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Novel Route to the Unsymmetrical Dialkyl Complex $CpW(NO)(CH_2SiMe_3)(CH_2CPh_3)$ and Formation of Metallacycles by Thermolysis of $CpW(NO)(CH_2SiMe_3)(CH_2CR_2Ph)$ (R = Me, Ph)

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Treatment of $CpW(NO)(CH_2SiMe_3)_2$ ($Cp = \eta^5\text{-}C_5H_5$) with $[Ph_3C]PF_6$ results in cleavage of the Si–C bond and formation of the unsymmetrical dialkyl complex $CpW(NO)(CH_2SiMe_3)(CH_2CPh_3)$ (**1**). Crystal data for **1**: $a = 10.930(2)$ Å, $b = 14.048(2)$ Å, $c = 9.357(2)$ Å, $\alpha = 92.781(16)°$, $\beta = 90.186(18)°$, $\gamma = 111.929(13)°$, $Z = 2$, space group $P\bar{1}$, $R = 0.041$, $R_w = 0.040$ for 3379 reflections with $I \geq 3\sigma(I)$. Complex **1** is thermally unstable and converts to the metallacyclic complex $CpW(NO)(CH_2C(C_6H_4)Ph_2)(NCMe)$ (**2**) in acetonitrile. Crystal data for **2**: $a = 13.632(4)$ Å, $b = 10.009(2)$ Å, $c = 16.081(2)$ Å, $\beta = 93.401(12)°$, $Z = 4$, space group $P2_1/c$, $R = 0.040$, $R_w = 0.046$ for 3427 reflections with $I \geq 3\sigma(I)$. The structures of **1** and **2** were solved by conventional heavy-atom methods and were refined by full-matrix least-squares procedures. In the presence of PPh_3, complex **1** thermally decomposes in CH_2Cl_2 to $CpW(NO)(CH_2C(C_6H_4)Ph_2)(PPh_3)$ (**4**). The neophyl analogue of **1**, $CpW(NO)(CH_2SiMe_3)(CH_2CMe_2Ph)$ (**5**), can be prepared from $CpW(NO)(CH_2SiMe_3)Cl$ and, like **1**, readily undergoes ortho metalation in the presence of PPh_3 and converts to $CpW(NO)(CH_2C(C_6H_4)Me_2)(PPh_3)$ (**6**).

Introduction

The chemistry of coordinatively and/or electronically unsaturated metal centers continues to be a prime focus in transition-metal organometallic chemistry.[1,2] Our recent efforts in this area have centered principally on the characteristic stoichiometric chemistry of hydrocarbon ligands attached to the 14-valence-electron fragments Cp′M(NO) (M = Mo, W; Cp′ = Cp ($\eta^5\text{-}C_5H_5$), Cp* ($\eta^5\text{-}C_5Me_5$)). In particular, we have expended considerable effort in developing the chemistry of the symmetric 16-electron complexes $Cp'M(NO)R_2$ (R = alkyl, aryl).[3] Subsequently, we developed methodology to synthesize asymmetric 16-electron complexes $Cp^*M(NO)(R)R'$[4,5] and were thus afforded the opportunity to study the comparative reactivity of two different hydrocarbyl ligands attached to the same metal center.[6] However, the preparation of the asymmetric hydrocarbyl complexes is nontrivial and presents significant synthetic challenges. In this paper, we report our serendipitous finding that reaction of $CpW(NO)(CH_2SiMe_3)_2$ with trityl cation affords the asymmetric dialkyl complex $CpW(NO)(CH_2SiMe_3)(CH_2CPh_3)$. We also describe some thermal reactions of this complex and its related analogue $CpW(NO)(CH_2SiMe_3)(CH_2CMe_2Ph)$, processes which result in the formation of new metallacyclic complexes.

Experimental Section

All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions using an atmosphere of dinitrogen. General procedures routinely employed in these laboratories have been described in detail previously.[7] $CpW(NO)(CH_2SiMe_3)_2$ was prepared according to the literature procedure.[8] $[Ph_3C]PF_6$ (Aldrich) was recrystallized from CH_2Cl_2/hexanes prior to use. $(PhMe_2CCH_2)_2Mg{\cdot}X(\text{dioxane})$ was prepared and handled according to methodology presented in ref 7. Acetonitrile (BDH) was twice distilled from CaH_2, and PPh_3 (Strem) was used as received. ^{19}F NMR spectra were obtained on a Varian XL-300 NMR spectrometer operating at 282 MHz with external CF_3COOH as reference.

Preparation of $CpW(NO)(CH_2SiMe_3)(CH_2CPh_3)$ (1). $CpW(NO)(CH_2SiMe_3)_2$ (1.15 g, 2.50 mmol) and $[Ph_3C]PF_6$ (1.16 g, 3.00 mmol) were dissolved in CH_2Cl_2 (75 mL) to form a red-brown solution that was stirred at room temperature overnight. The resulting brown solution was concentrated in vacuo to approximately 15 mL, was treated with 2 drops of deaerated water, and was applied to the top of a silica gel column (3 × 12 cm) made up in 1:1 CH_2Cl_2/hexanes. The same mixture of solvents was used as the initial eluent, but then the proportion of CH_2Cl_2 was gradually increased to 100%. A yellow band was eluted first and yielded a pale yellow residue upon removal of the solvent. This residue consisted mainly of Ph_3COH. Spectroscopic data for Ph_3COH: IR (Nujol mull) ν_{OH} 3470 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.5–7.0 (m, 15H, C_6H_5), 2.20 (s, 1H, OH); low-resolution mass spectrum (probe temperature 120 °C) m/z 260 [P^+].

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Continued elution of the column with CH_2Cl_2 provided a red band that appeared as a purple eluate. Removal of the solvent from the eluate under reduced pressure produced a purple glass which was extracted with hexanes (2 × 50 mL). Filtration and concentration of the combined hexanes extracts in vacuo induced the precipitation of a purple solid. Further deposition of product was effected by cooling of the concentrated solution to −40 °C for 1 h. The solid product was isolated by removing the mother liquor with a cannula. In this manner analytically pure complex 1 (0.30 g, 0.48 mmol, 19% yield) was isolated as a purple, crystalline solid.

To obtain samples of 1 for reactivity studies, the final reaction mixture was taken to dryness, suspended in Et_2O, treated with H_2O, and filtered through a Florisil column supported on a frit. The ether filtrate was then used directly in further reactions. *The approximate yield of 1 was 30–60%.*

Data for complex 1 are as follows. Anal. Calcd for $C_{29}H_{33}NOSiW$: C, 55.86; H, 5.33; N, 2.25. Found: C, 56.15; H, 5.21; N, 2.11. IR (Nujol mull): ν_{NO} 1572 cm^{-1}. IR (CH_2Cl_2): ν_{NO} 1580 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.6–7.0 (m, 15H, C_6H_5), 4.89 (s, 5H, Cp), 3.53 (d, 1H, $CH_aH_bCPh_3$, $^2J_{HH}$ = 12.8 Hz), 2.40 (d, 1H, $CH_aH_bSiMe_3$, $^2J_{HH}$ = 9.0 Hz), 1.28 (dd, 1H, $CH_aH_bCPh_3$, $^2J_{HH}$ = 12.8 Hz, $^4J_{HH}$ = 2.0 Hz), 0.29 (s, 9H, $SiMe_3$), −0.76 (dd, 1H, $CH_aH_bSiMe_3$, $^2J_{HH}$ = 9.0 Hz, $^4J_{HH}$ = 2.0 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 150.5 (C_{ipso}), 127.9, 127.5, 125.6 (C_{aryl}), 102.3 (C_5H_5), 86.4 (CH_2 $^2J_{WH}$ = 102 Hz), 58.1 (CH_2, $^2J_{WH}$ = 81 Hz), 62.8 (CPh_3), 2.9 ($Si(CH_3)_3$). Melting point: 96 °C dec.

