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Water-Induced Isomerization of CpW(NO)(*o*-tolyl)$_2$ to CpW(O)(N-*o*-tolyl)(*o*-tolyl) and Related Chemistry[†]

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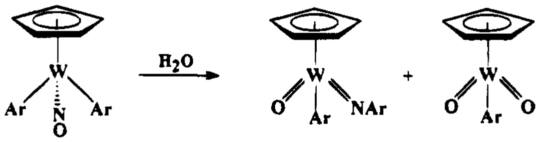
Treatment of a THF solution of CpW(NO)(*o*-tolyl)$_2$ (**1**) with H_2O affords a structural isomer of **1**, namely CpW(O)(N-*o*-tolyl)(*o*-tolyl) (**2**), in 30% isolated yield as well as the expected product, CpW(O)$_2$(*o*-tolyl) (**3**), in low isolated yield (10%). Complexes **2** and **3** are formed in a ratio of approximately 1:1 upon treatment of a C_6D_6 solution of **1** with D_2O. Similar treatment of **1** with $^{18}OH_2$ results in the production of unlabeled complex **2**, thereby establishing the intramolecular nature of the water-catalyzed isomerization of **1** to **2**. The characteristic reactivity of CpW(NO)(*o*-tolyl)$_2$ toward various classes of reagents has been investigated to determine if the conversion of **1** to **2** can be effected with reagents other than water. In general, this reactivity has been found to be similar to that exhibited by other Cp′W(NO)R$_2$ (Cp′ = Cp or Cp*; R = alkyl or aryl) complexes, and treatment of **1** with reagents other than water does not result in isomerization of the organometallic reactant. The isomerization is also dependent upon the nature of the Cp ligand, the metal, and the aryl groups as evidenced by the fact that treatment of the related diaryl complexes, CpW(NO)(*p*-tolyl)$_2$, CpW(NO)Ph$_2$, CpMo(NO)(*o*-tolyl)$_2$, and Cp*W(NO)(*o*-tolyl)$_2$, with water does not result in the production of their arylimido oxo structural isomers. Consequently, the water-induced isomerization of **1** to **2** remains a unique chemical process. Crystals of CpW(NO)(*o*-tolyl)$_2$ (**1**) and CpW(O)(N-*o*-tolyl)(*o*-tolyl) (**2**) have been subjected to X-ray crystallographic analyses.

Introduction

Cleavage of the N−O bond in metal-bound nitric oxide is both of fundamental significance in inorganic chemistry and of relevance to biological and environmental chemistry.[1] We have recently encountered such nitrosyl N−O bond cleavage under a variety of mild conditions while investigating the characteristic chemistry of 16-valence-electron complexes which contain Cp′M(NO) (Cp′ = η^5-C$_5$H$_5$ (Cp) or η^5-C$_5$Me$_5$ (Cp*); M = Mo or W) fragments.[2] The first, and still the most intriguing, example of nitrosyl N−O bond cleavage observed in our laboratories involves the novel isomerization that occurs as part of the overall conversion depicted in eq 1.[3] This isomerization of the 16-valence-electron diaryl nitrosyl compound (1) to a thermodynamically more stable 18-valence-electron arylimido oxo complex (2) is intriguing since it could conceivably proceed via intramolecular nitrosyl-ligand N−O bond cleavage. Consequently, we decided to investigate transformation 1 and related chemistry in some detail. Presented in this paper are the results of our attempts to delineate the scope of this conversion as well as our investigations into the nature of the chemical entities capable of inducing this isomerization. Finally, we also compare the reactivity of CpW(NO)(*o*-tolyl)$_2$ with various classes of reagents to the reaction chemistry exhibited by related diaryl and dialkyl complexes.



1 **2** **3** (1)

Ar = *o*-tolyl

Experimental Section

General Procedures Routinely Employed in the Legzdins Laboratories. All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions under an atmosphere of prepurified dinitrogen or argon unless otherwise specified. 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.[4] The gloveboxes used during this work were two Vacuum Atmospheres Models HE-43-2 and HE-

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[†] Dedicated to Prof. Dr. Max Herberhold on the occasion of his 60th birthday.

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493 and an Innovative Technologies Labmaster 130 two-station glovebox equipped with a cold well, freezer, and rotary evaporator. Some reactions were performed in a bomb, here defined as a thick-walled glass vessel with a Kontes greaseless Teflon stopcock and a side-arm for vacuum-line attachment. Filtrations were performed through columns supported on a medium-porosity glass frit. The column supports, which had been oven-dried and cooled in vacuo, included Celite 545 diatomaceous earth (Fisher), Florisil (Fisher, 60–100 mesh), or alumina (Fisher, neutral, activity I).

Solvents were either distilled from appropriate drying agents and purged with dinitrogen or argon for 15 min prior to use or were directly vacuum transferred from the drying agent.[5] CH_2Cl_2 was doubly distilled from P_2O_5. Et_2O was distilled from CaH_2 and sodium/benzophenone. Hexanes were distilled from CaH_2 and sodium/benzophenone/tetraglyme. Pentane was distilled from sodium/benzophenone/tetraglyme. THF was vacuum transferred from sodium/benzophenone. CH_3CN was vacuum transferred from CaH_2. $CDCl_3$ was dried over P_2O_5 and filtered through a short column of alumina (Woelm neutral, activity 1). Other deuterated solvents were dried over activated 4 Å molecular sieves, thrice freeze–pump–thaw degassed, and filtered through Celite.

All IR samples were run as solutions in NaCl cells or as Nujol mulls between NaCl plates. IR spectra were recorded on an ATI Mattson Genesis Series FTIR spectrometer, interfaced to a 486DX-33 PC using WinFIRST software. NMR spectra were obtained on either a Bruker AC-200 or Varian Associates XL-300 spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra are referenced to the residual proton or natural abundance carbon signal(s) of the solvent employed. $^{31}P\{^1H\}$ NMR spectra are referenced to external $P(OMe)_3$ set as 141 ppm downfield from 85% aqueous H_3PO_4. Mrs. M. T. Austria, Ms. L. K. Darge, and Dr. S. O. Chan assisted in obtaining the NMR data. Low-resolution mass spectra (EI, 70 eV) were recorded on a Kratos MS50 spectrometer using the direct-insertion method. Fast-atom bombardment (6 kV ion source, 7–8 kV xenon FAB gun) mass spectra were recorded on an AEI MS9 spectrometer using 3-nitrobenzyl alcohol as matrix. All mass spectra were recorded by Dr. G. K. Eigendorf and the staff of the mass spectroscopy laboratory. Elemental analyses were performed by Mr. P. Borda of the UBC Department of Chemistry.

