# Concurrent N-H and α-C-H Bond Activations of Pyrrolidine and Piperidine under Ambient Conditions by 18e Tungsten Allyl Nitrosyl Complexes

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**Supporting Information**

## Experimental Procedures

**General Methods**. All reactions and subsequent manipulations involving organometallic reagents were performed under anaerobic and anhydrous conditions either under high vacuum or an inert atmosphere of prepurified dinitrogen. Purification of inert gases was achieved by passing them first through a column containing MnO and then a column of activated 4 Å molecular sieves. Conventional glovebox and vacuum-line Schlenk techniques were utilized throughout. The gloveboxes utilized were Innovative Technologies LabMaster 100 and MS-130 BG dual-station models equipped with freezers maintained at – 30 $^{o}$C. Most of the reactions were performed in thick-walled glass vessels possessing Kontes greaseless stopcocks and side-arm inlets for vacuum-line attachment. Small-scale reactions and NMR spectroscopic analyses were conducted in J. Young NMR tubes which were also equipped with Kontes greaseless stopcocks. All solvents were dried with appropriate drying agents under a dinitrogen atmosphere and were distilled prior to use, or they were transferred directly under vacuum from the appropriate drying agent. Hydrocarbon solvents, diethyl ether, and tetrahydrofuran were dried and distilled from sodium benzophenone ketyl. Commercially available ($CH_2$=CH—CHMe)MgCl (Aldrich, 0.5 M in THF) and ($CH_2$=CMe—$CH_2$)MgCl (Aldrich, 0.5 M in THF) were transformed into the corresponding diallylmagnesium reagents in the usual manner.[1] Cp*W(NO)($CH_2CMe_3$)Cl[2] and Cp*W(NO)($CH_2CMe_3$)($\eta^3$-3,3-$Me_2C_3H_3$) (**1**)[3] were prepared according to published procedures. The synthesis of ($CH_2$=CMe—$CH_2$)MgCl from cinnamyl bromide (Aldrich) and magnesium (Strem) was carried out in a manner similar to that described previously for the synthesis of other allylmagnesium reagents,[3] and it was converted into the

bis(allyl)magnesium reagent in the usual manner.[1,3] The progress of most reactions was monitored by NMR spectroscopy, and the isolated yields of all new complexes have not been optimized.

All IR samples were prepared as Nujol mulls, and their spectra were recorded on a Thermo Nicolet 4700 FT-IR spectrometer. NMR spectra were recorded at room temperature on Bruker AV-300, AV-400 or AMX-500 spectrometers. All chemical shifts are reported in ppm, and all coupling constants are reported in Hz. $^{1}$H NMR spectra are referenced to the residual protio isotopomer present in a particular solvent, and $^{13}$C NMR spectra are referenced to the natural-abundance carbon signal of the solvent employed. Where necessary, $^{1}$H-$^{1}$H COSY, $^{1}$H-$^{1}$H NOEDS, $^{1}$H-$^{13}$C HMQC, $^{1}$H-$^{13}$C HMBC, and $^{13}$C APT experiments were carried out to correlate and assign $^{1}$H and $^{13}$C NMR signals. Low-resolution mass spectra (EI, 70 eV) were recorded by the staff of the UBC mass spectrometry facility using a Kratos MS-50 spectrometer. Elemental analyses were performed by Mr. Minaz Lakha of the UBC microanalytical facility.

**Preparation of Cp*W(NO)($CH_2CMe_3$)($NC_4H_7$-2-$Me_2CCH=CH_2$) (2).** Complex **2** was prepared by stirring a solution of **1** (97.1 mg, 0.199 mmol) in pyrrolidine (2 mL) for 17 h at room temperature. The final reaction mixture was taken to dryness in vacuo, and the residue was dissolved in a minimum of pentane. The pentane solution was chromatographed on a column of alumina (1 x 3 cm) with pentane as eluant to develop a single orange band that was eluted and collected. Concentration of the eluate under reduced pressure and cooling at -30 °C overnight resulted in the deposition of **2** as an orange crystalline solid (58.1 mg, 52% yield).