^{19}F and ^{31}P NMR Spectral Monitoring of the Formation of $CpW(NO)(CH_2SiMe_3)(CH_2CPh_3)$ (1). A reddish brown solution of $CpW(NO)(CH_2SiMe_3)_2$ (0.050 mmol) and $[Ph_3C]PF_6$ (0.080 mmol) was prepared in CD_2Cl_2 (0.8 mL) in a glovebox. Initial spectra were recorded, and then the reaction was allowed to proceed for 2 h, at which time final spectra were recorded. Spectral assignments, chemical shifts, and coupling constant data are summarized below.

^{31}P NMR (CD_2Cl_2): δ −35.5 (q, OPF_3, $^1J_{PF}$ = 1072 Hz), −139.6 (dp, 2 × base-PF_5), −143.8 (br septet, PF_6^-, $^1J_{PF}$ = 704 Hz). ^{19}F NMR (CD_2Cl_2): δ 3.4 (br d, PF_6^-, $^1J_{PF}$ = 704 Hz), −6.4 and −6.8 (dp, F_{axial} for 2 × base-PF_5, $^1J_{PF}$ = 739, 802 Hz, $^2J_{FF}$ = 60 Hz), 8.7 (dd, $F_{equatorial}$ of base-PF_5, $^1J_{PF}$ = 802 Hz, $^2J_{FF}$ = 60 Hz), 8.0 (dd, $F_{equatorial}$ of base-PF_5, $^1J_{PF}$ = 796 Hz, $^2J_{FF}$ = 60 Hz), −12.8 (d, OPF_3, $^1J_{PF}$ = 1065 Hz), −82.2 (decet with Si satellites, Me_3SiF, $^1J_{SiF}$ = 220 Hz, $^3J_{HF}$ = 8 Hz).

Thermal Decomposition of $CpW(NO)(CH_2SiMe_3)(CH_2CPh_3)$ (1) in Noncoordinating Solvents. A benzene solution (10 mL) of 1 (0.10 g, 0.16 mmol) was left undisturbed for 5 days at ambient temperatures. During this time, the color of the solution changed from purple to amber, and a tan precipitate formed. The solvent was removed from the final reaction mixture in vacuo. An IR spectrum (Nujol mull) of the solid residue showed bands assignable to terminal nitrosyl ligands at 1594, 1578, 1561, and 1547 cm^{-1}. A ^{1}H NMR spectrum of the residue in C_6D_6 showed resonances attributable to a mixture of several different Cp-containing compounds. These products were not investigated further. In separate experiments, monitoring of the reaction in C_6D_6, $CDCl_3$, or CD_2Cl_2 by ^{1}H NMR spectroscopy showed that all the CH_2SiMe_3 groups were converted to Me_4Si (TMS, δ 0.00).

Thermal Decomposition of $CpW(NO)(CH_2SiMe_3)(CH_2CPh_3)$ (1) in MeCN: Preparation of $CpW(NO)(CH_2C(C_6H_4)Ph_2)(NCMe)$ (2). A solution of 1 (0.30 g, 0.48 mmol) in MeCN (10 mL) was left undisturbed for 3 weeks at room temperatures. After that time the reaction mixture consisted of an amber solution over transparent, brick red crystals of 2 suited for X-ray crystallographic analysis (0.20 g, 73% yield). The formation of TMS as the other product in this reaction was confirmed by ^{1}H NMR monitoring of its progress in CD_3CN.

Anal. Calcd for $C_{27}H_{24}N_2OW$: C, 56.27; H, 4.20; N, 4.86. Found: C, 56.61; H, 4.30; N, 4.70. IR (KBr): ν_{NO} 1574, 1559 cm^{-1}. Low-resolution mass spectrum (probe temperature 180 °C): *m/z* 535 [P$^+$]. Complex 2 was insoluble in C_6D_6, CD_3CN, CD_3NO_2, or CD_2Cl_2, thereby making spectroscopic characterization difficult.

Reaction of $CpW(NO)(CH_2SiMe_3)(CH_2CPh_3)$ (1) with PMe_3: Preparation of $CpW(NO)(CH_2SiMe_3)(CH_2CPh_3)(PMe_3)$ (3). A purple solution (ν_{NO} 1607 cm^{-1}) of 1 (0.08 g, 0.13 mmol) in Et_2O (5 mL) at room temperature was treated with excess PMe_3 (0.2 mL, 2 mmol), thereby causing an immediate color change to yellow (ν_{NO} 1580 cm^{-1}). Addition of hexanes (5 mL) and cooling of the reaction mixture to −78 °C for 1 h induced the precipitation of a yellow solid, which turned pink when the mother liquor was removed and the solid was subjected to reduced pressure for a few minutes. Redissolution of the solid in C_6D_6 or $CDCl_3$ in the absence of excess phosphine led to purple solutions characteristic of the organometallic starting material. A ^{1}H NMR spectrum ($CDCl_3$) of 1 in the presence of a large excess of PMe_3 was obtained, thus providing further solution characterization of the adduct, 3. ^{1}H NMR: δ 7.5–7.0 (m, 15H, C_6H_5), 4.94 (d, 5H, Cp, $^3J_{HP}$ = 2.5 Hz), 3.04 (dd, 1H, CH, $^2J_{HH}$ = 15.0 Hz, $^3J_{HP}$ = 2.5 Hz), 1.40 (d, 9H, $P(CH_3)_3$, $^2J_{HP}$ = 9.0 Hz), 0.04 (s, 9H, $Si(CH_3)_3$). Resonances attributable to the other three methylene protons are presumably obscured by those due to the excess of uncoordinated PMe_3 (δ 1.00 ppm, d, J = 3.0 Hz).

Thermolysis of the PMe_3 adduct (3) in refluxing toluene containing 5 equiv of PMe_3 produced a mixture of thermal decomposition products.

Decomposition of $CpW(NO)(CH_2SiMe_3)(CH_2CPh_3)$ (1) in the Presence of PPh_3: Preparation of $CpW(NO)(CH_2C(C_6H_4)Ph_2)(PPh_3)$ (4). A purple solution of 1 (0.30 g, 0.48 mmol) and PPh_3 (0.39 g, 1.5 mmol) in hexanes/CH_2Cl_2 (10:1, 20 mL) was heated in a sealed vessel at 55 °C for 12 h. The resulting yellow solution was taken to dryness in vacuo, and the residue was washed with hexanes (5 × 25 mL). The residue was then dissolved in Et_2O (40 mL), filtered through Celite (1 × 4 cm), and concentrated in vacuo to incipient crystallization. Maintaining the concentrated ether solution at −30 °C overnight induced the precipitation of 4 (0.15 g, 39% yield) as a microcrystalline yellow solid.

