Coordinatively Unsaturated W(IV)−Bis(pyridine) Complexes, a Reactive Source of W(IV)

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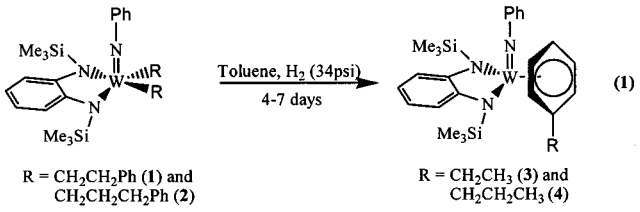
Addition of 2 equiv of a σ-donor ligand (L = pyridine, 4-picoline, or quinoline) to complexes of the type [W(NPh)(η^4-arene)(*o*-$(Me_3SiN)_2C_6H_4$)] (arene = $CH_3CH_2C_6H_5$ (**3**), $CH_3CH_2CH_2C_6H_5$ (**4**)) gave the W(IV)L_2 compounds, [W(NPh)(*o*-$(Me_3SiN)_2C_6H_4$)$(C_5H_5N)_2$] (**5**), [W(NPh)(*o*-$(Me_3SiN)_2C_6H_4$)(p−$C_6H_7N)_2$] (**6**), and [W(NPh)(*o*-$(Me_3SiN)_2C_6H_4)(C_9H_7N)_2$] (**7**)**.** Synthesis of compounds **5** and **6** by Na° reduction of [W(NPh)(*o*-$(Me_3SiN)_2C_6H_4)Cl_2$] in the presence of 3 equiv of L (L = **5**, pyridine or **6**, 4-picoline) is also presented. Compounds **5**, **6**, and **7** display hindered rotation of the donor ligands about the W−N bonds, resulting from a steric interaction with the Me_3Si groups of the diamide ligand. The coordinative unsaturation of **5** and **6** has also been explored. Compounds **5** and **6** readily react with either CO and PMe_3 to generated the six coordinate complexes [W(NPh)(*o*-$(Me_3SiN)_2C_6H_4)(C_5H_5N)_2$(CO)] (**8a**), [W(NPh)(*o*-$(Me_3SiN)_2C_6H_4)(C_6H_7N)_2$(CO)] (**8b**), [W(NPh)(*o*-$(Me_3SiN)_2C_6H_4)$-$(C_5H_5N)(PMe_3)_2$] (**10a**), and [W(NPh)(*o*-$(Me_3SiN)_2C_6H_4)(C_6H_7N)(PMe_3)_2$] (**10b**), respectively.

Introduction

In the course of our recent studies of the reactivity of β-hydrogen containing W(VI)−dialkyl complexes of the type W(NPh)(*o*-$(Me_3SiN)_2C_6H_4)R_2$ (where R = CH_2CH_3, CH_2CMe_3)[1,2] with H_2,[3] we have established that d^2 tungsten−arene complexes with the general formula W(NPh)(η^4-arene)(*o*-$(Me_3SiN)_2C_6H_4$) (arene = $CH_3CH_2C_6H_5$ (**3**), $CH_3CH_2CH_2C_6H_5$ (**4**)) can be synthesized by hydrogenolysis of the β-hydrogen containing dialkyl complexes W(NPh)(*o*-$(Me_3SiN)_2C_6H_4)(CH_2CH_2C_6H_5)_2$ (**1**) and W(NPh)(*o*-$(Me_3SiN)_2C_6H_4)$ $(CH_2CH_2CH_2C_6H_5)_2$ (**2**), eq 1.[4]



Since its beginnings in the mid 50's, the chemistry of transition metal π-arene complexes has been investigated in considerable detail.[5] Reports have demonstrated that a coordinated arene can behave as a spectator ligand, labile ligand, or substrate ligand.[6] For these reasons, we became interested in examining the chemistry of the chelate stabilized W(IV)−arene complexes **3** and **4**. To our disappointment, the reactivity of compounds **3** and **4** has been limited, presumably due to a robust metal−arene interaction. However, as has been observed and well studied for other arene compounds,[7−10] compounds **3** and **4** are susceptible to arene displacement by σ-donor ligands. In continuation of our earlier work with W(IV)−arene compounds,[4] we report the synthesis of a series of coordinatively unsaturated W(IV)L_2 compounds through arene displacement and initial reactivity studies that suggest these compounds are a more reactive source of W(IV) than the arene complexes.

Experimental Section

General Methods. All experimental procedures were conducted under an inert atmosphere, either in a N_2-filled drybox or by using standard Schlenk techniques under an argon atmosphere. Anhydrous tetrahydrofuran, pentane, and toluene were purchased from Sigma-Aldrich, passed over a column of activated alumina, stored over 4 Å molecular sieves, and degassed prior to use. Pyridine, 4-picoline, and quinoline were degassed and stored over 4 Å molecular sieves prior to use. PMe_3 was purchased from Sigma-Aldrich and used without further purification, and CO was passed over a column of activated 4 Å sieves prior to use. W(NPh)[*o*-$(Me_3SiN)_2C_6H_4]CH_2CH_2Ph)_2$[1] (**1**) and W(NPh)-[*o*-$(Me_3SiN)_2C_6H_4](CH_2CH_2CH_2Ph)_2$ (**2**)[4] were prepared according to previously reported literature procedures. All other reagents were obtained from Aldrich Chemicals and used as received unless otherwise noted.

^1H, ^{13}C, and ^{31}P NMR spectra were obtained on Varian Gemini 300, VXR 300, or Mercury 300 instruments in C_6D_6 solutions, referenced to residual solvent peaks, and reported relative to TMS. We have been unable to obtain satisfactory elemental analyses of compounds **5, 6, 7, 8**(**a,b**)**, 9**(**a,b**), and **10**(**a,b**). The carbon and nitrogen data are typically

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1−1.5% below the calculated values even for multiply recrystallized samples, while the hydrogen data are within the acceptable range. We suspect that the formation of W carbide and nitride during the combustion process is responsible for these results. Proton NMR spectra are included as Supporting Information.

