrosilylation reaction (Table 1, entry 6). These comparisons demonstrate the uniqueness of the bidentate silyl-functionalized NHC ligand with respect to the traditional carbonyl ligand and also monodentate NHC ligands. Further studies on the mechanism and scope of this catalytic hydrosilylation reaction are currently under way. We believe that the special electronic properties of the silyl-functionalized carbene ligands are the key factors in the unique performance of the cobalt catalyst in the hydrosilylation reaction.

In conclusion, we have developed a sequential cobalt-mediated C−H activation and silylation protocol for the preparation of silyl-donor-functionalized NHC–cobalt complexes. These silyl-donor-functionalized NHC complexes effect the hydrosilylation of 1-octene with $PhSiH_3$ with very high activity and good selectivity. These properties are superior to those of $[Co_2(CO)_8]$ and $[(IPr_2Me_2)_2CoPh_2]$ and thus indicate the potential use of this new type of strongly electron donating ligand in catalyst design.

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[26] An excess amount of $PhSiH_3$ was used to ensure full conversion of the olefin, as the formation of polyphenylsilanes was observed when the majority of the olefin had been consumed.

[27] The complex *trans*-$[(IPr_2Me_2)_2CoPh_2]$ (**6**) was prepared by the treatment of $[(IPr_2Me_2)_2CoCl_2]$ with PhMgBr and was fully characterized by various spectroscopic methods. See the Supporting Information for details.