

Lewis-Base-Stabilized Dichlorosilylene: A Two-Electron σ -Donor Ligand

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The first structurally described cobalt(I) Lewis-base-stabilized silylene complex $[\text{Co}(\text{CO})_3\{\text{SiCl}_2(\text{IPr})\}_2]^+[\text{CoCl}_3(\text{THF})]^-$ [**1**; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] was prepared by applying the two-electron σ -donor ligand $\text{SiCl}_2(\text{IPr})$ through coordination with $\text{Co}_2(\text{CO})_8$. The bonding situation between ligand $\text{SiCl}_2(\text{IPr})$ and the cobalt(I) metal center in $[\text{Co}(\text{CO})_3\{\text{SiCl}_2(\text{IPr})\}_2]^+$ of **1** was investigated by ^1H NMR and IR spectroscopy, single-crystal X-ray structural analysis, and density functional theoretical calculations.

An important part of the art of organometallic chemistry is to select suitable ligands to influence the electronic and steric properties of the complexes to favor the desired reactivity. N-Heterocyclic carbenes (NHCs) as representatives of strong two-electron σ -donor ligands have been successfully used in a number of catalytic transformations.¹ Apparently, small changes in the ligand properties can entirely change the chemistry. Silylenes, as heavier analogues of carbenes, are divalent neutral silicon species that nominally have a singlet ground state ($^1\text{A}_1$), with the lone pair of electrons as the highest occupied molecular orbital and an empty p orbital as the lowest unoccupied molecular orbital.² Consequently, silylenes are capable of behaving as σ -donor/ π -acceptor ligands resembling triorganophosphines (PR_3). The important breakthrough is the synthesis and structure of $\text{Ni}(\text{CO})_2(\text{NHSi})_2$ [$\text{NHSi} = (\text{tBuNCH}=\text{CHN}^t\text{Bu})\text{Si}$] published in 1994,³ which is derived from the coordination of two free NHSi ligands to a nickel center instead of other indirect preparative methods.⁴ Since then, the incorporation of stable silylenes as ligands for

transition metals has become an active area of research,^{5,6} even though, except stable N-heterocyclic silylenes, other types of silylene ligands were still extremely scarce until now.⁶

Dihalosilylenes as high-temperature molecules have attracted academic and industrial interest for decades.⁷ However, because of the extreme instability and rapid polymerization of dihalosilylenes at ambient temperature,^{8,9} as far as we know, the study of stable dihalosilylenes serving as free ligands that coordinate to metals has not been reported in the literature.¹⁰ Recently, we synthesized the first Lewis-base-stabilized dichlorosilylene $\text{SiCl}_2(\text{IPr})$ [IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]¹¹ and investigated the

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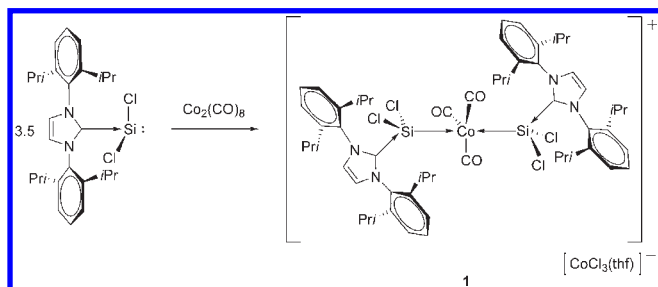
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Scheme 1. Synthesis of Cobalt Carbonyl Lewis-Base-Stabilized Dichlorosilylene Complex **1**

reactivity of $\text{SiCl}_2(\text{IPr})$ toward Lewis acid^{11c} $\text{B}(\text{C}_6\text{F}_5)_3$, from which we are inspired to explore the coordination behavior of $\text{SiCl}_2(\text{IPr})$ to transition metals. Herein we report on the synthesis and characterization of the first cobalt carbonyl Lewis-base-stabilized dichlorosilylene complex.

