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New Azasilatranes: Bidentate and Tridentate Coordination Modes of the Novel Ligand $EtOSi(Ph_2PNCH_2CH_2)_2(HNCH_2CH_2)N$

Dietrich Gudat, Lee M. Daniels, and John G. Verkade*

Gilman Hall, Iowa State University, Ames, Iowa 50011

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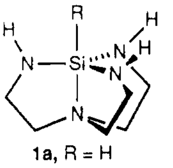
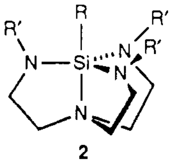
The synthesis and characterization of $EtOSi(Ph_2PNCH_2CH_2)_2(HNCH_2CH_2)N$ (ethoxy-*N*,*N*′-bis(diphenylphosphino)azasilatrane, the title compound **3b**) is reported. Its reactions with sulfur and MeI proceed easily via quaternization at the phosphorus sites to give the bis(phosphonium) salt and the bis(phosphine) sulfide, respectively. Synthesis and characterization of the coordination compounds $(\mathbf{3b})Ni(CO)_2$, $(\mathbf{3b})PtCl_2$, $(\mathbf{3b})M(CO)_4$ (M = Mo, W), and $(\mathbf{3b})M(CO)_3$ (M = Mo, W) give evidence for the existence of two possible coordination modes; one wherein **3b** behaves as a bidentate (P,P′) ligand and the other as a tridentate (P,P′,O) ligand. The latter coordination mode provides a rare example of coordination of a silyl ether to a transition metal. NMR spectroscopic studies in solution and the solid state establish the presence of transannular Si–N bonding and hypercoordination at silicon. Solid-state ^{31}P NMR spectra give direct evidence for the presence of a twisted, helically chiral conformation of the silatranyl cage, which in solution is lost as a consequence of rapid conformational mobility on the NMR time scale. These findings are further corroborated by the results of crystal structure determinations of the bis(phosphine) sulfide and $(\mathbf{3b})PtCl_2$. Crystals of the bis(phosphine) sulfide are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell having dimensions $a = 11.552$ (3) Å, $b = 19.661$ (3) Å, $c = 15.199$ (3) Å, $\beta = 107.35$ (1)°, and $d_{calcd} = 1.311$ g/cm^3. Crystals of $(\mathbf{3b})PtCl_2$ are monoclinic, space group $C2/m$, $Z = 2$, $d_{calcd} = 1.48$ g/cm^3, with unit cell dimensions $a = 15.117$ (2) Å, $b = 17.270$ (2) Å, $c = 9.791$ (2) Å, and $\beta = 105.20$ (2)°.

Introduction

By analogy to silatranes,[1] azasilatranes of type **1**[2] feature a hypercoordinate silicon atom in a nearly trigonal-bipyramidal (tbp) environment owing to the bonding interaction between the Si and the axial nitrogen (N_{ax}) atom below. As we have shown recently,[3] the scope of azasilatrane chemistry is expanded considerably by the presence of N_{eq} substituents (e.g., Me, $SiHMe_2$, $SiMe_3$) in **2**. In addition to cyclocondensation reactions starting from N,N′,N″-substituted tris(β-aminoethyl)amines, compounds of type **2** are also accessible via substitution reactions on azasilatranes **1** with reactive halides. Interestingly, substitution of the hydrogen on the equatorial NH functions exerts a strong influence on the degree of transannular $N_{eq} \rightarrow Si$ interaction, with the observed weakening of this bond being correlated with steric crowding among bulky substituents attached to both the Si and N_{eq} atoms.[4]



1a, R = H
b, R = Me
c, R = OEt



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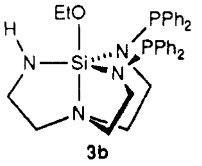

3b

As part of our investigation of the scope of equatorial NH substitution reactions in systems of type **1**, it was of interest to explore the use of halides of other than group 14 elements. Here, we report the reaction of **1c**[3] with diphenylchlorophosphine leading to the isolation of the novel *N*,*N*′-bis(diphenylphosphino)azasilatrane **3b** via the spectroscopically detected monosubstituted intermediate **3a**. The chemical reactivity and complexing properties of **3b** are described.

Experimental Section

All reactions were carried out with strict exclusion of moisture. Solvents were dried by standard methods and distilled before use. Commercially available chlorodiphenylphosphine, sulfur, and methyl iodide (Aldrich) were used without purification. Nickel tetracarbonyl (Strem Chemicals) was purified by trap to trap condensation before use. Ethoxyazasilatrane,[3] (cycloheptatriene)tricarbonylmolybdenum,[5] (η^5-mesitylene)tricarbonyltungsten,[5] bis(piperidine)tetracarbonylmolybdenum,[6] (η^2-cyclooctadiene)tetracarbonyltungsten,[7] and (η^2-cyclooctadiene)dichloroplatinum[5] were prepared according to published procedures. Solution NMR spectra were recorded on Nicolet NT300 (^1H, ^{13}C) or Bruker WM 200 (^{31}P, ^{29}Si, ^{195}Pt) instruments using deuterated solvents as the internal lock and TMS (for ^1H, ^{13}C, ^{29}Si) or H_3PO_4 (^{31}P) as external standards. K_2PtCl_4 was used as a secondary external standard for ^{195}Pt NMR spectra. For the measurement of solid-state NMR spectra, polycrystalline samples (ca. 50–200 mg) were mixed with Al_2O_3. Spectra were obtained on a Bruker MSL 300 spectrometer (operating at 121.5 MHz (^{31}P), 75.49 MHz (^{13}C), or 59.62 MHz (^{29}Si)) under proton decoupling, with use of the CP-MAS technique. A 90° pulse was employed with mixing times for polarization transfer of 5.00 ms for ^{13}C and ^{29}Si and 4.00 ms for ^{31}P. Spinning rates were in the range of 4–5 kHz. Chemical shifts were referenced to external TMS (^{13}C, ^{29}Si) or H_3PO_4 (^{31}P). The solid-state ^{31}P and ^{29}Si NMR data are collected in Table I. Mass spectra were recorded on Kratos MS-50 (70 eV EI, high-resolution conditions) and Finnigan 4000 (70 eV, EI, CI) mass spectrometers. Values of *m*/*e* of metal-containing fragments are based on the most abundant isotope, viz. ^{96}Mo and ^{184}W. IR spectra were recorded on an IBM 98 FT-IR spectrometer. Solid samples were measured as CsI or KBr pellets, and solution spectra were obtained from dilute CH_2Cl_2 or THF solutions with use of CaF_2 cells. Microanalyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Ethoxy-*N*,*N*′-bis(diphenylphosphino)azasilatrane (3b). To a stirred solution of 0.99 g (4.6 mmol) of ethoxyazasilatrane

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Table I. ^{31}P and ^{29}Si CP-MAS Solid-State NMR Data for Ethoxy-*N*,*N'*-bis(diphenylphosphino)azasilatrane (3b) and Its Derivatives

compd	$\delta(^{31}\mathrm{P})$, ppm	$\delta(^{29}\mathrm{Si})$, ppm
3b	46.0 40.1	−89.2
$[\mathrm{Me_2}(\mathbf{3b})]\mathrm{I_2}$ (**4b**)	49.0 41.6	−94.6
$\mathrm{S_2}(\mathbf{3b})$ (**5b**)	65.7 63.7	−85.0
$(\mathbf{3b})\mathrm{Ni(CO)_2}$ (**6**)	82.6 79.3	−78.9
$(\mathbf{3b})_2\mathrm{PtCl_2}$ (**7**)	41.5[a] 36.3[b]	−92.8
$(\mathbf{3b})\mathrm{Mo(CO)_4}$ (**8**)	82.1 79.0	−77.6
$(\mathbf{3b})\mathrm{W(CO)_4}$ (**9**)	66.4 62.9	−77.7
$(\mathbf{3b})\mathrm{Mo(CO)_3}$ (**10**)	80.4	−83.4
$(\mathbf{3b})\mathrm{W(CO)_3}$ (**11**)	75.9 74.6	−80.4

[a] $^1J_{\mathrm{PtP}}$ = 4.54 kHz. [b] $^1J_{\mathrm{PtP}}$ = 4.51 kHz.

