ORGANOMETALLICS

Volume 19, Number 17, August 21, 2000

Communications

Two Trigonal Ni(silylene)$_3$ Complexes

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Received February 7, 2000

*Summary: Two homoleptic Ni(silylene)$_3$ complexes, **1a** and **2a**, have been synthesized and characterized by X-ray crystallography. Due to steric constraints only three silylenes coordinate to the nickel, generating novel complexes that are trigonal planar at the nickel center.*

Stable carbenes form an important new class of organometallic ligands, with properties similar to those of phosphines.[1] Carbenes have been employed in place of phosphines in several transition-metal catalysts, in some cases providing superior catalysis.[2] Stable silylenes (**1**−**3**; Chart 1) are also isolobal with phosphines and can likewise act as ligands in transition-metal complexes, but much less is known about silylene−metal complexes.[3−5]

In 1994 we reported the synthesis of a tetracoordinate silylene−nickel complex, Ni(**1**)$_2$(CO)$_2$, from the reaction of **1** with nickel tetracarbonyl.[4] Subsequently Gehrhus, Lappert, and co-workers published the mixed complex Ni(**3**)$_3$PPh$_3$ as well as the homoleptic tetrahedral complex Ni(**3**)$_4$, the latter being synthesized from the reaction of **3** with bis(1,5-cyclooctadiene)nickel (Ni(COD)$_2$).[5] We have now carried out the reactions of Ni(COD)$_2$ with **1** and **2**,[6] leading to the new homoleptic complexes Ni(**1**)$_3$ and Ni(**2**)$_3$ (eq 1).[7] X-ray crystallographic studies show that in these complexes the three ligands surround the nickel atom in a trigonal-planar arrangement (Figures 1 and 2).[8]

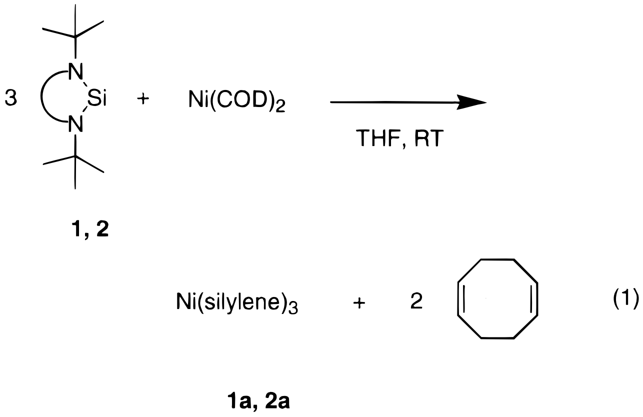
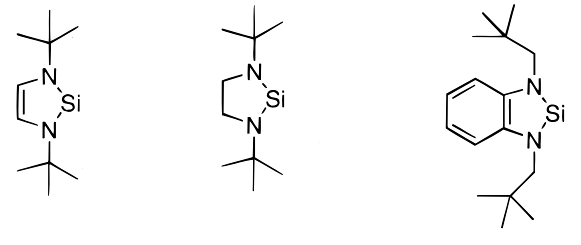


Chart 1



The different structures obtained for the homoleptic silylene complexes probably reflect the differing steric bulkiness of the silylene ligands. Using Ni(**2**)$_3$ as example, the angle between the methyl group carbons

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(1) For a recent review see: Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162.

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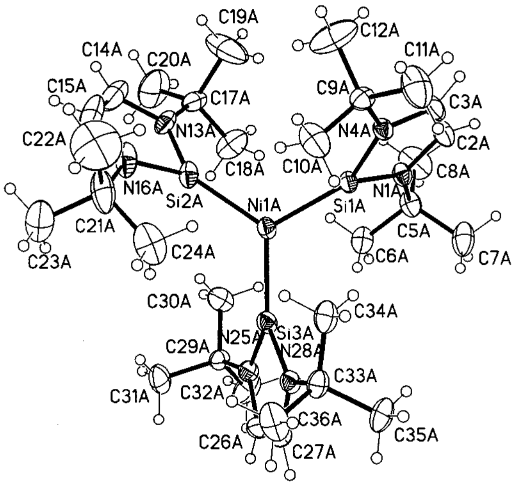

Figure 1. Structure of **1a** (thermal displacement ellipsoids drawn at 50% probability level). Selected bond distances (pm) and angles (deg): Ni(1A)–Si(1A), 214.28(12); Ni(1A)–Si(2A), 215.36(13); Ni(1A)–Si(3A), 215.80(13); Si(1A)–N(1A), 173.7(3); Si(1A)–N(4A), 174.3(3); N(1A)–C(2A), 139.9(5); C(2A)–C(3A), 132.4(5); Si(1A)–Ni(1A)–Si(2A), 116.04(5); Si(2A)–Ni(1A)–Si(3A), 124.63(5); Si(1A)–Ni(1A)–Si(3A), 119.32(5).