The reaction of 2 equiv of $\text{SiCl}_2(\text{IPr})$ with $\text{Co}_2(\text{CO})_8$ in toluene at room temperature afforded air- and moisture-sensitive blue crystals of $[\text{Co}(\text{CO})_3\{\text{SiCl}_2(\text{IPr})\}_2]^+[\text{CoCl}_3(\text{THF})]^-$ (**1**, where THF = tetrahydrofuran; Scheme 1). The ratio of the starting materials is different in comparison to that in Scheme 1, due to the problem of separating the products. The relatively high yield (74%) of **1** demonstrates that $\text{SiCl}_2(\text{IPr})$ functions as a coordinate ligand as well as a chlorinating and oxidizing agent. In contrast to the anion formed only by disproportionation in $[\text{Co}(\text{CO})_3(\text{L})_2]^+[\text{Co}(\text{CO})_4]^-$ ($\text{L} = \text{PR}_3$ and NHC),^{12,13} the anion $[\text{CoCl}_3(\text{THF})]^-$ in **1** is exclusively generated even if an excess of $\text{Co}_2(\text{CO})_8$ was used. Compound **1** is soluble in THF but insoluble in benzene and toluene. **1** has been characterized by NMR, IR and UV-vis spectroscopy, elemental analysis, and single-crystal X-ray analysis.

The molecular structure of **1** is shown in Figure 1. The formal oxidation states of cobalt in the cationic and anionic moieties are 1+ and 2+, respectively. The cation adopts a slightly distorted trigonal-bipyramidal geometry, with three carbonyl ligands occupying the equatorial plane and two $\text{SiCl}_2(\text{IPr})$ ligands arranged in the apical positions. $[\text{Co}(\text{CO})_3\{\text{SiCl}_2(\text{IPr})\}_2]^+$ has essentially C_2 symmetry. The cobalt atom in the anion is pseudotetrahedrally coordinate. The $\text{Si1}-\text{Co1}-\text{Si2}$ moiety is close to linear [$176.78(5)^\circ$]. Notably, to the best of our knowledge, no crystal structure of the cobalt(I) silylene complex has been described in the literature.¹⁴ The $\text{Co}-\text{Si}$ bond lengths of 2.2278(13) and 2.2276(12) Å in **1** are slightly shorter than those of covalently bonded $\text{Co}-\text{Si}$ units [range of 2.254(4) Å for $\text{Cl}_3\text{SiCo}(\text{CO})_4$ to 2.381(7) Å for $\text{H}_3\text{SiCo}(\text{CO})_4$]^{15,16} and longer by ca. 0.04 Å than that observed in the seven-coordinate cobalt silylene complex [2.1848(8) Å].¹⁷ This suggests that the Lewis-base-stabilized dichlorosilylene ligand $\text{SiCl}_2(\text{IPr})$ can be considered

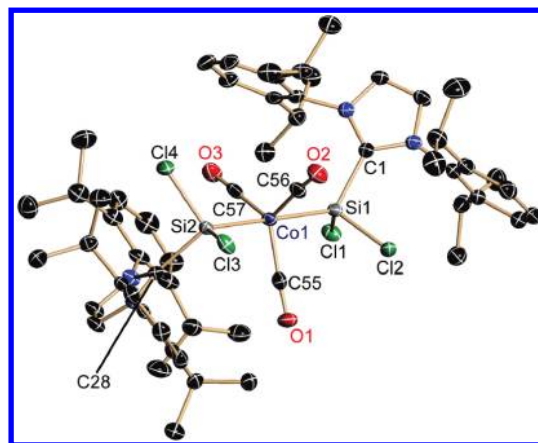


Figure 1. Anisotropic displacement parameters of **1**, depicted at the 50% probability level. Hydrogen atoms and the counterion $[\text{CoCl}_3(\text{THF})]^-$ have been omitted for clarity. Selected bond lengths (Å) and angles (deg): $\text{Co1}-\text{Si1}$ 2.2278(13), $\text{Co1}-\text{Si2}$ 2.2276(12), $\text{Co1}-\text{C55}$ 1.767(4), $\text{Co1}-\text{C56}$ 1.773(5), $\text{Co1}-\text{C57}$ 1.773(4), $\text{Si1}-\text{Cl1}$ 2.0635(16), $\text{Si1}-\text{Cl2}$ 2.0846(15), $\text{Si1}-\text{C1}$ 1.944(4), $\text{Si2}-\text{Cl3}$ 2.0696(15), $\text{Si2}-\text{Cl4}$ 2.0778(15), $\text{Si2}-\text{C28}$ 1.952(4); $\text{Si1}-\text{Co1}-\text{Si2}$ 176.78(5), $\text{Co1}-\text{Si1}-\text{C11}$ 109.64(6), $\text{Co1}-\text{Si1}-\text{Cl2}$ 115.54(6), $\text{Co1}-\text{Si2}-\text{Cl3}$ 110.58(6), $\text{Co1}-\text{Si2}-\text{Cl4}$ 115.13(6), $\text{Cl1}-\text{Si1}-\text{Cl2}$ 104.09(7), $\text{Cl3}-\text{Si2}-\text{Cl4}$ 103.11(6).