Characterization data for **2**: IR ($cm^{-1}$) 1561 (s, $\nu_{NO}$). MS (LREI, *m*/*z*, probe temperature 120 °C) 558 [$P^+$, $^{184}W$], 489 [P-allyl$^+$, $^{184}W$]. $^1H$ NMR (500 MHz, $C_6D_6$) $\delta$ 0.67 (d, $^2J_{HH}$ = 14.09, 1H, C*H*$_2$CMe$_3$), 1.06 (s, 3H, Me$_2$C), 1.17 (s, 3H, Me$_2$C), 1.18 (d, $^2J_{HH}$ = 14.09, 1H, C*H*$_2$CMe$_3$), 1.36 (s, 9H, CMe$_3$), 1.48-1.61 (m, 3H, pyrrolidine H), 1.67 (s, 15H, $C_5Me_5$), 1.80-1.89 (m, 1H, pyrrolidine H), 3.00 (m, 1H, pyrrolidine NCH$_2$), 3.20 (m, 1H, pyrrolidine NCH$_2$), 4.89-5.00 (m, 3H, pyrrolidine NCH and *H*$_2$C=CH). 5.81 (dd, $^3J_{HH}$ = 17.5, $^3J_{HH}$ = 10, 1H, H$_2$C=C*H*). $^{13}C\{^1H\}$ NMR (125 MHz, $C_6D_6$) $\delta$ 10.0 ($C_5$*Me*$_5$), 23.6 (Me$_2$*C*) 23.8 (pyrrolidine CH$_2$), 24.0 (*Me*$_2$C) 24.5 (*Me*$_2$C), 28.0 (pyrrolidine CH$_2$), 34.4 (CH$_2$C*Me*$_3$), 37.1 (CH$_2$*C*Me$_3$), 54.4 (*C*H$_2$CMe$_3$), 58.9 (pyrrolidine NCH$_2$), 85.0 (pyrrolidine NCH), 110.2 ($C_5$Me$_5$), 111.8 (*C*H$_2$=CH), 146.4 (CH$_2$=*C*H). Anal. Calcd. for $C_{24}H_{42}N_2OW$: C, 51.62; H, 7.58; N, 5.02. Found: C, 51.93; H, 7.90; N, 5.01.

**Preparation of Cp*W(NO)(CH$_2$CMe$_3$)(NC$_5$H$_9$-2-Me$_2$CCH=CH$_2$) (3).** Complex **3** was prepared by stirring a solution of **1** (90.3 mg, 0.185 mmol) in piperidine (2 mL) for 1 week at room temperature. The final reaction mixture was taken to dryness, and the residue was dissolved in a minimum amount of pentane. This solution was then chromatographed on a column of alumina (1 x 3 cm) with pentane as eluant to obtain an orange eluate that was collected. Concentration of the eluate under reduced pressure and cooling to -30 °C overnight resulted in the deposition of **3** as orange crystals.

Characterization data for **3**: IR ($cm^{-1}$) 1564 (s, $\nu_{NO}$). MS (LREI, *m*/*z*, probe temperature 120 °C) 572 [$P^+$, $^{184}W$], 503 [P-allyl$^+$, $^{184}W$]. $^1H$ NMR (500 MHz, $C_6D_6$) $\delta$ 1.10 (s, 3H, Me$_2$C), 1.20 (m, 1H, piperidine H), 1.23 (s, 3H, Me$_2$C), 1.29 (d, $^2J_{HH}$ = 5.92,

