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N-Heterocyclic Carbene Stabilized Dichlorosilylene Transition-Metal Complexes of V(I), Co(I), and Fe(0)

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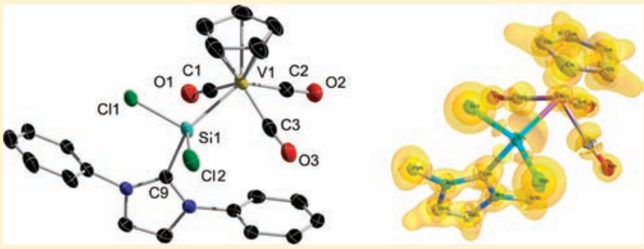
Supporting Information



ABSTRACT: Reactions of N-heterocyclic carbene stabilized dichlorosilylene IPr·$SiCl_2$ (**1**) (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) with (η^5-C_5H_5)V$(CO)_4$, (η^5-C_5H_5)Co$(CO)_2$, and $Fe_2(CO)_9$ afford dichlorosilylene complexes IPr·$SiCl_2$·V$(CO)_3$(η^5-C_5H_5) (**2**), IPr·$SiCl_2$·Co(CO)(η^5-C_5H_5) (**3**), and IPr·$SiCl_2$·Fe$(CO)_4$ (**4**), respectively. Complexes **2**−**4** are stable under an inert atmosphere, are soluble in common organic solvents, and have been characterized by elemental analysis and multinuclear (^{1}H, ^{13}C, and ^{29}Si) NMR spectroscopy. Molecular structures of **2**−**4** have been determined by single crystal X-ray crystallographic studies and refined with nonspherical scattering factors.

INTRODUCTION

N-heterocyclic carbenes (NHCs) have proven highly versatile σ-donor ligands for transition-metal (TM) complexes[1,2] and as effective Lewis bases to stabilize reactive main group element species[3,4] and as organocatalysts on their own right.[5] Use of NHCs as spectator ligands, particularly as alternatives to phosphines (R_3P), resulted in a second generation of Grubbs catalysts.[6] This is one of the remarkable developments in organometallic chemistry. Similarly, chemistry of TM−silylene complexes has attracted considerable attention[7] during the last two decades. TM−silylene complexes have been proposed as intermediates in catalytic hydrosilylation,[8] dehydrosilylation of organosilicon compounds,[9] redistribution of substituents on organosilicon compounds,[10] and deoligomerization of disilanylmetal complexes to monosilyl derivatives.[11] In general, silylenes are compounds with a neutral divalent silicon atom, and therefore, they are highly reactive species to be isolated at normal laboratory conditions.[12] Coordination to a TM center offers a convenient synthetic approach to trap or to generate such highly reactive species.[13] Remarkable contributions to this field have been made by Tilley and others.[7,14] Availability of the first stable N-heterocyclic silylene (NHSi)[15] and its application as a ligand for TM complexes introduced a direct method to prepare TM−silylene complexes.[16−20] Among acyclic silylenes, dichlorosilylene ($SiCl_2$) is one of the extremely reactive species and has academic and industrial importance. $SiCl_2$ readily polymerizes to $(SiCl_2)_n$ or decomposes to Si and $SiCl_4$.[21] Therefore access to TM complexes containing $SiCl_2$ as a ligand is rare and based on indirect multistep methods.[22] Moreover, these reactions often lead to a mixture of several products. In general, silylenes (e.g., SiX_2, X = halogen, H, alkyl, or aryl) are divalent neutral silicon species with the lone pair of electrons as the highest occupied molecular orbital (HOMO) and an empty p-orbital as the lowest unoccupied molecular orbital (LUMO) in the singlet ground (^{1}A) state. Therefore, silylenes can in principle behave as Lewis acids as well as Lewis bases and are known to possess an ambiphilic nature.[23] Very recently, we isolated the first Lewis-base stabilized dichlorosilylene[4] IPr·$SiCl_2$ (**1**) (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) in very good yield by reductive dehydrochlorination of $HSiCl_3$ using NHC. This method was the basis for developing silylene chemistry on a broader scale, without using alkali metals for the reduction. However even more important was the increase in the yield of silylene. Compound **1** consists of a three coordinate silicon atom containing a stereoactive lone pair of electrons. Therefore, **1** should serve as a convenient and readily available source of a neutral σ-donor ligand for TM complexes. In **1**, NHC is a Lewis base, and $SiCl_2$ behaves as a Lewis acid. Ambiphilic nature of $SiCl_2$, in which it behaves as a Lewis acid as well as a Lewis base at the same time, has been already demonstrated in our previous reports.[19,20,23] We have investigated the properties of **1** as a Lewis base,[23] and its oxidative addition to organic substrates,[24] functionalization of NHC,[25] and use of **1** as a σ-donor ligand for the TM complexes $[Co(CO)_3\{SiCl_2(IPr)\}_2][CoCl_3(THF)]$ **A**[19] and $Ni(CO)_2\{SiCl_2(IPr)\}_2$ **B**.[20] Formation of an ionic (**A**) and a neutral (**B**) bis-silylene complex further convinced us to continue our studies on the chemistry of TM complexes containing **1** as a ligand. A survey of literature reveals that there are only a few complexes, such as $(CO)_5VSiH_3$, (η^5-C_5H_5)$_2$V$(SiCl_3)_2$, (η^5-C_5H_5)V(N^{t}Bu)(NH^{t}Bu)Si$(SiMe_3)_3$, and (η^5-C_5H_5)V(L)(SiHRR′) (L = 1,2-bis(dimethylphosphino)ethane; R = Ph or