as a strong σ donor accompanied by weak π -accepting properties. The average $\text{Co}-\text{CO}$ bond distance of 1.771(5) Å in **1** is similar to those reported for $[\text{Co}(\text{CO})_3(\text{PPh}_3)_2]^+[\text{PF}_6]^-$ [1.778(10) Å (av)] and $[\text{Co}(\text{CO})_3(\text{IMes})_2]^+[\text{Co}(\text{CO})_4]^-$ [$\text{IMes} = 1,3$ -bis(2,4,6-trimethylphenyl)imidazol-2-ylidene; 1.790(6) Å (av)].^{13,18}

The geometries of the two silicon atoms in **1** can be described as distorted tetrahedral. Compared with the calculated $\text{LP}_{\text{Si}}-\text{Si}-\text{Cl}$ ($\text{LP}_{\text{Si}} = \text{lone-pair density}$) bond angle in $\text{SiCl}_2(\text{IPr})$ [122.65° (av)], the $\text{Co}-\text{Si}-\text{Cl}$ bond angle in **1** [$112.72(6)^\circ$ (av)] is smaller.¹¹ The $\text{Cl}-\text{Si}-\text{Cl}$ bond angle of $103.60(7)^\circ$ (av) in **1** is comparable to that in $\text{SiCl}_2(\text{IPr})$ [$97.25(6)^\circ$]. The mean $\text{Si}-\text{Cl}$ and $\text{Si}-\text{C}$ bond lengths in **1** [2.0739(16) and 1.948(4) Å] are significantly shorter than those observed in $\text{SiCl}_2(\text{IPr})$ [2.1664(16) Å (av) and 1.985(4) Å], which is probably caused by an increased Lewis acidity of the silicon center due to σ -electron donation from Lewis-base-stabilized silylene to the cobalt atom.

Compound **1** displays abnormal resonances in the ^1H NMR spectrum at room temperature, which might be caused by the d^7 cobalt(II) tetrahedral anion.¹⁹ These resonances shifted by different extents from +50 to -90°C and became broader at lower temperature. The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **1** exhibited a singlet at 44.11 ppm. The characteristic downfield shift $\Delta\delta$ of 25.05 ppm from the free $\text{SiCl}_2(\text{IPr})$ ligand (19.06 ppm) demonstrates coordination of $\text{SiCl}_2(\text{IPr})$ to the cobalt center,^{51,6b,11} which reveals the ambiphilicity of Lewis-base-stabilized silylene in **1**. Consistent with $\text{ArHSiCo}(\text{CO})\text{Cp}$ [$\text{Ar} = 2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4$, $\delta = 95.00$ ppm; $\text{Ar} = 8-(\text{Me}_2\text{NCH}_2)\text{C}_{10}\text{H}_6$, $\delta = 85.99$ ppm], **1** features quite

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(19) ^1H NMR of **1** (500 MHz, $\text{THF}-d_8$, 50°C): δ -4.82, -0.63, 0.40, 0.73, 1.15, 2.04, 5.85, 6.59, 6.87, 7.31, 7.53, 9.69. ^1H NMR (500 MHz, $\text{THF}-d_8$, 25°C): δ -6.28, -1.04, 0.37, 0.78, 1.17, 2.08, 6.11, 6.52, 6.78, 7.35, 7.57, 9.95. ^1H NMR (500 MHz, $\text{THF}-d_8$, 0°C): δ -7.49, -1.41, 0.36, 0.84, 1.19, 2.13, 6.45, 6.68, 7.40, 7.60, 10.36. ^1H NMR (500 MHz, $\text{THF}-d_8$, -50°C): δ -8.91, -1.98, 0.39, 1.29, 2.41, 6.25, 7.55, 12.93. ^1H NMR (500 MHz, $\text{THF}-d_8$, -90°C): δ 0.86, 1.41, 2.60, 5.82, 7.77.

