Inorganic Chemistry
Article

Inorg. Chem. **2010**, *49*, 10199–10202 **10199**
DOI: 10.1021/ic101556s

Facile Syntheses of Silylene Nickel Carbonyl Complexes from Lewis Base Stabilized Chlorosilylenes[†]

Gašper Tavčar, Sakya S. Sen, Ramachandran Azhakar, Andrea Thorn, and Herbert W. Roesky*

Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, 37077 Göttingen, Germany

Received August 2, 2010

Two silylene nickel carbonyl complexes of composition $\mathbf{L}\cdot\mathrm{Ni(CO)_3}$ (**1**) {**L** = PhC(N*t*Bu)$_2$SiCl} and $\mathbf{L'}_2\cdot\mathrm{Ni(CO)_2}$ (**2**) { **L′** = RSiCl$_2$, R = (1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene)} were prepared by reacting 1 equivalent of Ni(CO)$_4$ with 1 equivalent of heteroleptic chlorosilylene **L** for **1** and with 2 equivalents of carbene stabilized dichlorosilylene **L′** for **2** in toluene at room temperature. Both complexes **1** and **2** were characterized by single-crystal X-ray analysis, NMR and IR spectroscopy, EI-MS spectrometry, and elemental analysis.

Introduction

Transition-metal silylene complexes are of great interest due to their similarity to transition-metal carbene complexes because the latter serve as extremely successful catalysts for many organic transformations.[1] In organosilicon chemistry, these silylene metal complexes are postulated as catalytic intermediates in a number of metal-catalyzed silylene transfer reactions.[2,3] In 1987, Tilley and co-workers reported on two base-stabilized silylene complexes, (CO)$_4$FeSi(O*t*Bu)$_2${(O)P-[NMe$_2$]$_3$} and {Cp*[Me$_3$P]$_2$RuSiPh$_2$[MeCN]}$^+$.[4] Another promising route to prepare metal-silylene complexes is the utilization of N-heterocyclic silylenes (NHSi's). This approach is due to the significant p-electron donation from the adjacent nitrogen lone pairs into empty p orbitals on silicon, which leads to a strong stabilization of the NHSi's. NHSi's can be considered as ligands having donor and acceptor properties.[5,6] As a result, they can form stable transition metal complexes with back bonding from the metal to the silicon center.

In 1994, West and co-workers isolated Ni(CO)$_2$(NHSi)$_2$ [NHSi = (*t*BuNCH=CHN*t*Bu)Si] from the reaction of NHSi with Ni(CO)$_4$ in a molar ratio of 2:1.[7] The success of this reaction enthroned silylene as the pre-eminent ligand in transition metal chemistry and established the concept that NHSi's may resemble phosphines as ligands for transition metals. Since then, there has been a burgeoning interest in reactions of stable silylenes with transition metals.[6,8−11]

[†] Dedicated to Professor Wolfgang Kaim on the occasion of his 60th birthday.

[*] Author to whom correspondence should be addressed: E mail: hroesky@gwdg.de.

(1) (a) Nolan, S. P. In *N-Heterocyclic Carbenes in Synthesis*; Wiley-VCH: Weinheim, Germany, 2006. (b) Glorius, F. In *N-Heterocyclic Carbenes in Transition Metal Catalysis*; Springer-Verlag: Berlin, 2007. (c) Clavier, H.; Nolan, S. P. *Annu. Rep. Prog. Chem., Sect B: Org. Chem.* **2007**, *103*, 193–222. (d) Weskamp, T.; Böhm, V. P. W.; Herrmann, W. A. *J. Organomet. Chem.* **2000**, *600*, 12–22. (e) Jafarpour, L.; Nolan, S. P. *Adv. Organomet. Chem.* **2000**, *46*, 181–222. (f) Harrold, N. D.; Waterman, R.; Hillhouse, G. L.; Cundari, T. R. *J. Am. Chem. Soc.* **2009**, *131*, 12872–12873. (g) Sinha, A.; Rahaman, S. M. W.; Sarkar, M.; Saha, B.; Daw, P.; Bera, J. K. *Inorg. Chem.* **2009**, *48*, 11114–11122. (h) Lee, Y.; Li, B.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 11625–11633.