1c in 20 mL of benzene was added 1.03 g (10.2 mmol) of triethylamine, followed by 2.02 g (9.20 mmol) of chlorodiphenylphosphine. Precipitation of a white solid began immediately. After the mixture was stirred for 2 h at room temperature, the precipitated salt was filtered and washed twice with 5 mL of benzene. The resulting solution was concentrated in vacuo until the product began to precipitate. Ten milliliters of *n*-hexane was added, and the precipitate was collected by filtration. After it was washed several times with small portions of *n*-hexane and dried in vacuo, 2.00 g of spectroscopically pure product was obtained as a white powder (yield 75%, mp 169–173 °C). A sample of the product was recrystallized from benzene/hexane to give white needles (same melting point): MS (EI) *m*/*e* (relative intensity) 584 (12), 583 (12), 507 (41), 463 (19), 398 (100), 356 (36), 278 (34), 186 (39), 183 (39), 108 (72), 107 (29); HRMS (EI) calcd for $\mathrm{C_{32}H_{38}N_4P_2OSi}$ ($\mathrm{M^+}$) 584.229 03, found 584.227 72, calcd for ($\mathrm{M^+ - H}$) 583.221 20, found 583.221 46; ^{31}P NMR ($\mathrm{CD_2Cl_2}$) δ 50.1; ^{29}Si NMR ($\mathrm{CD_2Cl_2}$) δ −83.0 (t, $^2J_{\mathrm{PSi}}$ = 33 Hz); ^{13}C NMR ($\mathrm{CD_2Cl_2}$) δ 142.4 (d, J_{PC} = 26 Hz, Ph), 141.7 (d, J_{PC} = 26 Hz, Ph), 133.2 (d, J_{PC} = 21 Hz, Ph), 131.8 (d, J_{PC} = 20 Hz, Ph), 128.2 (d, J_{PC} = 4 Hz, Ph), 128.2 (Ph), 127.7 (Ph), 58.6 (t, J_{PC} = 6 Hz, $\mathrm{O}C\mathrm{H_2}$), 52.3 ($\mathrm{N}C\mathrm{H_2}$), 52.4 ($\mathrm{N}C\mathrm{H_2}$), 42.3 (d, J = 9 Hz, $\mathrm{N}C\mathrm{H_2}$), 37.3 ($\mathrm{N}C\mathrm{H_2}$), 18.6 ($\mathrm{C}C\mathrm{H_3}$); ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 7.52–7.45 (m, 8 H, Ph), 7.42–7.20 (m, 12 H, Ph), 3.76 (q, J = 6.9 Hz, 2 H, $\mathrm{OC}H_2$), 3.08 (t, J = 6.0 Hz, 2 H, $\mathrm{NC}H_2$), 2.96 (m, 2 H, $\mathrm{NC}H_2$), 2.80 (m, 2 H, $\mathrm{NC}H_2$), 2.61 (t, J = 6.0 Hz, 2 H, $\mathrm{NC}H_2$), 2.30 (m, 2 H, $\mathrm{NC}H_2$), 2.17 (m, 2 H, $\mathrm{NC}H_2$), 1.35 (t, J = 6.7 Hz, 1 H, NH), 1.08 (t, J = 6.9 Hz, 3 H, $\mathrm{CC}H_3$). Solid-state NMR data are listed in Table I.

Ethoxy-*N*,*N'*-bis(diphenylphosphinothioyl)azasilatrane (5b). A solution of 200 mg (0.34 mmol) of ethoxy-*N*,*N'*-bis(diphenylphosphino)azasilatrane (**3b**) in 5 mL of benzene was treated with 22 mg (0.09 mmol, 2 equiv) of $\mathrm{S_8}$ and stirred for 20 min at room temperature. The clear solution thus obtained was concentrated to a volume of 3 mL and 3 mL of hexane was carefully added to avoid mixing of the two solvents. Colorless needles formed within 48 h, which were collected by filtration, washed with a small amount of hexane, and dried in vacuo (yield 47%, mp 195 °C): MS (EI) *m*/*e* (relative intensity) 648 (0.4), 618 (0.5), 606 (0.6), 548 (22), 332 (46), 260 (100), 217 (97), 183 (26), 139 (65), 112 (48), 99 (59), 44 (94); MS (CI, $\mathrm{NH_3}$) *m*/*e* (relative intensity) 649 (31), 579 (100); ^{31}P NMR ($\mathrm{C_6D_6}$) δ 66.5; ^{29}Si NMR ($\mathrm{C_6D_6}$) δ −81.0 (t, $^2J_{\mathrm{PSi}}$ = 10 Hz); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 136.7 (d, J = 102 Hz, Ph), 136.0 (d, J = 103 Hz, Ph), 132.7 (d, J = 11 Hz, Ph), 132.1 (d, J = 11 Hz, Ph), 130.8 (d, J = 3 Hz, Ph), 130.3 (d, J = 3 Hz, Ph), 127.9 (d, J = 13 Hz, Ph), 127.4 (d, J = 13 Hz, Ph), 57.5 ($\mathrm{O}C\mathrm{H_2}$), 55.9 ($\mathrm{N}C\mathrm{H_2}$), 55.67 (d, J = 2 Hz, $\mathrm{N}C\mathrm{H_2}$), 45.3 (d, J = 2 Hz, $\mathrm{N}C\mathrm{H_2}$), 38.3 ($\mathrm{N}C\mathrm{H_2}$), 18.6 ($\mathrm{C}C\mathrm{H_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) δ 8.10 (m, 4 H, Ph), 7.70 (m, 4 H, Ph), 7.40 (m, 8 H, Ph), 7.24 (m, 4 H, Ph), 3.34 (m, 4 H, $\mathrm{NC}H_2$), 3.15 (t, J = 6.0 Hz, 2 H, $\mathrm{NC}H_2$), 2.99 (m, 4 H, $\mathrm{NC}H_2$), 2.55 (m, 2 H, $\mathrm{NCH_2}$), 2.40 (q, $^3J_{\mathrm{HH}}$ = 6.9 Hz, 2 H, $\mathrm{OC}H_2$), 0.92 (br, 1 H, $\mathrm{N}H$), −0.04 (t, $^3J_{\mathrm{HH}}$ = 6.9 Hz, 3 H, $\mathrm{CC}H_3$). Solid-state NMR data are listed in Table I.

