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

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ABSTRACT: Reactions of N-heterocyclic carbene stabilized dichlorosilylene IPr·SiCl2 (1) (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) with \((\eta^5-C_5H_5)V(CO)_{14}\), \((\eta^5-C_5H_5)Co(CO)_{12}\), and \(Fe_2(CO)_9\) afford dichlorosilylene complexes IPr·SiCl2·V(CO)\((\eta^5-C_5H_5)\) (2), IPr·SiCl2·Co(CO)\((\eta^5-C_5H_5)\) (3), and IPr·SiCl2·Fe(CO)\((\eta^5-C_5H_5)\) (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 (\(^1H\), \(^13C\), and \(^29Si\)) 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 \(\sigma\)-donor ligands for transition-metal (TM) complexes \(^5,^6\) and as effective Lewis bases to stabilize reactive main group element species \(^5,^4\) and as organocatalysts on their own right. \(^7\) Use of NHCs as spectator ligands, particularly as alternatives to phosphines (\(\text{R}_3\text{P}\)), resulted in a second generation of Grubbs catalysts. \(^8\) 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, \(^6\) dehydroxylation of organosilicon compounds, \(^9\) redistribution of substituents on organosilicon compounds, \(^10\) and deoligomerization of disilanyl-metal 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 \((\text{SiCl}_2)\), 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 \(\pi\)-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 \(\sigma\)-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 \(\sigma\)-donor ligand for the TM complexes \([\text{Co}(\text{CO})_3\{\text{SiCl}_2\text{(IPr)}\}]_2[\text{CoCl}_3(\text{THF})]\) \(^19\) and Ni(\(\text{CO})_2\{\text{SiCl}_2\text{(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)\(_3\)VSiH\(_3\), \((\eta^5-C_5H_5)V(\text{SiCl}_3)_{22}\), \((\eta^5-C_5H_5)V(\text{N}’\text{Bu})(\text{NH}’\text{Bu})\text{Si}(\text{Me}_3)_{3}\), and \((\eta^5-C_5H_5)V(\text{L})_2(\text{SiHRR})_2(L = 1,2\text{-bis(dimethylphosphino)ethane}; \text{R} = \text{Ph or} \quad\text{Me})\).
Mes, and $R' = \text{Ph or H}$), containing vanadium—silicon bonds which have been characterized by X-ray crystallographic studies.\textsuperscript{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.\textsuperscript{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—or carbene complexes, TM—silylene complexes derived from stable silylenes are still elusive. Herein, we report on a convenient access to TM complexes ($M = 687$): C, 61.13; H, 6.01; N, 4.07. Found (%): C, 61.01; H, 5.87; N, 4.27.\textsuperscript{1}H NMR (200 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ 1.32 (d, $J = 6.64$ Hz, 12H, CH$_3$), 1.68 (d, $J = 6.66$ Hz, 12H, CHMe$_2$), 3.00 (q, $J = 6.76$ Hz, 4H, CHMe$_2$), 4.49 (q, $J = 6.84$ Hz, 4H, CHMe$_2$), 7.20 (s, 2H, NCH), 7.36–7.42 (m, 4H, CH$_2$), 7.50–7.56 (m, 2H, CH$_2$) ppm. $^{13}$C$_{\text{H}}$ NMR (125 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ 22.78 (CHMe$_2$), 26.30 (CHMe$_2$), 25.61 (CHMe$_2$), 82.17 (C$_H$), 124.87 (NCH), 125.23, 125.82, 126.11, 129.54, 131.67, 132.48, 134.76 (C$_H$), 146.33 ($\text{ipso-C}_H$), 153.01 (NCH) 205.97 (br, CO) ppm. $^{29}$Si NMR (99 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ 31.86 ppm.

## 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$_3$SiCl$_2$ (1) was prepared according to the method given in the literature. Without further purification, ($\eta^5$-C$_5$H$_5$)V(CO)$_2$ ($\eta^5$-C$_5$H$_5$)Co(CO)$_2$ (2), IPr$_3$SiCl$_2$Co(CO)$_2$ ($\eta^5$-C$_5$H$_5$)$_2$ (3), and IPr$_3$SiCl$_2$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.