1H, C*H*$_2$CMe$_3$), 1.36 (m, 1H, piperidine H), 1.41 (s, 9H, CMe$_3$), 1.50 (m, 1H, piperidine H), 1.69 (d, $^2J_{HH}$ = 5.92, 1H, C*H*$_2$CMe$_3$), 1.69 (s, 15H, C$_5$Me$_5$), 1.72-1.75 (m, 2H, piperidine H), 2.03-2.05 (m, 1H, piperidine H), 3.01 (br d, 1H, piperidine NCH$_2$), 3.63 (td, $^3J_{HH}$ = 12, $^4J_{HH}$ = 3.2, 1H, piperidine NCH$_2$), 4.91 (d, $^3J_{HH}$ = 10.7, 1H, *H*$_2$C=CH), 4.96 (d, $^3J_{HH}$ = 17.4, 1H, *H*$_2$C=CH) 5.09-5.11 (br ,1H, piperidine NCH). 6.05 (dd, $^3J_{HH}$ = 17.46, $^3J_{HH}$ = 10.7, 1H, CH$_2$=C*H*). $^{13}$C{$^1$H} NMR (125 MHz, C$_6$D$_6$) $\delta$ 10.0 (C$_5$*Me*$_5$), 20.4 (piperidine CH$_2$), 23.5 (*Me*$_2$C), 26.4 (piperidine CH$_2$), 26.6 (*Me*$_2$C), 27.6 (piperidine CH$_2$), 34.6 (CH$_2$C*Me*$_3$), 37.0 (CH$_2$*C*Me$_3$), 49.4 (*C*H$_2$CMe$_3$), 56.0 (piperidine NCH$_2$), 81.4 (piperidine NCH), 110.3 (*C*$_5$Me$_5$), 110.8 (*C*H$_2$=CH), 148.9 (CH$_2$=*C*H). The signal for CH$_2$=CH-*C*Me$_2$ is probably obscured. Anal. Calcd. for C$_{25}$H$_{44}$N$_2$OW: C,52.45; H, 7.75; N, 4.89. Found: C, 52.18; H, 7.74; N, 5.29.

**Preparation of Cp*W(NO)(CH$_2$CMe$_3$)($\eta^3$-CH$_2$CMeCH$_2$) (4).** Complexes **4, 6** and **8** were synthesized and isolated in a similar manner, and the preparation of complex **4** is described here as a representative example. In a glovebox a 100-mL Schlenk tube was charged with a magnetic stir bar and Cp*W(NO)(CH$_2$CMe$_3$)Cl (1.00g, 2.20 mmol). A 350-mL Schlenk tube was then charged with a magnetic stir bar and (CH$_2$CMeCH$_2$)$_2$Mg·x(dioxane) (titre = 113.0 g / mol R, 0.25g, 0.5 equiv). On a vacuum line, Et$_2$O (approx. 40 mL and 60 mL) was vacuum-transferred onto the Cp*W(NO)(CH$_2$CMe$_3$)Cl and the diallylmagnesium reagents, respectively. The Et$_2$O above the Cp*W(NO)(CH$_2$CMe$_3$)Cl was allowed to melt, and this resulted in the formation of a purple solution which was kept cold with a dry ice/acetone bath. This purple solution was then cannulated dropwise into the 350-mL Schlenk tube containing the magnesium reagent that was kept in a liquid N$_2$ bath. The rate of addition was slow

enough to allow the added solution to freeze upon contact with the frozen $Et_2O$. Additional $Et_2O$ (2 x 10 mL) was used to wash the 100 mL-Schlenk tube to ensure quantitative transfer of the $Cp^*W(NO)(CH_2CMe_3)Cl$ reactant. After the addition of the $Cp^*W(NO)(CH_2CMe_3)Cl$ solution was finished, the mixture was stirred for 45 min while being maintained in the dry ice/acetone bath. The solution gradually turned brown, with the concomitant formation of a brown suspension of Mg salts. The dry ice/acetone bath was then removed, and the solvent was evaporated from the final mixture in vacuo. The residue was extracted with hexanes (4 x 100 mL), and the combined extracts were transferred to the top of a neutral activated alumina (I) column (2 x 5 cm) made up in hexanes and supported on a medium or high porosity frit. The column was eluted with 1:1 hexanes/$Et_2O$, and the resulting yellow band was collected. Solvent was removed from the eluate in vacuo to obtain a light yellow microcrystalline powder which was recrystallized from 3:1 pentane/$Et_2O$ at –30 °C in multiple crops to obtain light yellow, long needles of **4.** The crystals were washed with small amounts of cold pentane (-30 °C, 2 x 5 mL) and dried in vacuo. Yield 0.65 g (62%).