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Mes, and R′ = Ph or H), containing vanadium−silicon bonds which have been characterized by X-ray crystallographic studies.[26] Moreover, to the best of our knowledge no vanadium−silylene complex has been isolated so far. The lack of progress in this area is due to the paramagnetic properties of most vanadium complexes.[26] Therefore, we became interested in exploring the chemistry of TM, especially vanadium, complexes using **1** as a ligand. Ligand substitution reactions are essential for the application of TM organometallic compounds as homogeneous catalysts. Compared to the TM−carbene complexes, TM−silylene complexes derived from stable silylenes are still elusive. Herein, we report on a convenient access to TM−silylene complexes $IPr\cdot SiCl_2\cdot V(CO)_3(\eta^5\text{-}C_5H_5)$ (**2**), $IPr\cdot SiCl_2\cdot Co(CO)(\eta^5\text{-}C_5H_5)$ (**3**), and $IPr\cdot SiCl_2\cdot Fe(CO)_4$ (**4**) by ligand substitution reaction. Complexes **2**−**4** have been characterized by elemental analyses and NMR spectroscopy. Molecular structures of **2**−**4** have been established by single crystal X-ray crystallography. Complex **2** is the first vanadium−silylene complex which is structurally characterized by single crystal X-ray crystallography. The quality of the X-ray structures in terms of accuracy and precision has been improved by using nonspherical scattering factors.

■ EXPERIMENTAL SECTION

General Procedures. All syntheses and manipulations were performed under an inert atmosphere of nitrogen using Schlenk line techniques or a glovebox. The solvents used were purified by MBRAUN MB SPS-800 solvent purification system. NHC stabilized dichlorosilylene $IPr\cdot SiCl_2$ (**1**) was prepared[4] according to the method given in the literature. Without further purification, $(\eta^5\text{-}C_5H_5)V(CO)_4$, $(\eta^5\text{-}C_5H_5)Co(CO)_2$, (abcr GmbH & Co. KG) and $Fe_2(CO)_9$ (Aldrich) were used as received. C_6D_6 (Na/benzophenone ketyl) and CD_2Cl_2 (CaH_2) were distilled under nitrogen prior to use. ^1H, ^{13}C, ^{29}Si, and ^{51}V NMR spectra were recorded using Bruker Avance DPX 200 or Bruker Avance DRX 500 spectrometer. ^{51}V NMR chemical shifts are reported relative to $VOCl_3$ as an external reference. Elemental analyses were obtained from the Analytical Laboratory of the Institute of Inorganic Chemistry at the University of Göttingen.