Synthesis of W(NPh)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)(C$_5$H$_5$N)$_2$ (5). Pyridine (0.13 mL, 1.57 mmol) was added dropwise to a room-temperature toluene solution of **4** (0.51 g, 0.79 mmol). Upon addition of pyridine, the solution became dark purple in color. The mixture was stirred for 1 h at which time the solvent was stripped off, and the resulting solid was dried in vacuo for 1 h. Subsequent washing with several portions of cold pentane (0 °C), followed by drying the remaining solid in vacuo, yielded 0.39 g (73%) of **5** as a dark purple solid. ^{1}H NMR (25 °C, C_6D_6): δ 0.45 (s, 18H, SiMe$_3$), 4.97 (t, 2H, *p*-C$_5$H$_5$N), 5.71 (d, 2H, *o*-C$_5$H$_5$N), 6.28 (t, 4H, *m*-C$_5$H$_5$N), 6.90 (m, 1H, *p*-W≡NC$_6$H$_5$), 7.03 (m, 2H, *o*-pdaC$_6$H$_4$), 7.10−7.12 (m, 4H, *o*,*m*-W≡NC$_6$H$_5$), 7.41 (m, 2H, *m*-pdaC$_6$H$_4$), 7.82 (d, 2H, *o*-C$_5$H$_5$N). ^{13}C NMR (25 °C, C_6D_6): δ 5.58 (SiMe$_3$), 118.64 (*o*-pdaC$_6$H$_4$), 118.66 (*m*-pdaC$_6$H$_4$), 121.62 (*m*-C$_5$H$_5$N), 122.17 (*m*-C$_5$H$_5$N), 124.23 (*p*-W≡NC$_6$H$_5$), 124.65 (*o*-W≡NC$_6$H$_5$), 127.75 (*m*-W≡NC$_6$H$_5$), 129.40 (*p*-C$_5$H$_5$N), 137.91 (*o*-C$_5$H$_5$N), 142.14 (*o*-C$_5$H$_5$N), 152.08 (pda C$_6$H$_4$), 158.76 (W≡NC$_6$H$_5$).

Synthesis of 5 From W(NPh)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)Cl$_2$. To a dispersion of Na° (0.17 g, 7.24 mmol) in THF was added a THF solution of W(NPh)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)Cl$_2$ (2.16 g, 3.62 mmol) and pyridine (0.88 mL, 10.09 mmol) at room temperature. The mixture was stirred for 30 min, during which time the solution changed from bright to dark purple in color. The solvent was removed under reduced pressure, and the resulting solid was extracted with toluene. Subsequent evaporation of the toluene and drying in vacuo gave 2.25 g (91%) of **5**.

Synthesis of W(NPh)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)(*p*-C$_6$H$_7$N)$_2$ (6). 4-Picoline (0.07 mL, 0.77 mmol) was added dropwise to a room-temperature toluene solution of **4** (0.25 g, 0.39 mmol). Upon addition of 4-picoline, the solution became dark-purple in color. The mixture was stirred for 1 h at which time the solvent was stripped off, and the resulting solid was dried in vacuo for 1 h. Subsequent washing with several portions of cold pentane (0 °C), followed by drying the remaining solid in vacuo, yielded 0.20 g (73%) of **6** as a dark purple solid. ^{1}H NMR (C_6D_6, 25 °C): δ 0.50 (s, 18H, SiMe$_3$), 2.37 (s, 3H, C$_6$H$_7$N), 5.78 (d, 2H, *o*-C$_6$H$_7$N), 6.28 (t, 4H, *m*-C$_6$H$_7$N), 6.93 (m, 1H, *p*-W≡NC$_6$H$_5$), 7.07 (m, 2H, *o*-pdaC$_6$H$_4$), 7.10−7.14 (m, 4H, *o*,*m*-W≡NC$_6$H$_5$), 7.48 (m, 2H, *m*-pdaC$_6$H$_4$), 7.88 (d, 2H, *o*-C$_6$H$_7$N). ^{13}C NMR (C_6D_6, 25 °C): δ 5.79 (SiMe$_3$), 17.75 (*p*-CH$_3$(C$_6$H$_7$N)), 118.51 (*o*-pdaC$_6$H$_4$), 118.64 (*m*-pdaC$_6$H$_4$), 123.84 (*m*-C$_6$H$_7$N), 124.52 (*m*-C$_6$H$_7$N), 126.52 (*p*-W≡NC$_6$H$_5$), 128.02 (*o*-W≡NC$_6$H$_5$), 128.89 (*m*-W≡NC$_6$H$_5$), 129.66 (*p*-C$_6$H$_7$N), 141.13 (*o*-C$_6$H$_7$N), 142.26 (*o*-C$_6$H$_7$N), 152.88 (pdaC$_6$H$_4$), 159.29 (W≡NC$_6$H$_5$).

Synthesis of 6 From W(NPh)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)Cl$_2$. To a dispersion of Na° (0.16 g, 7.24 mmol) in THF was added a THF solution of W(NPh)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)Cl$_2$ (2.14 g, 3.62 mmol) and 4-picoline (0.88 mL, 10.09 mmol) at room temperature. The mixture was stirred for 30 min, during which time the solution changed from bright to dark purple in color. The solvent was removed under reduced pressure, and the resulting solid extracted with toluene. Subsequent evaporation of the toluene and drying in vacuo gave 2.41 g (93%) of **6**.

Synthesis of W(NPh)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)(C$_9$H$_7$N)$_2$ (7). Quinoline (0.09 mL, 0.77 mmol) was added dropwise to a room-temperature toluene solution of **4** (0.25 g, 0.39 mmol). Upon addition of quinoline, the solution became turquoise in color. The mixture was stirred for 1 h at which time the solvent was stripped off, and the resulting solid was dried in vacuo for 1 h. Subsequent washing with several portions of cold pentane (0 °C), followed by drying the remaining solid in vacuo, yielded 0.19 g (63%) of **7** as a black solid. ^{1}H NMR (25 °C, C_6D_6): δ 0.38 (s, 18H, SiMe$_3$), 5.00 (d, 2H, C$_9$H$_7$N), 5.55 (d, 2H, C$_9$H$_7$N), 6.38 (m, 2H, C$_9$H$_7$N), 6.49 (m, 2H, C$_9$H$_7$N), 6.76 (m, 4H, C$_9$H$_7$N), 6.97 (m, 1H, p−W≡NC$_6$H$_5$), 7.05 (m, 2H, *o*-pdaC$_6$H$_4$), 7.25 (m, 2H, *m*-W≡NC$_6$H$_5$), 7.39 (m, 2H, *m*-pdaC$_6$H$_4$), 7.51 (d, 2H, *o*-W≡NC$_6$H$_5$), 8.91 (d, 2H, C$_9$H$_7$N). ^{13}C NMR (25 °C, C_6D_6): δ 5.49 (SiMe$_3$), aromatic; 116.08, 118.64, 118.85, 125.05, 125.17, 125.33, 125.95, 126.40, 129.66, 129.81, 131.29, 135.48, 142.90, 150.20.