Anal. Calcd for $C_{43}H_{36}NOPW$: C, 64.74; H, 4.55; N, 1.76. Found: C, 64.99; H, 4.68; N, 1.70. IR (Nujol mull): ν_{NO} 1586 (sh), 1576 (s), 1564 (s) 1553 (m) cm^{-1}. ^{1}H NMR (C_6D_6): δ 8.04 (d, 1H, aryl H, J_{HH} = 7.2 Hz), 7.8, 7.5, 7.4 (m, 3 × 1H, aryl H), 7.2–7.0 (m, 25H, aryl H), 4.70 (d, 5H, Cp, J_{HP} = 1.8 Hz), 3.59 (dd, 1H, CH_aH_b, $^2J_{HH}$ = 13.2 Hz, $^3J_{HP}$ = 5.4 Hz), 2.41 (dd, 1H, CH_aH_b, $^2J_{HH}$ = 13.2 Hz, $^3J_{HP}$ = 16.5 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 30.40 (s, $^1J_{PW}$ 207 Hz). Low-resolution mass spectrum (probe temperature 200 °C): *m/z* 797 [P$^+$], 535 [P$^+$ − PPh_3].

Preparation of $CpW(NO)(CH_2SiMe_3)(CH_2CMe_2Ph)$ (5). $CpW(NO)(CH_2SiMe_3)_2$ (2.30 g, 5.00 mmol) was dissolved in MeCN (30 mL) in a 300-mL reaction vessel. The vessel was then evacuated and back-filled with H_2 (1 atm). Overnight the resulting burgundy solution turned amber red. The solvent was then removed in vacuo, and the residue was dissolved in Et_2O. The ether solution was cooled to −78 °C and treated with HCl (2 equiv as a 0.75 M ether solution) until the solution was deep blue.[9] The resulting reaction mixture containing $CpW(NO)(CH_2SiMe_3)Cl$ was taken to dryness under reduced pressure, and the residue was then extracted with pentane (5 × 20 mL). The combined extracts were filtered through a column of Celite (2 × 8 cm) supported on a medium-porosity frit. The blue pentane filtrate was taken to dryness in vacuo and then redissolved in cold Et_2O (30 mL, −40 °C). The solution was then treated with $(PhMe_2CCH_2)_2Mg{\cdot}X(dioxane)$ (2.0 mmol, 0.8 equiv) dissolved in cold Et_2O (20 mL, −40 °C). The stirred reaction mixture was slowly warmed to room temperature over the course of 30 min. After this time the reaction mixture consisted of a cloudy red-brown solution. The volume of the solution was reduced in vacuo to about 20 mL, and the mixture was then filtered through a

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(9) This sequence of reactions converts $CpW(NO)(CH_2SiMe_3)_2$ to $CpW(NO)(CH_2SiMe_3)Cl$ via the alkyl azomethine complex $CpW(NO)(CH_2SiMe_3)(NC\{H\}Me)$. For details of a related transformation refer to the preparation of $Cp^*W(NO)(CH_2SiMe_3)Cl$ in ref 4.

column of Florisil (2 × 3 cm) supported on a frit. The column was washed with Et_2O until the purple product band was completely eluted. The solvent was then removed in vacuo from the eluate, and the residue was redissolved in pentane. The pentane solution was filtered through Celite (1 × 2 cm), concentrated, and placed in a freezer to induce crystallization. After several days at −30 °C, 620 mg (25% yield based on CpW(NO)$(CH_2SiMe_3)_2$) of maroon crystals of **5** was isolated by removing the mother liquor with a cannula.

Anal. Calcd for $C_{19}H_{29}NOSiW$: C, 45.70; H, 5.85; N, 2.80. Found: C, 46.03; H, 5.96; N, 2.70. IR (Nujol mull): ν_{NO} 1574 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.43 (d, 2H, aryl H, J_{HH} = 9.6 Hz), 7.21 (t, 2H, aryl H, J_{HH} = 7.5 Hz), 7.06 (t, 1H, H_{para}, J_{HH} = 7.2 Hz), 4.93 (s, 5H, Cp), 4.01 (d, 1H, CH_2, $^2J_{HH}$ = 11.1 Hz), 1.88 (d, 1H, CH_2, $^2J_{HH}$ = 9.6 Hz, $^3J_{HP}$ = 16.5 Hz), 1.79 and 1.68 (s, 2 × 3H, $C(CH_3)_2$), 0.27 (s, 9H, $Si(CH_3)_3$), −0.46 (dd, 1H, CH_2, $^2J_{HH}$ = 9.6 Hz, $^4J_{HH}$ = 2.4 Hz), −1.54 (dd, 1H, CH_2, $^2J_{HH}$ = 11.1 Hz, $^4J_{HH}$ = 2.4 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 152.90 (C_{ipso}), 126.08, 125.93, 125.68 (C_{aryl}), 101.49 (Cp), 99.89 (CH_2CMe_2Ph, $^1J_{WC}$ = 87.1 Hz), 53.41 (CH_2SiMe_3, $^1J_{WC}$ = 84.2 Hz), 46.58 (CMe_2), 33.86 and 31.56 (2 × $C(CH_3)$), 2.87 ($Si(CH_3)_3$). Low-resolution mass spectrum (probe temperature 150 °C): *m/z* 499 [P^+].

Thermal Decomposition of CpW(NO)(CH_2SiMe_3)(CH_2CMe_2Ph) (5) in the Presence of PPh_3: Preparation of CpW(NO)($CH_2C(C_6H_4)Me_2$)(PPh_3) (6). CpW(NO)(CH_2SiMe_3)(CH_2CMe_2Ph) (0.23 g, 0.47 mmol) and PPh_3 (0.20 g, 0.76 mmol) were weighed into a Rotoflo-capped reaction vessel. Hexanes (30 mL) was added, and the reaction vessel was then immersed in a 55 °C oil bath. After 24 h of thermolysis without stirring, the originally purple reaction mixture consisted of an amber supernatant solution over a large quantity of yellow needles. The needles **6** (0.26 g, 82% yield) were isolated by removing the supernatant liquid with a cannula and washing the product with pentane (2 × 20 mL). The complex was then recrystallized from CH_2Cl_2/hexanes.

Anal. Calcd for $C_{33}H_{32}NOPW$: C, 58.85; H, 4.79; N, 2.08. Found: C, 58.28; H, 4.77; N, 1.94. IR (Nujol mull): ν_{NO} 1576 (s), 1568 (s), 1557 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.5 (br m, 15H, PPh_3), 7.0 (m, 4H, metallacycle aryl H), 5.48 (d, 5H, Cp, J_{HP} = 1.8 Hz), 2.07 (vt, 1H, CH_aH_b, $^2J_{HH}$ = 13.8 Hz, $^3J_{HP}$ = 13.8 Hz), 1.59 (dd, 1H, CH_aH_b, $^2J_{HH}$ = 13.8 Hz, $^3J_{HP}$ = 12.3 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 165.92, 162.1 (d, J_{PC} = 10.7 Hz), 142.36, 135.44, 132.5 (br), 131.6 (br), 129.0 (br), 125.47, 123.91, 123.78 (C_{aryl}), 99.85 (C_5H_5), 47.90 (d, CH_2, J_{PC} = 13.4 Hz), 34.84, 33.57 (2 × $C(CH_3)$), $C(CH_3)_2$ not observed. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 28.24 (s, $^1J_{PW}$ = 212 Hz). Low-resolution mass spectrum (probe temperature 250 °C): *m/z* 673 [P^+], 411 [$P^+ - PPh_3$].