(2) Lewis, K. M.; Rethwisch, D. G. In *Catalyzed Direct Reactions of Silicon*; Elsevier: Amsterdam, The Netherlands, 1993.

(3) (a) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351–1374. (b) Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213–232. (c) Gauvin, F.; Harrod, J. F.; Woo, H. G. *Adv. Organomet. Chem.* **1998**, *42*, 363–405. (d) Corey, J. Y. *Adv. Organomet. Chem.* **2004**, *51*, 1–52. (e) Tilley, T. D. *Comments Inorg. Chem.* **1990**, *10*, 37–46. (e) Fürstner, A.; Krause, H.; Lehmann, C. W. *Chem. Commun.* **2001**, *22*, 2372–2373. (f) Calimano, E.; Tilley, T. D. *J. Am. Chem. Soc.* **2009**, *131*, 11161–11173. (g) Prévost, M.; Woerpel, K. A. *J. Am. Chem. Soc.* **2009**, *131*, 14182–14183. (h) Ohmura, T.; Masuda, K.; Takase, I.; Suginome, M. *J. Am. Chem. Soc.* **2009**, *131*, 16624–16625.

(4) (a) Zybill, C.; Müller, G. *Angew. Chem.* **1987**, *99*, 683–684. Ibid. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 669−670. (b) Straus, D. A.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 5872–5873.

(5) (a) Li, R.-E.; Sheu, J.-H.; Su, M.-D. *Inorg. Chem.* **2007**, *46*, 9245–9253. (b) Bharatam, P. V.; Moudgil, R.; Kaur, D. *Inorg. Chem.* **2003**, *42*, 4743–4749. (c) Bharatam, P. V.; Moudgil, R.; Kaur, D. *Organometallics* **2002**, *21*, 3683–3690.

(6) Schmedake, T. A.; Haaf, M.; Paradise, B. J.; Millevolte, A. J.; Powell, D.; West, R. *J. Organomet. Chem.* **2001**, *636*, 17–25.

(7) Haaf, M.; Hayashi, R.; West, R. *J. Chem. Soc., Chem. Commun.* **1994**, 33–34.

(8) (a) West, R.; Denk, M. *Pure Appl. Chem.* **1996**, *68*, 785–788. (b) Feldman, J. D.; Mitchell, G. P.; Nolte, J.-O.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 11184–11185. (c) Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Maciejewski, H. *Organometallics* **1998**, *17*, 5599–5601. (d) Petri, S. H. A.; Eikenberg, D.; Neumann, B.; Stammler, H.-G.; Jutzi, P. *Organometallics* **1999**, *18*, 2615–2618. (e) Schmedake, T. A.; Haaf, M.; Paradise, B. J.; Powell, D.; West, R. *Organometallics* **2000**, *19*, 3263–3265. (f) Dysard, J. M.; Tilley, T. D. *Organometallics* **2000**, *19*, 4726–4732. (g) Clendenning, S. B.; Gehrhus, B.; Hitchcock, P. B.; Moser, D. F.; Nixon, J. F.; West, R. *J. Chem. Soc., Dalton Trans.* **2002**, 484–490. (h) Amoroso, D.; Haaf, M.; Yap, G. P. A.; West, R.; Fogg, D. E. *Organometallics* **2002**, *21*, 534–540. (i) Avent, A. G.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Maciejewski, H. *J. Organomet. Chem.* **2003**, *686*, 321–331.

(9) Haaf, M.; Schmedake, T. A.; West, R. *Acc. Chem. Res.* **2000**, *33*, 704–714.

(10) (a) Yang, W.; Fu, H.; Wang, H.; Chen, M.; Ding, Y.; Roesky, H. W.; Jana, A. *Inorg. Chem.* **2009**, *48*, 2058–2060. (b) Li, J.; Merkel, S.; Henn, J.; Meindl, K.; Döring, A.; Roesky, H. W.; Ghadwal, R. S.; Stalke, D. *Inorg. Chem.* **2010**, *49*, 775–777.

(11) Meltzer, A.; Präsang, C.; Driess, M. *J. Am. Chem. Soc.* **2009**, *131*, 7232–7233.