Synthesis of W(NPh)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)Ph$_2$. W(NPh)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)Cl$_2$ (1.0 g, 1.68 mmol) was dissolved in 50 mL of Et$_2$O and cooled to −78 °C. Two equivalents of PhMgCl (1.12 mL, 3.36 mmol) was then added by syringe. The reaction was allowed to warm to room temperature and stir for 2 h, during which time the solution became brown in color and a precipitate formed. The solvent was then removed under reduced pressure, and the remaining brown−orange solid was dried in vacuo. The solid was then extracted with pentane and filtered until the filtrate was clear. The solution was concentrated to 10 mL and cooled to −78 °C for 3 h. The resulting orange solid was isolated by filtration and dried in vacuo to yield 0.77 g (68%) of W(NPh)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)Ph$_2$ as a orange crystalline solid. ^{1}H NMR (25 °C, C_6D_6): δ 0.12 (s, 18H, SiMe$_3$), 6.80−7.66 (m, 19H, aromatic). ^{13}C NMR (25 °C, C_6D_6): δ 0.72 (SiMe$_3$), aromatic: 123.14, 124.93, 125.69, 125.80, 128.18, 129.09, 131.67, 136.71, 156.25, 196.30. Anal. Calcd for C$_{32}$H$_{41}$N$_3$Si$_2$W: C, 54.31; H, 5.84; N, 5.94. Found: C, 53.98; H, 5.61; N, 5.69.

Synthesis of W(NPh)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)(C$_5$H$_5$N)$_2$(CO) (8a). An ampule fitted with a Teflon valve was charged with W(NPh)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)(C$_5$H$_5$N)$_2$ (**5**) (0.20 g, 0.29 mmol) and toluene (40 mL). The mixture was frozen in liquid N_2, and the flask was evacuated. Upon warming to room temperature, the flask was charged with CO (20 psi). The solution immediately turned brown in color. After stirring at room temperature for 30 min, the reaction solvent was removed, and the resulting solid was extracted with pentane. The filtrate was dried in vacuo for 3 h to give 0.13 g (65%) of **8a** as a dark-brown crystalline solid. ^{1}H NMR (C_6D_6, 25 °C): δ 0.35 (s, 9H, SiMe$_3$), 0.37 (s, 9H, SiMe$_3$), 6.26 (t, 4H, *m*-C$_5$H$_5$N), 6.46 (t, 2H, *p*-C$_5$H$_5$N), 6.65 (m, 2H, *o*-pdaC$_6$H$_4$), 6.86−7.10 (m, 5H, aromatic), 7.29 (d, 2H, *o*-W≡NC$_6$H$_5$), 8.77 (d, 4H, *o*-C$_5$H$_5$N). ^{13}C NMR (C_6D_6, 25 °C): δ 3.79 (SiMe$_3$), 4.20 (SiMe$_3$), aromatic; 115.62, 118.60, 119.16, 121.01, 124.02, 124.31, 125.03, 129.63, 137.08, 149.73, 150.64, 154.03, 158.57, 281.05 (C≡O). IR ν_{CO} = 1889 cm^{-1}.

Synthesis of W(NPh)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)(C$_6$H$_7$N)$_2$(CO) (8b). Following the procedure used for the synthesis of **8a**, W(NPh)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)(p−C$_6$H$_7$N)$_2$ (**6**) (0.75 g, 1.05 mmol) was exposed to a positive pressure (20 psi) of C≡O. Compound **8b** (0.58 g, 76%) was isolated as a dark-brown crystalline solid. ^{1}H NMR (C_6D_6, 25 °C): δ 0.41 (s, 9H, SiMe$_3$), 0.45 (s, 9H, SiMe$_3$), 1.47 (s, 6H, C$_6$H$_7$N), 6.17 (d, 4H, C$_6$H$_7$N), 6.65 (m, 2H, *o*-pdaC$_6$H$_4$), 6.88 (t, 1H, *p*-W≡NC$_6$H$_5$), 6.94−7.13 (m, 6H, aromatic), 7.34 (d, 2H, *o*-W≡NC$_6$H$_5$), 8.77 (d, 4H, C$_6$H$_7$N). ^{13}C NMR (C_6D_6, 25 °C): δ 3.89 (SiMe$_3$), 4.29 (SiMe$_3$), 20.44 (C$_6$H$_7$N) aromatic; 115.53, 118.62, 119.16, 121.00, 124.07, 124.91, 125.20, 129.60, 138.22, 149.25, 150.87, 153.64, 158.84, 283.91 (C≡O). IR ν_{CO} = 1878 cm^{-1}.

Synthesis of W(NPh)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)(C$_5$H$_5$N)(PMe$_3$)(CO) (9a). W(NPh)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)(C$_5$H$_5$N)$_2$(CO) (**8a**) (0.30 g, 0.42 mmol) was dissolved in pentane at room temperature, and to the resulting solution was added PMe$_3$ (0.04 mL, 0.42 mmol). The solution was allowed to stir at room temperature for 30 min. The reaction solvent was removed, and the resulting solid was extracted with pentane. The filtrate was dried in vacuo to give **9a** (0.22 g, 74%) as a dark-brown solid. ^{1}H NMR (C_6D_6, 25 °C): δ 0.21 (s, 9H, SiMe$_3$), 0.30 (s, 9H, SiMe$_3$), 0.97 (d, 9H, PMe$_3$, $^2J_{P-H}$ = 9.0 Hz), 6.38 (t, 2H, *m*-C$_5$H$_5$N), 6.80−7.12 (m, 8H, aromatic), 7.24 (d, 2H, *o*-W≡NC$_6$H$_5$), 8.70 (d, 2H, *o*-C$_5$H$_5$N). ^{13}C NMR (C_6D_6, 25 °C): δ 3.15 (SiMe$_3$), 3.70 (SiMe$_3$), 16.65 (PMe$_3$, $^1J_{P-C}$ = 28.4 Hz), aromatic; 114.98, 118.44, 118.52, 121.26, 122.99, 123.23, 123.82, 129.08, 137.20, 148.75, 150.90, 151.70, 158.21, 271.50 (C≡O). ^{31}P NMR (C_6D_6, 25 °C): δ −10.76 (PMe$_3$, $^1J_{W-P}$ = 188.8 Hz). IR ν_{CO} = 1905 cm^{-1}