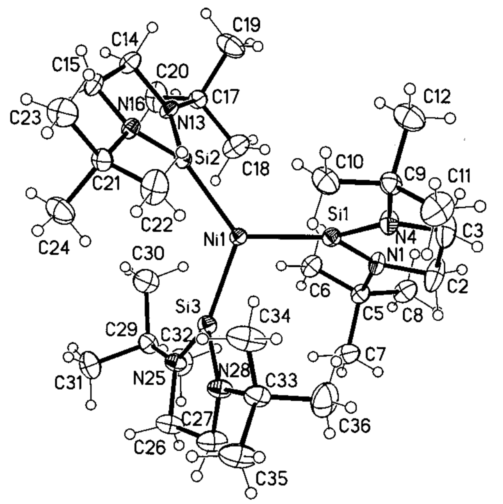

Figure 2. Structure of **2a** (thermal displacement ellipsoids drawn at 50% probability level). Selected bond distances (pm) and angles (deg): Ni(1)–Si(1), 214.43(8); Ni(1)–Si(2), 217.51(8); Ni(1)–Si(3), 215.37(8); Si(1)–N(1), 172.8(2); Si(1)–N(4), 172.4(2); N(1)–C(2), 146.5(3); C(2)–C(3), 151.9(4); Si(1)–Ni(1)–Si(2), 126.02(3); Si(2)–Ni(1)–Si(3), 124.66(3); Si(1)–Ni(1)–Si(3), 109.23(3); N(1)–Si(1)–N(4), 92.52(11).

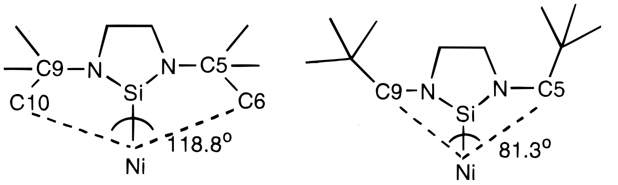

Figure 3. Steric effects of varying N-substituents on silylene. The cone angle for a neopentyl substituent is approximated using the angle of the quaternary carbon (∠C(5)–Ni(1)–C(9) = 81.3°). With *tert*-butyl as the substituent the cone angle is too large for tetrahedral substitution (∠C(10)–Ni(1)–C(6) = 118.8°).

C(6) and C(10) and the silicon atom (Figure 3) provides a measure of the steric constraint. This angle is 118.8° in Ni(**2**)$_3$, large enough to prevent tetrasubstitution. The crystal structure of Ni(**3**)$_4$ has not been published, but the corresponding steric constraint can be approximated by the C(9)–Ni–C(5) angle in Ni(**2**)$_3$, 81.3°. This should allow four molecules of **3** to coordinate to nickel, giving the more typical tetrahedral complex.

A similar effect is observed with homoleptic nickel

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(6) Syntheses of **1** and **2** followed established procedures; see: (a) Haaf, M. H.; Schmiedl, A.; Schmedake, T. A.; Powell, D. R.; Millevolte, A. J.; Denk, M.; West, R. *J. Am. Chem. Soc.* **1998**, *120*, 12714. (b) Haaf, M.; Schmedake, T. A.; Paradise, B. J.; West, R. *Can. J. Chem.*, in press.

(7) Synthesis of **1a**: into a 100 mL Schlenk flask, the unsaturated silylene **1** (0.50 g, 2.6 mmol) and bis(cyclooctadiene)nickel(0) (0.175 g, 0.64 mmol) were added. Under ice cooling and vigorous stirring, 5 mL of THF was added to the flask. The solution rapidly became dark red. Proton NMR indicated the presence of unreacted silylene, free cyclooctadiene, and a new product formed in virtually quantitative yield. The solvent was evaporated in vacuo, and the flask was gently heated (60 °C) to remove the unreacted silylene and cyclooctadiene from the reaction mixture. The remaining red solid was redissolved in toluene, affording a clear, dark red solution. X-ray-quality crystals became apparent after cooling the solution for 48 h. ^{1}H NMR (C_6D_6, 293 K): δ 1.543 (s, 18H), 6.600 (s, 2H). ^{13}C NMR (C_6D_6, 293 K): δ 33.488 ($C(\mathbf{C}H_3)_3$), 53.824 ($\mathbf{C}(CH_3)_3$), 118.196 ($\mathbf{C}{=}\mathbf{C}$).^{29}Si NMR (C_6D_6, 293 K): δ 110.553. Yield after recrystallization: 0.236 mg (57% based on Ni(COD)$_2$). Due to the extreme reactivity of the complex, satisfactory elemental analyses could not be obtained. Synthesis of **2a**: Into a 150 mL flask containing 0.500 g (2.53 mmol) of saturated silylene **2**, 50 mL of THF was added. In a separate flask 0.175 g Ni(COD)$_2$ (0.64 mmol) was dissolved in 25 mL of THF. The flasks were then cooled to 0 °C and combined via cannula. The reaction mixture was warmed to room temperature and stirred for 1 h, generating **2a** quantitatively with respect to Ni(COD)$_2$ according to the NMR. The flask was then pumped to dryness and heated to 70 °C under vacuum to remove cyclooctadiene and unreacted silylene. The residue was redissolved in toluene and filtered. Slow cooling of a saturated toluene solution afforded X-ray-quality crystals of **2a**. ^{1}H NMR (C_6D_6, 293 K): δ 1.469 (s, 18H), 3.150 (s, 4H). ^{13}C NMR (C_6D_6, 293 K): δ 32.208 ($C(\mathbf{C}H_3)_3$), 45.888 ($\mathbf{C}H_2$), 52.499 ($\mathbf{C}(CH_3)_3$).^{29}Si NMR (C_6D_6, 293 K): δ 144.57. Yield after recrystallization: 0.270 mg (65% based on Ni(COD)$_2$). Due to the extreme reactivity of the complex, satisfactory elemental analyses could not be obtained.