Table 1. Comparison of Carbonyl IR Bands in Various Cations of $[\text{Co}(\text{CO})_3(\text{L})_2]^+ \text{X}^-$

L	X ⁻	$\bar{\nu}(\text{CO})$ (cm ⁻¹) ^{a,b}
SiCl ₂ (IPr)	[CoCl ₃ (THF)] ⁻	2052 (vw), 1994 (s), 1969 (s)
P ⁿ Bu ₃ ²⁰	[Co(CO) ₄] ⁻	2066 (vw), 1997 (s), 1983 (s)
PPh ₃ ²⁰	[Co(CO) ₄] ⁻	2071 (vw), 2014 (s), 2001 (s)
P(<i>p</i> -MeC ₆ H ₄) ₃ ²⁰	[PF ₆] ⁻	2073 (vw), 2009 (sh), 2001 (s) ^c
IMes ¹³	[Co(CO) ₄] ⁻	1981 (mw) ^{c,d}

^a Nujol mull, unless indicated otherwise. ^b v, very; m, medium; w, weak; s, strong; sh, shoulder. ^c THF. ^d E' band.

different ²⁹Si{¹H} NMR resonances from those of covalently bonded metal silyl complexes (below 150 ppm).¹⁴

The IR spectrum of **1** recorded as a Nujol mull shows three bands attributed to carbonyl groups on cobalt(I) and a weak A₁' band centered at 2052 cm⁻¹ along with two strong bands at 1994 and 1969 cm⁻¹ for the E' mode. The well-split of the three distinct bands is characteristic for C₂ symmetry of the cationic moiety [Co(CO)₃{SiCl₂(IPr)}₂]⁺.^{20,21} In a comparison of analogous complexes containing [Co(CO)₃(PR₃)₂]⁺, the coordinate CO in **1** as a "reporting group" features lower stretching frequencies (Table 1). According to Tolman's method, this indicates higher electron density on the cobalt (I) center in [Co(CO)₃{SiCl₂(IPr)}₂]⁺ of **1**.²² Moreover, we can deduce that the Lewis-base-stabilized dichlorosilylene SiCl₂(IPr) is either a stronger two-electron σ donor or a weaker π acceptor than PR₃.^{5g,23} We can state that the electron-donating to electron-accepting ratio for SiCl₂(IPr) is distinctly larger than that for PR₃. For the same reason, SiCl₂(IPr) and IMes possess the similar ratios of electron donation to electron acceptance.

The THF solution of **1** exhibits two characteristic absorptions at 587 and 693 nm, which are ascribed to the d-d transition from the ground state ⁴A₂ to the ⁴T₁(P) state of the pseudotetrahedral cobalt(II) anionic moiety.²⁴ Though the expected band should be around 600 nm, the spin-orbit coupling causes a splitting of this band into two parts. Thus, the cationic moiety [Co(CO)₃{SiCl₂(IPr)}₂]⁺ of **1** shows essentially no absorption beyond $\lambda > 400$ nm, consistent with that observed for [Co(CO)₃(P*n*Bu₃)₂]⁺[ClO₄]⁻.²⁰

In order to explore the electronic structure and bonding properties of the cationic moiety in complex **1**, density functional theoretical calculations were performed for the cation singlet, in which the isopropyl groups were substituted by methyl groups, with exchange-correlation functional B²⁵P86²⁶ and the 6-31G* basis set employing polarization functions for non-hydrogen atoms with *Gaussian03*.²⁷ After geometry optimization starting from the crystal coordinates, the calculated structural parameters compare well with experimental values (see the Supporting Information).

Natural bond orbital²⁸ analysis assigns a single weak covalent Co-Si bond with occupation 1.82226 from one of the two silicon atoms, and the other silicon atom is described in terms of a strongly donating silicon lone pair (occupation 1.05441; no covalent bond here). The donation is into the same empty predominantly s-type orbital [s (88.95%) p^{0.00} (0.09%) d^{0.12} (10.95%) f^{0.00} (0.01%)] on cobalt into which also the carbonyl carbon atoms donate their lone pairs. Additionally, for the same silicon atom, there is another donation into the antibonding covalent Co-Si bond. Both donation modes lead to a distinct stabilization energy (see the Supporting Information). The Co-Si bonds, however, are chemically equivalent, so the complete characteristics of the Co-Si bond are given by an average of two (or even more) contributing natural Lewis structures. This leads to a strong σ -donating silicon lone pair.

In summary, we use the two-electron σ -donor ligand SiCl₂(IPr) for synthesis of the first structural characterized cobalt(I) Lewis-base-stabilized silylene complex **1** through coordination with Co₂(CO)₈. The Lewis-base-stabilized dichlorosilylene SiCl₂(IPr) can be considered as a strong σ donor accompanied by a weak π -accepting ability.

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Supporting Information Available: Experimental preparation, computational details, and a CIF file for compound **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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