Procedures Specific to This Work. The organometallic reagents, $Cp'M(NO)Cl_2$ (M = Mo or W), were prepared by established procedures.[6] $Cp'Mo(NO)Cl_2$ complexes were further purified by Soxhlet extraction with CH_2Cl_2, and the $Cp'W(NO)Cl_2$ complexes were stored at −30 °C and used within a few months of preparation. *tert*-Butylamine (Aldrich) and isopropyl alcohol (BDH) were subjected to two freeze–pump–thaw cycles and dried over CaH_2. *p*-Tolyl isocyanate was vacuum transferred from P_2O_5. All $(aryl)_2Mg{\cdot}x(dioxane)$ complexes were prepared by a modification[7] of the standard methodology,[8] and the complexes $Cp^*W(NO)Ph_2$ and $Cp^*W(NO)(p\text{-tolyl})_2$ were prepared by established procedures.[7] D_2O (MSD, 99.8% D), $^{18}OH_2$ (Aldrich, 97% ^{18}O), elemental sulfur (Fisher), and CO (Matheson CP grade) were used as received.

Preparation of CpW(NO)(*o*-tolyl)₂ (1). THF (10 mL) was vacuum transferred onto a mixture of $CpW(NO)Cl_2$ (350 mg, 1.00 mmol) and $(o\text{-tolyl})_2Mg{\cdot}x(dioxane)$ (2.00 mmol of *o*-tolyl) at −196 °C. The reaction mixture was stirred while being slowly warmed to 0 °C until there was no noticeable starting material remaining in the flask (approximately 10 min). The final purple solution was taken to dryness in vacuo, and Et_2O (100 mL) was vacuum transferred onto the remaining purple residue. This purple solution was filtered quickly through Florisil (3 × 3 cm). The volume of the purple filtrate was reduced in vacuo, and the resulting solution was placed in a freezer (−30 °C) overnight. Purple needles of the desired complex (150 mg, 33% yield) were isolated by cannulating away the mother liquor.

Anal. Calcd for $C_{19}H_{19}NOW$: C, 49.48; H, 4.15; N, 3.04. Found: C, 49.19; H, 4.21; N, 3.05. IR (Nujol mull): ν_{NO} 1599 cm^{-1}. ^1H NMR (C_6D_6): δ 7.56–7.02 (m, 8H, Ar *H*), 6.11 (s, 5H, C_5H_5), 2.67 (s, 6H, 2 × *Me*). Low-resolution mass spectrum (probe temperature 120 °C): *m/z* 461 [P^+].

Isolation of CpW(O)(N-*o*-tolyl)(*o*-tolyl) (2). A solution of $CpW(NO)(o\text{-tolyl})_2$ (generated from 1.00 mmol $CpW(NO)Cl_2$) in THF was prepared as above. This solution was treated with excess H_2O (0.1 mL) at −70 °C. As the stirred reaction mixture was warmed to room temperature, its color changed from purple to brown. This mixture was taken to dryness in vacuo, and the residue was extracted with Et_2O (2 × 25 mL). The extracts were filtered through Florisil (3 × 5 cm). The resulting yellow filtrate was taken to dryness under reduced pressure, and the remaining residue was triturated with hexanes to obtain a yellow powder which was dissolved in Et_2O. Concentration and cooling of this solution to −30 °C led to the deposition of 138 mg (30% yield) of analytically pure **2**.

Anal. Calcd for $C_{19}H_{19}NOW$: C, 49.48; H, 4.15; N, 3.04. Found: C, 49.59; H, 4.30; N, 2.91. IR (Nujol mull): $\nu_{W=O}$ 897 (vs), also 1476 (s), 1379 (m), 1117 (m), 1022 (m), 1007 (m), 841 (m), 824 (s), 766 (s), and 750 (m) cm^{-1}. ^1H NMR (C_6D_6): δ 7.90 (dd, 1H, o-Ar *H*), 7.24–6.77 (m, 7H, Ar *H*), 5.72 (s, 5H, C_5H_5), 2.48 (s, 3H, *Me*), 2.32 (s, 3H, *Me*). Low-resolution mass spectrum (probe temperature 120 °C): *m/z* 461 [P^+].

Isolation of CpW(O)₂(*o*-tolyl) (3). Product **3** was obtained by elution with acetone of the Florisil column used during the isolation of **2** (vide supra). Solvent was evaporated from the acetone eluate to obtain a microcrystalline off-white solid which was crystallized from CH_2Cl_2/hexanes. Complex **3** was typically isolated in low yields (5–10% based on $CpW(NO)Cl_2$).

Anal. Calcd for $C_{12}H_{12}O_2W$: C, 38.73; H, 3.25. Found: C, 38.82; H, 3.30. IR (Nujol mull): 947 (m), 901 (m), 845 (w), 818 (w) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.58 (dd (J_{HH} = 3.2 and 12.4 Hz), 1H, *o*-Ar *H*), 7.32 (m, 2H, Ar *H*), 7.19 (m, 1H, Ar *H*), 7.06 (m, 1H, Ar *H*), 6.52 (s, 5H, C_5H_5), 2.29 (s, 3H, *Me*). Low-resolution mass spectrum (probe temperature 120 °C): *m/z* 372 [P^+].

Reaction of CpW(NO)(*o*-tolyl)₂ with ¹⁸OH₂ or D₂O. Solutions of $CpW(NO)(o\text{-tolyl})_2$ (46 mg, 0.10 mmol) in C_6D_6 (0.7 mL) were treated with excess $^{18}OH_2$ or D_2O (0.05 mL). The solutions changed in color from purple to brown in a few seconds. The reaction mixtures were worked-up as described in the preceding paragraphs, and the resulting solids were characterized by mass spectrometry and ^1H NMR spectroscopy. In both cases, ^1H NMR spectroscopy indicated that two products had been formed in the approximate ratio of 1:1. These two products were identified as complexes **2** and **3** by comparisons to authentic samples. The mass spectrum of the solid isolated from the reaction with $^{18}OH_2$ exhibited a parent envelope at *m/z* 461 (probe temperature 120 °C).

Preparation of CpW(NO)(η^2-C{O}-*o*-tolyl)(*o*-tolyl) (4). A solution of $CpW(NO)(o\text{-tolyl})_2$ (generated from 1.00 mmol $CpW(NO)Cl_2$) in THF was prepared as described above. The stirred reaction mixture was treated with excess CO at room temperature, whereupon the solution changed from purple to yellow in a matter of seconds. This yellow solution was taken to dryness in vacuo, and the resulting yellow residue was triturated in CH_2Cl_2 (40 mL). The resulting mixture was filtered through Florisil (3 × 5 cm). Hexanes (30 mL) were added to the filtrate, the volume of the solution was reduced in vacuo, and the final solution was placed in a freezer (−30

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°C) overnight. Yellow-orange crystals of the desired complex (250 mg, 51% yield) were then isolated by removing the supernatant solution by cannulation and drying the crystals in vacuo.