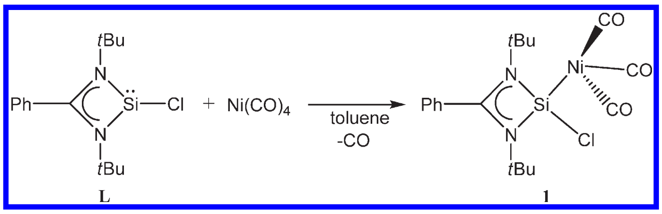
The carbene transition metal complexes are serving as powerful catalysts for several organic transformations; therefore, the study of silylene−metal complexes seems promising. Moreover, such compounds may also be studied as precursors for preparing silicon−metal alloys by chemical vapor deposition.[9]

Recently, we reported the facile synthesis of tricoordinate stable heteroleptic chlorosilylene $PhC(N\textit{t}Bu)_2SiCl$ (**L**)[12] and N-heterocyclic carbene stabilized dichlorosilylene ($RSiCl_2$, R = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene) (**L′**).[13] These compounds can be considered as tamed silicon dichloride[14] having one or two reactive Si−Cl bonds compared to other dicoordinate stable silylenes. Previously, we also showed that tricoordinate silylene is capable of forming silylene transition metal complexes. For example, treatment of $PhC(N\textit{t}Bu)_2SiO\textit{t}Bu$ with $Fe_2(CO)_9$ yielded $PhC(N\textit{t}Bu)_2SiO\textit{t}Bu \cdot Fe(CO)_4$,[10a] whereas **L′**, when reacted with $Co_2(CO)_8$, yielded $[Co(CO)_3\{\mathbf{L'}\}_2]^+[CoCl_3(THF)]^-$.[10b] To gain further insight into the structure and bonding of silylene units bearing unsupported Si−M bonds (M = transition metal), we embarked on extending our investigation to $Ni(CO)_4$. Unlike chromium hexacarbonyl (d^6, saturated), iron pentacarbonyl (d^8, saturated), and cobalt carbonyl (d^9, unsaturated), $Ni(CO)_4$ (d^{10}, saturated) is the most labile and most reactive toward ligand exchange. The rate of exchange is first order, and proportional to the concentration of $Ni(CO)_4$.[15] Very recently, Driess et al. documented the formation of silylene−nickel carbonyl complex $R'Si \cdot Ni(CO)_3$ [R = $CH[(C{=}CH_2)CMe(NAr)_2]$, Ar = 2,6-$\textit{i}Pr_2C_6H_3$][11] and showed its remarkable reactivity toward H_2S, NH_3, $\textit{i}PrNH_2$, and $H_2NNH(Ph)$.[16] In all of these reactions, the $Ni(CO)_3$ group played the role of an umbrella by using the lone pair of electrons of silicon. In view of these results, we selected $Ni(CO)_4$ and probed its reaction with **L** and **L′**, respectively.

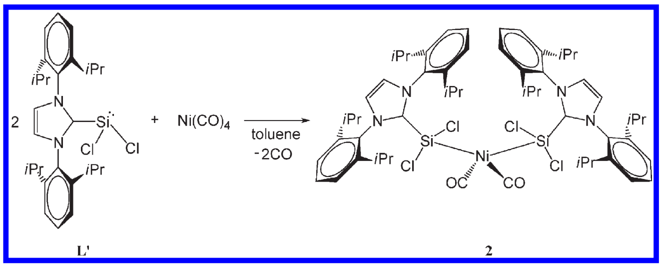
Results and Discussion

Synthetic and Spectroscopic Aspects. The synthetic strategy for the title compounds involves the one-pot reaction of $Ni(CO)_4$ with the starting materials **L** and **L′**, respectively. In **L**, the silicon exhibits a tricoordinate site (2N, 1Cl) and can act as a two-electron donor. In **L′**, the silicon is stabilized by an N-heterocyclic carbene and features a tricoordinate center with a lone pair of electrons on silicon (1C, 2Cl). The reactions of $Ni(CO)_4$ with **L** and **L′** are straightforward, which afforded silylene nickel carbonyl complexes **1** and **2**, respectively. In case of **L**, the reaction proceeds from a 1:1 molar ratio to afford $\mathbf{L} \cdot Ni(CO)_3$ (**1**), where one carbonyl group was displaced (Scheme 1), whereas in **L′**, the reaction proceeds with 1:2 equivalents to afford $\mathbf{L'}_2Ni(CO)_2$ (**2**) with the displacement of two CO molecules (Scheme 2). Both products are extremely air- and moisture-sensitive and immediately decompose when exposed to air. Complexes **1** and **2** are soluble in solvents like diethyl ether, toluene, and THF. The number of carbonyl groups displaced from $Ni(CO)_4$ might be due to electronic factors of the ligand. A practical consequence is that the elimination of CO can be fine-tuned by alteration of the substituents on the nitrogen atoms of the silylene ligand.