Synthesis of $IPr\cdot SiCl_2\cdot V(CO)_3(\eta^5\text{-}C_5H_5)$ (2). To a Schlenk flask containing $IPr\cdot SiCl_2$ (**1**) (0.59 g, 1.21 mmol) and $(\eta^5\text{-}C_5H_5)V(CO)_4$ (0.28 g, 1.22 mmol) was added toluene (40 mL) at room temperature with constant stirring. The reaction mixture was further stirred for 12 h. A small amount of insoluble material was removed by filtration. The volatiles from the red filtrate were removed under vacuum to obtain a brown solid. The solid was dissolved in toluene (20 mL) and stored at −35 °C in a freezer to yield compound $IPr\cdot SiCl_2\cdot V(CO)_3(\eta^5\text{-}C_5H_5)$ (**2**) as red crystals (0.61 g, 73%). Anal. calcd (%) for $C_{35}H_{41}Cl_2N_2O_3SiV$ (M = 687): C, 61.13; H, 6.01; N, 4.07. Found (%): C, 61.01; H, 5.87; N, 4.09. ^1H NMR (200 MHz, C_6D_6, 298 K): δ 0.94 (d, *J* = 6.84 Hz, 12H, $CHMe_2$), 1.56 (d, *J* = 6.62 Hz, 12H, $CHMe_2$), 2.99 (q, *J* = 6.70 Hz, 4H, $CHMe_2$), 4.65 (s, 5H, C_5H_5), 6.37 (s, 2H, NC*H*), 6.98−7.24 (m, 6H, C_6H_3) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 298 K): δ 22.63 ($CHMe_2$), 26.43 ($CHMe_2$), 29.19 ($CHMe_2$), 91.07 (C_5H_5), 124.77 (NCH), 125.63, 126.39, 129.27, 131.26, 135.13, 137.84 (C_6H_3), 145.58 (*ipso*-C_6H_3) ppm. ^1H NMR (200 MHz, CD_2Cl_2, 298 K): δ 1.10 (d, *J* = 6.80 Hz, 12H, $CHMe_2$), 1.41 (d, *J* = 6.62 Hz, 12H, $CHMe_2$), 2.83 (q, *J* = 6.70 Hz, 4H, $CHMe_2$), 4.57 (s, 5H, C_5H_5), 7.20 (s, 2H, NC*H*), 7.36−7.51 (m, 6H, C_6H_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2, 298 K): δ 22.42 ($CHMe_2$), 26.33 ($CHMe_2$), 29.14 ($CHMe_2$), 90.78 (C_5H_5), 124.70 (NCH), 125.19, 127.00, 128.38, 129.19, 131.11, 134.97, 138.17 (C_6H_3), 145.58 (*ipso*-C_6H_3), 158.10 (NCN), 259.20−263.03 (br, CO) ppm. ^{29}Si NMR (99 MHz, CD_2Cl_2, 298 K): δ 88.70 ppm. ^{51}V NMR (78 MHz, CD_2Cl_2, 298 K): δ −1593.46 ppm.

Synthesis of $IPr\cdot SiCl_2\cdot Co(CO)(\eta^5\text{-}C_5H_5)$ (3). A toluene solution of $(\eta^5\text{-}C_5H_5)Co(CO)_2$ (0.25 g, 1.39 mmol) was added to a stirred solution of $IPr\cdot SiCl_2$ (**1**) (0.67 g, 1.37 mmol) at 0 °C with constant stirring. Stirring of the reaction mixture was continued at room temperature for 12 h. Volatiles were removed under vacuum to obtain an orange solid. Recrystallization from a mixture of dichloromethane (10 mL) and *n*-hexane (10 mL) solution at −35 °C afforded complex **4** as orange-yellow crystals (0.51 g, 58%). Anal. calcd for $C_{33}H_{41}Cl_2CoN_2OSi$ (M = 639): C, 61.97; H, 6.46; N, 4.38. Found (%): C, 61.89; H, 6.38; N, 4.27. ^1H NMR (200 MHz, CD_2Cl_2, 298 K): δ 1.32 (d, *J* = 6.84 Hz, 12H, $CHMe_2$), 1.68 (d, *J* = 6.66 Hz, 12H, $CHMe_2$), 3.00 (q, *J* = 6.76 Hz, 4H, $CHMe_2$), 4.49 (s, 5H, C_5H_5), 7.20 (s, 2H, NC*H*), 7.36−7.42 (m, 4H, C_6H_3), 7.50−7.56 (m, 2H, C_6H_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2, 298 K): δ 22.98 ($CHMe_2$), 26.30 ($CHMe_2$), 29.66 ($CHMe_2$), 82.17 (C_5H_5), 124.87 (NCH), 125.23, 125.82, 126.11, 129.54, 131.67, 132.48, 134.76 (C_6H_3), 146.33 (*ipso*-C_6H_3), 155.01 (NCN) 205.97 (br, CO) ppm. ^{29}Si NMR (99 MHz, CD_2Cl_2, 298 K): δ 31.86 ppm.