X-ray Crystallographic Analyses of CpW(NO)(CH_2SiMe_3)(CH_2CPh_3) (1) and CpW(NO)($CH_2C(C_6H_4)Ph_2$)(NCMe) (2). Crystallographic data for complexes **1** and **2** are collected in Table I. Purple crystals of complex **1** were grown from Et_2O/hexanes, whereas pale orange crystals of complex **2** were formed directly by allowing a solution of **1** to stand unstirred in MeCN for several weeks at room temperature. The final unit-cell parameters were obtained by least-squares analysis of 2(sin θ)/λ values for 25 strong reflections with 2θ = 20–25° for **1**. Constrained least-squares refinement of 25 reflections with 2θ = 36–42° gave final cell parameters for **2**. The intensities of three standard reflections, measured every 200 reflections throughout the data collections, remained constant for **1** and decreased uniformly by about 3% for **2**. The data were processed[10] and corrected for absorption using the Gaussian integration method.[11]

Both structures were solved by heavy-atom methods, the coordinates of the heavy atoms being determined from the Patterson functions and those of the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. All non-hydrogen atoms of both complexes were refined with anisotropic thermal parameters; hydrogen atoms were fixed in idealized positions (C(sp^2)–H = 0.97 Å; C(sp^3)–H = 0.98 Å, $B_H = 1.2B_{bonded\ atom}$), except for the four methylene protons of complex **1**, which were successfully refined. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 12. Final atomic coordinates and equivalent isotropic thermal parameters and selected bond lengths and angles appear in Tables II and III, respectively. Hydrogen atom parameters, anisotropic thermal parameters, and complete tables of bond lengths and bond angles and torsion angles, are included as supplementary material. Views of the solid-state molecular structures of complexes **1** and **2** are displayed in Figures 1 and 2, respectively.

Table I. Crystallographic and Experimental Data for Complexes 1 and 2[a]

	1	2
formula	$C_{29}H_{33}NOSiW$	$C_{27}H_{24}N_2OW$
fw	623.52	576.35
color, habit	purple, plate	orange, plate
cryst dimens (mm^3)	0.08 × 0.20 × 0.60	0.08 × 0.23 × 0.25
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a (Å)	10.930(2)	13.632(4)
b (Å)	14.048(2)	10.009(2)
c (Å)	9.357(2)	16.081(2)
α (deg)	92.781(16)	90
β (deg)	90.186(19)	93.401(12)
γ (deg)	111.929(13)	90
V (Å^3)	1330.8(9)	2190.1(8)
Z	2	4
d_{calcd} (Mg/m^3)	1.56	1.75
F(000)	620	1128
μ(Mo Kα) (cm^{-1})	46	56
T(K)	294	294
transmissn factors	0.37–0.72	0.30–0.67
scan type	ω–2θ	ω–2θ
scan range (deg in ω)	0.80 + 0.35 tan θ	1.05 + 0.35 tan θ
scan speed (deg/min)	1.26–10.06	1.68–10.06
data collected	$\pm h,\pm k,\pm l$	$-h,-k,\pm l$
$2\theta_{max}$ (deg)	55	55
cryst decay (%)	negligible	3
no. of unique rflns	6077	5183
no. of reflns with $I > 3\sigma(I)$	3379	3427
no. of variables	298	280
R	0.041	0.040
R_w	0.040	0.046
GOF	1.19	1.61
max Δ/σ (final cycle)	0.024	0.029
residual density (e/Å^3)	−0.57 to +1.48	−3.35 to +2.84

[a] Additional details: CAD4-F diffractometer; MoKα radiation ($\lambda_{K\alpha}$ = 0.710 69 Å); background counts at each end of the scan (scan/background time ratio 2:1); function minimized $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o)^2$; $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum F_o^2]^{1/2}$; GOF = $[\sum w(|F_o| - |F_c|)^2/(\text{no. of degrees of freedom})]^{1/2}$. Values given for R, R_w, and GOF are based on those reflections with $I > 3\sigma(I)$.

Results and Discussion

Synthesis of CpW(NO)(CH_2SiMe_3)(CH_2CPh_3): Novel Mode of Reactivity of the Trityl Cation. Previous studies in our laboratories have shown that Cp′M(NO)R_2

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[10] ENPROC, a data reduction program for intensities measured on an Enraf-Nonius CAD4 diffractometer (written in FORTRAN IV, University of British Columbia, 1978).

[11] (a) The computer programs used were locally written programs for data processing and locally modified versions of the following: ORFLS, full-matrix least-squares, and ORFFE, function and errors, by W. R. Busing, K. O. Martin, and H. A. Levy; FORDAP, Patterson and Fourier syntheses, by A. Zalkin; ORTEPII, illustrations, by C. K. Johnson. (b) Coppens, P.; Leiserowitz, L.; Rabinovich, D. *Acta Crystallogr.* **1965**, *18*, 1035. (c) Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1967**, *22*, 457.

[12] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K. (present distributor Kluwer Academic Publishers: Dordrecht, The Netherlands), 1974; Vol. IV, pp 99–102, 149.

Table II. Final Positional (Fractional ×10⁴, W × 10⁵) with Equivalent Isotropic Thermal Parameters (*U*, ×10³ Å²) for Complexes 1 and 2

atom	*x*	*y*	*z*	U_{eq}
		Complex 1		
W	30277(4)	26637(3)	31647(4)	37
Si	33859(26)	15322(21)	63193(26)	56
O	2374(7)	3976(5)	5381(7)	78
N	2547(7)	3357(5)	4490(7)	49
C1	5235(9)	3725(9)	3124(10)	68
C2	5168(9)	2782(9)	2533(12)	64
C3	4469(10)	2599(8)	1230(11)	68
C4	4080(9)	3424(8)	1054(10)	60
C5	4574(10)	4112(7)	2184(13)	66
C6	3017(11)	1401(8)	4364(10)	52
C7	1273(8)	2140(7)	1864(10)	37
C8	162(8)	2543(6)	1758(8)	36
C9	4753(11)	2765(9)	6833(12)	93
C10	3855(12)	434(10)	6842(12)	90
C11	1881(11)	1508(10)	7260(12)	87
C12	−1017(8)	1794(6)	839(8)	36
C13	−1056(9)	873(6)	226(10)	51
C14	−2124(9)	250(6)	−638(11)	59
C15	−3142(9)	529(7)	−929(9)	51
C16	−3112(9)	1432(8)	−327(11)	67
C17	−2083(9)	2048(7)	558(11)	57
C18	−406(7)	2681(6)	3233(8)	41
C19	−818(9)	3492(7)	3577(9)	54
C20	−1367(10)	3580(9)	4865(12)	71
C21	−1503(10)	2870(11)	5854(11)	78
C22	−1143(11)	2061(9)	5531(11)	74
C23	−609(9)	1953(7)	4242(9)	51
C24	795(8)	3549(6)	973(8)	38
C25	742(9)	3541(7)	−519(9)	49
C26	1481(11)	4402(8)	−1246(10)	65
C27	2222(11)	5289(8)	−514(14)	72
C28	2271(9)	5313(7)	962(12)	61
C29	1567(9)	4461(6)	1692(10)	51
		Complex 2		
W	42663(2)	21027(3)	14571(2)	25
O	5238(5)	−435(7)	981(4)	50
N1	4825(5)	574(7)	1219(4)	30
N2	5388(5)	2384(7)	2440(4)	35
C1	4544(9)	4394(10)	1315(6)	52
C2	5200(7)	3736(10)	845(7)	48
C3	4655(9)	3112(9)	179(6)	54
C4	3663(8)	3373(10)	282(6)	50
C5	3604(8)	4216(10)	982(6)	52
C6	5970(7)	2563(8)	2967(5)	34
C7	6713(8)	2753(10)	3634(6)	46
C8	3529(6)	1720(9)	2637(4)	34
C9	2383(6)	1841(9)	2540(4)	30
C10	2036(6)	3291(8)	2489(5)	32
C11	1184(7)	3662(11)	2036(5)	45
C12	850(8)	4959(13)	2017(6)	58
C13	1357(9)	5918(11)	2456(7)	59
C14	2208(9)	5602(11)	2901(7)	55
C15	2544(7)	4309(10)	2930(6)	45
C16	1949(6)	1128(10)	3295(5)	34
C17	2079(8)	−220(11)	3412(6)	50
C18	1769(8)	−868(11)	4100(6)	53
C19	1305(8)	−155(13)	4705(6)	55
C20	1144(7)	1163(14)	4593(5)	57
C21	1461(7)	1837(10)	3892(5)	44
C22	2125(6)	1106(8)	1713(4)	30
C23	2829(6)	1182(8)	1129(4)	27
C24	2598(7)	576(9)	357(5)	34
C25	1711(7)	−87(9)	185(5)	40
C26	1039(7)	−162(11)	793(6)	47
C27	1251(7)	441(11)	1554(5)	44