Ethoxy-*N*,*N'*-bis(methyldiphenylphosphonio)azasilatrane Diiodide (4b). To a solution of 200 mg (0.34 mmol) of **3b** in 5 mL of $\mathrm{CH_2Cl_2}$ was added 0.35 mL of methyl iodide. After 25 min at room temperature, 10 mL of hexane was added, and the white precipitate that formed was collected by filtration and dried in vacuo. Recrystallization from $\mathrm{CH_2Cl_2}$/hexane yielded 169 mg (57% yield) of **4b**·$\mathrm{CH_2Cl_2}$ as colorless crystals (decomposition >250 °C): ^{31}P NMR ($\mathrm{CD_2Cl_2}$) δ 46.9; ^{29}Si NMR ($\mathrm{CD_2Cl_2}$) δ −94.6 (t, $^2J_{\mathrm{PSi}}$ = 10 Hz); ^{13}C NMR (DMSO-d_6) δ 134.0 (d, J = 2 Hz, Ph), 133.7 (Ph), 132.6 (d, J = 10 Hz, Ph), 131.8 (d, J = 11 Hz, Ph), 129.5 (Ph), 129.2 (d, J = 3 Hz, Ph), 126.5 (d, J = 70 Hz, Ph), 124.0 (d, J = 76 Hz, Ph), 59.0 ($\mathrm{O}C\mathrm{H_2}$), 54.9 ($\mathrm{N}C\mathrm{H_2}$), 50.0 ($\mathrm{N}C\mathrm{H_2}$), 47.5 (d, J = 10 Hz, $\mathrm{N}C\mathrm{H_2}$), 44.5 (d, J = 2 Hz, $\mathrm{N}C\mathrm{H_2}$), 15.7 ($\mathrm{C}C\mathrm{H_3}$), 14.8 (d, $^1J_{\mathrm{PC}}$ = 71 Hz, $\mathrm{P}C\mathrm{H_3}$); ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 7.99 (m, 4 H, Ph), 7.86–7.63 (m, 12 H, Ph), 7.61–7.53 (m, 4 H, Ph), 3.59 (m, 2 H, $\mathrm{NC}H_2$), 3.46 (dt, 2 H, $\mathrm{NC}H_2$), 3.24 (m, 2 H, $\mathrm{NC}H_2$), 2.99 (m, 2 H), 2.88 (m, 2 H, $\mathrm{NCH_2}$), 3.27 (d, $^2J_{\mathrm{PH}}$ = 14.2 Hz, 6 H, $\mathrm{PC}H_3$), 1.80 (q, $^3J_{\mathrm{HH}}$ = 7.0 Hz, 2 H, $\mathrm{OC}H_2$), 1.52 (br, 1 H, NH), 0.25 (t, $^3J_{\mathrm{HH}}$ = 7.0 Hz, 3 H, $\mathrm{CC}H_3$). Solid-state NMR data are listed in Table I. Anal. Calcd for $\mathrm{C_{34}H_{44}I_2N_4OP_2Si{\cdot}CH_2Cl_2}$: C, 44.08; H, 4.65; N, 5.88. Found: C, 42.56; H, 4.66; N, 6.02.

***cis*-(Ethoxy-*N*,*N'*-bis(diphenylphosphino)azasilatrane-*P*,*P'*)dichloroplatinum (7).** A solution of 120 mg (0.21 mmol) of ethoxy-*N*,*N'*-bis(diphenylphosphino)azasilatrane (**3b**) in 1.2 mL of $\mathrm{CH_2Cl_2}$ was added to a stirred solution of 77 mg (0.21 mmol) of (cyclooctadiene)platinum dichloride in 1.3 mL of $\mathrm{CH_2Cl_2}$ at room temperature. The resulting clear solution was kept at 5 °C for 24 h. The precipitated colorless solid was then collected by filtration, washed once with a small amount of benzene, and dried in vacuo, yielding 95 mg (54%) of product as a colorless, microcrystalline solid (mp 190–200 °C dec): ^{31}P NMR (DMSO) δ 40.0 ($^1J_{\mathrm{PPt}}$ = 4493 Hz); ^{195}Pt NMR (DMSO) δ 274 (t, $^1J_{\mathrm{PPt}}$ = 4488 Hz); ^{1}H NMR (DMSO-d_6) δ 8.27 (m, 4 H, Ph), 7.56 (m, 4 H, Ph), 7.44 (m, 12 H, Ph), 2.91 (m, 2 H, $\mathrm{NC}H_2$), 2.84 (m, 2 H, $\mathrm{NC}H_2$), 2.67 (m, 4 H, $\mathrm{NC}H_2$), 2.55 (m, 4 H, $\mathrm{NCH_2}$), 2.29 (q, $^3J_{\mathrm{HH}}$ = 6.9 Hz, 2 H, $\mathrm{OCH_2}$), 2.16 (br, 1 H, NH), −0.44 (t, $^3J_{\mathrm{HH}}$ = 6.9 Hz, 3 H, $\mathrm{CH_3}$); IR (CsI) 3448 (m, NH), 304 (m, NH), 279 cm^{-1} (m, PtCl). Slow cooling of a hot saturated DMSO solution produced block-shaped crystals, which were used for an X-ray crystal structure determination.

(Ethoxy-*N*,*N'*-bis(diphenylphosphino)azasilatrane-*P*,*P'*)dicarbonylnickel (6). Tetracarbonylnickel (0.4 mL) was added via syringe to a stirred solution of 45 mg (0.76 mmol) of **3b** in 5 mL of benzene at room temperature. Evolution of CO began immediately, and the solution was stirred for an additional 1 h. After 3 mL of hexane was slowly added, the mixture was stored at 5 °C overnight. The precipitate that was formed was collected by filtration, washed with a small amount of hexane, and dried in vacuo, to give 250 mg (47%) of product as a light yellow powder (dec pt 175–180 °C): MS (EI) *m*/*e* (relative intensity) 584 (18, ligand), no reproducible metal-containing peaks detectable; ^{31}P NMR ($\mathrm{C_6D_6}$) δ 81.5; ^{29}Si NMR ($\mathrm{CH_2Cl_2}$) δ −76.7 (t, $^2J_{\mathrm{PSi}}$ = 21 Hz); ^{13}C NMR ($\mathrm{CD_2Cl_2}$) δ 201.8 (t, J = 8 Hz, $C\mathrm{O}$), 200.2 (t, J = 3 Hz, $C\mathrm{O}$), 144.3 (m, J = 15 Hz, Ph), 141.1 (m, J = 14 Hz, Ph), 134.0 (t, J = 8 Hz, Ph), 131.3 (t, J = 9 Hz, Ph), 129.2 (Ph), 128.3 (Ph), 128.1 (t, J = 5 Hz, Ph), 127.5 (t, J = 5 Hz, Ph), 59.5 ($\mathrm{O}C\mathrm{H_2}$), 57.3 ($\mathrm{N}C\mathrm{H_2}$), 55.5 ($\mathrm{N}C\mathrm{H_2}$), 45.6 (d, J = 4 Hz, $\mathrm{N}C\mathrm{H_2}$), 38.8 ($\mathrm{N}C\mathrm{H_2}$), 17.7 ($\mathrm{C}C\mathrm{H_3}$); ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 7.74 (m, 4 H, Ph), 7.56 (m, 4 H, Ph), 7.37 (m, 12 H, Ph), 3.24 (m, 2 H, $\mathrm{NC}H_2$), 3.07 (m, 2 H, $\mathrm{NC}H_2$), 2.80 (m, 4 H, $\mathrm{NC}H_2$), 2.56 (ddd, 2 H, $\mathrm{NC}H_2$), 2.26 (ddd, 2 H, $\mathrm{NC}H_2$), 3.05 (q, $^3J_{\mathrm{HH}}$ = 6.9 Hz, 2 H, $\mathrm{OC}H_2$), 1.31 (br, 1 H, NH), 0.30 (t, $^3J_{\mathrm{HH}}$ = 6.9 Hz, 3 H, $\mathrm{CC}H_3$); IR ($\mathrm{CH_2Cl_2}$) 1991 (s, CO), 1926 cm^{-1} (s, CO); IR (KBr) 3430 (m, NH), 1982 (s, CO), 1918 cm^{-1} (s, CO). Solid-state NMR data are listed in Table I. Anal. Calcd for $\mathrm{C_{34}H_{38}N_4NiO_3P_2Si}$: C, 57.89; H, 6.29; N, 7.94. Found: C, 56.16; H, 5.21; N, 7.86.