Scheme 1. Synthesis of **1**



Scheme 2. Synthesis of **2**



The coordination of the Ni atom to silicon resulted in a downfield chemical shift in the ^{29}Si NMR spectrum. The silylene−nickel complex of **1** resonates at δ 62.69 ppm (^{29}Si NMR of **L**: 14.16 ppm), while in **2** it is observed at δ 43.19 ppm (^{29}Si NMR of **L′**: 19.06 ppm). The downfield chemical shift is due to the deshielding upon coordination of the nickel atom to silicon. These values are consistent with those reported for base-stabilized silylene transition metal complexes (δ 40.30 ppm for $PhC(N\textit{t}Bu)_2SiO\textit{t}Bu \cdot Fe(CO)_4$ and δ 44.25 ppm for $[Co(CO)_3\{\mathbf{L'}\}_2]^+[CoCl_3(THF)]^-$).[10a,b] The ^1H NMR spectrum of **1** exhibits two sets of resonances: one for *t*Bu and another for phenyl protons [δ 1.06 ppm (^1H NMR of **L**: 1.08 ppm) and δ 6.71−6.95 ppm (^1H NMR of **L**: 6.78−7.05 ppm)], whereas in **2** the $-CH(CH_3)_2$ protons resonate at 0.96 and 1.51 ppm (^1H NMR for $-CH(CH_3)_2$ of **L′**: 1.01 and 1.43 ppm), $-CH(CH_3)_2$ at 2.94 ppm (^1H NMR for $-CH(CH_3)_2$ of **L′**: 2.79 ppm), and NC*H* at 6.23 ppm (^1H NMR for NC*H* of **L′**: 6.36 ppm). The ^{13}C NMR spectrum reveals the presence of carbonyl groups, resonating at δ 199.31 ppm for **1** and δ 202.51 ppm for **2**. Compound **1** shows the molecular ion in the EI-MS spectrum at *m*/*z* 438, while compound **2** exhibits only fragments. The CO stretching frequencies for **1** (1984 cm^{-1} and 1969 cm^{-1}) and for **2** (1974 cm^{-1} and 1921 cm^{-1}) are very close to the reported CO stretching frequencies for previously mentioned silylene metal carbonyl complexes and deviate significantly from that of $Ni(CO)_4$ (2060 cm^{-1}).[17] On the basis of these wave numbers, we can argue that the C−O bond energy in **1** is

---

(12) (a) So, C.-W.; Roesky, H. W.; Magull, J.; Oswald, R. B. *Angew. Chem.* **2006**, *118*, 4052–4054. Ibid. *Angew. Chem., Int. Ed.* **2006**, *45*, 3948–3950. (b) Sen, S. S.; Roesky, H. W.; Stern, D.; Henn, J.; Stalke, D. *J. Am. Chem. Soc.* **2010**, *132*, 1123–1126.

(13) Ghadwal, R. S.; Roesky, H. W.; Merkel, S.; Henn, J.; Stalke, D. *Angew. Chem.* **2009**, *121*, 5793–5796. Ibid. *Angew. Chem., Int. Ed.* **2009**, *48*, 5683 − 5686.

(14) (a) Schmeisser, M.; Voss, P. *Z. Anorg. Allg. Chem.* **1964**, *334*, 50–56. (b) Koe, J. R.; Powell, D. R.; Buffy, J. J.; Hayase, S.; West, R. *Angew. Chem.* **1998**, *110*, 1514–1515. Ibid. *Angew. Chem., Int. Ed.* **1998**, *37*, 1441–1442. (c) Weidenbruch, M. *Angew. Chem.* **2006**, *118*, 4347–4348. Ibid. *Angew. Chem., Int. Ed.* **2006**, *45*, 4241 − 4242.