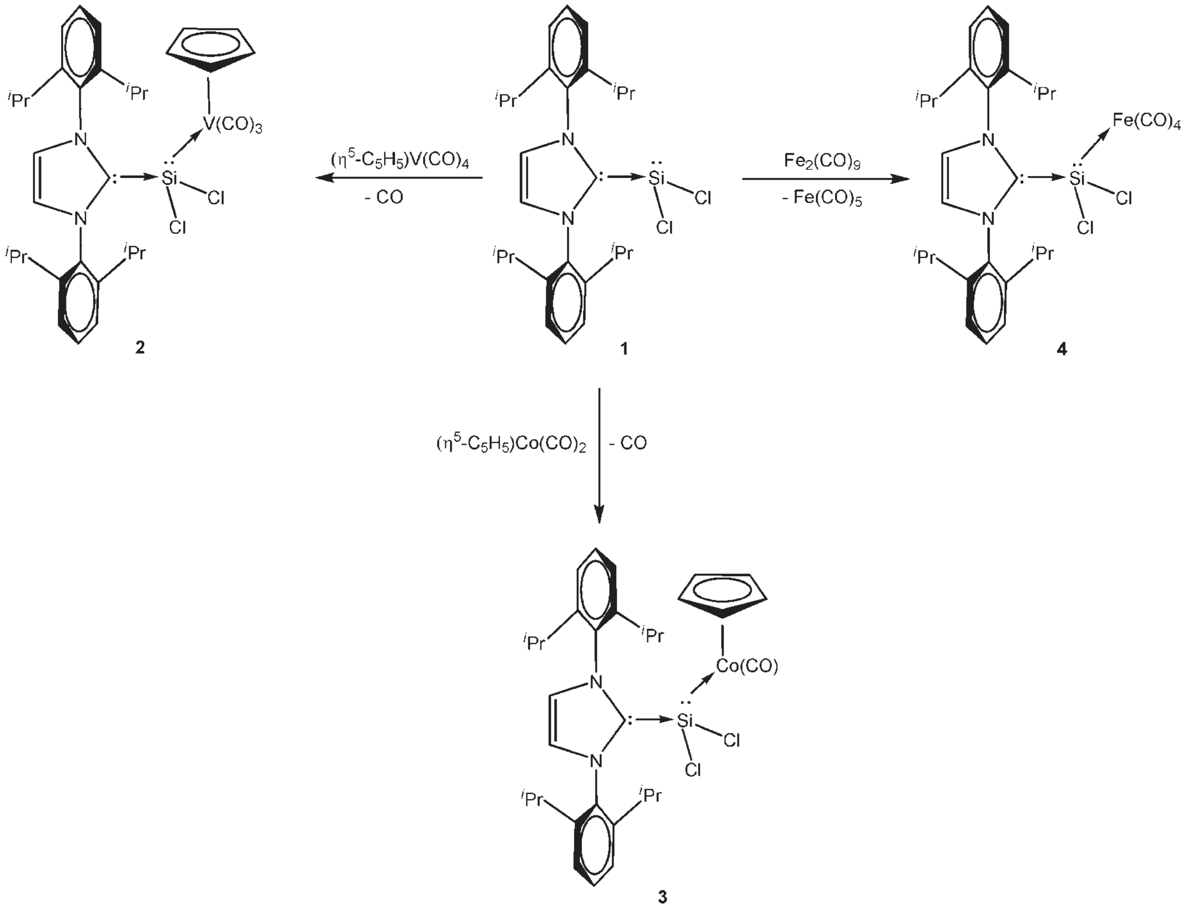
Synthesis of $IPr\cdot SiCl_2\cdot Fe(CO)_4$ (4). Toluene (50 mL) was added to a mixture of $IPr\cdot SiCl_2$ (**1**) (1.56 g, 3.20 mmol) and $Fe_2(CO)_9$ (1.16 g, 3.19 mmol) in a Schlenk flask at room temperature. After 12 h of stirring, all volatiles were removed under vacuum to obtain a brown solid. Recrystallization from a solution of dichloromethane (15 mL) and *n*-hexane (10 mL) at −35 °C afforded complex **4** as colorless crystals (1.02 g, 48%). Anal. calcd for $C_{31}H_{36}Cl_2FeN_2O_4Si$ (M = 655): C, 56.80; H, 5.54; N, 4.27. Found (%): C, 56.71; H, 5.43; N, 4.22. ^1H NMR (200 MHz, CD_2Cl_2, 298 K): δ 1.13 (d, *J* = 6.70 Hz, 12H, $CHMe_2$), 1.41 (d, *J* = 6.54 Hz, 12H, $CHMe_2$), 2.72 (m, 4H, $CHMe_2$), 7.15 (s, 2H, NC*H*), 7.30−7.51 (m, 6H, C_6H_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2, 298 K): δ 22.74 ($CHMe_2$), 26.51 ($CHMe_2$), 29.46 ($CHMe_2$), 125.02 (NCH), 125.51, 127.99, 128.58, 131.15, 134.13 (C_6H_3), 145.96 (*ipso*-C_6H_3) 214.95 (CO) ppm. ^{29}Si NMR (99 MHz, CD_2Cl_2, 298 K): δ 59.19 ppm. ^1H NMR (500 MHz, C_6D_6, 298 K): δ 0.92 (d, *J* = 6.69 Hz, 12H, $CHMe_2$), 1.44 (d, *J* = 6.54 Hz, 12H, $CHMe_2$), 2.77 (m, 4H, $CHMe_2$), 6.36 (s, 2H, NC*H*), 6.99−7.28 (m, 6H, C_6H_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 298 K): δ 22.76 ($CHMe_2$), 26.05 ($CHMe_2$), 29.12 ($CHMe_2$), 124.61 (NCH), 125.63, 126.53, 127.81, 129.65, 130.91, 132.02, 134.15 (C_6H_3), 146.62 (*ipso*-C_6H_3) 191.56, 215.81 (CO) ppm. ^{29}Si NMR (99 MHz, C_6D_6, 298 K): δ 59.20 ppm.