***cis*-(Ethoxy-*N*,*N'*-bis(diphenylphosphino)azasilatrane-*P*,*P'*)tetracarbonylmolybdenum (8).** A solution of 153 mg (0.260 mmol) of **3b** in 4 mL of THF was added to 110 mg (0.290 mmol) of bis(piperidine)tetracarbonylmolybdenum. After the mixture was stirred for 10 min at room temperature, the insoluble material present was removed by centrifugation. The clear supernatant solution was separated and 5 mL of hexane added. After the mixture was stored at 4 °C for 3 days, orange-brown crystals separated from the solution, together with a small amount of a white powder. The crystals were collected, rinsed with a small amount of benzene/hexane (1:1), and dried in vacuo, giving 85 mg (41%) of product (dec pt 165–175 °C): MS (desorption CI, NH_3) *m/e* (relative intensity) 766 (8, $M^+ - CO$), 738 (1, $M^+ - 2CO$), 243 (13), 203 (22), 187 (100); ^{31}P NMR (CD_2Cl_2) δ 85.2; ^{13}C NMR (CD_2Cl_2) δ 217.8 (m, J = 22 Hz, CO), 213.0 (t, J = 10 Hz, *C*O), 209.2 (t, J = 11 Hz, *C*O), 143.8 (m, J = 26 Hz, Ph), 140.1 (m, J = 32 Hz, Ph), 132.8 (m, J = 13 Hz, Ph), 131.4 (m, J = 14 Hz, Ph), 129.3 (Ph), 128.9 (Ph), 128.1 (Ph), 127.8 (m, J = 11 Hz, Ph), 59.6 (OCH_2), 56.5 (NCH_2), 54.8 (NCH_2), 48.9 (NCH_2), 37.5 (NCH_2), 16.9 (CCH_3); ^1H NMR (CD_2Cl_2) δ 7.83 (m, 4 H, Ph), 7.51 (m, 4 H, Ph), 7.50–7.31 (m, 12 H, Ph), 3.14 (dt, 2 H, NCH_2), 3.02 (m, 2 H, NCH_2), 2.88 (m, 4 H, NCH_2), 2.78 (m, 2 H, NCH_2), 2.67 (m, 2 H, NCH_2), 2.66 (q, $^3J_{HH}$ = 7.0 Hz, 2 H, OCH_2), 1.48 (br, 1 H, N*H*), −0.14 (t, $^3J_{HH}$ = 7.0 Hz, 3 H, CCH_3); IR (CH_2Cl_2) 2017 (m), 1917 (vs, CO), 1886 (s, CO), 1861 cm^{-1} (s, CO); IR (KBr) 3437 (m, NH), 2014 (m, CO), 1911 (s, CO), 1877 (s, CO), 1848 cm^{-1} (s, CO). Solid-state NMR data are listed in Table I.

The IR and NMR data suggested the presence of small amounts (ca. 5%) of *fac*-(ethoxy-*N*,*N'*-bis(diphenylphosphino)azasilatrane-*P*,*P'*,*O*)tricarbonylmolybdenum (**10**), which could not be removed by further recrystallization from the tetracarbonyl complex.

***cis*-(Ethoxy-*N*,*N'*-bis(diphenylphosphino)azasilatrane-*P*,*P'*)tetracarbonyltungsten (9).** To a solution of 214 mg (0.370 mmol) of **3b** in 4 mL of THF was added 160 mg (0.400 mmol) of (cyclooctadiene)tetracarbonyltungsten. The mixture was shaken until a clear solution formed and kept in the dark for 3 days at room temperature. Hexane (4.0 mL) was then added. The yellow precipitate was filtered, washed with a small amount of benzene and hexane, and dried in vacuo, to give 175 mg (54% yield) of product as a yellow powder (dec pt 185–190 °C): MS (desorption CI, NH_3, *m/e* lower than 400 neglected) *m/e* (relative intensity) 853 (11, MH^+), 585 (13, ligand)H^+), 405 (100); IR (THF) 2013 (m, CO), 1907 (vs, CO), 1881 (s, CO), 1863 cm^{-1} (s, CO); IR (KBr) 3437 (m, NH), 2008 (m, CO), 1898 (s, CO), 1869 (s, CO), 1841 cm^{-1} (s, CO); ^{31}P NMR (CD_2Cl_2) δ 68.3 ($^1J_{PW}$ = 262 Hz); ^{13}C NMR (CD_2Cl_2) δ 208.8 (m, J = 12 Hz, *C*O), 206.8 (t, $^2J_{PC}$ = 9 Hz, *C*O), 202.8 (t, $^2J_{PC}$ = 8 Hz, CO), 143.4 (m, J = 34 Hz, Ph), 139.5 (m, J = 39 Hz, Ph), 132.9 (m, J = 12 Hz, Ph), 131.6 (m, J = 14 Hz, Ph), 129.5 (Ph), 129.1 (Ph), 128.1 (m, J = 8 Hz, Ph), 127.8 (m, J = 12 Hz, Ph), 56.5 (NCH_2), 54.7 (NCH_2), 43.8 (NCH_2), 37.4 (NCH_2), 58.7 (OCH_2), 16.8 (CCH_3); ^1H NMR (CD_2Cl_2) δ 7.85 (m, 4 H, Ph), 7.54 (m, 4 H, Ph), 7.38 (m, 12 H, Ph), 3.14 (m, 2 H, NCH_2), 3.03 (m, 2 H, NCH_2), 2.89 (m, 4 H, NCH_2), 2.79 (m, 2 H, NCH_2), 2.68 (m, 2 H, NCH_2), 2.64 (q, $^3J_{HH}$ = 7.0 Hz, 2 H, OCH_2), 1.51 (br, 1 H, N*H*), −0.19 (t, $^3J_{HH}$ = 7.0 Hz, 3 H, CCH_3). Solid-state NMR data are listed in Table I. Anal. Calcd for $C_{36}H_{38}N_4O_5P_2SiW$: C, 49.10; H, 4.35; N, 6.36. Found: C, 48.22; H, 4.17; N, 6.01.

***fac*-(Ethoxy-*N*,*N'*-bis(diphenylphosphino)azasilatrane-*P*,*P'*,*O*)tricarbonylmolybdenum (10).** A solution of 250 mg (0.430 mmol) of **3b** was added via syringe to a stirred solution of 120 mg (0.440 mmol) of (cycloheptatriene)tricarbonylmolybdenum in 6 mL of benzene. A yellow precipitate began to form after a few minutes. The mixture was stirred for an additional 1 h, after which the precipitate was collected by filtration, washed thoroughly with benzene, and dried in vacuo, yielding 165 mg (45%) of product as a yellow, microcrystalline solid (mp 215 °C dec): MS (desorption CI, NH_3) *m/e* (relative intensity) 767 (1, MH^+), 187 (100); ^{31}P NMR (CD_2Cl_2) δ 79.1; ^{13}C NMR (solid state in Al_2O_3, CP-MAS) δ 230.9 (*C*O), 220.8 (CO), 143.2 (Ph), 134.3 (Ph), 131.4 (Ph), 127.0 (Ph), 72.3 (OCH_2), 48.0 (NCH_2), 47.6 (NCH_2), 39.7 (NCH_2), 35.2 (NCH_2), 15.6 (CCH_3); ^1H NMR (CD_2Cl_2) δ 7.70–7.10 (m, 20 H, Ph), 3.75 (q, $^3J_{HH}$ = 7.0 Hz, 2 H, OCH_2), 3.39 (m, 2 H, NCH_2), 3.20 (m, 2 H, NCH_2), 2.91 (m, 4 H, NCH_2), 2.76 (m, 2 H, NCH_2), 2.42 (m, 2 H, NCH_2), 1.5 (br, 1 H, N*H*), 1.08 (t, $^3J_{HH}$ = 7.0 Hz, 3 H, CCH_3); IR (CH_2Cl_2) 1923 (s, CO), 1821 (m, CO), 1785 cm^{-1} (m, CO); IR (KBr) 3441 (m, NH), 1915 (s, CO), 1809 (s, CO), 1790 cm^{-1} (s, CO). Solid-state NMR data are listed in Table I.

***fac*-(Ethoxy-*N*,*N'*-bis(diphenylphosphino)azasilatrane-*P*,*P'*,*O*)tricarbonyltungsten (11). Method A.** A solution of 125 mg (0.210 mmol) of **3b** was added to a solution of 86 mg (0.220 mmol) of (mesitylene)tricarbonyltungsten in 6 mL of benzene. The clear yellow solution was irradiated for 3 h with a 275-W UV lamp. A yellow solid slowly precipitated, which was collected by filtration, washed thoroughly with benzene, and dried in vacuo, giving 33 mg (18%) of product as a yellow, microcrystalline solid (mp 210 °C dec).