(15) Hegedus, L. S. In *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Mill Valley, CA, 1994.

(16) Meltzer, A.; Inoue, S.; Präsang, C.; Driess, M. *J. Am. Chem. Soc.* **2010**, *132*, 3038–3046.

(17) Braga, D.; Grepioni, F.; Orpen, A. G. *Organometallics* **1993**, *12*, 1481–1483.

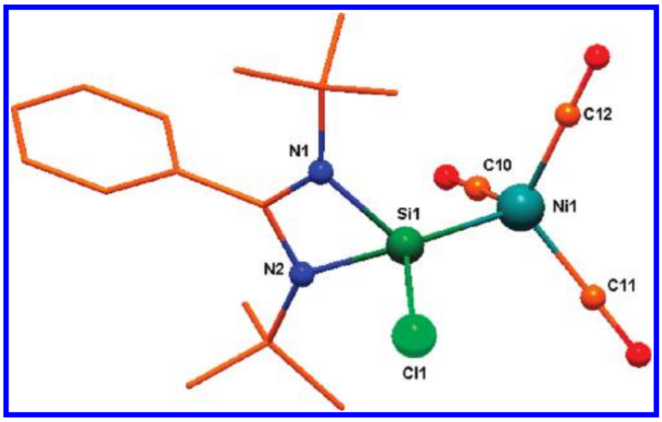


Figure 1. Crystal structure of **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni1−Si1 2.2111(8), Ni1−C10 1.795(2), Ni1−C11 1.7967(19), Ni1−C12 1.798(2), Cl1−Si1 2.1149(7), Si1−N1 1.8456(15), Si1−N2 1.8373(15); C10−Ni1−C11 114.39(9), C10−Ni1−C12 114.47(9), C11−Ni1−C12 110.48(8), C10−Ni1−Si1 102.67(7), C11−Ni1−Si1 105.66(6), C12−Ni1−Si1 108.31(6), N2−Si1−N1 71.15(7), N2−Si1−Cl1 102.23(5), N1−Si1−Cl1 102.24(5), N2−Si1−Ni1 123.18(5), N1−Si1−Ni1 125.63(5), Cl1−Si1−Ni1 120.87(3), N2−Si1−C26 35.72(6), N1−Si1−C26 35.81(6), Cl1−Si1−C26 109.08(5).

slightly higher compared to that of **2**. This result is consistent with the π-bonding argument, which states that greater positive charge on nickel results in less back bonding of electron density into the π^* orbitals of the CO ligand.