Synthesis of W(NPh)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)(C$_6$H$_7$N)(PMe$_3$)(CO) (9b). Following the procedure used for the synthesis of **9a**, W(NPh)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)(p−C$_6$H$_7$N)$_2$(CO) (**8a**) (0.25 g, 0.34 mmol) was reacted with PMe$_3$ (0.04 mL, 0.34 mmol) at room temperature. Compound **9b** (0.21 g, 87%) was isolated as a dark-brown crystalline solid. ^{1}H NMR (C_6D_6, 25 °C): δ 0.25 (s, 9H, SiMe$_3$), 0.34 (s, 9H, SiMe$_3$), 0.99 (d, 9H, PMe$_3$, $^2J_{P-H}$ = 9.3 Hz), 1.53 (s, 3H, C$_6$H$_7$N), 6.29 (d, 2H, C$_6$H$_7$N), 6.74−7.05 (m, 7H, aromatic), 7.26 (d, 2H, *o*-W≡NC$_6$H$_5$), 8.63 (d, 2H, C$_6$H$_7$N). ^{13}C NMR (C_6D_6, 25 °C): δ 3.69 (SiMe$_3$), 4.25 (SiMe$_3$), 17.00 (PMe$_3$, $^1J_{P-C}$ = 27.9 Hz), 20.66 (C$_6$H$_7$N), aromatic; 115.42, 118.91, 119.00, 121.74, 123.52, 123.64, 124.96, 125.42, 129.56, 149.39, 151.50, 151.86, 158.79, 273.20 (C≡O). ^{31}P NMR (C_6D_6, 25 °C): δ −10.71 (PMe$_3$, $^1J_{W-P}$ = 188.0 Hz). IR ν_{CO} = 1903 cm^{-1}.

Synthesis of W(NPh)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)(C$_5$H$_5$N)(PMe$_3$)$_2$ (10a). W(NPh)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)(C$_5$H$_5$N)$_2$ (**5**) (0.20 g, 0.29 mmol) was placed in a Schlenk tube and dissolved in toluene (40 mL). To this solution was added 2 equiv of PMe$_3$ (0.06 mL, 0.59 mmol) at room temperature. An immediate color change from purple to dark brown was observed. The mixture was stirred at room temperature for 30 min, at which time the reaction solvent was removed, and the resulting brown solid was extracted with pentane. The filtrate was dried in vacuo for 3 h. Compound **10a** (0.15 g, 67%) was isolated as a dark-brown crystalline solid. ^{1}H NMR (C$_6$D$_6$, 25 °C): δ 0.13 (s, 9H, SiMe$_3$), 0.19 (s, 9H, SiMe$_3$), 1.10 (d, 9H, PMe$_3$, $^2J_{P-H}$ = 7.8 Hz), 1.43 (d, 9H, PMe$_3$, $^2J_{P-H}$ = 6.3 Hz), 6.40 (t, 1H, C$_5$H$_5$N), 6.51 (t, 1H, C$_5$H$_5$N), 6.70−7.10 (m, 8H, aromatic), 7.32 (d, 2H, *o*-W≡NC$_6$H$_5$), 8.52 (d, 1H, C$_5$H$_5$N), 8.79 (d, 1H, C$_5$H$_5$N). ^{13}C NMR (C$_6$D$_6$, 25 °C): δ 4.16 (SiMe$_3$), 6.22 (SiMe$_3$), 22.39 (PMe$_3$, $^1J_{P-C}$ = 24.5 Hz), 26.26 (PMe$_3$, $^1J_{P-C}$ = 22.4 Hz), aromatic; 113.96, 118.66, 118.85, 120.95, 121.40, 121.56, 122.02, 125.07, 129.36, 136.40, 149.16, 152.23, 153.59, 155.62, 160.24. ^{31}P NMR (C$_6$D$_6$, 25 °C): δ −40.31 (PMe$_3$, $^1J_{W-P}$ = 157.9 Hz, $^2J_{P-P}$ = 10.0 Hz), −24.09 (PMe$_3$, $^1J_{W-P}$ = 190.0 Hz, $^2J_{P-P}$ = 10.0 Hz).

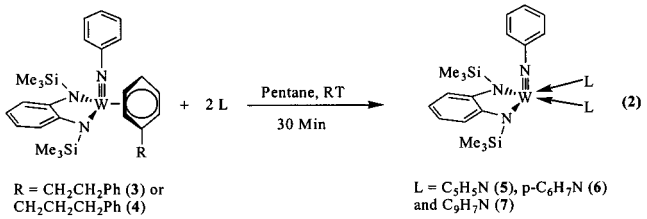
Synthesis of W(NPh)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)(C$_6$H$_7$N)(PMe$_3$)$_2$ (10b). Following the procedure used for the synthesis of **10a**, W(NPh)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)(p−C$_6$H$_7$N)$_2$ (**6**) (0.20 g, 0.28 mmol) was reacted with PMe$_3$ (0.06 mL, 0.56 mmol). Compound **10b** (0.19 g, 86%) was isolated as a dark-brown crystalline solid. ^{1}H NMR (C$_6$D$_6$, 25 °C): δ 0.17 (s, 9H, SiMe$_3$), 0.24 (s, 9H, SiMe$_3$), 1.11 (d, 9H, PMe$_3$, $^2J_{P-H}$ = 8.1 Hz), 1.46 (d, 9H, PMe$_3$, $^2J_{P-H}$ = 6.3 Hz), 1.83 (s, 3H, C$_6$H$_7$N), 6.24 (d, 1H, C$_6$H$_7$N), 6.69 (d, 1H, C$_6$H$_7$N), 6.76 (t, 1H, *p*-W≡NC$_6$H$_5$), 6.85−7.10 (m, 8H, aromatic), 8.51 (d, 1H, C$_6$H$_7$N), 8.72 (d, 1H, C$_6$H$_7$N). ^{13}C NMR (C$_6$D$_6$, 25 °C): δ 4.20 (SiMe$_3$), 6.28 (SiMe$_3$), 20.14 (C$_6$H$_7$N), 22.72 (PMe$_3$, $^1J_{P-C}$ = 24.2 Hz), 26.25 (PMe$_3$, $^1J_{P-C}$ = 22.4 Hz), aromatic; 113.90, 118.64, 118.87, 120.98, 121.43, 121.50, 122.04, 124.91, 125.11, 129.37, 148.48, 152.14, 153.49, 155.79, 160.43. ^{31}P NMR (C$_6$D$_6$, 25 °C): δ −39.93 (PMe$_3$, $^1J_{W-P}$ = 159.0 Hz, $^2J_{P-P}$ = 10.0 Hz), −24.09 (PMe$_3$, $^1J_{W-P}$ = 192.5 Hz, $^2J_{P-P}$ = 10.0 Hz).