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) with Esd's in Parentheses for Complexes 1 and 2

	Complex 1		
	Bond Lengths		
W–N	1.740(7)	Si–C6	1.859(9)
W–C6	2.141(10)	O–N	1.240(8)
W–C7	2.132(8)	C7–C8	1.524(11)
W–Cp	2.050(5)		
	Bond Angles		
N–W–C6	99.4(4)	W–N–O	170.2(6)
N–W–C7	98.7(3)	W–C6–Si	122.5(5)
C6–W–C7	107.5(4)	W–C7–C8	131.0(6)
	Complex 2		
	Bond Lengths		
W–N1	1.762(7)	C8–C9	1.566(11)
W–N2	2.152(7)	C9–C22	1.542(10)
W–C8	2.232(8)	C22–C23	1.385(10)
W–C23	2.201(8)	C22–C27	1.376(12)
W–Cp	2.049(5)	C23–C24	1.401(10)
O–N1	1.228(9)	C24–C25	1.393(12)
N2–C6	1.140(10)	C25–C26	1.381(13)
C6–C7	1.443(12)	C26–C27	1.379(12)
	Bond Angles		
N1–W–N2	88.6(3)	C8–C9–C22	102.9(6)
N1–W–C8	105.0(3)	C9–C22–C23	115.3(7)
N1–W–C23	88.5(3)	W–C23–C22	120.2(5)
N2–W–C8	74.6(3)	W–C23–C24	123.0(6)
N2–W–C23	144.6(3)	C22–C23–C24	116.7(7)
C8–W–C23	72.1(3)	C23–C24–C25	122.0(7)
W–N1–O	173.8(6)	C24–C25–C26	119.3(7)
W–N2–C6	178.2(7)	C25–C26–C27	119.5(8)
N2–C6–C7	178.5(9)	C22–C27–C26	120.7(8)
W–C8–C9	113.6(5)		

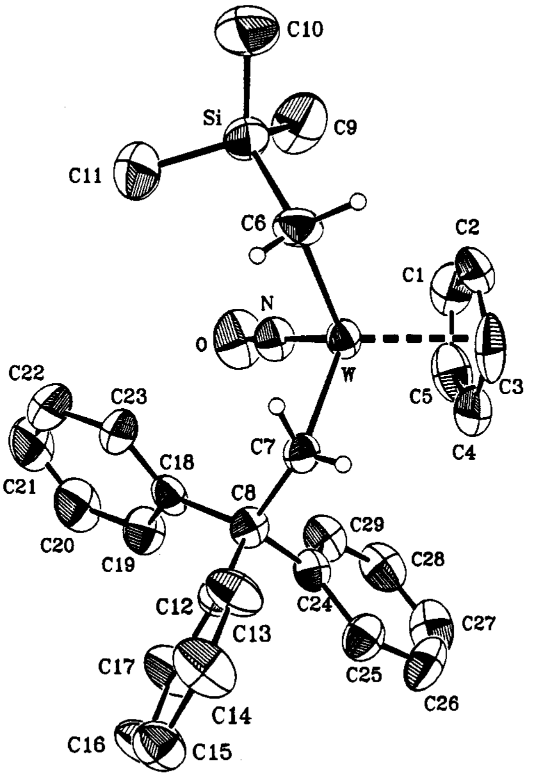


Figure 1. View of CpW(NO)(CH_2SiMe_3)(CH_2CPh_3) (1; 50% probability thermal ellipsoids are shown for the non-hydrogen atoms).

species are very reactive with a variety of substrates.[3] For example, Lewis bases generally coordinate to the metal centers of these 16-electron coordinatively unsaturated species and Lewis acids coordinate to the nitrosyl oxygen of these complexes (eq 1). The Lewis-acid adducts readily reconvert to starting materials. Thus, hydrolysis of the adducts formed by CpW(NO)(CH_2SiMe_3)$_2$ invariably regenerates the dialkyl complex.[13] In this paper we report an exception to this latter generalization, namely a Lewis-acid adduct of CpW(NO)(CH_2SiMe_3)$_2$ which undergoes a novel chemical transformation.

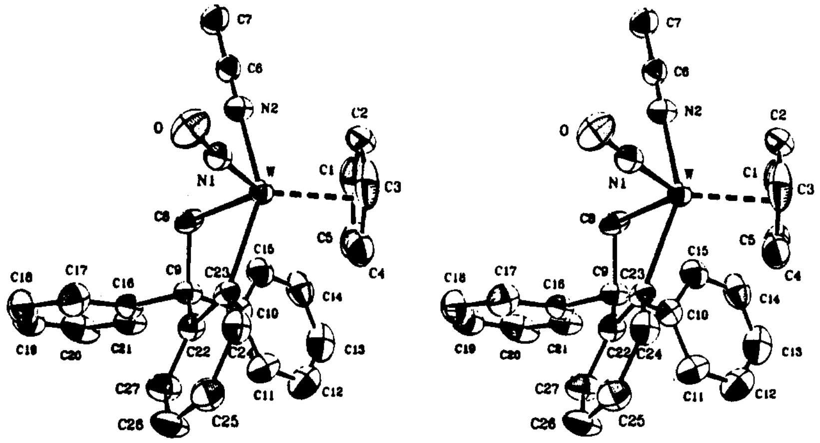
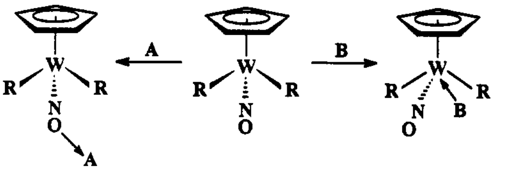


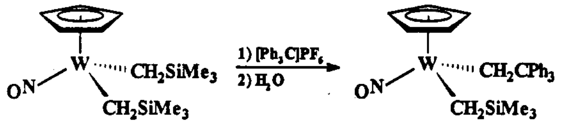
Figure 2. Stereoview of $CpW(NO)(CH_2C(C_6H_4)Ph_2)(NCMe)$ (**2**; 50% probability thermal ellipsoids are shown for the nonhydrogen atoms).