Structural Characterization. The molecular structures of **1** and **2** are shown in Figures 1 and 2. Important bond lengths and angles are provided in the legends of the figures. Both compounds crystallize in the monoclinic $P2_1/c$ space group (Table 1). In both structures, the silicon atoms are tetra-coordinate and adopt distorted tetrahedral geometry. In **1**, the four sites are occupied by two nitrogen atoms from the amidinato ligand, one chlorine, and one nickel atom, while in **2** they are occupied by one carbon, two chlorine, and one nickel atom. In both compounds, Ni also displays distorted tetrahedral geometry. In **1**, the coordination environment at the Ni atom is derived from one Si and three C atoms of the carbonyl groups, but **2** features a coordination environment of two Si and two C atoms of the carbonyl groups. The Si−Ni bond length in **1** is 2.2111(8) Å. In **2**, they are 2.1955(9) Å and 2.1854(7) Å. These bond lengths are comparable with those of other silylene nickel complexes.[7,16] The Si−Ni bonds in the two complexes are 0.14 Å and 0.16 Å shorter than the sum of the covalent radii of Si (1.11 Å) and Ni (1.24 Å). A similar decrease in bond length is also observed in the Si−Fe bond in the PhC(N*t*Bu)$_2$SiO*t*Bu·Fe(CO)$_4$ (2.23 Å) complex,[10a] which is 0.2 Å shorter than the sum of the covalent radii of Si (1.11 Å) and Fe (1.32 Å) and the Si−Co bond (2.22 Å) in $[\mathrm{Co(CO)_3\{SiCl_2\,\mathbf{L}'\}_2}]^+[\mathrm{CoCl_3(THF)}]^-$,[10b] which is 0.15 Å shorter compared to the sum of covalent radii of silicon and cobalt. These results indicate some possible π-backbonding within the Ni−Si bond. There is a slight change in the Ni−C bond lengths when compared with that of the precursor. The average Ni−C bond length in Ni(CO)$_4$ is 1.817(2) Å,[17] whereas in **1**, the Ni−C$_{\mathrm{av}}$ bond distance is 1.796(2) Å. The deviation is more in **2**, where the mean Ni−C bond length is 1.764(2) Å. A similar kind of variation is also observed in the Ni−C bonds of Ni(CO)$_2$(NHSi)$_2$ [NHSi = (*t*BuNCH═CHN*t*Bu)Si].[7] Moreover, we observed a variation of the bond lengths and the angles of the ligand when coordinated to nickel. For comparison are given the bond length of Si−Cl in **1**, 2.1149(7) Å [Si−Cl of **L** 2.156(1) Å], and the cone angle (∠N−Si−N) is 71.210(2)° [∠N−Si−N of **L** 71.15(7)°].[12a] The Si−Cl$_{\mathrm{av}}$ distance in **2** is 2.1280(9) Å [Si−Cl$_{\mathrm{av}}$ of **L′** 2.1664(17) Å], and ∠Cl−Si−Cl$_{\mathrm{av}}$ is 98.63(4)° [∠Cl−Si−Cl$_{\mathrm{av}}$ in **L′** 97.25(6)°].[13]

Conclusion

The chlorosilylenes **L** and **L′** are versatile ligands for the synthesis of silylene nickel carbonyl complexes. The nature of the ligand indicates the displacement of carbonyl groups from the Ni(CO)$_4$ under the same experimental conditions. In the case of **L**, one carbonyl group is displaced to yield **L**·Ni(CO)$_3$ (**1**), but with **L′**, two carbonyl groups are displaced to yield **L′**$_2$·Ni(CO)$_2$ (**2**). The above versatile and diverse nature of two silylenes can be utilized as a scaffold for the preparation of other different transition metal silylene complexes. Moreover, one can also pursue the reactivities of **1** and **2** with reactive Si−Cl bonds after coordinating to the lone pair of electrons, which will provide synthetic access to other fascinating silicon compounds.

Experimental Section

All manipulations were carried out in an inert atmosphere of dinitrogen using standard Schlenk techniques and in a dinitrogen-filled glovebox. Solvents were purified using the MBRAUN solvent purification system MB SPS-800. All chemicals were purchased from Aldrich and used without further purification. **L** and **L′** were prepared as proposed in the literature,[12b,13] as was Ni(CO)$_4$.[18] ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded with a Bruker Avance DPX 200 or a Bruker Avance DRX 500 spectrometer, using C$_6$D$_6$ as a solvent. Chemical shifts δ are given relative to SiMe$_4$. EI-MS spectra were obtained using a Finnigan MAT 8230 instrument. IR spectra were recorded on Bio-Rad Digilab FTS7 spectrometer in the range 4000−350 cm^{-1} as nujol mulls. Elemental analyses were performed by the Institut für Anorganische Chemie, Universität Göttingen. Melting points were measured in a sealed glass tube on a Büchi B-540 melting point apparatus.