Characterization data for **4**: IR ($cm^{-1}$) 1563 (s, $\nu_{NO}$). MS (LREI, *m*/*z*, probe temperature 120 °C) 475 [$P^+$, $^{184}W$]. $^1H$ NMR (400 MHz, $C_6D_6$) $\delta$ 0.56 (br d, $^2J_{HH}$ = 2.7, 1H, allyl $CH_2$), 1.06 (d, $^2J_{HH}$ = 13.0, 1H, C*H*$_2$CMe$_3$), 1.35 (s, 9H, $CMe_3$), 1.50 (s, 15H, $C_5Me_5$), 1.73 (d, $^2J_{HH}$ = 13.0, 1H, C*H*$_2$CMe$_3$), 1.79 (br s, 1H, allyl $CH_2$), 2.02 (dd, $^2J_{HH}$ = 2.7, $^4J_{HH}$ = 4.2, 1H, allyl $CH_2$), 2.28 (s, 3H, allyl Me), 3.52 (br d, $^4J_{HH}$ = 4.2, 1H, allyl $CH_2$). $^{13}C\{^1H\}$ NMR (100 MHz, $C_6D_6$) $\delta$ 9.9 ($C_5$*Me*$_5$), 21.8 (allyl Me), 27.4 (*C*H$_2$CMe$_3$), 35.0 (CH$_2$C*Me*$_3$) 37.4 (CH$_2$*C*Me$_3$), 43.5 (allyl $CH_2$), 74.5 (allyl $CH_2$), 106.5 (*C*$_5$Me$_5$), 129.5

(allyl *C*Me). Anal. Calcd. for $C_{19}H_{33}NOW$: C, 48.01; H, 7.00; N, 2.95. Found: C, 48.13; H, 7.12; N, 3.17.

**Preparation of Cp*W(NO)($CH_2CMe_3$)($NC_4H_7$-2-$CH_2CMe=CH_2$) (5).** Complex **5** was synthesized and purified in a manner similar to that described for **2** (vide supra). Complex **4** (95.0 mg, 0.200 mmol) was dissolved in pyrrolidine (2 mL), and the mixture was stirred under a gentle flow of $N_2$ for 64 h, after which time the volatiles were removed in vacuo. The orange-yellow residue was redissolved in a minimum of pentane and chromatographed on alumina using 3:1 pentane/$Et_2O$ as eluant. The orange band that developed was eluted from the column and collected, and the solvent was removed in vacuo. NMR spectroscopy revealed that the residue was an approx. 60:40 mixture of **4** (starting material) and **5**. The yellow-orange solid was extracted with cold pentane (-30 °C, 2 x 3 mL), and the extracts were reduced in volume. Complex **5** was fractionally crystallized as fine yellow-orange rods (18 mg, 16%). Longer reaction times led to the decomposition of **5** into an intractable white solid.

Characterization data for **5**: IR ($cm^{-1}$) 1563 (s, $\nu_{NO}$). MS (LREI, *m*/*z*, probe temperature 120 °C) 544 [$P^+$, $^{184}W$], 489 [P-allyl$^+$, $^{184}W$]. $^1H$ NMR (400 MHz, $C_6D_6$) $\delta$ 0.79 (d, $^2J_{HH}$ = 14.0, 1H, C*H*$_2$CMe$_3$), 0.97 (d, $^2J_{HH}$ = 14.0, 1H, C*H*$_2$CMe$_3$), 1.39 (s, 9H, $CH_2C$*Me*$_3$), 1.47 (m, 1H, pyrrolidine $CH_2$), 1.65 (s, 15H, $C_5Me_5$), 1.70 (m, 1H, pyrrolidine $CH_2$), 1.95 (t, $^3J_{HH}$ = 11.6, 1H, $H_2C$=CMe—C*H*$_2$), 1.96 (s, 3H, $H_2C$=C*Me*), 2.74 (dd, $^3J_{HH}$ = 4.0, $^3J_{HH}$ = 11.6, 1H, $H_2C$=CMe—C*H*$_2$), 3.03 (m, 2H, pyrrolidine $NCH_2$), 4.80-4.83 (overlapping br s, 2H, *H*$_2$C=CMe), 5.14 (m, 1H, pyrrolidine NCH). Other pyrrolidine $CH_2$ signals are obscured. $^{13}C\{^1H\}$ NMR (100 MHz, $C_6D_6$) $\delta$ 9.6 ($C_5$*Me*$_5$), 22.2 ($H_2C$=C*Me*),

26.0 (pyrrolidine $CH_2$), 31.0 (pyrrolidine $CH_2$), 34.6 ($CH_2C\mathit{Me}_3$), 37.3 ($CH_2\mathit{C}Me_3$), 50.1 ($H_2C$=CMe—$\mathit{C}H_2$), 57.9 (pyrrolidine N$\mathit{C}H_2$), 58.4 ($\mathit{C}H_2CMe_3$), 75.0 (pyrrolidine NCH), 109.7 ($\mathit{C}_5Me_5$), 112.2 ($H_2\mathit{C}$=CMe), 144.5 ($H_2C$=$\mathit{C}$Me). Anal. Calcd. for $C_{23}H_{40}N_2OW$: C, 50.74; H, 7.41; N, 5.15. Found: C, 50.63; H, 7.38; N, 5.03.