■ RESULTS AND DISCUSSION

Synthesis and Characterization. Reaction of $IPr\cdot SiCl_2$ (**1**) with $(\eta^5\text{-}C_5H_5)V(CO)_4$, $(\eta^5\text{-}C_5H_5)Co(CO)_2$, and $Fe_2(CO)_9$ afforded NHC stabilized dichlorosilylene complexes $IPr\cdot SiCl_2\cdot V(CO)_3(\eta^5\text{-}C_5H_5)$ (**2**), $IPr\cdot SiCl_2\cdot Co(CO)(\eta^5\text{-}C_5H_5)$ (**3**), and $IPr\cdot SiCl_2\cdot Fe(CO)_4$ (**4**), respectively (Scheme 1).

Complexes **2**−**4** are crystalline solids, soluble in common organic solvents, and stable under an inert atmosphere. These complexes were characterized by elemental analyses and ^1H, ^{13}C, and ^{29}Si NMR spectroscopic studies. ^1H NMR spectra of **2**−**4** show two sets of resonances for methyl protons ($CHMe_2$) of isopropyl groups, whereas methine protons appear as a multiplet. Imidazole backbone protons exhibit a singlet and show solvent dependence. Complexes **2** and **3** each show a singlet for cyclopentadienyl (C_5H_5) protons. $^{13}C\{^1H\}$ NMR spectra of **2**−**4** exhibit usual resonances for the IPr ligand. In the ^{13}C NMR spectra (in CD_2Cl_2) of **2** and **3**, a resonance at δ 90.78 and 82.17 ppm, respectively, may be assigned for each cyclopentadienyl group. Complex **2** exhibits a broad ^{29}Si NMR signal at δ 88.70 ppm due to the presence of paramagnetic vanadium. Similar broadening can also be seen in the $^{13}C\{^1H\}$ NMR spectrum of **2** for carbonyl groups (δ 259.20−263.03 ppm).

Scheme 1



However, resonances for the IPr ligand in **2** exhibit without any broadening. ^{51}V NMR resonance for **2** appears at δ −1593.46 ppm, which is consistent with those observed for analogues vanadium complexes.[26] For the carbonyl group, **3** and **4** show ^{13}C NMR resonances between δ 191 and 219 ppm. ^{29}Si NMR spectra of **3** and **4** exhibit a resonance at 31.86 and 59.20 ppm, which is consistent with those observed for TM−silylene complexes.[19,20]

Single Crystal X-ray Structure Determination. *Single Crystal X-ray Structures.* Molecular structures of compounds **2**−**4** were established by single-crystal X-ray crystallographic studies and corresponding ORTEP-representations are shown in Figures 1−3. Crystallographic data for **2**−**4** are summarized in Table 1. All crystals were measured on a Bruker three-circle diffractometer equipped with a SMART 6000 CCD area detector and a CuKα rotation anode. Integrations were performed with SAINT.[27] Intensity data for all compounds were corrected for absorption and scaled with SADABS.[28] Structures were solved by direct methods and initially refined by full-matrix least-squares methods on F^2 with the program SHELXL-97,[29] utilizing anisotropic displacement parameters for nonhydrogen atoms. The structural model was improved by a subsequent refinement with nonspherical scattering factors,[30] which was initiated by converged IAM parameter values. The scattering-factor model used in this refinement was based on the Hansen and Coppens multipole formalism.[31] For compounds **2** and **4** hydrogen atoms were included in the model by constraints via a riding model,and in case of **3**, hydrogen atoms were refined freely. Instead of adjusting the respective multipole parameters to the experimental data, which requires Bragg data to a high resolution, multipole parameters were predicted from theoretical calculations on each whole molecule, using the density functional theory (DFT) functional B3LYP and 6-31 g* as the basis set. This procedure is different to the fragment-based invariom approach.[32] Prior to refinement with XDLSM as part of the XD suite,[33] input files were processed with the program InvariomTool.[32] The criterion for observed reflections was [$I > 3\sigma(I)$]. Only positional and displacement parameters of nonhydrogen atoms were adjusted in the nonspherical atom refinement, so that the number of parameters was not increased in comparison to the IAM. Bond distances to hydrogen atoms were set to values from geometry optimization.[34] These aspherical atom refinements share the benefits of a conventional charge density refinement. For all compounds, parameter precision (as indicated by parameter standard deviations) and figures of merit improve. Anisotropic displacement parameters (ADPs) become deconvoluted from electron density, and an interpretable electron density model was obtained (Figures 1−3). Calculated deformation densities show the expected electron density accumulations in bonding regions. Valence-shell charge concentrations (VSCC) of σ-donation can also be localized by calculating and interpreting the Laplacian of the electron density. These results are presented for compounds **2**−**4** (Figures 1−3).