(1)

A = Lewis acid; B = Lewis base

Addition of $[Ph_3C]PF_6$ to a purple CH_2Cl_2 solution of $CpW(NO)(CH_2SiMe_3)_2$ (ν_{NO} at 1566 cm^{-1}) results in the formation of red-brown $[CpW(CH_2SiMe_3)_2(NO\rightarrow CPh_3)]PF_6$. Neither solution nor solid-state IR spectroscopy permits the clear assignment of ν_{NO} for this isonitrosyl adduct, since bands attributable to ν_{CC} of the phenyl rings obscure the nitrosyl region of the IR spectrum. We have been unable to isolate this adduct to date, but we have found that upon hydrolysis it not only liberates $CpW(NO)(CH_2SiMe_3)_2$ but also converts to the unsymmetrical dialkyl complex $CpW(NO)(CH_2SiMe_3)(CH_2CPh_3)$ (**1**). The rational synthesis of **1** (eq 2) is conducted by allowing trityl hexafluorophosphate and $CpW(NO)(CH_2SiMe_3)_2$ to react at room temperature overnight in CH_2Cl_2, then adding water,[14] and finally chromatographing the final purple reaction mixture on silica. Complex **1** is isolable in low to moderate yields (10–40%) as a crystalline, diamagnetic solid which can be handled in air for short periods of time and stored under N_2 indefinitely without noticeable decomposition. Its solutions, however, are air- and heat-sensitive (vide infra). The spectroscopic properties of **1** are consistent with its formulation and are similar to those exhibited by other asymmetric dialkyl complexes we have prepared previously.[4,5] Four sets of resonances attributable to methylene-type protons appear in the ^1H NMR spectrum of the complex. Interestingly, an additional coupling of 2 Hz is evident between one of the methylene protons in one alkyl group and one proton of the other. We have previously ascribed this phenomenon to "W" coupling.[5] Such long-range, four-bond couplings of 1–4 Hz are well known in H–C–C–C–H systems that are held rigidly in a coplanar W-shaped conformation.[15]



(2)

1

The reaction to form complex **1** (eq 2) is not particularly clean. This is partly due to the fact that **1** is formed fairly slowly in solution and thermally decomposes somewhat during the course of the reaction. ^{31}P and ^{19}F NMR spectroscopy of the reaction mixture in CD_2Cl_2 indicates that the major byproducts of the reaction are PF_5 and Me_3SiF. Furthermore, these spectra show resonances attributable to PF_6^-, OPF_3 (possibly resulting from hydrolysis of PF_5),[16] and two kinds of base–PF_5 adducts. The chemical shifts and coupling data observed for each species are collected in the Experimental Section and agree reasonably well with published data.[16,17] The ^{19}F NMR resonances due to the base–PF_5 adducts are distinctive[18] and are typical of octahedral phosphorus complexes, but the true nature of these species remains to be conclusively ascertained.

The redox properties of **1** have been investigated by cyclic voltammetry and have been found to be comparable to those exhibited by other $Cp'M(NO)R_2$ (R = alkyl, aryl) complexes.[3] Qualitatively, $CpW(NO)(CH_2SiMe_3)(CH_2CPh_3)$ exhibits reversible reduction and irreversible oxidation behavior, features attributable to the nonbonding nature of its LUMO.[3,19] In CH_2Cl_2, complex **1** is reduced electrochemically at −1.50 V vs Ag wire.[20] For comparison, the parent complex $CpW(NO)(CH_2SiMe_3)_2$ is similarly reduced at −1.61 V under similar experimental conditions.[21]

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[13] In this respect, Cp_3Er, MgI_2,[8] $AlMe_3$,[8] and HBF_4 form isonitrosyl-type complexes with the complex $CpW(NO)(CH_2SiMe_3)_2$, which has a ν_{NO} (Nujol mull) band at 1541 cm^{-1}. The nitrosyl-stretching frequency in the adducts appears to be dependent on the hardness of the Lewis acid employed. Thus, $[CpW(NO)(CH_2SiMe_3)_2]\cdot Cp_3Er$ displays a rather high-energy ν_{NO} of 1507 cm^{-1}, whereas $[CpW(NO)(CH_2SiMe_3)_2]\cdot HBF_4$ displays a low-energy ν_{NO} of 1404 cm^{-1}. Additionally, the colors of the adducts shift from red to orange to yellow as the hardness of the Lewis acid increases.

[14] Failure to hydrolyze the reaction mixture reduces the yield of **1** substantially. However, we believe that water is not necessary for the conversion but merely serves to liberate any of complex **1** that exists as an isonitrosyl adduct in the reaction mixture.

[15] Becker, E. D. *High Resolution NMR, Theory and Applications*; 2nd ed.; Academic Press: New York, 1980; p 104.

[16] Schmutzler, R. *Adv. Fluorine Chem.* **1965**, *5*, 31.

[17] (a) ^{19}F chemical shifts: Elmsley, J. W.; Phillips, L. *Prog. NMR Spectrosc.* **1971**, *7*, 1. (b) ^{31}P chemical shifts: Mavel, G. *Annu. Rep. NMR Spectrosc.* **1973**, *5B*, 1.

[18] Both of these resonances consist of a doublet of doublets (due to four equatorial fluorines, coupled to P and F_{axial}) and a doublet of pentets (due to one axial fluorine, coupled to P and four $F_{equatorial}$) in a 4:1 ratio.

[19] Legzdins, P.; Rettig, S. J.; Sánchez, L.; Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* **1985**, *107*, 1411.

This observation implies that a CH_2CPh_3 ligand exerts electronic effects toward the W center similarly to the CH_2SiMe_3 group.

The solid-state molecular structure of 1 has been established by a single-crystal X-ray crystallographic analysis. In terms of the intramolecular metric parameters about its metal center, $CpW(NO)(CH_2SiMe_3)(CH_2CPh_3)$ resembles $CpW(NO)(CH_2SiMe_3)_2$[8] very closely. Selected data are summarized in Table III, and an ORTEP diagram of 1 is shown in Figure 1. Complex 1 is chiral and crystallizes with one molecule of each enantiomer per unit cell, there being no unusual inter- or intramolecular interactions.[22] The ortho hydrogens of the phenyl rings, in particular, might have been expected to interact with the 16-electron metal center, since the complex decomposes thermally via an ortho-metalation reaction (vide infra).[23] The tungsten–carbon bond of the $W–CH_2SiMe_3$ moiety is not significantly longer (i.e. 0.026 Å) in 1 than the average of the two analogous bonds in $CpW(NO)(CH_2SiMe_3)_2$. The C6–W–C7 angle that defines the vacant coordination site at the metal center in this complex is 107.5(4)°, the smallest that we have yet observed, thereby indicating that complex 1 is a relatively weak Lewis acid at tungsten.[3]

Other reactions of transition-metal–alkyl complexes with trityl cation are well known and have been extensively studied. Typically, one of the following reactivity patterns is observed:

(i) alkyl abstraction from a metal center[24]

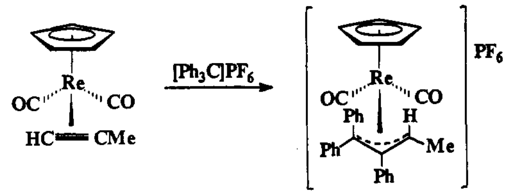
$$M—R + Ph_3C^+ \rightarrow [M]^+ + Ph_3C–R \qquad (3)$$

(ii) hydride abstraction from either the α-[25] or β-position[26] of an alkyl ligand

$$M—CH_2R + Ph_3C^+ \rightarrow [M{=}CHR]^+ + Ph_3C—H \quad (4)$$

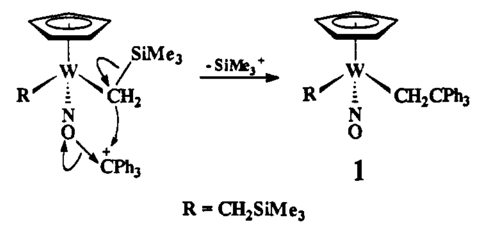
$$M—CH_2CH_2R + Ph_3C^+ \rightarrow [M—(\eta^2\text{-}CH_2{=}CHR)]^+ + Ph_3C—H \quad (5)$$