Synthesis of 1. The prepared 0.64 M solution of Ni(CO)$_4$ in diethyl ether (1.75 mL, 1.12 mmol) was added to the solution of **L** (0.31 g, 1.05 mmol) in toluene (50 mL) at ambient temperature. The color of the solution changed slowly from yellow to colorless. The mixture was stirred overnight. The reaction mixture was then filtered through Celite, and the solution was concentrated and stored at 4 °C overnight to yield colorless crystals of **1** (0.25 g, 54.5%). Mp 168−175 °C. Elemental analysis (%) calcd for C$_{18}$H$_{23}$ClN$_2$NiO$_3$Si (438): C, 49.40; H, 5.30; N, 6.40. Found: C, 50.71; H, 5.95; N, 6.68. ^{1}H NMR (200 MHz, C$_6$D$_6$, 25 °C): δ 1.06 (s, 18H, C(C*H*$_3$)$_3$), 6.71−6.95 (m, 5H, C$_6$*H*$_5$) ppm. ^{13}C{^{1}H} NMR (125.75 MHz, C$_6$D$_6$, 25 °C): δ 30.87 C(*C*H$_3$)$_3$, 54.8 (*C* (CH$_3$)$_3$), 125.64, 127.81, 128.0, 128.65, 129.28, 130.94 (*C*$_6$H$_5$), 171.13 (N*C*N), 199.31 (*C*O) ppm. ^{29}Si{^{1}H} NMR (99.36 MHz, C$_6$D$_6$, 25 °C): δ 62.69 ppm. EI-MS: *m*/*z* 438 (100%). FT-IR (Nujol, cm^{-1}): wave number 1984 (s), 1969 (s).

Synthesis of 2. The prepared 0.64 M solution of Ni(CO)$_4$ in diethyl ether (1.75 mL, 1.12 mmol) was added to the solution of **L′** (1.09 g, 2.24 mmol) in toluene (50 mL) at ambient temperature. The color of the solution changed slowly from brown to yellow. The mixture was stirred for 12 h. The reaction mixture was then filtered through Celite, and the solution was concentrated and stored at room temperature overnight to yield bright yellow crystals of **2**·toluene (0.89 g, 73%). Mp 165−170 °C. For

---

(18) Jolly, P. W.; Wilke, G. In *The Organic Chemistry of Nickel*; Academic Press: New York, 1974.

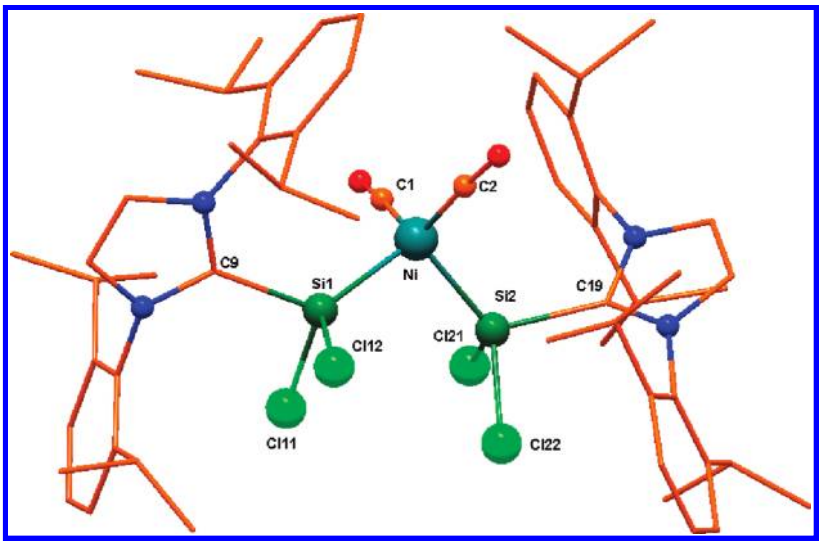


Figure 2. Crystal structure of **2**·toluene. Hydrogen atoms and one toluene molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni−C2 1.764(2), Ni−C1 1.765(3), Ni−Si2 2.1854(7), Ni−Si1 2.1955(9), Si1−C9 1.985(2), Si1−Cl11 2.1183(8), Si1−Cl12 2.1443(10), Si2−C19 2.002(2), Si2−Cl22 2.1197(8), Si2−Cl21 2.1296(9); C2−Ni−C1 125.81(11), C2−Ni−Si2 111.44(7), C1−Ni−Si2 97.59(7), C2−Ni−Si1 110.41(8), C1−Ni−Si1 107.18(8), C19−Si2−Cl22 100.15(7), C19−Si2−Cl21 99.58(7), Cl22−Si2−Cl21 97.67(4), C19−Si2−Ni 116.02(6), Cl22−Si2−Ni 122.01(3), Cl21−Si2−Ni 117.39(3).