The reaction was also performed in a sealed vessel in order to detect the $H_2$ being evolved. A 250-mL bomb was charged with complex **4** (approx 35.0 mg) and a small stir bar. Pyrrolidine (approx 5 mL) was added via vacuum transfer, and the contents were stirred for 1 day. The volatiles, including an appropriate amount of pyrrolidine (approx. 0.75 mL), were then vacuum-transferred into a J-Young NMR tube equipped with a $C_6D_6$ capillary. The presence of $H_2$ was indicated by a singlet at 4.79 ppm in the $^1$H NMR spectrum. This chemical shift was confirmed by recording the $^1$H NMR spectrum of a separately prepared sample of $H_2$ in pyrrolidine in a J-Young NMR tube equipped with a $C_6D_6$ capillary.

**Preparation of Cp*W(NO)($CH_2CMe_3$)($\eta^3$-$CH_2CHCHMe$) (6).** Complex **6** was synthesized from Cp*W(NO)($CH_2CMe_3$)Cl (1.00g, 2.20 mmol) and ($CH_2CHCHMe)_2Mg\cdot x$(dioxane) (0.5 equiv) in a manner similar to that described for **4** above. Since complex **6** is thermally unstable, cold solvents (-30 °C) had to be employed throughout its extraction and subsequent chromatography in order to minimize its decomposition. Thus, the crude product was extracted with pentane (4 x 50 mL), and the alumina column was washed with 3:1 pentane/$Et_2O$. The orange eluate was collected, the solvent was removed in vacuo, and the residue was crystallized from 5:1 pentane/$Et_2O$ at –30 °C overnight to obtain **6** as orange-yellow crystalline clusters.

The solids were washed with small amounts of cold pentane (-30 °C, 2 x 5 mL) and then dried in vacuo. Yield 0.45 g (43%).

Characterization data for **6**: IR ($cm^{-1}$) 1594 (s, $\nu_{NO}$). MS (LREI, *m*/*z*, probe temperature 120 °C) 475 [$P^+$, $^{184}W$]. $^1H$ NMR (400 MHz, $C_6D_6$) $\delta$ 0.89 (d, $^2J_{HH}$ = 13.2, 1H, C*H*$_2$CMe$_3$), 1.01 (m, 1H, allyl C*H*Me), 1.32 (s, 9H, CMe$_3$), 1.48 (s, 15H, $C_5Me_5$), 1.56 (d, $^3J_{HH}$ = 14.0, 1H, allyl $CH_2$), 1.59 (d, $^2J_{HH}$ = 13.2, 1H, C*H*$_2$CMe$_3$), 1.89 (d, $^3J_{HH}$ = 6.0, 3H, allyl Me), 3.67 (d, $^3J_{HH}$ = 7.2 1H, allyl $CH_2$), 4.97 (ddd, $^3J_{HH}$ = 7.2, $^3J_{HH}$ = 9.4, $^3J_{HH}$ = 14.0, 1H, allyl CH). $^{13}C\{^1H\}$ NMR (100 MHz, $C_6D_6$) $\delta$ 9.5 ($C_5$*Me*$_5$), 16.9 (allyl Me), 27.9 (*C*H$_2$CMe$_3$), 34.6 (CH$_2$C*Me*$_3$), 39.3 (CH$_2$*C*Me$_3$), 52.4 (allyl *C*HMe), 74.3 (allyl $CH_2$), 106.0 (*C*$_5$Me$_5$), 114.6 (allyl *C*H). Anal. Calcd. for $C_{19}H_{33}NOW$: C, 48.01; H, 7.00; N, 2.95. Found: C, 47.88; H, 7.32; N, 3.24.