There are also some more esoteric, and probably unexpected, reactions of trityl cation with organometallic species that have been reported in the chemical literature. For instance, Tilley has shown that trityl cation will abstract hydride from the Cp* ring of $Cp^*Ru(PMe_3)_2Me$ to give the fulvene complex $[(\eta^4\text{-}C_5Me_4CH_2)Ru(PMe_3)_2Me]BPh_4$.[27] Very recently, Casey has shown that trityl cation will add to a coordinated alkyne and then undergo extensive rearrangement (eq 6).[28] Reaction 2 thus



(6)

represents a new type of reactivity for $[Ph_3C]PF_6$ and establishes a transformation of a silicon-containing ligand that is, to the best of our knowledge, unprecedented in transition-metal organometallic chemistry.[29] Transformation 2 formally involves the removal of the anionic ligand "$[CpW(NO)(CH_2SiMe_3)(=CH_2)]^-$" from a silicon center by an electrophile. Although such electrophilic cleavage processes have been extensively used in synthetic organic chemistry for the formation of new carbon–carbon bonds,[29b] reaction 2 represents the first application of $SiMe_3^+$ (a better leaving group than H^+)[30] as a leaving group in a transition-metal-alkyl complex. A plausible mechanism for this process involves the initial cationic adduct, $[CpW(CH_2SiMe_3)_2(NO{\rightarrow}CPh_3)]^+$, undergoing intramolecular aliphatic electrophilic attack in a manner as depicted in eq 7. The ejected trimethylsilyl cation could



(7)

then abstract fluoride from the counterion to give Me_3SiF and PF_5, both of which are detectable in the reaction mixture. Consistent with the above hypothesis is the fact that reactions of organosilicon compounds described as "electrophilic" do not generally take place with electrophilic attack at Si but, more often, at a remote center.[31] The Si-containing leaving group is then subject to nucleophilic attack, in this case by PF_6^-. Presumably, PF_6^- is not critical for reaction 2 to occur, since $CpW(NO)(CH_2SiMe_3)_2$ fails to react with $[NH_4]PF_6$ over the course of 1 day. In closing this section, it may be noted that the reverse of reaction 2, namely the removal of an alkyl group from silicon by a transition-metal cation, has been reported.[32]

Reactions Related to Reaction 2. As an extension of this work, we attempted to effect reactions similar to conversion 2 by using other carbocations as electrophiles. However, the reaction of $CpW(NO)(CH_2SiMe_3)_2$ with *tert*-butyl cation (generated in situ from *tert*-butyl chloride and $AlCl_3$) does not provide the anticipated neopentyl complex, $CpW(NO)(CH_2SiMe_3)(CH_2CMe_3)$. Instead, com-

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[20] Electrochemical conditions: $[1] = 1 \times 10^{-4}$ M; $[[n\text{-}Bu_4N]PF_6] = 0.1$ M. For further details of the electrochemical apparatus see: Dryden, N. H.; Legzdins, P.; Rettig, S. J.; Veltheer, J. E. *Organometallics* **1992**, *11*, 2583.

[21] The only experimental change was that the reference electrode in this case was SCE; see: Herring, F. G.; Legzdins, P.; Richter-Addo, G. B. *Organometallics* **1989**, *8*, 1485.

[22] The shortest $W–H_{methylene}$ interaction is 2.10(8) Å. The shortest intermolecular approach is 2.32 Å between hydrogen atoms attached to C17 and C27.

[23] However, the shortest $W–H_{ortho}$ interaction is that with the hydrogen attached to C29 at 3.36 Å.

[24] For example, M–R = $(CO)_4(PPh_3)Mn–Me$ (see: Harris, P. J.; Knox, S. A. R.; McKinney, R. J.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1978, 1009) or M–R = $Cp^*_2ZrMe_2$.[27]

[25] For example, $M–CH_2R = CpRe(NO)(PPh_3)(CH_2Ph)$; see: Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865.

[26] For example, $M–CH_2CH_2R = CpFe(CO)_2(CH_2CH_2CH_3)$; see: Green, M. L. H.; Nagy, P. L. I. *J. Organomet. Chem.* **1963**, *1*, 58.

[27] Straus, D. A.; Zhang, C.; Tilley, T. D. *J. Organomet. Chem.* **1989**, *369*, C13.

[28] Casey, C. P.; Yi, C. S.; Gavney, J. A., Jr. *J. Organomet. Chem.* **1993**, *443*, 111.

[29] Both nucleophiles and electrophiles, either inorganic or organic, are well-known to attack silicon–carbon bonds; see: (a) Bazant, V.; Chvalovský, V.; Rathouský, J. *Organosilicon Compounds*; Academic: New York, 1965; Vol. 1. (b) Parnes, Z. N.; Bolestova, G. I. *Synthesis* **1984**, 991.

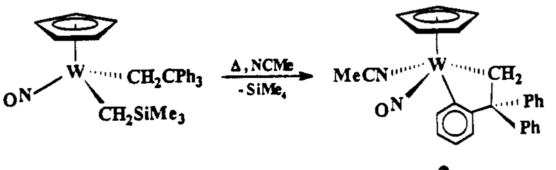
[30] March, J. *Advanced Organic Chemistry*; Wiley-Interscience: New York, 1985; Chapter 11.

[31] Bassindale, A. R.; Taylor, P. G. *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley-Interscience: New York, 1989; Vol. 1, Chapter 13, p 840.

[32] Kelly, L. F.; Narula, A. S.; Birch, A. J. *Tetrahedron Lett.* **1980**, *21*, 871.

plete decomposition of the organometallic reactant occurs. Similarly, treatment of $\mathrm{CpW(NO)(CH_2SiMe_3)_2}$ with $\mathrm{[C_7H_7]BF_4}$ results in decomposition. These preliminary investigations suggest that reaction 2 is evidently not of general applicability, since there are a number of reaction pathways accessible to the organometallic starting material under the existing experimental conditions.

Ortho-Metalation Reactions by Thermal Decomposition of $\mathrm{CpW(NO)(CH_2SiMe_3)(CH_2CPh_3)}$. (a) In Organic Solvents. While the prototypal bis((trimethylsilyl)methyl) complex $\mathrm{CpW(NO)(CH_2SiMe_3)_2}$ is reasonably thermally stable,[33] the mixed complex $\mathrm{CpW(NO)(CH_2SiMe_3)(CH_2CPh_3)}$ (1) is substantially more thermally active. In noncoordinating solvents such as $\mathrm{C_6D_6}$, $\mathrm{CDCl_3}$, and $\mathrm{CD_2Cl_2}$, 1 decomposes in about 1 week at room temperature to an intractable light brown powder. ^{1}H NMR spectroscopy of reaction solutions shows that all $\mathrm{CH_2SiMe_3}$ groups are converted to TMS and that a number of other organometallic species are formed. In contrast, an unstirred solution of 1 in acetonitrile (a coordinating solvent) slowly deposits transparent, brick red crystal of 2 over the course of several weeks at room temperature (eq 8). The evolution of TMS as the other product in reaction 8 is confirmed by monitoring of reaction 8 in $\mathrm{CD_3CN}$ by ^{1}H NMR spectroscopy.