X-ray Experimental for Compounds 6 and 8a. Crystals of **6** suitable for diffraction studies were obtained from an unstirred pentane reaction mixture at room temperature. Crystals of **8a** were obtained from a concentrated Et$_2$O solution that was stored at −40 °C for 1 week. Data were collected at 173 K on a Siemens SMART PLATFORM equipped with A CCD area detector and a graphite monochromator utilizing Mo Kα radiation (λ = 0.71073 Å). Cell parameters were refined using up to 8192 reflections. A hemisphere of data (1381 frames) was collected using the ω-scan method (0.3° frame width). The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability (maximum correction on *I* was < 1%). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structures were solved by the direct methods in *SHELXTL5*[11] and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. For compound **6,** the N1 imido and the N5 methylpyridyl ligands are slightly disordered in their planes but could not be resolved. This is evidenced by the larger than normal and elongated thermal ellipsoids of their atoms. A total of 351 parameters were refined in the final cycle of refinement using 6092 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 2.48% and 5.63%, respectively. Refinement was done using F^2. For compound **8a**, the asymmetric unit consists of one complex and a half diethyl ether disordered over a center of inversion (1/2 ether in the asymmetric unit). The ether was refined in two parts and their occupancy was fixed at 50% due to symmetry. A total of 369 parameters were refined in the final cycle of refinement using 6907 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 3.07% and 7.48%, respectively. Refinement was done using F^2. Details of data collection, solution, and refinement are given in Table 3.

Results and Discussion

Arene Displacement Reactions. Pentane solutions of the W(IV)−arene complexes W(NPh)[*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)](η^4-ethylbenzene) (**3**) and W(NPh)[*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)](η^4-propylbenzene) (**4**) rapidly react with 2 equiv of pyridine, 4-picoline, or quinoline at room temperature, giving W(NPh)(*o*-(Me$_3$SiN)$_2$-C$_6$H$_4$)(C$_5$H$_5$N)$_2$ (**5**) and W(NPh)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)(*p*-C$_6$H$_7$N)$_2$ (**6**) as dark purple solids and W(NPh)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)-(C$_9$H$_7$N)$_2$ (**7**)as a black solid in good yield (60−75%), eq 2.



Additional purification of the crude products is possible through subsequent washings with cold pentane (0 °C) followed by drying the resulting solid in vacuo. The room temperature ^{1}H and ^{13}C NMR spectra of **5**, **6**, and **7** are consistent with monomeric L$_2$ adducts where the donor ligands are coordinated in an η^1(N) fashion. In particular, upon coordination the resonances for the donor ligand protons are shifted upfield with respect to the free ligand.[12] Interestingly, the ortho ring protons of the nitrogen donor ligands display significantly different chemical shifts (5.69 and 7.80 ppm, for **5**), Figure 1, suggesting that there is hindered rotation of the rings about the W−N bonds with respect to the time scale of the NMR experiment. In addition, it is important to note that at 300 MHz the meta protons appear as overlapping triplets (6.28 ppm), however, at 500 MHz two triplets are observed. The corresponding carbon atoms are resolved at 300 MHz and resonate at 121.62 and 122.17 ppm, respectively.

The structure of the L$_2$ adducts was confirmed by an X-ray diffraction analysis of a single crystal of **6**, grown from an unstirred reaction mixture in pentane at room temperature, Figure 2. Selected bond lengths and angles are presented in Table 1. The coordination geometry about the W atom in **6** is best described as distorted square pyramidal, with the W atom displaced 0.69 Å out of the N2−N3−N4−N5 plane. The W−N1 bond length of 1.753(3) Å is consistent with typical W−N imido bond lengths,[2,4,13] and the W−N(pic) distances of 2.083(3) and

Table 1. Selected Bond Distances (Å) and Angles (Deg) for **6**

W−N1	1.753(3)	N3−W−N2	78.34(10)
W−N3	2.060(2)	N5−W−N4	80.33(10)
W−N2	2.062(3)	N2−W−N5	87.91(10)
W−N5	2.083(3)	N3−W−N4	88.80(10)
W−N4	2.109(3)	C1−N1−W	169.7(3)

Table 2. Selected Bond Distances (Å) and Angles (Deg) for **8a**

W−N1	1.787(3)	N1−W−C29	84.62(16)
W−N2 cis imido	2.139(3)	C29−W−N3	86.83(15)
W−N3 trans imido	2.112(3)	C29−W−N2	164.10(4)
W−N4	2.203(3)	N1−W−N2	110.34(14)
W−N5	2.215(3)	N2−W−N3	78.08(12)
W−C29	1.985(4)	C29−W−N4	96.07(14)
C29−O1	1.165(5)	C29−W−N5	88.85(15)
N1−W−N5	92.67(14)	N3−W−N4	89.23(12)
N1−W−N5	92.18(14)	N3−W−N5	86.63(12)
N4−W−N5	173.39(12)	N2−W−N5	88.77(12)
		N2−W−N5	85.34(13)

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Table 3. Crystal Data and Structure Refinement Details for **6** and **8a**