Anal. Calcd for $C_{20}H_{19}NO_2W$: C, 49.10; H, 3.91; N, 2.86. Found: C, 49.18; H, 3.89; N, 2.80. IR (Nujol mull): 1584 (s), 1532 (s), 1219 (m), 925 (m), 819 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 8.26 (dd, 1H, *o*-Ar *H*), 7.74 (m, 2H, Ar *H*), 7.60 (m, 1H, Ar *H*), 7.48 (m, 1H, Ar *H*), 7.22 (m, 1H, Ar *H*), 7.11 (m, 2H, Ar *H*), 5.91 (s, 5H, C_5H_5), 2.83 (s, 3H, *Me*), 2.44 (s, 3H, *Me*). ^{13}C (CD_2Cl_2): δ 273.36 (*C*O), 161.39, 149.17 (2 × C_{ipso}), 142.03, 140.59, 140.52, 138.36, 136.77, 132.16, 129.51, 127.42, 125.79, 124.66 (10 × C_{aryl}), 100.61 (C_5H_5), 26.15, 21.14 (2 × *Me*). Low-resolution mass spectrum (probe temperature 120 °C): *m/z* 489 [P$^+$], 461 [P$^+$ − CO].

Preparation of CpW(NO)(*o*-tolyl)$_2$(PMe$_3$) (5). A solution of CpW(NO)(*o*-tolyl)$_2$ (generated from 1.00 mmol of CpW(NO)Cl$_2$) in THF was prepared as described above. The stirred reaction mixture was treated with approximately 1 atm of PMe$_3$ at room temperature, whereupon the solution changed from purple to yellow/brown in approximately 5 s. The reaction mixture was taken to dryness in vacuo, and the remaining brown residue was triturated in CH_2Cl_2 (10 mL). The resulting yellow powder was dissolved in CH_2Cl_2 (10 mL), and this solution was filtered through alumina I (3 × 3 cm). Hexanes (5 mL) were added to the filtrate, the volume of the solution was reduced in vacuo, and the final solution was placed in a freezer (−30 °C) overnight. The desired complex deposited as a yellow powder (360 mg, 67% yield) and was isolated by removing the supernatant solution by cannulation.

Anal. Calcd for $C_{22}H_{28}NOPW$: C, 49.18; H, 5.25; N, 2.61. Found: C, 48.96; H, 5.25; N, 2.57. IR (Nujol mull): 1587 (s), 1303 (m), 1281 (m), 954 (m), 826 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$) (60:40 mixture of cis and trans isomers): δ 7.8 (m, *o*-Ar *H*), 7.2−6.8 (m, Ar *H*), 5.59 (s, C_5H_5), 5.56 (s, C_5H_5), 2.47 (s, *Me*), 2.33 (s, 3H, *Me*), 0.89, 0.79 (d ($^2J_{HP}$ = 9.3 Hz), 2 × P*Me*$_3$). Low-resolution mass spectrum (probe temperature 170 °C): *m/z* 461 [P$^+$ − PMe$_3$].

Generation of CpW(NO)(*o*-tolyl)(NHCMe$_3$) (6). Complex **1** (70 mg, 0.15 mmol) in CH_2Cl_2 (2 mL) was treated with excess Me$_3$CNH$_2$. There was no immediate color change, and there was no change evident in the ν_{NO} band in the solution IR spectrum. However, stirring of this solution at room temperature for 2 d resulted in a change in color from purple to orange. Cooling of the final solution to −30 °C afforded a dark orange powder which was identified by its physical properties as complex **6**. In solution this complex exists as a mixture of two isomers in the ratio 5:1. Only data for the major isomer are presented below.

^{1}H NMR ($CDCl_3$): δ 9.4 (s, 1H, N*H*), 7.7 (m, 1H, Ar *H*), 7.2 (m, 1H, Ar *H*), 7.0 (m, 2H, Ar *H*), 5.95 (s, 5H, C_5H_5), 2.24 (s, 3H, *Me*), 1.33 (s, 9H, C*Me*$_3$). ^{13}C ($CDCl_3$): δ 144.18, 141.40, 128.88, 126.28, 124.32 (5 × C_{aryl}), 102.60 (Cp), 64.99 (*C*Me$_3$), 33.02 (C*Me*$_3$), 28.69 (Ar *Me*). Low-resolution mass spectrum (probe temperature 120 °C): *m/z* 442 [P$^+$].

Generation of CpW(NO)(*o*-tolyl)(OCHMe$_2$) (7). A solution of CpW(NO)(*o*-tolyl)$_2$ (30 mg, 0.065 mmol) in $CDCl_3$ (0.7 mL) in an NMR tube was treated with an excess of Me$_2$CHOH (5 mg, 0.08 mmol). The solution changed color from purple to deep red in a matter of seconds. The reaction produced one major Cp-containing product (>95 %) as judged by ^{1}H NMR spectroscopy. The contents of the NMR tube were poured into a Schlenk tube and were taken to dryness. The resulting red solid was extremely air- and moisture-sensitive, and satisfactory mass spectral and elemental analysis data could not be obtained.

IR (Nujol mull): 1602 (br) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.6 (m, 1H, Ar *H*), 7.2 (m, 1H, Ar *H*), 7.1 (m, 2H, Ar *H*), 6.1 (s, 5H, C_5H_5), 5.4 (m, 1H, −C*H*−), 2.31 (s, 3H, *Me*), 1.30 (m, 6H, 2 × *Me*). ^{13}C ($CDCl_3$): δ 144.53, 137.40, 129.69, 127.49, 124.58 (5 × C_{aryl}), 104.55 (Cp), 85.34 (O*C*HMe$_2$), 27.02 (OCH*Me*$_2$), 26.61 (Ar *Me*), 26.08 (OCH*Me*$_2$).

Preparation of CpW(NO)(SAr)$_2$ (Ar = *o*-Tolyl (8), *p*-Tolyl (9)). A solution of CpW(NO)(*o*-tolyl)$_2$ (generated from 1.00 mmol of CpW(NO)Cl$_2$) in THF was prepared as described above. The stirred reaction mixture was treated with excess S$_8$ (80 mg, 2.5 equiv of S) at room temperature, whereupon the solution changed from purple to red in about 10 s. This red solution was taken to dryness in vacuo, and the resulting dark red residue was triturated in Et$_2$O (30 mL). This mixture was filtered through Florisil (3 × 5 cm). The volume of the filtrate was reduced in vacuo, and the resulting solution was placed in a freezer (−30 °C) overnight. Dark red crystals of the desired complex (270 mg, 51% yield) were isolated by removing the supernatant solution by cannulation.

Anal. Calcd for $C_{19}H_{19}NOS_2W$: C, 43.44; H, 3.64; N, 2.67. Found: C, 43.52; H, 3.65; N, 2.61. IR (Nujol mull): 1616 (s), 825 (m), 744 (m) cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.62 (d, 2H, *o*-Ar *H*), 7.10 (m, 6H, Ar *H*), 5.06 (s, 5H, C_5H_5), 2.51 (s, 6H, 2 × *Me*). ^{13}C (CD_2Cl_2): δ 161.39, 149.17 (2 × C_{ipso}), 142.03, 140.59, 140.52, 138.36, 136.77, 132.16, 129.51, 127.42, 125.79, 124.66 (10 × C_{aryl}), 100.61 (C_5H_5), 21.14 (*Me*). Low-resolution mass spectrum (probe temperature 120 °C): *m/z* 525 [P$^+$].