(8)

1 2

The ortho-metalated complex 2 is air-stable for short periods of time and is completely insoluble in all common organic solvents, a feature which has prevented its characterization by the usual spectroscopic methods. Its IR spectrum (KBr) shows two possible nitrosyl-stretching frequencies at 1574 and 1559 cm^{-1}.[34] The only means of establishing the molecular structure of 2 was by a single-crystal X-ray crystallographic analysis. Fortunately, the crystals that deposited from the reaction mixture were of suitable quality. An ORTEP diagram of the solid-state molecular structure of 2 is shown in Figure 2. Two isomers, differing in the arrangement of the NO and MeCN ligands relative to the unsymmetrical metallacycle, are possible. However, only the isomer in which the nitrosyl ligand is *trans* to the W–CH$_2$ bond and the acetonitrile group is *trans* to the W–aryl bond is found in the crystal studied. Selected bond lengths and angles for 2 are given in Table III. The newly formed tungsten–carbon bond (W–C23) is 2.201(8) Å in length, comparable to the W–aryl bond lengths in the related $\mathrm{Cp^*W(NO)}$(*o*-tolyl)$_2$, which average 2.13 Å.[7] The three phenyl rings attached to C9 exhibit bond angles with that carbon of 102.9(6)–112.5(7)° (mean 109.5°), thus indicating there is little distortion from ideal tetrahedral geometry. The angle at the methylene carbon (W–C8–C9), however, is markedly more acute than the analogous W–C7–C8 angle in complex 1, i.e. 113.6(5) versus 131.0(6)°. This feature is in accord with the strain associated with the formation of a five-membered metallacycle. Both the nitrile and nitrosyl ligands in complex 2 are essentially linear with W–N1–O = 173.8(6)° and W–N2–C6 = 178.2(7)°. The observed insolubility of this complex is somewhat puzzling, since the crystal structure shows no unusual packing features. As in complex 1, there are no unusually close intermolecular contacts, the closest approach of 2.39 Å being between hydrogen atoms attached to C7 and C25.

The formation of 2 by reaction 8 is an example of the well-known ortho-metalation reaction.[35] The alternate cyclometalation reaction to form $\mathrm{CpW(NO)(CH_2SiMe_2CH_2)(NCMe)}$ is not observed, even though precedents for such a reaction do exist.[36] In this case, however, the latter reaction course is expected to be less thermodynamically favorable than the cyclometalation of a phenyl-containing ligand, since aromatic C–H bonds are known to be easier to activate than aliphatic ones.[37] Furthermore, ortho metalation of 1 produces a five-membered metallacycle, whereas cyclometalation of a trimethylsilyl group would produce a more strained four-membered metallacycle. The propensity of 1 to ortho metalate clearly accounts for its greater thermal instability as compared to $\mathrm{CpW(NO)(CH_2SiMe_3)_2}$.

(b) In the Presence of $\mathrm{PMe_3}$. Treatment of a solution of 1 in $\mathrm{Et_2O}$ or $\mathrm{CDCl_3}$ with an excess of $\mathrm{PMe_3}$ results in a change in color from purple to yellow, which is attributed to formation of the phosphine adduct $\mathrm{CpW(NO)(CH_2SiMe_3)(CH_2CPh_3)(PMe_3)}$ (3). Due to the steric bulk and the relatively weak Lewis acidity of 1, this adduct is very labile. Like other phosphine dialkyl complexes that we have previously prepared, this adduct readily loses its phosphine ligand in vacuo or in solutions in the absence of excess phosphine.[8] Thus, a ^{1}H NMR spectrum of 3 can only be obtained if a large excess of $\mathrm{PMe_3}$ is added to the sample. On the basis of spectroscopic evidence, however, there is no ambiguity as to the identity of the compound. The fact that $\mathrm{PMe_3}$ can coordinate to 1 precludes formation of a metallacyclic complex analogous to 2 upon thermolysis. The $\mathrm{PMe_3}$ adduct does undergo slow and unclean decomposition, but it is much slower than for 1 (35% after 8 months at room temperature) and occurs without evolution of TMS. This relative stability is as expected, since oxidative addition of a C–H bond requires a vacant coordination site at the metal center.[35,38] Not surprisingly, therefore, coordination of $\mathrm{PMe_3}$ to 1 prevents ortho metalation of the $\mathrm{CH_2CPh_3}$ ligand.

(c) In the Presence of $\mathrm{PPh_3}$. Since thermolysis of the $\mathrm{PMe_3}$ adduct does not lead to $\mathrm{CpW(NO)(CH_2C(C_6H_4)Ph_2)(PMe_3)}$, the direct analogue of 2, we next utilized $\mathrm{PPh_3}$ (a more sterically demanding phosphine) as a trapping agent during the thermolysis of 1. $\mathrm{PPh_3}$ does not coordinate to the metal center in 1, and thermolysis of 1 in the presence of an excess of $\mathrm{PPh_3}$ leads to the formation of yellow $\mathrm{CpW(NO)(CH_2C(C_6H_4)Ph_2)(PPh_3)}$ (4). Unlike the nitrile complex 2, compound 4 is soluble in common nonaliphatic organic solvents, thus permitting the spectroscopic characterization of the metallacyclic ligand. The

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[33] This complex will thermally decompose to $\mathrm{CpW(O)({=}CHSiMe_3)(CH_2SiMe_3)}$, but the conversion takes several months; see: Legzdins, P.; Rettig, S. J.; Sánchez, L. *Organometallics* **1985**, *4*, 1470.

[34] Two IR bands can be explained by either one being ν_{CC} attributable to the arylated ligand or by the possibility of two isomers, i.e. one in which the W–aryl bond is trans to the NCMe ligand and one in which it is cis.

[35] See ref 1, Chapter 5 and references contained therein.

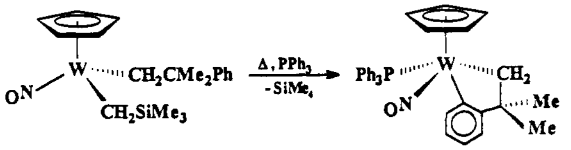
[36] Bruno, J. W.; Smith, B. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40.

[37] Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.

[38] Ibers, J. A.; DiCosimo, R.; Whitesides, G. M. *Organometallics* **1982**, *1*, 13.

^1H NMR spectrum of 4 in C_6D_6 reveals that the four aryl protons on the activated ring resonate downfield of the protons on the normal phenyl rings and appear as a doublet (δ 8.1 ppm) and three complex multiplets (δ 7.8, 7.5, 7.4 ppm). The two diastereotopic methylene protons appear as doublets of doublets at δ 3.59 ($^2J_{HH}$ = 13.2 Hz, $^3J_{HP}$ = 5.4 Hz) and 2.41 ($^2J_{HH}$ = 13.2 Hz, $^3J_{HP}$ = 16.5 Hz) ppm.

The dimethyl analogue of complex 4 is easily prepared in a similar manner by thermolysis of the requisite precursor, $CpW(NO)(CH_2SiMe_3)(CH_2CMe_2Ph)$ (5), at 55 °C in hexanes containing an excess of PPh_3 (eq 9). As expected, the resulting complex 6 is yellow and exhibits spectroscopic properties very similar to those of 4.



(9)

5 **6**

Summary. This work has established a new mode of reaction of $[Ph_3C]PF_6$ with a transition-metal–alkyl complex. Furthermore, it has demonstrated that ortho metalation of phenyl-containing alkyl ligands is facile at the 16-electron metal centers extant in $CpW(NO)(alkyl)_2$ complexes.

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Supplementary Material Available: Tables of hydrogen atom coordinates, anisotropic thermal parameters, all bond lengths and bond angles, torsion angles, and intermolecular contacts for complexes 1 and 2 (14 pages). Ordering information is given on any current masthead page.

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