Complex **2** is the first example of a vanadium−silylene complex that has been characterized by single crystal X-ray

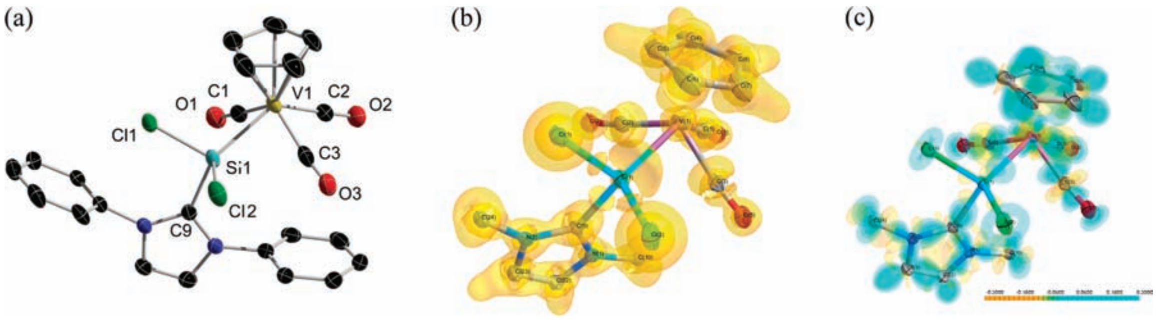


Figure 1. (a) ORTEP-representation of the molecular structure of **2**. ADPs are depicted at the 50% probability level. Isopropyl groups and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si(1)−C(9) 1.98452(2), Si(1)−Cl(1) 2.1120(8), Si(1)−Cl(2) 2.1264(10), V(1)−Si(1) 2.4043(7), V(1)−C(1) 1.9223(2), V(1)−C(4) 2.2649(3); and C(1)−V(1)−Si(1) 127.97(8), C(3)−V(1)−Si(1) 76.32(8), C(9)−Si(1)−Cl(1) 98.35(7), C(9)−Si(1)−Cl(2) 96.53(7), Cl(1)−Si(1)−Cl(2) 99.61(3), C(9)−Si(1)−V(1) 129.99(7). (b) Isosurface plot of the Laplacian $\nabla^2\rho(r)$ [e$Å^{-5}$] of the electron density of **2** from aspherical atom refinement with an isosurface value of 0.2 e/$Å^5$. Phenyl, isopropyl groups, and hydrogen atoms were omitted for clarity. The VSCCs from σ-donation are visible on the C(9)−Si(1) and Si(1)−V(1) bonds. (c) Deformation electron density plot[35] of **2**.