**Preparation of Cp*W(NO)(CH$_2$CMe$_3$)(NC$_4$H$_7$-2-CHMeCH=CH$_2$) (7).** Complex **7** was synthesized in a manner similar to that described above for the preparation of complex **5**. Thus, complex **6** (71.0 mg, 0.149 mmol) was dissolved in pyrrolidine (2 mL), and the mixture was stirred under a gentle flow of $N_2$ for 1 day, after which time the volatiles were removed in vacuo. The orange-yellow residue was redissolved in a minimum of pentane and chromatographed on alumina using 3:1 pentane/$Et_2O$ as eluant. The orange band that developed was eluted from the column and collected, and the solvent was removed in vacuo. Complex **7** was recrystallized from pentane at –30 °C overnight to obtain orange-yellow microcrystals (18 mg, 22%).

Characterization data for **7**: IR ($cm^{-1}$) 1563 (s, $\nu_{NO}$). MS (LREI, *m*/*z*, probe temperature 120 °C) 544 [$P^+$, $^{184}W$], 489 [P-allyl$^+$, $^{184}W$]. $^1H$ NMR (400 MHz, $C_6D_6$) $\delta$ 0.72 (d, $^2J_{HH}$ = 14.4, 1H, C*H*$_2$CMe$_3$), 0.88 (d, $^3J_{HH}$ = 6.8, 3H, $H_2C$=CH—CH*Me*), 1.10 (d, $^2J_{HH}$ = 14.4, 1H, C*H*$_2$CMe$_3$), 1.35 (obscured, 2H, pyrrolidine $CH_2$), 1.37 (s, 9H, $CMe_3$), 1.48 (m, 1H, pyrrolidine $CH_2$), 1.67 (s, 15H, $C_5Me_5$), 1.70 (obscured, 1H, pyrrolidine $CH_2$), 2.79 (m, 1H, $H_2C$=CH—C*H*Me), 3.02 (m, 2H, pyrrolidine $NCH_2$), 5.01-5.03 (m, 2H, pyrrolidine NCH and *H*$_2$C=CH), 5.16 (d, $^3J_{HH}$ = 17.2, 1H, *H*$_2$C=CH), 5.99 (ddd, $^3J_{HH}$ = 7.2, $^3J_{HH}$ = 10.4, $^3J_{HH}$ = 17.2,1H, $H_2C$=C*H*). $^{13}C\{^1H\}$ NMR (100 MHz, $C_6D_6$) $\delta$ 9.8 ($C_5$*Me*$_5$), 14.6 ($H_2C$=CH—CH*Me*), 25.5 (pyrrolidine $CH_2$), 28.7 (pyrrolidine $CH_2$), 34.5 ($CH_2$C*Me*$_3$), 37.1 ($CH_2$*C*$Me_3$), 45.6 ($H_2C$=CH—*C*HMe), 55.1 (*C*$H_2CMe_3$), 58.6 (pyrrolidine $NCH_2$), 80.6 (pyrrolidine NCH), 109.9 (*C*$_5Me_5$), 114.1 ($H_2$*C*=CH), 142.9 ($H_2C$=*C*H). Anal. Calcd. for $C_{23}H_{40}N_2OW$: C, 50.74; H, 7.41; N, 5.15. Found: C, 51.03; H, 7.50; N, 4.94.

**Preparation of Cp*W(NO)($CH_2CMe_3$)($\eta^3$-$CH_2CHCHPh$) (8).** Complex **8** was synthesized from Cp*W(NO)($CH_2CMe_3$)Cl (0.50g, 1.10 mmol) and ($CH_2CHCHPh)_2Mg\cdot x$(dioxane) (0.5 equiv) in a manner similar to that described for **4** above. The crude product was extracted with pentane (3 x 30 mL), and the alumina column was washed with 3:1 pentane/$Et_2O$. The orange eluate was collected, the solvent was removed in vacuo, and the residue was crystallized from pentane at –30 °C overnight to obtain **8** as orange rods. The crystals were washed with small amounts of cold pentane (-30 °C, 2 x 2 mL) and then dried in vacuo. Yield 0.25 g (43%).