CpW(NO)(S-*p*-tolyl)$_2$ (9) was prepared by using the same methodology as described above for complex **8**. Thus, treatment of CpW(NO)(*p*-tolyl)$_2$ generated in situ with excess S$_8$ afforded a dark red solution. Dark red crystals of complex **9** (230 mg, 45% yield) were isolated in a similar manner.

Anal. Calcd for $C_{19}H_{19}NOS_2W$: C, 43.44; H, 3.64; N, 2.67. Found; C, 43.59; H, 3.63; N, 2.74. IR (Nujol mull): 1614 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.6 (s (br), 4H, *o*-Ar *H*), 6.92 (d ($^3J_{HH}$ = 7.8 Hz), 4H, *p*-Ar *H*), 5.02 (s, 5H, C_5H_5), 2.05 (s, 6H, 2 × *Me*). Low-resolution mass spectrum (probe temperature 120 °C): *m/z* 525 [P$^+$].

Preparation of CpW(NO)(η^2-N(*p*-tolyl)C{O}-*o*-tolyl)(*o*-tolyl) (10). A sample of CpW(NO)(*o*-tolyl)$_2$ (46 mg, 0.10 mmol) in toluene (5 mL) was treated with an excess of *p*-tolyl isocyanate (25 mg, 0.18 mmol). The color of the solution changed from purple to yellow in a matter of seconds. Hexanes (5 mL) were added to the final reaction mixture, and the sample was placed in a freezer (−35 °C) overnight. A yellow microcrystalline powder of the desired complex (37 mg, 63% yield) was then isolated by decanting the supernatant solution and drying the powder in vacuo.

Anal. Calcd for $C_{27}H_{26}N_2O_2W$: C, 54.56; H, 4.41; N, 4.71. Found: C, 54.52; H, 4.54; N, 4.60. IR (Nujol mull): 1586 (s), 1573 (s), 1558 (m), 1394 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.04 (m, 1H, Ar *H*), 7.3−6.9 (m, 11H, Ar *H*), 5.81 (s, 5H, C_5H_5), 2.58 (s, 3H, *Me*), 2.34 (s, 3H, *Me*) 2.31 (s, 3H, *Me*). Low-resolution mass spectrum (probe temperature 120 °C): *m/z* 594 [P$^+$].

Reaction of Cp*W(NO)(*o*-tolyl)$_2$ with D$_2$O. A solution of Cp*W(NO)(*o*-tolyl)$_2$ (53 mg, 0.10 mmol) in C_6D_6 (0.7 mL) was treated with excess D$_2$O (0.05 mL). The solution changed color from purple to brown in a few minutes. One major Cp*-containing product was produced in 95% yield (based on integration) as judged by ^{1}H NMR spectroscopy. This product was identified as Cp*W(O)$_2$(*o*-tolyl) on the basis of its characteristic ^{1}H NMR, IR, and mass spectral data.[9]

In Situ Treatment of CpW(NO)(*p*-tolyl)$_2$ with H$_2$O. A solution of CpW(NO)(*p*-tolyl)$_2$ was generated in THF from CpW(NO)Cl$_2$ (1.0 mmol) and (*p*-tolyl)$_2$Mg·*x*(dioxane) and was treated with excess H$_2$O (0.1 mL). The solution changed in color from dark blue to brown in a few seconds. The final reaction mixture was taken to dryness in vacuo, and the residue remaining was triturated in Et$_2$O (30 mL). The resulting yellow mixture was filtered through alumina I (3 × 3 cm). The filtrate was taken to dryness under reduced pressure to obtain a light yellow powder which was identified as 4,4′-dimethylbiphenyl (30 mg, 16% yield) by its ^{1}H NMR and mass spectra: ^{1}H NMR (C_6D_6): δ 7.44 (d, 2H, Ar *H*), 7.03 (d, 2H, Ar *H*), 2.14 (s, 3H, *Me*); low-resolution mass spectrum

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(9) Legzdins, P.; Lundmark, P. J.; Phillips, E. C.; Rettig, S. J.; Veltheer, J. E. *Organometallics* **1992**, *11*, 2991.

(probe temperature 120 °C): *m/z* 182 [P$^+$]. No organometallic product was isolated.

In Situ Treatment of CpW(NO)Ph$_2$ with H$_2$O. CpW(NO)Ph$_2$ was generated in THF from CpW(NO)Cl$_2$ (1.0 mmol) and Ph$_2$Mg$\cdot x$(dioxane) and was treated with excess H$_2$O (0.1 mL). The solution changed from dark blue to green to brown in a matter of seconds. The final reaction mixture was taken to dryness in vacuo, and the residue remaining was triturated in Et$_2$O (30 mL). The resulting yellow mixture was filtered through alumina I (3 × 3 cm). The filtrate was taken to dryness under reduced pressure to obtain a light yellow powder. Its IR and mass spectra indicated the material to be CpW(O)$_2$Ph. IR (Nujol mull): 950, 904 cm^{-1}. Low-resolution mass spectrum (probe temperature 180 °C): *m/z* 358 [P$^+$].

In Situ Treatment of CpMo(NO)(*o*-tolyl)$_2$ with H$_2$O. A THF solution of CpMo(NO)(*o*-tolyl)$_2$ was generated in a manner similar to its tungsten analogue (vide supra). This solution was treated at −20 °C with excess H$_2$O (0.1 mL). The purple color characteristic of the diaryl complex quickly changed to dark red. This solution was taken to dryness in vacuo, and the residue remaining was triturated with Et$_2$O (20 mL). The resulting red mixture was filtered through Florisil (3 × 3 cm). The filtrate was taken to dryness under reduced pressure, and the residue was triturated in hexanes to obtain a dark red powder. On the basis of its IR and mass spectra, the product was identified as [CpMo(NO)(*o*-tolyl)]$_2$(μ-O). IR (Nujol mull): ν_{NO} 1622 cm^{-1} and also 813 cm^{-1}. Low-resolution mass spectrum (probe temperature 120 °C): *m/z* 580 [P$^+$]. Attempts to obtain this complex analytically pure have to date been unsuccessful.

X-ray Crystallographic Analysis of CpW(O)(N-*o*-tolyl)(*o*-tolyl) (2). A prismatic yellow crystal of **2** was mounted in a thin-walled glass capillary and was transferred to a Rigaku AFC6S diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda_{K\alpha}$ = 0.710 69 Å). Final unit-cell parameters for the complex were obtained by least-squares analysis of setting angles for 25 reflections, 25.1 ≤ 2θ ≤ 29.7°. The intensities of three standard reflections were measured every 200 reflections during the data collection. These intensities remained constant throughout, thereby indicating crystal and electronic stability; no decay correction was therefore applied. The data were corrected for Lorentz and polarization effects and for absorption using the azimuthal scan method.[10] Pertinent crystallographic and experimental parameters for the complex are summarized in Table 1.