### RESULTS AND DISCUSSION

#### Synthesis of IPr$_3$SiCl$_2$-Co(CO)$_2$($\eta^5$-C$_5$H$_5$)$_2$ (2).
To a Schlenk containing IPr$_3$SiCl$_2$ (1) (0.59 g, 1.21 mmol) and ($\eta^5$-C$_5$H$_5$)V(CO)$_2$ (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 $\sim$35 °C in a freezer to yield complex IPr$_3$SiCl$_2$-V(CO)$_2$ ($\eta^5$-C$_5$H$_5$)$_2$ (2) as red crystals (0.61 g, 73%). Anal. calc. (%): for C$_{35}$H$_{41}$Cl$_2$N$_2$O$_3$SiV (M = 687): C, 61.13; H, 6.01; N, 4.07. Found (%): C, 61.01; H, 5.87; N, 4.27. $^1$H NMR (200 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ 1.32 (d, $J = 6.64$ Hz, 12H, CH$_3$), 1.68 (d, $J = 6.66$ Hz, 12H, CHMe$_2$), 3.00 (q, $J = 6.76$ Hz, 4H, CHMe$_2$), 4.49 (q, $J = 6.84$ Hz, 4H, CHMe$_2$), 7.20 (s, 2H, NCH), 7.36–7.42 (m, 4H, CH$_2$), 7.50–7.56 (m, 2H, CH$_2$) ppm. $^{13}$C$_{\text{H}}$ NMR (75 MHz, C$_6$D$_6$, 298 K): $\delta$ 22.78 (CHMe$_2$), 26.30 (CHMe$_2$), 25.61 (CHMe$_2$), 82.17 (C$_H$), 124.87 (NCH), 125.23, 125.82, 126.11, 129.54, 131.67, 132.48, 134.76 (C$_H$), 146.33 ($\text{ipso-C}_H$), 153.01 (NCH) 205.97 (br, CO) ppm. $^{29}$Si NMR (99 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ 31.86 ppm. $^{29}$Si NMR (99 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ 31.86 ppm.
However, resonances for the IPr ligand in 2 exhibit without any broadening. $^{51}$V NMR resonance for 2 appears at $\delta = -1593.46$ ppm, which is consistent with those observed for analogues vanadium complexes. For the carbonyl group, 3 and 4 show $^{13}$C NMR resonances between $\delta = 191$ 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. 

**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. Intensity data for all compounds were corrected for absorption and scaled with SADABS. Structures were solved by direct methods and initially refined by full-matrix least-squares methods on $F^2$ with the program SHELXL-97, utilizing anisotropic displacement parameters for nonhydrogen atoms. The structural model was improved by a subsequent refinement with nonspherical scattering factors, 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. 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. Prior to refinement with XDLSM as part of the XD suite, input files were processed with the program InvariomTool. 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. 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 $\sigma$-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
crystallography (Figure 1a). Complex 2 crystallizes in the monoclinic space group \( \text{P2}(1) / n \) and features a distorted square-pyramidal geometry defined by the \( \text{C}_9\text{H}_5 \) centroid around the vanadium atom. Silicon is four coordinate and displays a
distorted tetrahedral geometry. The coordination environment around vanadium consists of three carbonyl groups, one (η⁵-C₅H₅), 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, indicating a contribution of π-back bonding. The Cl–Si–Cl bond angle in 2 (99.63(4)°) is comparable to that in I (97.25(6)°). The mean Si–Cl bond length (av 2.1192(11) Å) and Si bond lengths (av 2.1664(16) Å), which may be interpreted as increased Lewis acidity of the silicon due to the π-electron donation to the vanadium atom. The V–C(η⁵-C₅H₅)) intratetrahedral bond distances (2.250 to 2.287 Å) are similar to the corresponding distances in vanadocene (av 2.26 Å). The C–Si–V bond angle is 129.99(7)°.

The molecular structure of complex 3 is shown in 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 Si–Fe bond distance in 4 (2.2315(13) Å) is comparable to those observed in silylene–iron complexes. The average Si–Cl bond length (av 2.0916(16) Å) 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)-SiCl₂·V(CO)₃(η⁵-C₅H₅) (2), (IPr)-SiCl₂·Co(CO)(η⁵-C₅H₅) (3), and (IPr)-SiCl₂·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/Å³ with step sizes of $0.1$ e/Å³, as indicated in the legend. Phenyl, isopropyl groups, and hydrogen atoms were omitted for clarity.

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