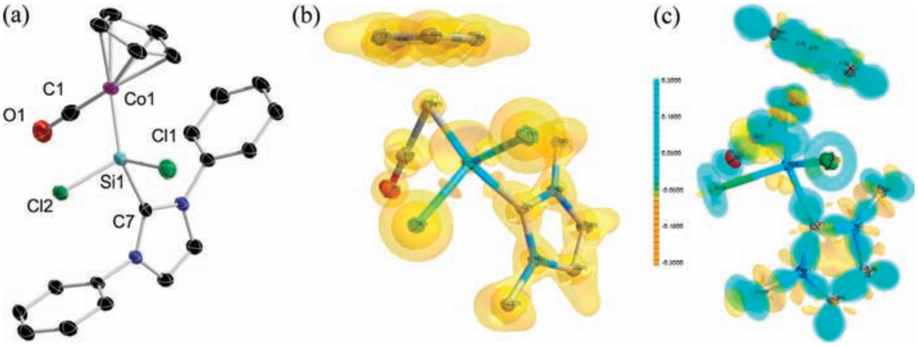


Figure 2. (a) ORTEP representation of the molecular structure of **3**. Anisotropic displacement parameters are depicted at the 50% probability level. Isopropyl groups and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si(1)−Cl(2) 2.0989(4), Si(1)−Cl(1) 2.1127(5), C(7)−Si(1) 1.96059(16), Si(1)−Co(1) 2.1349(4); and Si(1)−Co(1)−C(6) 98.68(5), C(7)−Si(1)−Cl(2) 101.10(4), C(7)−Si(1)−Cl(1) 96.83(4), Cl(2)−Si(1)−Cl(1) 100.42(2), C(7)−Si(1)−Co(1) 121.17(4), Cl(2)−Si(1)−Co(1) 115.68(2), Cl(1)−Si(1)−Co(1) 117.88(2). (b) Isosurface plot of the Laplacian $\nabla^2\rho(r)$ [e$Å^{-5}$] from nonspherical atom refinement of **3** with an isosurface value of 0.2 e/$Å^5$. Phenyl, isopropyl groups, and hydrogen atoms are omitted for clarity. The VSCCs from σ-donation are clearly visible on the C(5)−Si(1) and Si(1)−Co(1) bonds. (c) Deformation electron density plot[35] of **3**.

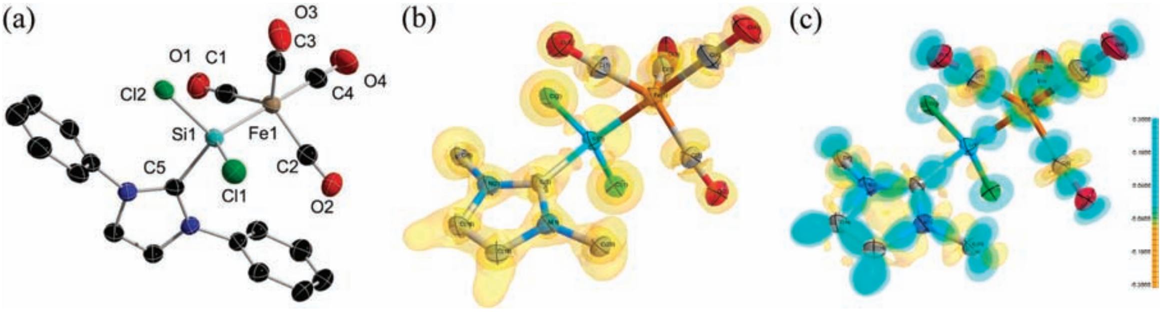


Figure 3. (a) ORTEP representation of the molecular structure of **4**. Anisotropic displacement parameters are depicted at the 50% probability level. Isopropyl groups and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si(1)−Cl(2) 2.0890(12), Si(1)−Cl(1) 2.0965(14), C(5)−Si(1) 1.958(3), Si(1)−Fe(1) 2.229(11); and Si(1)−Fe(1)−C(4) 176.84(18), C(5)−Si(1)−Cl(2) 101.16(12), C(5)−Si(1)−Cl(1) 99.03(12), Cl(2)−Si(1)−Cl(1) 102.10(5), C(5)−Si(1)−Fe(1) 121.73(12), Cl(2)−Si(1)−Fe(1) 112.97(5), Cl(1)−Si(1)−Fe(1) 116.92(5). (b) Isosurface plot of the Laplacian $\nabla^2\rho(r)$ of the electron density of **4** from aspherical atom refinement with an isosurface value of 0.2 e/$Å^5$. Phenyl, isopropyl groups, and hydrogen atoms are omitted for clarity. The VSCCs from σ-donation are visible on C(5)−Si(1) and Si(1)−Fe(1) bonds. (c) Deformation electron density plot of **4**.

crystallography (Figure 1a). Complex **2** crystallizes in the monoclinic space group *P*2(1)/*n* and features a distorted square-pyramidal geometry defined by the C_5H_5 centroid around the vanadium atom. Silicon is four coordinate and displays a

Table 1. Crystallographic Data and Structure Refinement for 2−4

	2·toluene	**3**·0.5 benzene	**4**
formula	$C_{42}H_{49}Cl_2N_2O_3SiV$	$C_{36}H_{44}Cl_2CoN_2OSi$	$C_{31}H_{36}Cl_2FeN_2O_4Si$
Fw	779.76	678	655.48
CCDC	826487	826486	826488
cryst size/mm	0.20 × 0.13 × 0.02	0.01 × 0.01 × 0.01	0.20 × 0.12 × 0.12
cryst syst	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/n$	*Pbca*	*Fdd*2
T/°C	−173	−173	−173
a/Å	10.2337(2)	15.4231(3)	33.7046(11)
b/Å	19.3235(3)	18.8135(4)	38.9594(13)
c/Å	20.2250(4)	23.9576(4)	10.2939(4)
α/°	90	90	90
β/°	92.7920(10)	90	90
γ/°	90	90	90
V/Å^3	3994.76(13)	6951.6(2)	13517.0(8)
D_{calcd}/g cm^{-3}	1.297	1.297	1.288
Z	4	8	16
wavelength/ Å	1.54178	1.54178	1.54178
abs coeff/mm^{-1}	3.907	5.842	5.661
θ range/°	3.16−71.94	3.69−72.52	3.47−71.89
reflns collected/indep reflns	26872/7266 [R(int) = 0.0287]	22847/6840 [R(int) = 0.0760]	25685/5420 [R(int) = 0.0730]
max. and min transmn	0.3674 and 0.4696	0.7535 and 0.5685	0.2775 and 0.4690
final $R1$ indices	0.041	0.024	0.052
$wR2$ indices (all data)	0.056	0.027	0.060
largest diff peak and hole/e Å^3	0.828 and −0.455	0.312 and −0.159	0.952 and −0.326