Interpretation of the Patterson function yielded the coordinates of the heaviest atoms in the structure, and the full structure of the compound was then derived by conventional electron-density methods and was refined by full-matrix least-squares methods on *F*, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o)^2$. Hydrogen atoms were fixed in calculated positions with C−H = 0.98 Å and $U_H = 1.2U_{\text{bonded atom}}$. Non-hydrogen atoms were refined with anisotropic thermal parameters. A correction for secondary extinction was applied, the final value of the extinction coefficient being 1.48(6) × 10^{-7}. Complex neutral-atom scattering factors (for all atoms) and anomalous scattering corrections for the non-hydrogen atoms were taken from ref 11. Final positional and equivalent isotropic thermal parameters for the complex are given in Table 2, and selected bond lengths (Å) and bond angles (deg) are listed in Table 3. A view of the solid-state molecular structure of complex **2** is displayed in Figure 2.

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

compd	**2**[b]	**1**[c]
formula	C$_{19}$H$_{19}$NOW	C$_{19}$H$_{19}$NOW
fw	461.22	461.22
temp, K	294	205
color, habit	yellow, prism	purple, octagonal
cryst size, mm	0.06 × 0.15 × 0.32	0.09 × 0.21 × 0.23
cryst system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a, Å	13.509(3)	9.636(2)
b, Å	7.003(3)	14.634(2)
c, Å	18.436(3)	12.347(3)
β, deg	107.24(1)	107.72(2)
V, Å^3	1666(1)	1658.5
Z	4	4
ρ_{calc}, g/cm^3	1.839	1.847
F(000)	883.81	883.81
μ(Mo K_α), cm^{-1}	70.82	71.10
transm factors (relative)	0.65−1.00	0.233−0.549
scan type	$\omega-2\theta$	$\omega-2\theta$
scan range, deg in ω	1.31 + 0.35 tan θ	0.9 + 0.35 tan θ
scan rate, deg/min	32	0.82−3.3
data collcd	$+h,+k,\pm l$	$\pm h,+k,+l$
$2\theta_{max}$, deg	60	48
cryst decay, %	0	negligible
tot. reflcns	5238	2575
obsd reflcns	2539	2075
R	0.030	0.022
R_w	0.029	0.026
gof	1.21	1.188
max Δ/σ (final cycle)	0.03	0.02
resid density, e/Å^3	−0.84 to 0.65 (near W)	−0.62(11) to 0.76(11)[d]

[a] Function minimized $\Sigma w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$, and gof $= [\Sigma w(|F_o| - |F_c|)^2/(m-n)]^{1/2}$. Values given for *R*, R_w, and gof are based on those reflections with $I \geq 3\sigma(I)$ for complex **2** and $I \geq 2.5\sigma(I)$ for complex **1**. For complex **1**, $w = [\sigma(F_o)^2 + 0.0002F_o^2]^{-1}$. [b] Rigaku AFC6S diffractometer, Mo Kα radiation (λ = 0.710 69 Å), graphite monochromator, takeoff angle 6.0°, aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1, up to 8 rescans), $\sigma^2(F^2) = [S^2(C + 4B)]/Lp^2$ (*S* = scan rate, *C* = scan count, *B* = normalized background count). [c] Enraf Nonius CAD4F diffractometer. [d] 0.93 Å from W.

Table 2. Final Positional and Equivalent Isotropic Thermal Parameters (Å^2) for CpW(O)(N-*o*-tolyl)(*o*-tolyl) (2)

atom	*x*	*y*	*z*	B_{eq}[a]
W(1)	0.49362(2)	0.51470(3)	0.13169(1)	2.867(9)
O(1)	0.4942(4)	0.7486(6)	0.1018(3)	4.4(2)
N(1)	0.3814(4)	0.4067(8)	0.0713(3)	3.4(2)
C(1)	0.6789(5)	0.497(1)	0.1490(4)	5.0(3)
C(2)	0.6262(5)	0.348(1)	0.1017(4)	4.5(3)
C(3)	0.5903(5)	0.218(1)	0.1477(4)	4.2(3)
C(4)	0.6145(5)	0.295(1)	0.2206(4)	4.0(3)
C(5)	0.6705(5)	0.465(1)	0.220(4)	4.3(3)
C(6)	0.4339(5)	0.5353(8)	0.2276(3)	3.4(2)
C(7)	0.4537(6)	0.684(1)	0.2806(4)	5.0(3)
C(8)	0.4073(7)	0.683(1)	0.3404(4)	5.3(4)
C(9)	0.3472(7)	0.533(1)	0.3488(4)	5.9(4)
C(10)	0.3261(6)	0.387(1)	0.2976(5)	5.7(4)
C(11)	0.3703(6)	0.385(1)	0.2391(4)	4.5(3)
C(12)	0.2954(5)	0.318(1)	0.0232(3)	3.5(3)
C(13)	0.2015(6)	0.407(1)	0.0050(4)	4.3(3)
C(14)	0.1157(6)	0.316(1)	−0.0441(4)	5.5(4)
C(15)	0.1263(7)	0.141(2)	−0.0745(5)	6.1(4)
C(16)	0.2222(8)	0.054(1)	−0.0571(5)	6.4(4)
C(17)	0.3068(6)	0.137(1)	−0.075(4)	5.1(4)
C(18)	0.5182(8)	0.852(1)	0.2750(5)	7.3(5)
C(19)	0.1898(6)	0.594(1)	0.0367(5)	6.2(4)

[a] $B_{eq} = (8/3)\pi^2\Sigma\Sigma U_{ij}a_i^*a_j^*(a_ia_j)$.

X-ray Crystallographic Analysis of CpW(NO)(*o*-tolyl)$_2$ (1). Under a dry N$_2$ atmosphere, a dark-purple-colored octagonal plate of complex **1** was cleaved, and a fragment was wedged into a glass capillary tube with a trace of fluorocarbon

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(10) TEXSAN/TEXRAY structure analysis package which includes versions of the following: MITHRIL, integrated direct methods, by C. J. Gilmore; DIRDIF, direct methods for difference structures, by P. T. Beurskens; ORFLS, full-matrix least-squares, and ORFFE, functions and errors, by W. R. Busing, K. O. Martin, and H. A. Levy; ORTEP II, illustrations, C. K. Johnson.

(11) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.

Table 3. Selected Metrical Parameters for CpW(O)(N-o-tolyl)(o-tolyl) (2)

atoms	bond length (Å)	atoms	bond angle (deg)
W(1)-O(1)	1.729(4)	O(1)-W(1)-N(1)	106.8(2)
W(1)-N(1)	1.764(5)	O(1)-W(1)-C(6)	103.6(2)
W(1)-C(6)	2.155(6)	N(1)-W(1)-C(6)	95.0(2)
N(1)-C(12)	1.382(8)	W(1)-N(1)-C(12)	178.2(5)
W(1)-CP[a]	2.119(3)		

[a] CP refers to the unweighted centroid of the cyclopentadienyl ring.