	6	**8a**
empirical formula	C30 H41 N5 Si2 W	C31 H42 N5 O Si2 W
FW	711.71	748.73
temp.	173(2) K	173(2) K
wavelength	0.71073 Å	0.71073 Å
Cryst syst	monoclinic	triclinic
space group	*P*2(1)/c	*P*-1
unit cell dimensions	$a = 13.6142(7)$ Å $\alpha = 90°$ $b = 12.7895(6)$ Å $\beta = 101.720(1)°$ $c = 19.0541(1)$ Å $\gamma = 90°$	$a = 10.0740(7)$ Å $\alpha = 69.341(1)°$ $b = 12.0912(9)$ Å $\beta = 78.022(1)°$ $c = 15.336(1)$ Å $\gamma = 76.008(1)°$
volume	3248.4(3) Å^3	1680.6(2) Å^3
Z	4	2
density (calculated)	1.455 Mg/m^3	1.480 Mg/m^3
absorption coefficient	3.656 mm^{-1}	3.540 mm^{-1}
F(000)	1432	754
cryst size	0.30 × 0.18 × 0.06 mm^3	0.39 × 0.32 × 0.02 mm^3
θ range for data collection	1.93−27.50°	1.83−27.50°
index ranges	$-17 \le h \le 16$, $-16 \le k \le 14$, $-24 \le l \le 23$	$-13 \le h \le 12$, $-15 \le k \le 8$, $-19 \le l \le 18$
reflns collected	22571	11730
independent reflections	7453 [R(int) = 0.0352]	7565 [R(int) = 00399]
Completeness to $\theta = 27.49°$	99.9%	98.1%
absorption correction	integration	integration
max. and min. transmission	0.8168 and 0.4250	0.9287 and 0.3380
Refinement method	full-matrix least-squares on F^2	Full-matrix least-squares on F^2
data/restraints/parameters	7453/0/351	7565/0/369
GOF on F^2	1.034	1.061
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0248, wR2 = 0.0563	R1 = 0.0307, wR2 = 0.0748
R indices (all data)	R1 = 0.0366, wR2 = 0.0626	R1 = 0.0359, wR2 = 0.0801
largest diff. peak and hole	1.375 and −0.720 e.Å^{-3}	1.330 and −1.534 e.Å^{-3}

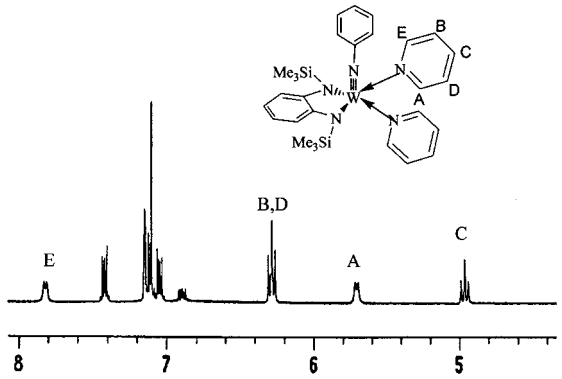

Figure 1. Room temperature ^{1}H NMR spectra of [W(NPh)[*o*-(Me$_3$SiN)$_2$C$_6$H$_4$](C$_5$H$_5$N)$_2$] (**5**) with pyridine ring proton assignments.

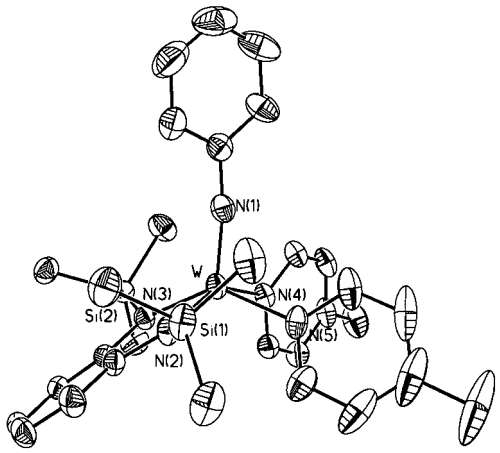

Figure 2. Molecular structure of [W(NPh)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)(*p*-C$_6$H$_7$N)$_2$] (**6**), showing 50% thermal ellipsoids and the atom labeling scheme.

2.109(3) Å are shorter than what is typically found (2.30 Å) for W−N(py) bond lengths.[12,14−16]

Bonding Explanation for Hindered Rotation in 5, 6, and 7. The structural data for **6** combined with a basic understanding of the bonding in these complexes provides an explanation for the unexpected slow rotation of the pyridine rings at room temperature that is observed in the ^{1}H NMR spectra of **5**, **6**, and **7**. The conformation of the diamido ligand in **6** is significantly different from that observed in the W(VI) compounds we have previously studied.[2] In the W(VI) complexes, an angle of ca. 50° is formed by the plane defined by the W and two amide N atoms and the plane defined by the two amide N atoms and the phenylene ring. We suggested that the folding of the TMS$_2$pda ligand in the d^0 complexes arises because of π donation from the amide N atoms to the LUMO (d$_{xy}$) on the W center.[1] Maximum π donation occurs when the N p orbitals are rotated into the *xy* plane of the metal center. To approach this conformation, the ligand folds along the N−N vector, giving the observed structures. Recently, DFT calculations performed by Galindo[17] have confirmed these qualitative arguments.

In contrast to the W(VI) complexes, compound **6** has an almost planar diamide ligand (fold angle = 5.3°). The structural difference arises because in **6** the d$_{xy}$ orbital contains a pair of electrons. To avoid a filled−filled interaction between the d$_{xy}$ orbital and nitrogen p$_\pi$ orbitals, the nitrogen p$_\pi$ orbitals rotate out of the *xy* plane, away from the d$_{xy}$ orbital. Upon rotation, the diamide ligand is flattened. This conformation moves the SiMe$_3$ groups into the *xy* plane (The plane of the pyridine rings). This creates a steric interaction between the SiMe$_3$ groups and the Py ligands that is the source of the observed hindered rotation of the pyridine rings about the W−N bonds.