distorted tetrahedral geometry. The coordination environment around vanadium consists of three carbonyl groups, one (η^5-C_5H_5), and a neutral silylene ligand. The V−Si bond length (2.4045(8) Å) in **2** is shorter than those observed for vanadium−silyl (~2.56 Å) complexes,[26] indicating a contribution of π-back bonding. The Cl−Si−Cl bond angle in **2** (99.63(4)°) is comparable to that in **1** (97.25(6)°). The mean Si−Cl bond length (av 2.1192(11)°) in **2** is slightly shorter than that observed for **1** (av 2.1664(16) Å), which may be interpreted as increased Lewis acidity of the silicon due to the σ-electron donation to the vanadium atom. The V−C((η^5-C_5H_5)) interatomic bond distances (2.250 to 2.287 Å) are similar to the corresponding distances in vanadocene (av 2.26 Å).[36] The C−Si−V bond angle is 129.99(7)°.

The molecular structure of complex **3** is shown in the Figure 2a. Complex **3** crystallizes in the orthorhombic space group *Pbca* with half a benzene molecule in the asymmetric unit. The silicon atom is four coordinate and features a distorted tetrahedral geometry. The cobalt atom assumes distorted trigonal planar coordination geometry defined by the C_5H_5 centroid, the CO ligand, and the silylene (**1**) ligand. The Co−Si bond length of 2.1348(5) Å is shorter than those reported for $[Co(CO)_3\{SiCl_2(IPr)\}_2][CoCl_3(THF)]$ (2.2278(13) and 2.2276(12) Å).[19] The Si−Cl (av 2.1062(6) Å) and Si−C (1.9564(16) Å) bond lengths are shorter than those observed in **1** (av 2.1664(16) and 1.985(4) Å). The C−Si−Co bond angle is 121.23(5)°.

The molecular structure of complex **4** is shown in Figure 3a. Complex **4** crystallizes in orthorhombic space group *Fdd*2. The geometry around the iron atom is distorted trigonal bipyramidal with three equatorial positions occupied by carbonyl groups and each of the two axial positions by a carbonyl group and a silylene ligand. The silicon center is four coordinate and features a distorted tetrahedral geometry. The Si−Fe bond distance in **4** (2.2315(13) Å) is comparable to those observed in silylene−iron complexes.[17,22] The average Si−Cl bond length (av 2.0916(16)°) in **4** is slightly shorter than those observed for **1** (av 2.1664(16) Å) and **2** (av 2.1192(11)°). The Si−C-(carbene) bond distance (1.949(4) Å) is shorter than that obtained for **1** (1.985(4) Å) and **2** (1.984(3) Å). The axial Si−Fe−C bond angle is almost linear (177.01(19)°).

■ CONCLUSION

A direct method to prepare dichlorosilylene complexes $IPr\cdot SiCl_2\cdot V(CO)_3(\eta^5\text{-}C_5H_5)$ (**2**), $IPr\cdot SiCl_2\cdot Co(CO)(\eta^5\text{-}C_5H_5)$ (**3**), and $IPr\cdot SiCl_2\cdot Fe(CO)_4$ (**4**) is reported. Complexes **2**−**4** have been characterized by elemental analyses and NMR spectroscopy. Molecular structures of **2**−**4** have been established by single crystal X-ray crystallography and subsequent aspherical atom refinement. Complex **2** is the first structurally characterized vanadium−silylene complex. The ambiphilic nature of dichlorosilylene is demonstrated in TM complexes **2**−**4**.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Crystallographic data for complexes **2**−**4** as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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(35) Deformation electron density plot, which shows the difference between the total electron density (as modelled by the nonspherical scattering factors) and the independent atom model. Deformation density represents the nonspherical part of the electron density and highlights the covalent character of most bonds. Values of isosurface range from −0.3 to 0.3 e/Å^3 with step sizes of 0.1 e/Å^3, as indicated in the legend. Phenyl, isopropyl groups, and hydrogen atoms were omitted for clarity.

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