Method B. A solution of 367 mg (0.630 mmol) of **3b** and 254 mg (0.620 mmol) of (cyclooctadiene)tetracarbonyltungsten in 12 mL of benzene in a 100-mL flask equipped with a reflux condenser and a gas outlet was irradiated for 2 h with a 275-W UV lamp. A yellow solid precipitated, which was filtered, washed several times with warm benzene, and dried in vacuo, giving 305 mg (57%) of product as a yellow, microcrystalline powder (mp 210 °C dec). According to IR and NMR spectroscopic data, the product contained a small amount (ca. 5%) of the tetracarbonyl complex, which could not be separated by prolonged washings with benzene or THF from the product: MS (desorption CI, NH_3) *m/e* (relative intensity) 853 (1, MH^+), 187 (100); ^{31}P NMR (pyridine-d_5) δ 73.0 ($^1J_{PW}$ = 229 Hz); ^{13}C NMR (solid state in Al_2O_3, CP-MAS) δ 221.2 (*C*O), 216.5 (*C*O), 214.0 (*C*O), 143.0 (Ph), 134.2 (Ph), 130.6 (Ph), 126.9 (Ph), 74.6 (OCH_2), 49.4 (NCH_2), 47.6 (NCH_2), 39.8 (NCH_2), 35.9 (NCH_2), 15.3 (CCH_3); ^1H NMR (pyridine-d_5) δ 7.84 (m, 8 H, Ph), 7.50–7.30 (m, 12 H, Ph), 4.16 (q, $^3J_{HH}$ = 7.0 Hz, 2 H, OCH_2), 3.34 (m, 2 H, NC*H*), 3.09 (m, 2 H, NCH_2), 2.98 (m, 2 H, NCH_2), 2.88 (t, 2 H, NCH_2), 2.70 (m, 2 H, NCH_2), 2.48 (m, 2 H, NCH_2), 2.50 (br, 1 H, NH), 1.23 (t, $^3J_{HH}$ = 7.0 Hz, 3 H, CCH_3); IR (CH_2Cl_2) 1915 (s, CO), 1812 (m, CO), 1780 cm^{-1} (m, CO); IR (KBr) 3462 (m, NH), 1907 (s, CO), 1801 (s, CO), 1780 cm^{-1} (s, CO). Solid-state NMR data are listed in Table I. Anal. Calcd for $C_{35}H_{38}N_4O_4P_2SiW$: C, 49.31; H, 4.49; N, 6.57. Found: C, 48.45; H, 4.30; N, 6.97.

Reaction of *fac*-(3b)M(CO)$_3$ (M = Mo, W) with CO. Approximately 20 mg of the title metal complexes was suspended in 5 mL of CH_2Cl_2, and a slow stream of CO was bubbled through each solution for 10 min. Each mixture was then centrifuged and the IR spectrum of its yellow supernatant recorded in the carbonyl region: *fac*-LMo(CO)$_3$ reaction 2017 (m), 1917 (vs), 1886 (s), 1861 (s) cm^{-1} (*cis*-LMo(CO)$_4$), 1820 (sh), 1790 (w) cm^{-1} (*fac*-(L)Mo(CO)$_3$); *fac*-LW(CO)$_3$ reaction, 2020 (s), 1995 (s) cm^{-1} (not assigned), 1913 (m), 1879 (w), 1855 (w), cm^{-1} (*cis*-(L)W(CO)$_4$), 1813 (w), 1781 (w) cm^{-1} (*fac*-LW(CO)$_3$). Prolonged reaction times did not give complete conversion of the tricarbonyl into tetracarbonyl complexes.

Crystal Structure Solution of S$_2$(3b) (5b). A colorless crystal was sealed in a glass capillary. Pertinent crystallographic parameters are given in Table II. The data were corrected for Lorentz and polarization effects, for absorption, and for a slight decay as indicated by intensity standards (11.5%). The structure solution was given by direct methods (SHELXS-86[8]) and was refined by using the CAD4-SDP[9] programs. The positions of all 42 nonhydrogen atoms were taken from the direct-methods E-map. Hydrogen atoms were placed in calculated positions for all nonmethyl carbon atoms with isotropic temperature factors set equal to 1.3 times the isotropic equivalent factors for the attached carbon atoms. Hydrogen atoms were used only for the calculation of structure factors. The final residuals for 379 variables refined with 3359 data for which $I > 3\sigma(I)$ were R = 0.0439 and R_w = 0.0616.

Crystal Structure Solution of (3b)PtCl$_2$ (7). A colorless crystal of **7** was sealed in a glass capillary for data collection. Crystallographic parameters are summarized in Table II. The structure was solved by using direct methods (SHELXS-86[8]) and refined by using the SHELX-76[10] package. Although the diffractometer data were of high quality, a substantial amount of disorder involving the complex and several molecules of DMSO in the lattice complicated the solution and refinement of the structure. Details are given in the supplementary material. The final dis-

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(8) Sheldrick, G. M. SHELX-86; Institut für Anorganische Chemie der Universität: Göttingen, FRG, 1986.

(9) Enraf-Nonius Structure Determination Package; Enraf-Nonius: Delft, Holland.

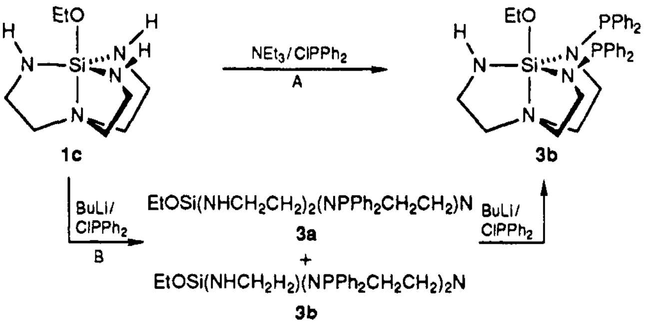
(10) Sheldrick, G. M. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., Van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978.

Table II. Crystal Data Summary for 5b and 7

	kb	7
formula	$C_{32}H_{38}N_4OSiP_2S_2$	$C_{32}H_{38}N_4OSiP_2Cl_2Pt \cdot 3.2C_2H_6OS$
fw	648.85	1100.72
space group	$P2_1/c$	$C2/m$
a, Å	11.522 (3)	15.117 (2)
B, Å	19.661 (3)	17.270 (2)
c, Å	15.199 (3)	9.791 (2)
β, deg	107.35 (1)	105.20 (2)
V, Å^3	3286 (1)	2467 (1)
Z	4	2
d_{calcd}, g/cm^3	1.311	1.48
cryst size, mm	0.4 × 0.4 × 0.5	0.1 × 0.1 × 0.15
μ(Mo Kα), cm^{-1}	3.17	32.7
data collecn instrument	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)	Mo K, (λ = 0.71073 Å)
orientation rflns: no.; range (2θ), deg	25; $18 < 2\theta < 31$	25; $17 < 2\theta < 32$
temp, °C	22 (1)	22 (1)
scan method	θ–2θ	θ–2θ
data collecn range, 2θ, deg	4.0–50.0	4.0–45.0
no. of unique data		
total no.	5780	1684
no. with $I > 3\sigma(I)$	3359	1658
no. of params refined	379	112
transmissn factors: max, min (ψ scans)	0.999, 0.966	0.999, 0.924
R^a	0.0439	0.0652
$R_w{}^b$	0.0616	0.0894
quality-of-fit indicator^c	1.15	3.86
largest shift/esd, final cycle	0.01	0.02
largest peak, e/Å^3	0.30	1.23

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

Scheme I



crepancy indices were $R = 0.0652$ and $R_w = 0.0894$.