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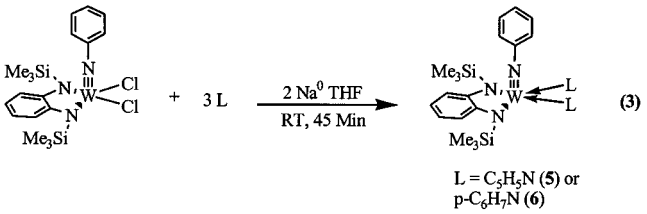
We have synthesized the complex W(NPh)[*o*-$(Me_3SiN)_2C_6H_4$]-Ph_2 as a W(VI) model of compounds **5**−**7**, and we observe free rotation of the phenyl rings about the W−C bonds. Because this compound has a d^0 electronic configuration, we would expect that the *o*-$(Me_3SiN)_2C_6H_4$ ligand is folded along the N−N vector as it is in all other M(VI) (M = Mo, W) complexes of this type. This folding of the ligand moves the $SiMe_3$ groups out of the *xy* plane of the molecule, thus relieving the steric congestion in the complex that would cause hindered rotation about the W−C bonds.

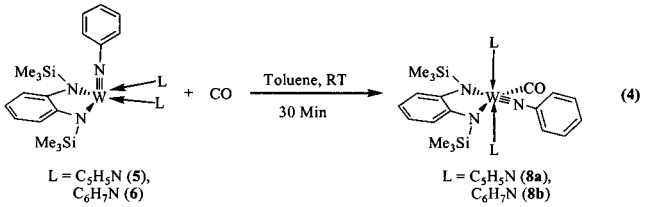
Na° Reduction of W(NPh)[*o*-$(Me_3SiN)_2C_6H_4$]Cl_2 with Pyridine or Picoline. Although our initial discovery of the W(IV)L_2 compounds through arene displacement from either **3** or **4** allowed us to characterize compounds **5, 6**, and **7**. To study their chemistry more easily, a more efficient synthetic pathway was necessary. In light of this, we have discovered that compounds **5** and **6** can be generated from W(NPh)(*o*-$(Me_3SiN)_2C_6H_4$)Cl_2 in one step. Na° reduction of a THF solution of the W(VI)−dichloride, in the presence of pyridine or 4-picoline, produces **5** and **6** with improved purity and yield (> 90%), eq 3.



(3)

Isolation of pure **5** and **6** is accomplished by removal of the THF in vacuo followed by toluene extraction to separate the desired products from NaCl, the major byproduct of the reaction. Subsequent removal of toluene from the filtrate solution followed by drying the resulting solid in vacuo for 3 h yields **5** and **6** as dark purple, crystalline solids.

Addition of a Sixth Ligand to W(IV)L_2. We have found that the W(IV)L_2 compounds are coordinatively unsaturated and readily accommodate additional ligands. For example, reaction of W(NPh)(*o*-$(Me_3SiN)_2C_6H_4$)$(C_5H_5N)_2$ (**5**) or W(NPh)(*o*-$(Me_3SiN)_2C_6H_4$)(*p*-$C_6H_7N)_2$ (**6**) with CO (20 psi) results in the rapid formation of the six coordinate complexes W(NPh)(*o*-$(Me_3SiN)_2C_6H_4$)$(C_5H_5N)_2$(CO) (**8a**) and W(NPh)(*o*-$(Me_3SiN)_2C_6H_4$)-$(C_6H_7N)_2$(CO) (**8b**), eq 4.



(4)

An X-ray diffraction study was performed on a single crystal of **8a**, which was grown from a concentrated Et_2O solution at −40 °C. The molecular structure is shown in Figure 3 and selected bond distances and angles are presented in Table 2. Complex **8a** adopts a pseudo-octahedral geometry about the W atom, with the pyridine groups occupying mutually trans positions. Consequently, the phenyl−imido is cis and trans to the $NSiMe_3$ groups, and CO occupies the remaining equatorial position. As a consequence of this geometrical arrangement of ligands (imido trans to amide), there is competition between the π-donation of the imido and amide ligands to the metal

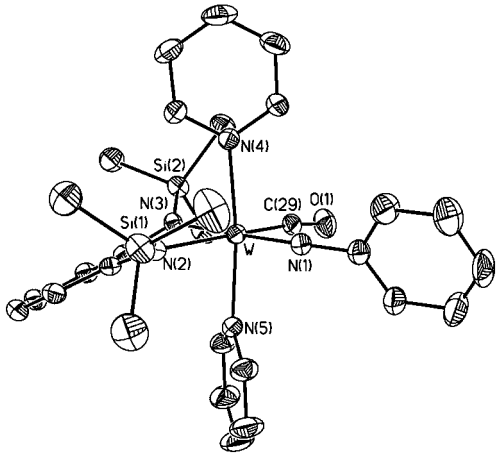


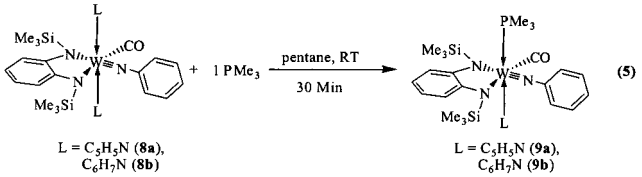
Figure 3. Molecular structure of [W(NPh)(*o*-$(Me_3SiN)_2C_6H_4$)$(C_5H_5N)_2$-(CO)] (**8a**), showing 50% thermal ellipsoids and the atom labeling scheme.

center. As a result, there is a slight lengthening of the W−N1-(imido) bond distance (1.787(3) Å) of **8a** in comparison to that observed for complex **6** (1.753(3) Å), where position trans to the imido is unoccupied. The largest distortions from a purely octahedral geometry are the N1−W−N2 (110.34(14)°) and N2−W−N3 (78.08(12)°) bond angles, which can be attributed to the restricted bite of the chelate ring.

The value of the CO stretching frequencies, $\nu_{CO} = 1890\ cm^{-1}$ (**8a**) and 1878 cm^{-1} (**8b**), are unusually low for what might be expected for high oxidation state (W(IV), d^2) complexes. It is likely that the ability of the W to backbond to the CO ligand is significantly enhanced relative to what might be expected because the amide N that is trans to the CO ligand is a π donor ligand, which enhances the backbonding thereby relieving an unfavorable Npπ−Wdπ filled−filled interaction.