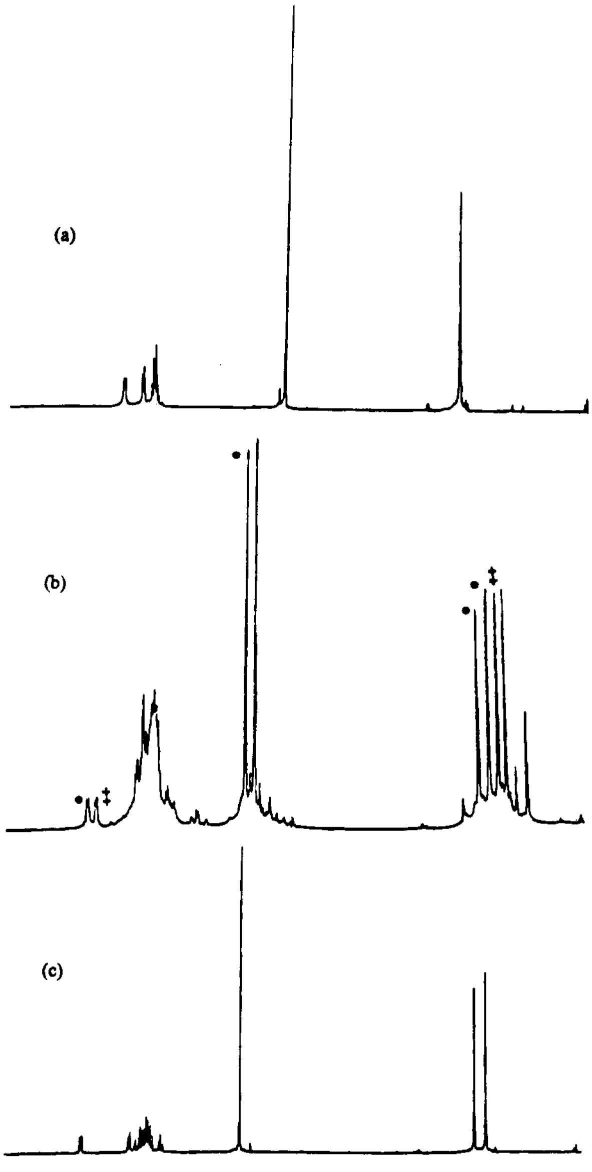

Figure 1. (a) 300 MHz ^{1}H NMR spectrum of CpW(NO)(o-tolyl)$_2$ (**1**) (C$_6$D$_6$). (b) 300 MHz ^{1}H NMR spectrum of the reaction mixture of D$_2$O and CpW(NO)(o-tolyl)$_2$ (**1**), where ● denotes CpW(O)(N-o-tolyl)(o-tolyl) (**2**) and ‡ denotes CpW(O)$_2$(o-tolyl) (**3**) (C$_6$D$_6$). (c) 300 MHz ^{1}H NMR spectrum of CpW(O)(N-o-tolyl)(o-tolyl) (**2**) (C$_6$D$_6$).

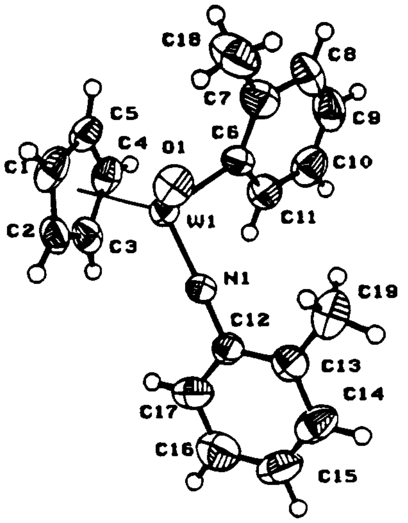

Figure 2. View of the solid-state molecular structure of complex **2**. Probability ellipsoids at the 33% level are shown.

grease as adhesive. The tube was sealed with a hot wire inside the glovebox. Data were recorded at 205 K with an Enraf Nonius CAD4F diffractometer equipped with an in-house modified low-temperature attachment and using graphite-monochromatized Mo Kα radiation. Two intensity standards were measured every 1 h of exposure time and showed intensity fluctuations of ±2% during the course of the measurements. The data were corrected for absorption by the Gaussian integration method, and corrections were carefully checked against ψ-scan measurements. Data reduction included corrections for intensity scale variation and for Lorentz and polarization effects.

Coordinates and anisotropic thermal parameters for all non-hydrogen atoms were refined. Hydrogen atoms were placed in calculated positions 0.95 Å from their respective carbon atoms and with isotropic temperature factors initially proportionate to the carbon-atom equivalent isotropic temperature factors. In subsequent cycles of refinement the coordinate shifts for the hydrogen atoms of the aryl and cyclopentadienyl rings were linked with those for their respectively bound carbon atoms. Each methyl group was refined as a rigid CH$_3$ group subject to restraints which maintained near axial symmetry for the respective CCH$_3$ fragment. Mean isotropic temperature factors were refined for each of five groups of hydrogen atoms, and the shifts were applied to the individual atomic values. An extinction parameter[12] was refined. A weighting scheme based on counting statistics was applied such that $\langle w(|F_o| - |F_c|)^2\rangle$ was nearly constant as a function of both $|F_o|$ and $(\sin\theta)/\lambda$. Final full-matrix least-squares refinement of 211 parameters for 2075 data ($I \geq 2.5\sigma(I)$) and 6 restraints converged at $R_F = 0.022$. The final maximum shift/error was 0.02. Crystallographic details are summarized in Table 1. The programs used for absorption corrections, data reduction, structure solution, refinement, and plot generation were from the NRCVAX Crystal Structure System.[13] Final refinement was made using CRYSTALS.[14] Complex scattering factors for neutral atoms[11] were used in the calculation of structure factors. Computations were carried out on MicroVAX-II and 80486 computers.

Rigid-body analysis[15] of the anisotropic thermal parameters of the molecule yielded $R_w = 0.079$ for the agreement between observed and calculated U_{ij} values with an rms discrepancy of 0.0012 Å. While there remained some significant residual observed thermal motion for a few of the cyclopentadienyl-carbon atoms and the outer carbon atoms of one of the o-tolyl groups C(21-27), further modeling of the internal motion was deemed to be unwarranted. Pertinent crystallographic and

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(14) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. CRYSTALS. Chemical Crystallography Laboratory, University of Oxford, Oxford, England, 1984.

(15) Schomaker, V.; Trueblood, K. N. *Acta Crystallogr.* **1968**, *B24*, 63.