Table 1. Crystal and Structure Refinement Parameters for Compounds **1** and **2**

parameter	**1**	**2**·toluene
empirical formula	$C_{18}H_{23}ClN_2NiO_3Si$	$C_{63}H_{80}Cl_4N_4NiO_2Si_2$
fw	437.61	1182.0
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	13.942(3)	15.072(3)
b (Å)	11.524(2)	17.701(4)
c (Å)	13.737(3)	24.500(5)
β (*deg*)	111.24(3)	95.46(3)
V (Å^3)	2057.2(7)	6507(2)
Z	4	4
ρ_{calcd} (g/cm^3)	1.413	1.207
F(000)	912	2504
μ (mm^{-1})	3.278	2.624
GOF on F^2	1.147	1.059
$R1$ [$I > 2\sigma(I)$]	0.0271, 0.0753	0.0391, 0.1066
$R1$, $wR2$ (all data)	0.0275, 0.0755	0.0489, 0.1146
largest diff peak/hole (e Å^{-3})	0.332/-0.228	0.537/-0.290

elemental analysis, **2**·toluene was treated under vacuum conditions overnight to remove the toluene molecule. Anal. calcd for $C_{56}H_{72}Cl_4N_4NiO_2Si_2$ (885.34): C, 61.71; H, 6.66; N, 5.14. Found: C, 59.89; H, 6.84; N, 4.49. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ 0.96 (d, 24 H, J = 6.7 Hz, $CH(C\mathit{H}_3)_2$), 1.51 (d, 24 H, J = 6.7 Hz, $CH(C\mathit{H}_3)_2$), 2.94 (sept, 4H, $C\mathit{H}(CH_3)_2$), 6.23 (s, 4H, $C\mathit{H}$), 6.95−7.26 (m, 12 H, $C_6\mathit{H}_3$) ppm. $^{13}C\{^1H\}$ NMR (125.75 MHz, C_6D_6, 25 °C): δ 23.22 ($CH(\mathit{C}H_3)_2$), 25.76 ($CH(\mathit{C}H_3)_2$), 29.33 ($\mathit{C}H(CH_3)_2$), 124.36 (N*C*H), 125.64, 124.95, 125.64, 128.51 129.28, 130.92, 135.17, 145.55, 163.58 (*C*$_6$H$_3$), 202.51 (*C*O) ppm. $^{29}Si\{^1H\}$ NMR (99.36 MHz, C_6D_6, 25 °C): δ 43.19 ppm. FT-IR(Nujol, cm^{-1}): wave number 1974 (s), 1921 (s).

Crystal Structure Determination. Crystals were mounted at 100 K on a Bruker Smart 6000 CCD diffractometer equipped with a rotating anode generator and Incoatec Helios optics using Cu Kα radiation (λ = 1.54178 Å). Both crystals belonged to the space group $P2_1/c$ and were intergrated with SAINT.[19] Empirical absorption correction was applied by SADABS,[20] and the structure solution by direct methods as well as refinement were executed using SHELX.[21]

For **1**, a colorless plate of 0.3 × 0.3 × 0.01 mm was mounted and a total of 36 195 reflections measured, of which 3491 were independent. The asymmetric unit consisted of one molecule of the amidinate silylene nickel carbonyl complex. All atoms except hydrogens were refined anisotropically by full-matrix least-squares methods on F^2 to give a final R factor of 2.75%. Hydrogen atoms were refined using a riding model.[21]

For **2**, the crystal selected was a brownish plate of 0.15 × 0.1 × 0.04 mm size. A total of 101 205 reflections were collected, of which 11 010 were unique. The asymmetric unit consisted of one molecule of **2** and one molecule of toluene. The latter was disordered to a high degree around the 2-fold axis. The disorder was resolved into five positions in the asymmetric unit; their occupancy was refined and fixed in later stages of the refinement. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods on F^2 to yield a final R factor of 4.89%. Hydrogen atoms were refined using a riding model.[21]

Acknowledgment. We are thankful to the Deutsche Forschungsgemeinschaft for supporting this work. G.T. and R.A. are thankful to the Alexander von Humboldt Stiftung for research fellowships.

Supporting Information Available: CIFs for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

---

(19) *SAINT*; Bruker AXS Inc.: Madison, WI, 2000.

(20) Sheldrick, G. M. *SADABS*; Universität Göttingen: Göttingen, Germany, 2000.

(21) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.