The room temperature ^{1}H NMR spectra of **8a** and **8b** display two peaks (0.34 and 0.37 ppm (**8a**), 0.41 and 0.45 ppm (**8b**)) that are assigned to inequivalent $Si(CH_3)_3$ groups. The inequivalence of the $Si(CH_3)_3$ groups is consistent with the structural result which places the $NSiMe_3$ groups cis and trans to the imido group.[3] In contrast to the ^{1}H NMR spectra of the W(IV)L_2 compounds **5**, **6**, and **7**, there is only one set of pyridine ring protons for **8a** and **8b** due to unhindered rotation and the equivalency of the rings in the octahedral geometry. The ^{13}C NMR spectra of **8a** and **8b** display resonances at 281 and 284 ppm, respectively, corresponding to the CO ligands.

Ligand Substitution Reactivity. Examination of the chemistry of the six-coordinate compounds **8a** and **8b** led to the observation that one of the N donor ligands is labile and can be displaced. This was demonstrated by the reaction of W(NPh)-(*o*-$(Me_3SiN)_2C_6H_4$)$(C_5H_5N)_2$(CO) (**8a**) and W(NPh)(*o*-$(Me_3SiN)_2C_6H_4$)$(C_6H_7N)_2$(CO) (**8b**) with PMe_3 to give the substitution products W(NPh)(*o*-$(Me_3SiN)_2C_6H_4$)(C_5H_5N)(CO)(PMe_3) (**9a**) and W(NPh)(*o*-$(Me_3SiN)_2C_6H_4$)(C_6H_7N)(CO)(PMe_3) (**9b**), eq 5.

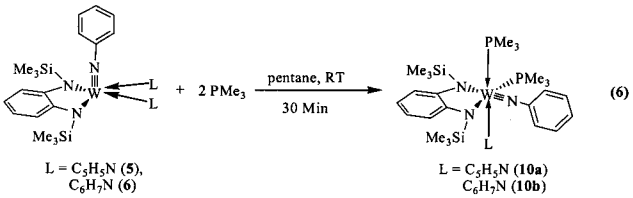


(5)

As was found for **8a** and **8b**, the ^{1}H NMR spectra of compounds **9a** and **9b** are consistent with rapidly rotating N donor ligands.

Due to the coordinative saturation of **8a** and **8b**, we believe that the reaction proceeds through a dissociative pathway in which a five coordinate W(NPh)(*o*-$(Me_3SiN)_2C_6H_4$)(CO)L intermediate is trapped by the incoming PMe_3 ligand.

In agreement with the proposed lability of one of the N donor ligands in the six coordinate complexes **8a** and **8b**, reaction of W(NPh)(*o*-$(Me_3SiN)_2C_6H_4$)$(C_5H_5N)_2$ (**5**) or W(NPh)(*o*-$(Me_3SiN)_2C_6H_4$)$(C_6H_7N)_2$ (**6**) with 2 equiv of PMe_3 results in the rapid formation of W(NPh)(*o*-$(Me_3SiN)_2C_6H_4$)$(C_5H_5N)(PMe_3)_2$ (**10a**) and W(NPh)(*o*-$(Me_3SiN)_2C_6H_4$)$(C_6H_7N)(PMe_3)_2$ (**10b**), respectively, with loss of 1 equiv of pyridine, eq 6.



(6)

Displacement of pyridine or 4-picoline by a second PMe_3 group to generate compounds **10a** and **10b** is preferred; this is demonstrated by the reaction of compound **5** or **6** with 1 equiv of PMe_3, which produces a 1:1 mixture of the bisphosphine complexes **10a** or **10b** and W(IV)L_2, as determined by NMR spectroscopy.

Similar to compounds **8a** and **8b**, the room temperature ^{1}H NMR spectra of **10a** and **10b** display two peaks (0.14 and 0.20 ppm (**10a**), 0.17 and 0.24 ppm (**10b**)) assigned to the inequivalent $Si(CH_3)_3$ groups, again due to a cis and trans orientation with respect to the imido group.[3] Unlike the previously described six-coordinate complexes, the N donor ligand of **10a** and **10b** display hindered rotation. The PMe_3 protons appear as doublets at 1.09 ppm ($^2J_{P-H}$ = 7.3 Hz) and 1.43 ppm ($^2J_{P-H}$ = 6.3 Hz) for **10a** and 1.12 ppm ($^2J_{P-H}$ = 8.1 Hz) and 1.46 ($^2J_{P-H}$ = 6.3 Hz) for **10b**, which is consistent with inequivalent PMe_3 groups. The ^{31}P NMR spectra of **10a** and **10b** confirm this inequivalence, as the PMe_3 groups appear as two doublets ($^2J_{P-P}$ = 9.5 Hz) for **10a** and ($^2J_{P-P}$ = 10.0 Hz) for **10b** that have ^{183}W satellites ($^1J_{W-P}$ = 190 and 158 Hz (**10a**), $^1J_{W-P}$ = 193 and 159 Hz (**10b**)). The small $^2J_{P-P}$ values are consistent with a cis orientation (axial and equatorial) of the PMe_3 groups,[18] leaving the pyridine group as the remaining ligand of the octahedral complex. A cis-orientation of the PMe_3 groups also accounts for the difference in the $^1J_{W-P}$ values. The larger $^1J_{W-P}$ value corresponds to the PMe_3 group which is trans to pyridine, and the smaller value for the PMe_3 trans to amide, as would be expected with the amide group having a greater trans influence than pyridine.

Summary and Conclusions

The Na° reduction of W(NPh)[*o*-$(Me_3SiN)_2C_6H_4$]Cl_2 in the presence of donor ligands such as pyridine or 4-picoline provides a simple and efficient means for producing the coordinatively unsaturated W(IV)L_2 compounds **8a** and **8b**. The reactions of compounds **5** and **6** with additional ligands, presented in this paper, serve to demonstrate the reactive nature of these compounds. In addition to the increased reactivity with respect to the W(IV)−arene complexes, the W(IV)L_2 compounds are, to our knowledge, very rare examples of bispyridine complexes with hindered rotation about the M−N(py) bonds. Based on our initial observations of the lability of the N donor ligands upon formation of six-coordinate complexes, we believe that these compounds will display very rich chemistry and are currently exploring this possibility.

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Supporting Information Available: X-ray crystallographic files for **6** and **8a**, in CIF format, and ^{1}H NMR spectra of compounds **5**−**10b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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