Characterization data for **8**: IR ($cm^{-1}$) 1578 (s, $\nu_{NO}$). MS (LREI, *m*/*z*, probe temperature 120 °C) 537 [$P^+$, $^{184}W$]. $^1H$ NMR (400 MHz, $C_6D_6$) $\delta$ 0.93 (br s, 1H, C*H*$_2$CMe$_3$), 1.24 (obscured, 1H, allyl H), 1.32 (br s, 9H, CMe$_3$), 1.43 (br s, 15H, $C_5Me_5$), 1.60 (br s, 1H, C*H*$_2$CMe$_3$), 2.11 (br s, 1H, allyl H), 3.74 (br s, 1H, allyl H), 5.53 (br s, 1H, allyl CH), 7.07-7.36 (br m, 5H, aryl H). $^{13}C\{^1H\}$ NMR (100 MHz, $C_6D_6$) $\delta$ 9.5 ($C_5$*Me*$_5$), 29.1 (*C*H$_2$CMe$_3$), 34.8 (CH$_2$C*Me*$_3$), 39.0 (CH$_2$*C*Me$_3$), 61.1 (allyl *C*HPh), 72.0 (allyl CH$_2$), 106.3 (*C*$_5$Me$_5$), 109.1 (allyl *C*H), 126.4 (aryl C), 127.2 (aryl C), 128.7 (aryl C), 137.4 (ipso C). Anal. Calcd. for $C_{19}H_{33}NOW$: C, 53.64; H, 6.56; N, 2.61. Found: C, 53.58; H, 6.32; N, 2.64.

**Preparation of Cp*W(NO)(CH$_2$CMe$_3$)(NC$_4$H$_7$-2-CHPhCH=CH$_2$) (9).** In a Schlenk tube, complex **8** (30.0 mg, 0.558 mmol) was dissolved in pyrrolidine (2 mL), and the mixture was stirred under a gentle flow of $N_2$ overnight (16 h), after which time the volatiles were removed in vacuo. Complex **9** was isolated from the crude reaction mixture by crystallization from pentane at –30 °C overnight to obtain a yellow-orange, microcrystalline solid (24 mg, 71%).

Characterization data for **9**: IR ($cm^{-1}$) 1562 (s, $\nu_{NO}$). MS (LREI, *m*/*z*, probe temperature 120 °C) 606 [$P^+$, $^{184}W$]. $^1H$ NMR (400 MHz, $C_6D_6$) $\delta$ 0.86 (d, $^2J_{HH}$ = 14.0, 1H, C*H*$_2$CMe$_3$), 1.07 (d, $^2J_{HH}$ = 14.0, 1H, C*H*$_2$CMe$_3$), 1.39 (s, 9H, CMe$_3$), 1.71 (s, 15H, $C_5Me_5$), 3.00-3.15 (m, 3H, PhC*H* and pyrrolidine NCH$_2$), 4.89 (dd, $^2J_{HH}$ = 1.4, $^3J_{HH}$ = 16.9, 1H, *H*$_2$C=CH), 5.02 (dd, $^2J_{HH}$ = 1.4, $^3J_{HH}$ = 10.0, 1H, *H*$_2$C=CH), 5.59 (m, 1H, pyrrolidine NCH), 6.78 (dt, $^3J_{HH}$ = 10.0, $^3J_{HH}$ = 16.9, 1H, H$_2$C=C*H*), 7.01 (m, 1H para CH), 7.11 (m, 2H, meta CH), 7.32 (m, 2H, ortho CH). Other pyrrolidine CH$_2$ signals are

obscured. $^{13}C\{^1H\}$ NMR (100 MHz, $C_6D_6$) $\delta$ 10.0 ($C_5Me_5$), 23.3 (pyrrolidine $CH_2$), 29.2 (pyrrolidine $CH_2$), 34.5 ($CH_2CMe_3$), 37.0 ($CH_2CMe_3$), 53.2 ($CH_2CMe_3$), 55.8 (pyrrolidine $NCH_2$), 56.1 (*C*HPh), 82.8 (pyrrolidine NCH), 110.3 ($C_5Me_5$), 115.2 ($H_2C$=CH), 126.6 (Ar C), 128.5 (Ar C), 129.1 (Ar C), 143.0 ($H_2C$=*C*H), 144.3 (Ar ipso C). Anal. Calcd. for $C_{28}H_{42}N_2OW$: C, 55.44; H, 6.98; N, 4.62. Found: C, 55.23; H, 7.20; N, 4.77.