Table 4. Final Positional and Equivalent Isotropic Thermal Parameters (Å^2) for CpW(NO)(*o*-tolyl)$_2$ (1) at 205 K

atom	x	y	z	B_{eq}[a]
W	0.316284(21)	0.185482(12)	0.026673(16)	0.0252
O	0.3351(4)	0.0619(3)	−0.1604(3)	0.0431
N	0.3288(5)	0.1179(3)	−0.0878(3)	0.0288
C(1)	0.2876(9)	0.2080(5)	0.2129(6)	0.0534
C(2)	0.1763(9)	0.1503(5)	0.1493(6)	0.0532
C(3)	0.2410(7)	0.0710(4)	0.1277(5)	0.0487
C(4)	0.3924(8)	0.0791(4)	0.1690(5)	0.0463
C(5)	0.4208(9)	0.1636(5)	0.2250(5)	0.0524
C(11)	0.1194(6)	0.2540(4)	−0.0710(4)	0.0315
C(12)	0.0028(6)	0.2169(3)	−0.1569(5)	0.0362
C(13)	−0.1053(6)	0.2748(4)	−0.2231(5)	0.0397
C(14)	−0.1002(6)	0.3681(4)	−0.2051(5)	0.0443
C(15)	0.0106(6)	0.4047(4)	−0.1189(6)	0.0450
C(16)	0.1158(6)	0.3471(4)	−0.0522(5)	0.0389
C(17)	−0.0093(7)	0.1157(3)	−0.1824(6)	0.0510
C(21)	0.5091(6)	0.2624(3)	0.0477(4)	0.0306
C(22)	0.6245(6)	0.2477(3)	0.0031(4)	0.0345
C(23)	0.7177(7)	0.3201(4)	−0.0011(5)	0.0453
C(24)	0.6989(8)	0.4046(5)	0.0378(6)	0.0512
C(25)	0.5936(8)	0.4197(4)	0.0892(6)	0.0497
C(26)	0.5020(6)	0.3487(4)	0.0968(5)	0.0372
C(27)	0.6547(7)	0.1556(4)	−0.0402(5)	0.0477

[a] B_{eq} is the cube root of the product of the principle axes of the thermal ellipsoid.

Table 5. Selected Metrical Parameters for CpW(NO)(*o*-tolyl)$_2$ (1) at 205 K

atoms	bond length (Å)	atoms	bond angle (deg)
W−N	1.759(4)	N−W−CP[a]	124.1
W−C(11)	2.160(5)	W−N−O	172.5(4)
W−C(21)	2.120(5)	N−W−C(11)	94.35(19)
W−CP[a]	2.030	N−W−C(21)	97.20(21)
N−O	1.229(6)	C(11)−W−C(21)	114.20(20)

[a] CP refers to the unweighted centroid of the cyclopentadienyl ring.

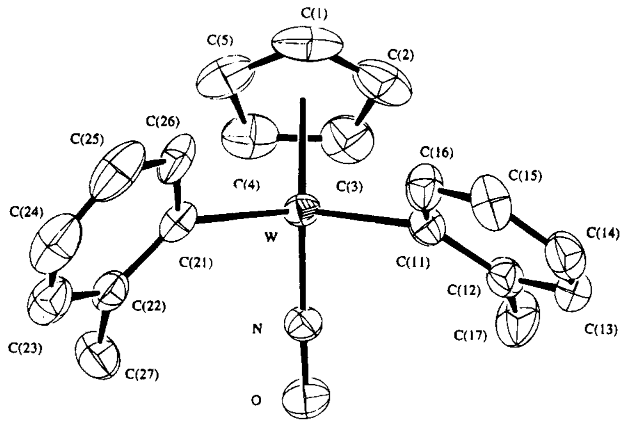

Figure 3. View of the solid-state molecular structure of complex **1**. Probability ellipsoids at the 50% level are shown.

experimental parameters for the complex are summarized in Table 1. Final positional and equivalent isotropic thermal parameters for the complex are given in Table 4, and selected bond lengths (Å) and bond angles (deg) are listed in Table 5. A view of the solid-state molecular structure of complex **1** is displayed in Figure 3.

Results and Discussion

Nitrosyl N−O Bond Cleavage. The cleavage of nitric oxide may be effected in the condensed phase, and this process has been viewed as a model for the catalytic degradation of nitrogen oxides.[16] The cleavage of bound nitric oxide (i.e. a nitrosyl ligand) can be viewed as a crude modeling of the crucial step in this process and is a fundamental transformation of interest in its own right since it permits the utilization of NO as a source of nitrogen and oxygen atoms in transition-metal chemistry. There have been several examples of nitrosyl-ligand N−O bond cleavage reported which involve the photolysis[17] or thermolysis[18] of mixtures of organometallic complexes to obtain mixed-metal nitrido cluster complexes. In addition, NO cleavage reactions involving metal cluster compounds are well-known.[19] Furthermore, there have been reports of the Lewis acid-induced conversion of a terminal nitrosyl ligand into terminal oxo and nitrido linkages, a process which has been termed intramolecular redox isomerization.[20] It has also been reported that nitric oxide can be used as a source of oxo ligands in an *intermolecular* fashion.[21] Very recently, Cummins and co-workers effected the synthesis of terminal chromium(VI) nitrido complexes, (RR′N)$_3$Cr≡N, via deoxygenation of the precursor nitrosyl complex, (RR′N)$_3$Cr(NO), using (THF)V(Mes)$_3$ as the oxygen-atom acceptor.[22] Finally, tandem mass spectrometry has demonstrated that $Cp_2Fe_2(NO)^+$ undergoes N−O bond cleavage, the resulting fragments being pyridine and $CpFe_2O^+$.[23]

In contrast to the examples of nitrosyl N−O cleavage mentioned in the preceding paragraph, the transformation depicted in eq 1 in the Introduction is quite intriguing since it involves the inducement of such cleavage by water. Of particular interest is the specific nature of conversion 1, namely, the following: (a) Is the isomerization of **1** to **2** an intermolecular or an intramolecular process? (b) What role does the H_2O play in this isomerization and what other agents induce this reactivity? (c) What other complexes containing an NO ligand may be induced to undergo this isomerization? We have endeavored to answer these questions by studying the characteristic chemistry of CpW(NO)(*o*-tolyl)$_2$ and some of its analogues with a variety of reagents. The closest analogues to **1** are those containing a different Cp′ ligand, a different metal center, or different aryl groups. The reactions of some of these analogues of **1** with H_2O have been investigated to determine the generality of conversion 1. Furthermore, the characteristic chemistry of **1** has been investigated to elucidate whether its reactivity with other reagents does or does not parallel that of other related diaryl and dialkyl systems. It should be emphasized here that complex **1** (the only member of the class of molecules CpM(NO)(aryl)$_2$ (M = Mo or W) that has been isolated to date) is quite difficult to handle due to its hydrolytic and thermal instability in solution and that the isolation

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(16) See, for example: (a) Gland, J. L.; Sexton, B. A. *Surf. Sci.* **1980**, *94*, 355. (b) Villarubia, J. S.; Ho, W. *J. Chem. Phys.* **1987**, *87*, 750.