Results and Discussion

Synthesis of 3b and Its Derivatives 4b and 5b. By analogy to the substitution reactions of azasilatranes 1a–c with chloroorganosilanes,[3] treatment of 1c with chlorodiphenylphosphine in benzene in the presence of triethylamine proceeds via P–N bond formation with preservation of the tricyclic atrane framework. Depending on the stoichiometry of the reactants, the product as analyzed by ^{31}P NMR spectroscopy consists either of a mixture of mono- and disubstituted azasilatranes 3a,b with unreacted 1c still present (ratio 1c:chlorodiphenylphosphine > 1:2; Scheme I, route A) or of pure disubstituted 3b (1c: chlorodiphenylphosphine ≥ 1:2, Scheme I, route B). Complete substitution of all three NH functionalities was not observed under the conditions described even when a large excess of chlorodiphenylphosphine was present. This behavior is comparable to the formation of only mono- and disubstitution products in the reaction of 1c and trimethylchlorosilane or phenyldimethylchlorosilane[3] and may be attributed to steric overcrowding in the hypothetical trisubstituted compounds.

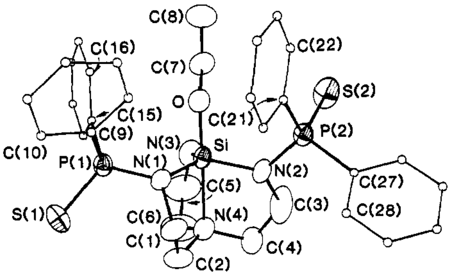
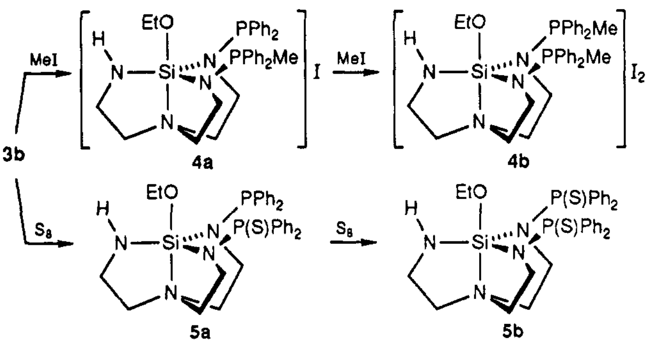


Figure 1. ORTEP drawing of **5b**, with the phenyl carbon atoms drawn as spheres of arbitrary size for clarity. The thermal ellipsoids are drawn at the 40% probability level. The labels for phenyl carbon atom numbering around the rings are shown only for the first two carbons.

Scheme II



A mixture of 3a,b (together with unidentified byproducts) was also observed spectroscopically after treatment of a benzene solution of 1c with 1 equiv of *n*-BuLi, followed by addition of 1 equiv of chlorodiphenylphosphine. Complete conversion of 3a into 3b was observed when a second equivalent of each of the last two reactants was added, thus further confirming the identity of the intermediate 3a (Scheme I, route B). Isolation of pure 3b was possible after reaction of 1c with 2 equiv each of triethylamine and chlorodiphenylphosphine (route A), separation of the precipitated ammonium salt, and precipitation of the product from hexane/benzene solutions. No attempts were made to isolate the intermediate 3a.

The constitution of 3b, which was obtained as a white microcrystalline solid, was unequivocally established by NMR spectroscopy and high-resolution MS. The product was found to be easily soluble in CH_2Cl_2, THF, and benzene, slightly soluble in ether, and insoluble in hexane. The chemical reactivity of 3b is typical of tertiary phosphines in that quaternization or oxidation reactions at phosphorus are easily achieved. Thus, treatment of a solution of 3b in CH_2Cl_2 with excess MeI smoothly afforded the novel bis(phosphonium) salt 4b (Scheme II). The corresponding monoalkylated species, 4a, was detected as an intermediate by monitoring the reaction by ^{31}P NMR spectroscopy, although we were unable to isolate it. Similarly, oxidation of 3b with 2 equiv of sulfur in benzene at ambient temperature gave the corresponding bis(phosphine) sulfide 5b, via the spectroscopically detectable intermediate 5a (Scheme II).

Both 4b and 5b were isolated by precipitation from their respective reaction mixtures upon addition of hexane, and their constitution was established by NMR and MS spectroscopies. In the case of 5b, the proposed molecular structure was further confirmed by X-ray crystallography (Figure 1). As with other azasilatranes,[3,11] the structure

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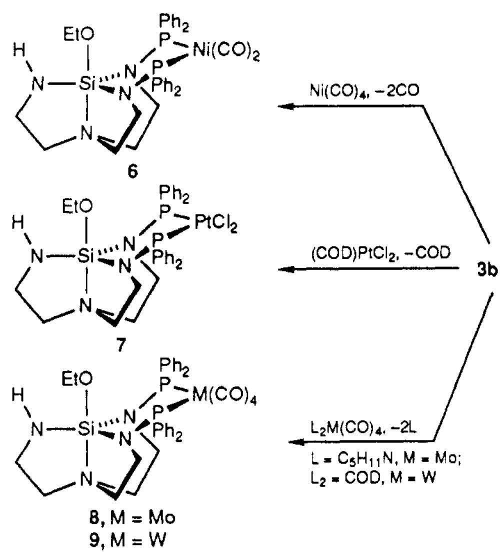
(11) Maharashvili, A.; Shklover, V. E.; Struchkov, Yu. T.; Lapsina, A.; Zelchan, G.; Lukevics, E. *J. Organomet. Chem.* 1988, *349*, 23.

Scheme III



of **5b** features a tricyclic skeleton of envelope-shaped five-membered rings arranged around the central Si-N$_{ax}$ bond. The coordination sphere of the Si atom is a distorted trigonal bipyramid, with the Si atom significantly displaced (0.287 (1) Å) above the plane formed by the three N$_{eq}$ atoms. The O-Si-N$_{ax}$ moiety is linear (O-Si-N = 178.2 (3)°). The Si-N$_{ax}$ distance (2.214 (3) Å) is consistent with a substantial transannular bonding interaction, although this bond is lengthened relative to that in EtOSi(NMeCH$_2$CH$_2$)$_3$N (**2c**; 2.135 (2) Å[3]). These data, together with the observed shortening of the Si-O distance (1.658 (3) Å in **5b** compared with 1.699 (2) Å in **2c**), indicate a decrease in bond strength of the dative N$_{ax}$ → Si bond in **5b** with a concomitant transfer of electron density from this bond into the collinear Si-O bond. The P=S and P—N bond distances in **5b** are normal for such compounds.[12]

Coordination Chemistry of 3b. Ligand **3b** reacts easily with transition-metal compounds of the type L$_n$ML'$_m$ (m = 2, 3, L' = olefins, amines, CO) with displacement of L' and formation of the corresponding phosphine complexes. Thus, treatment of THF solutions of Ni(CO)$_4$, Cl$_2$Pt(η^2-cyclooctadiene), (CO)$_4$Mo(piperidine)$_2$, and (CO)$_4$W(η^2-cyclooctadiene) with 1 equiv of **3b** gave the new complexes **6**–**9**, respectively (Scheme III), which were isolated as microcrystalline materials after concentration of the reaction mixtures and addition of hexane. In the case of **9**, the isolated product contained approximately 5% of a second component later identified as the tricarbonyl complex **10** (see below), which could not be separated and whose formation occurs by extrusion of a very labile CO ligand in solution. Whereas formation of **6**–**8** was complete within 20 min at room temperature, a longer reaction period of 2 days was required for **9**.