(8) Crystal data for **1a**: a colorless prism-shaped crystal of dimensions 0.38 × 0.32 × 0.30 mm was grown from THF at −20 °C. $C_{30}H_{60}N_6NiSi_3$: monoclinic, group $C2/c$, $a = 47.354(4)$ Å, $b = 12.2927(16)$ Å, $c = 18.982(2)$ Å, $V = 10939(2)$ Å^3, $Z = 12$, $T = 133(2)$ K, $D_{calcd} = 1.180$ Mg/m^3, $R(F) = 0.0489$ for 4878 observed reflections. All non-hydrogen atoms were refined with anisotropic displacement parameters. There are one and a half molecules per asymettric unit—the half-molecule sits on a crystallographic 2-fold axis. In one molecule, one *tert*-butyl group is disordered and modeled in two orientations with occupancies of 0.65(3) and 0.35(3) for the atoms C(22A)–C(24A) and C(22′)–C(24′), respectively. In the other molecule, one *tert*-butyl group is also disordered and modeled in two orientations with occupancies of 0.50(18) for both C(16B)–C(18B) and C(16′)–C(18′), respectively. Restraints on the positional and displacement parameters of the disordered atoms were required for the refinement to achieve convergence. Full crystallographic information is given in the Supporting Information. Crystal data for **2a**: a red prism-shaped crystal of dimensions 0.38 × 0.36 × 0.28 mm was grown from toluene at −20 °C. $C_{30}H_{66}N_6NiSi_3$: monoclinic, group $P2_1/n$, $a = 10.5740(8)$ Å, $b = 16.7611(14)$ Å, $c = 20.9670(17)$ Å, $V = 3683.2(5)$ Å^3, $Z = 4$, $T = 133(2)$ K, $D_{calcd} = 1.179$ Mg/m^3, $R(F) = 0.0418$ for 4908 observed reflections. All non-hydrogen atoms were refined with anisotropic displacement parameters. Full crystallographic information is given in the Supporting Information.

phosphine complexes. Coordinatively unsaturated, trigonal nickel phosphine complexes can be isolated with bulky phosphines, while less hindered phosphines afford the four-coordinate tetrahedral complexes. For example, crystallographic studies have confirmed the formation of trigonal-planar $Ni(PPh_3)_3$.[9] Also, the saturated germylene (the germanium analogue of **2**) has been reported to form $Ni(germylene)_3$ upon reaction with $Ni(COD)_2$, although a crystal structure has not yet been reported.[10]

The silicon atoms in Ni(**1**)$_3$ and Ni(**2**)$_3$ have trigonal-planar coordination, but the silylene rings are not coplanar with the $Ni(Si)_3$ planes. This is consistent with the description of this class of ligands as weak π-acceptors.[4] In both compounds the N−Si−N angles of the complexed silylenes are close to 90°, the values both predicted[11] and determined[12] for the free silylenes.

Although the unsaturated silylene **1** is believed to be less electrophilic than the saturated analogue **2**,[13] in the nickel complexes the Ni−Si bond lengths are essentially identical (the average bond length is 215.15(13) pm in Ni(**1**)$_3$ and 215.77(8) pm in Ni(**2**)$_3$). These are also similar to the Ni−Si distance in the tetrahedral complex Ni(**3**)$_3$(PPh_3).[5] The longer Ni−Si distances in Ni(**1**)$_2$(CO)$_2$, 220.7(2) and 221.6(2) pm,[4] may again reflect the steric repulsion between these bulkier silylene ligands in tetrahedral coordination.

Complexation to the metal center causes a deshielding of the silicon nucleus, resulting in a downfield shift of the ^{29}Si NMR. The ^{29}Si resonance for the saturated silylene **2** shifts from 118.9 ppm for the free silylene to 144.6 ppm for Ni(**2**)$_3$. Similarly, the resonance for the unsaturated silylene **1** shifts from 78.4 to 110.6 ppm upon formation of Ni(**1**)$_3$. The longer Ni−Si bonds in Ni(**1**)$_2$(CO)$_2$ are consistent with a smaller downfield shift (^{29}Si 97.5 ppm).

In summary, it appears that N-substitution plays an important role in metal silylene chemistry by affecting the bulkiness of the ligand, which can manifest itself in controlling the geometry of substitution or by lengthening the M−Si bonds, leading to less deshielding of the silicon nucleus.

Acknowledgment. This research was supported by the National Science Foundation and by the Organosilicon Research Center.

Supporting Information Available: Complete crystallographic and ^1H NMR data for compounds **1a** and **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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