**X-ray Crystallography.** Data collection for each compound was carried out at –100 ±1 °C on a Bruker X8 APEX diffractometer, using graphite-monochromated Mo K$\alpha$ radiation.

Data for **2** were collected to a maximum $2\theta$ value of 55.6° in 0.5° oscillations with 10.0 s exposures. The structure was solved by direct methods[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in fixed positions. The final cycle of full-matrix least-squares analysis was based on 12520 observed reflections and 264 variable parameters.

Data for **3** were collected to a maximum $2\theta$ value of 55.6° in 0.5° oscillations with 6.0 s exposures. The structure was solved by direct methods[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in fixed positions. The final cycle of full-matrix least-squares analysis was based on 6277 observed reflections and 272 variable parameters.

Data for **5** were collected to a maximum $2\theta$ value of 55.6° in 0.5° oscillations with 10.0 s exposures. The structure was solved by direct methods[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in fixed positions. The final cycle of full-matrix least-squares analysis was based on 5392 observed reflections and 248 variable parameters.

For each structure neutral-atom scattering factors were taken from Cromer and Waber.[5] Anomalous dispersion effects were included in $F_{calc}$;[6] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[7] The values for mass attenuation coefficients are those of Creagh and Hubbell.[8] All calculations were performed using SHELXL-97.[9] X-ray crystallographic data for all three structures are presented in Table 1.

**Table 1.** X-ray Crystallographic Data for Complexes **2**, **3** and **5**.

| Complex | **2** | **3** | **5** |
|---|---|---|---|
| | **Crystal Data** | | |
| Empirical formula | $C_{24}H_{42}N_2OW$ | $C_{25}H_{44}N_2OW$ | $C_{23}H_{40}N_2OW$ |
| Crystal Habit, color | Needle, orange | Prism, yellow | Prism, yellow |
| Crystal size (mm) | 0.20 × 0.10 × 0.05 | 0.35 × 0.30 × 0.25 | 0.40 × 0.175 × 0.075 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | $P2_1/n$ | $P2_1/c$ |
| Volume (Å$^3$) | 2418.6(8) | 2597.4(4) | 2347.98(14) |
| *a* (Å) | 11.732(3) | 10.776(1) | 12.6452(4) |
| *b* (Å) | 13.594(2) | 18.681(2) | 8.1081(3) |
| *c* (Å) | 15.641(3) | 13.048(1) | 22.9995(8) |
| $\alpha$(º) | 90 | 90 | 90 |
| $\beta$(º) | 104.161(8) | 98.560(5) | 95.311(2) |
| $\gamma$(º) | 90 | 90 | 90 |
| Z | 4 | 4 | 4 |
| Density (calculated) (mg/m$^3$) | 1.534 | 1.464 | 1.540 |
| Absorption coefficient (cm$^{-1}$) | 47.92 | 44.64 | 49.34 |
| $F_{000}$ | 1128 | 1160 | 1096 |
| | **Data Collection and Refinement** | | |
| Measured Reflections: Total | 159755 | 60650 | 36666 |
| Measured Reflections: Unique | 12520 | 6277 | 5392 |
| Final R Indices[a] | R1 = 0.0262, wR2 = 0.0665 | R1 = 0.0201, wR2 = 0.0502 | R1 = 0.0200, wR2 = 0.0500 |
| Goodness-of-fit on F$^{2b}$ | 0.938 | 1.065 | 1.061 |
| Largest diff. peak and hole (e$^-$ Å$^{-3}$) | 1.869 and -1.156 | 1.909 and -1.093 | 1.731 and -0.674 |

[a] R1 on $F = \Sigma \mid (|F_o| - |F_c|) \mid / \Sigma |F_o|$, ($I_o > 2\sigma(I_o)$); wR2 = $[(\Sigma ( F_o^2 - F_c^2 )^2 ) / \Sigma w(F_o^2 )^2]^{1/2}$ (all data); w = $[\sigma^2 F_o^2 ]^{-1}$; [b] GOF = $[\Sigma (w ( |F_o| - |F_c| )^2 ) / \textit{degrees of freedom} ]^{1/2}$.

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