Complexes **6**–**9** are air- and moisture-stable in the solid state and dissolve easily in benzene, DMSO, and chlorinated organic solvents. The solutions displayed increased sensitivity to hydrolysis and decomposed slowly at ambient temperature, even in the absence of moisture. Formulation of the products was inferred from analytical, MS, NMR, and IR spectroscopic data. In addition to multinuclear NMR studies (see below) significant information on the molecular constitution was obtained from the IR spectra. Thus, characteristic band patterns in the carbonyl region[13] (see experimental section for frequencies) indicate the presence of Ni(CO)$_2$ in **6** and *cis*-M(CO)$_4$ units in **8** and **9** (Figure 2), which suggest coordination of **3b** as a bidentate diphosphine chelating ligand. In the case of **7**, the presence of a *cis*-PtCl$_2$ unit was suggested on the basis of its characteristic Pt-Cl stretching bands[13] (304 and 279 cm^{-1}) and the overall structure was further confirmed by X-ray crystallography (see Figure 2). Although the bond data for **7** are of limited accuracy due to the presence of extensive disorder in the crystal (see Experimental Section and the supplementary material), the dominant features are clearly evident. The Pt atom adopts a slightly distorted square planar coordination geometry that shows the expected cis arrangement of the phosphine groups. The Pt-P (2.77 (1) Å) and Pt-Cl (2.37 (1) Å) distances appear to be in the normal range.[12] The six-membered chelate ring exhibits an almost planar arrangement of the Pt, P, and N atoms. The Pt-O distance (3.32 (3) Å) excludes substantial bonding interaction between these two atoms. The apparent mirror symmetry of the atrane cage is considered to be imposed by the stated disorder effects rather than by symmetry of individual molecules, and this precludes a more detailed discussion of conformational features of the cage system in this complex.

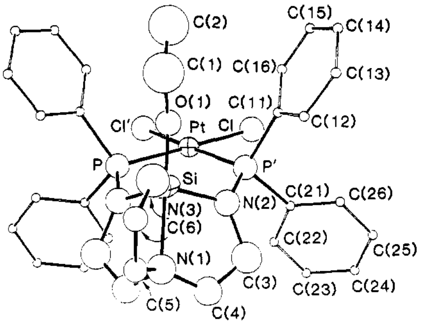
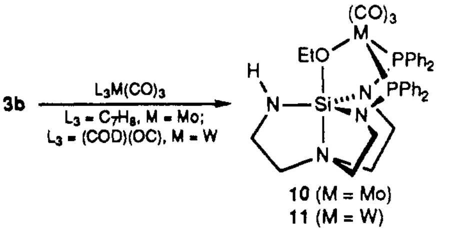


Figure 2. ORTEP drawing of **7**. Phenyl-group carbon atoms are represented as small circles for clarity. All other atoms are represented by 50% probability ellipsoids.

In contrast to the complexes **6**–**9** described above, a different type of coordination results from the reaction of **3b** and (η^3-cycloheptatriene)Mo(CO)$_3$ (reaction 1). Thus,



(1)

heating a benzene solution containing 1 equiv of each reactant to 30 °C for 1 h produced a yellow precipitate, which was identified as (**3b**)Mo(CO)$_3$ (**10**) by spectroscopic techniques. Formation of **10** or its tungsten analogue **11** was also observed during photolysis of THF solutions of the corresponding tetracarbonyl complexes **8** and **9**, respectively (reaction 2), or in the case of **11** via reaction of

$$8,\ 9 \underset{+\mathrm{CO}}{\overset{\mathrm{UV}\ -\mathrm{CO}}{\rightleftharpoons}} 10,\ 11 \qquad (2)$$

(CO)$_4$W(COD) and the free ligand **3b** under photolytic conditions. In the latter instance, the presence of **9** as an intermediate was established by ^{31}P NMR spectroscopic investigation of the reaction mixture. In contrast, (**3b**)-

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[12] Corbridge, D. E. C. *The Structural Chemistry of Phosphorus*; Elsevier Scientific Publishing: Amsterdam, 1974.

[13] Nakamoto, K. *IR and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; Wiley-Interscience: New York, 1978.

$Ni(CO)_2$ (**6**) was found to be stable with respect to loss of another CO under both thermal (refluxing toluene) and photolytic conditions.

The composition and constitution of **10** and **11** were established by analytical (**11**) and spectroscopic data (**10**, **11**). The CI mass spectra show characteristic clusters at m/e 767 (**10**) and 853 (**11**) whose intensity distribution matches the calculated isotopic patterns and that are assigned to $(M + H)^+$ ions. The IR spectra of these complexes display characteristic carbonyl bands[13] indicating the presence of *fac*-$M(CO)_3$ groups (see Experimental Section for frequencies). Both the MS and NMR spectra give no evidence for any ligands other than **3b** and carbonyls. In order to achieve the normally favored hexacoordination at the metal, bonding of the oxygen atom of the ethoxy group to the metal center is assumed (i.e., P,P′,O coordination). This assumption is in accord with certain differences in the NMR data of **10** and **11** in comparison with those of **6**–**9** featuring **3b** as a bidentate ligand (see below). The unusual coordination of the silyl ether group, allowing **3b** to function as a tridentate ligand in this case, is undoubtedly facilitated by both the chelate effect and the electron-releasing capability of the azasilatranyl group,[14,15] which results in enhanced nucleophilicity of the oxygen atom compared with that of alkyl-substituted silyl ethers. The lability of the metal–oxygen interaction in **10** and **11** is demonstrated by the easy substitution of stronger ligands. Hence, **10** and **11** react easily with carbon monoxide with displacement of the coordinated oxygen to give the tetracarbonyl complexes **8** and **9**, respectively, which were identified by their IR and ^{31}P NMR spectral data. In these spectra, however, are also absorptions of other, as yet unidentified, decomposition products.

NMR Spectroscopic Studies. Multinuclear (^1H, ^{13}C, ^{29}Si, ^{31}P, ^{195}Pt) NMR spectroscopy proved valuable in identifying the structural formulations of the new azasilatrane compounds **3b**–**11**. In addition, these data provide information on conformational aspects of the rather rigid molecular skeleton. NMR spectra were generally obtained on solution samples, with the exceptions of **7**, **10**, and **11**, where low solubilities precluded the accumulation of sufficient ^{13}C and ^{29}Si spectra. These data were therefore collected from solid samples under high-resolution CP/MAS conditions. ^{31}P data of all compounds were recorded in both solutions and the solid state (see Table I).

The ^1H NMR spectra of **3b**–**11** show, in addition to the signals of aromatic and NH protons, characteristic multiplets for the ethoxy substituent and the CH_2 protons of the methylene bridges. In accord with the effective mirror symmetry of these molecules in solution, the latter resonances show the expected AA′MM′ (NH-substituted rings) or ABMN (NP-substituted rings) spectral splittings. The chemical shifts of both the OCH_2 and CH_3 resonances occur in the normal range found for different N-substituted ethoxyazasilatranes[3] in the case of **3b**, **10**, and **11**, while for the other compounds, significant upfield shifts of 0.6–1.0 ppm are observed for both resonances. The origin of this effect lies in the magnetic anisotropy of the aromatic substituents at phosphorus. The strong shielding of the proton resonances can be correlated with the dominance of molecular conformations in solution wherein the ^1H nuclei of the ethoxy fragment are in close proximity to the π electron clouds of the aromatic rings and are thus subject to strong screening due to the ring current effect. Support for this hypothesis is provided by the crystal structures of **5b** and **7**, which exhibit the postulated conformation in the solid state. In the case of **10** and **11**, the study of molecular models rules out any such ring current effects on the ethoxy protons from the phenyl groups owing to the coordination of the oxygen atom to the metal center. The absence of this aromatic shift effect constitutes additional evidence for the tridentate coordination of the azasilatrane ligand in **10** and **11**.

In the ^{13}C NMR spectra, the absorptions assignable to the azasilatrane moiety are generally in close agreement with our data obtained previously for N-substituted ethoxyazasilatranes.[3] An exception, however, is observed for the OCH_2 resonances of **10** and **11**, which are significantly deshielded with respect to the narrow range (δ 56–59 ppm) commonly found for ethoxyazasilatranes.[3] This downfield shift is consistent with an increase in electron-withdrawing ability of the adjacent oxygen atom as a consequence of its coordination to the metal center. No screening effects due to the anisotropy of the aromatic systems were found in the ^{13}C NMR spectra, which is in accord with the expected larger distances between the phenyl groups and the ethoxy carbon atoms. The remaining resonances assignable to the phenyl groups and coordinated carbonyls display no unexpected characteristics.

The ^{29}Si spectra of **3b**–**11** (Table I) feature a single resonance in both the solution and solid state, with peak splitting due to coupling with the phosphorus nuclei. The chemical shifts are found in the upfield region characteristic for pentacoordinate silicon nuclei in an atrane structure,[1–4] thus establishing the presence of substantial transannular interaction in all cases. Chemical shift differences between spectra taken in solution and the solid state were found to be less than 7 ppm, indicating rather small variations of the cage structure in the different phases. The extremely high-field shift in the case of **7** parallels the rather short $Si–N_{ax}$ bond distance found in the crystal structure. An increase in transannular $Si–N_{ax}$ interaction with respect to that in the parent molecule **3b** ($\delta(^{29}Si)$ −89.2) may therefore also be postulated for dicationic **4b** ($\delta(^{29}Si)$ −94.6), whereas the opposite is found for the corresponding disulfide **5b** ($\delta(^{29}Si)$ −85.0). Coordination of the oxygen atom in **10** and **11** also produces an upfield shift with respect to the signals in the corresponding complexes **8** and **9**. This is indicative of a higher degree of transannular interaction in the former compounds, consistent with the formally stronger electron-withdrawing character of the coordinated EtO group.[1,14]

An interesting phenomenon is observed in the ^{31}P NMR spectra. Whereas in solution a single resonance is observed for all compounds studied, the solid-state spectra (with the exception of **10**) display two signals of equal intensity. In the case of **10**, a single broad line is found. Since the presence of different molecules occupying independent sites in the unit cell is ruled out by both the solid-state ^{29}Si NMR studies and the crystal structures of **5b** and **7**, the resonances must be assigned to two different ^{31}P nuclei present in each molecule. The chemical inequivalency in this case results from the twisted conformation of the atrane cage,[1,16] which introduces helical chirality of the atrane backbone and leads to a different environment for each phosphorus nucleus. In solution, this inequivalency is lost due to interconversion of the two enantiomers, which is rapid on the NMR time scale so that only an average signal is observed down to −80 °C. A similar splitting is observed for the ^{13}C resonances of the CO groups in **11**,

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(14) Such an effect was established by NMR spectroscopic studies for silatranes (Bellama, J. M.; Nies, D.; Ben Zvi, N. *Magn. Reson. Chem.* **1986**, *24*, 748).

(15) Garant, R.; Verkade, J. G. Submitted for publication.

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whereas in the case of **10** as well as for the resonances of the methylene carbon atoms of the atrane cage of both molecules, this effect is too small to be detected.

Conclusions. The new ligand **3b** is easily accessible via diphosphination of the azasilatrane precursor **1c**. The chemical reactivity of **3b** was found to be typical of tertiary phosphines, thus allowing facile alkylation, oxidation with sulfur, and complexation. The coordination compounds synthesized displayed two modes of attachment of the ligand to the metal center, with **3b** behaving as either a bidentate (P,P′ coordination) or tridentate (P,P′,O coordination) ligand. The latter mode represents the first example of metal coordination by a silatranyl ether group, and it is favored by both the chelate effect and the enhanced basicity at oxygen due to the transannular $N_{ax}\rightarrow$Si bond. The results of NMR spectroscopic studies in both solution and the solid state are consistent with the preservation of a transannular $N_{ax}\rightarrow$Si bond in all cases, with an increase in bond strength being observed as a consequence of either coordination of the axial oxygen atom to a metal center or accumulation of positive charge in the atrane cage.

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Supplementary Material Available: Description of the structure solution of **7** and tables of positional and anisotropic thermal parameters, bond lengths, least-squares planes, and bond angles for **5b** and **7** (20 pages); tables of calculated and observed structure factors (26 pages). Ordering information is given on any current masthead page.

Synthesis, Structure, and Properties of Dicarbonyl Bis(phosphine) 1,4-Diphenyltetraazabutadiene Complexes of Molybdenum and Tungsten

Soon W. Lee and William C. Trogler*

Department of Chemistry, D-006, University of California at San Diego, La Jolla, California 92093-0506

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The complexes $MoBr_2(CO)_2(PPh_3)_2$ and $MoBr_2(CO)_2(PEt_3)_2$ react with $[Li(THF)_x]_2[PhNN{=}NNPh]$ ($[Li(THF)_x]_2$(I)) to yield crystalline materials of formula $Mo(N(Ph)N{=}NNPh)(CO)_2(PPh_3)_2{\cdot}C_6H_6$ (III) and $Mo(N(Ph)N{=}NNPh)(CO)_2(PEt_3)_2$ (IV), respectively. The complex *trans*-$WBr_2(CO)_2(PPh_3)_2$ reacts with $[Li(THF)_x]_2[PhNN{=}NNPh]$ ($[Li(THF)_x]_2$(I)) to yield *trans*-$W(PPh_3)_2(CO)_4$ and the cyclic tetrazene complex $W(N(Ph)N{=}NNPh)(CO)_2(PPh_3)_2{\cdot}C_6H_6$ (IIIa). Dibromotetracarbonyltungsten reacts with 3 mol of PMe_3 to give $WBr_2(CO)_2(PMe_3)_3$ (IIa). Complex IIa reacts with I to exclusively yield $W(N(Ph)N{=}NNPh)(CO)_2(PMe_3)_2$ (IVa). The crystal structures of IIa, III, IIIa, IV, and IVa were determined through X-ray diffraction at room temperature: complex III crystallizes in the monoclinic crystal system, space group $C2$, with lattice constants a = 20.675 (8) Å, b = 9.946 (4) Å, c = 15.285 (9) Å, β = 130.54 (3)°, and Z = 2; IV crystallizes in the tetragonal system, space group $P4_32_12$, with lattice constants a = 13.000 (3) Å, c = 17.941 (6) Å, and Z = 4; IIa crystallizes in the orthorhombic system, space group $Pbca$, with lattice constants a = 8.938 (4) Å, b = 15.416 (5) Å, c = 29.974 (9) Å, and Z = 8; IIIa crystallizes in the monoclinic system, space group $C2$, with lattice constants a = 20.598 (10) Å, b = 9.976 (5) Å, c = 15.257 (7) Å, β = 130.49 (3)°, and Z = 2; IVa crystallizes in the monoclinic system, space group $P2_1$, with lattice constants a = 9.476 (3) Å, b = 11.902 (3) Å, c = 10.473 (3) Å, β = 90.93 (2)°, and Z = 2. Least-squares refinement of the structures led to R factors of 0.047 (III), 0.034 (IV), 0.048 (IIa), 0.059 (IIIa), and 0.072 (IVa). The coordination spheres of molybdenum and tungsten in III, IIIa, IV, and IVa can be described as distorted octahedrons with trans PR_3 groups. Complex IIa exhibits a monocapped-octahedral structure based on a *fac*-$WBr_2(CO)(PMe_3)_3$ group (bromines trans to two P) with CO capping the face defined by the three P atoms. This structure is maintained in solution as evidenced by a doublet and triplet in the ^{31}P NMR spectrum at δ −15.2 and −38.7, respectively, with J_{P-P} = 14.6 Hz. Complexes III, IIIa, IV, and IVa have formal 18-electron configurations if the tetraazabutadiene ligand is viewed as a neutral four-electron donor analogous to the diazabutadiene ligand. The structures of III, IIIa, IV, and IVa show a progressive increase in distortion from octahedral symmetry as the PR_3 groups become smaller. The distortion rotates the MN_4 metallacycle plane out of coplanarity with the two CO groups by as much as 30°. Electrochemical studies show that IV displays two reversible one-electron reductions. Electrochemical studies of IVa reveal only irreversible reduction processes. Complexes IV and IVa do not react with small two-electron-donating molecules (CO, PMe_3, and CH_3CN).

Introduction

Transition-metal complexes that have unsaturated metallacycles containing the 1,4-disubstituted tetraazabutadiene ligand (also called tetraazadiene, tetrazene, or tetrazenido) have attracted interest because of their novel bonding features.[1] Attention has focused on the delo-

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