(17) (a) Gibson, C. P.; Dahl, L. F. *Organometallics* **1988**, *7*, 543. (b) Gibson, C. P.; Bern, D. S.; Falloon, S. B.; Hitchens, T. K.; Cortopassi, J. E. *Organometallics* **1992**, *11*, 1742.

(18) Feasey, N. D.; Knox, S. A. R. *J. Chem. Soc., Chem. Commun.* **1982**, 1063.

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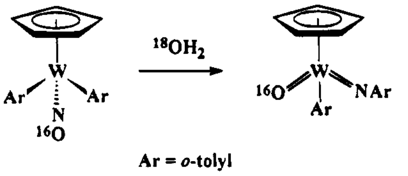
(21) The mechanism of this conversion is unclear and the fate of nitrogen of the nitric oxide has not been determined; see: Alt, H. G.; Hayen, H. I. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 497.

(22) Odom, A. L.; Cummins, C. C.; Protasiewicz, J. D. *J. Am. Chem. Soc.* **1995**, *117*, 6613.

(23) Schröder, D.; Müller, J.; Schwarz, H. *Organometallics* **1993**, *12*, 1972.

of some derivatives of **1** has been precluded by their extreme sensitivity.

Intramolecular Water-Induced N–O Bond Cleavage. The first question that is raised by the isomerization of **1** to **2** is whether the oxo ligand of **2** is the result of intramolecular cleavage of the nitrosyl ligand of **1** or intermolecular transfer from the water reactant. This point can be addressed by treating complex **1** with $^{18}OH_2$. The final reaction mixture is worked up in a manner similar to that outlined in the Experimental Section for complex **2**. The mass spectrometric characterization of this product reveals an isotopic envelope centered at m/z 461 which is identical to that obtained from treatment of **1** with nonlabeled water. The observed result thus indicates that the imido *and* oxo ligands of complex **2** have their origins in the initial nitrosyl ligand and that the isomerization of **1** to **2** probably occurs intramolecularly (eq 2).



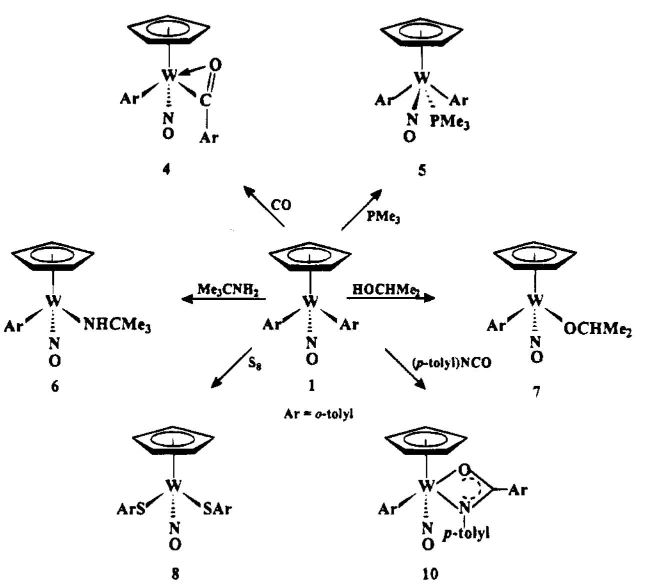
(2)

Treatment of complex **1** with D_2O affords results similar to those obtained with H_2O and $^{18}OH_2$. Monitoring of the reaction of complex **1** in C_6D_6 with approximately 1 equiv of D_2O by ^1H NMR spectroscopy (Figure 1) reveals that **1** is converted to complexes **2** and **3** in the approximate ratio of 1:1. Similar product ratios are obtained from similar treatment of **1** in C_6D_6 with H_2O and $^{18}OH_2$.[24] The results of the ^1H NMR spectroscopic and mass spectrometric investigations therefore indicate that the formation of **2** and **3** takes place via independent pathways.

Characteristic Chemistry of Complex 1. Complex **1** exhibits reactivity toward several classes of reagents among which are included Lewis acids and bases, Brønsted acids, and electrophiles (Scheme 1). The chemistry involved generally resembles that observed for other Cp'W(NO)R$_2$ systems such as CpW(NO)(CH$_2$SiMe$_3$)$_2$.[25]

(A) Reactivity toward Lewis Bases. One possible function of the water in inducing transformation 1 may involve initial coordination as a Lewis base to the metal center. If so, other Lewis bases may also serve to induce this isomerization. However, the reaction of **1** with CO, a typical Lewis base, produces a monoinserted 18-valence-electron acyl–aryl complex, **4**. This complex is similar to the products obtained from the insertion of CO into related dialkyl[26] and diaryl[5] complexes. This insertion of CO into an M–C$_{aryl}$ bond of complex **1** is more facile than for some analogous dialkyl complexes as evidenced by the much shorter reaction times for the aryl system. This difference in reactivity indicates that the metal center of **1** is more accessible and/or the metal center of **1** is a more potent Lewis acid than that in the related dialkyl complexes.[27] Complex **1** also reacts with PMe$_3$, another typical Lewis base, at room temperature to afford the 1:1 PMe$_3$ adduct, **5**. Similar adducts of PMe$_3$ with Cp*-containing diaryls have been previously reported.[5] Complex **5** is formulated as the four-legged piano-stool adduct containing a terminal nitrosyl ligand on the basis of its ^1H NMR and IR spectra (e.g. ν_{NO} (Nujol mull): 1587 cm^{-1}). Its ^1H NMR spectrum (see Experimental Section) also indicates that this adduct exists as a 60:40 mixture of isomers in solution. Like other adducts of this type,[26] **5** is probably the trans isomer with the Lewis base trans to the nitrosyl ligand in the metal's coordination sphere, and the isomers in solution are the rotamers resulting from hindered rotation about the two W–*o*-tolyl bonds. Attempts to induce the thermal isomerization of **5** to its imido oxo isomer by warming benzene solutions of **5** simply result in its thermal decomposition to an intractable mixture. Furthermore, when solutions of complex **1** in a variety of solvents (e.g. C_6D_6, CDCl$_3$, and THF-d_8) are allowed to decompose thermally at room temperatures in the absence of a trapping agent, the ^1H NMR spectra of the final solutions exhibit a large number of peaks attributable to Cp resonances, thereby indicating that many products are formed.

Scheme 1



(B) Reactivity toward RNH$_2$ and R'OH. It is possible that the reactivity of a Brønsted acid such as *tert*-butylamine with complex **1** may parallel that exhibited by water. At room temperature there is no initial adduct formation between the amine and the complex as determined by IR spectroscopy. Consistently, the color of the reaction mixture does not change from the initial purple color upon addition of the amine. However, the reaction mixture does change to yellow when cooled to approximately −50 °C, a feature consistent with adduct formation occurring only at low temperatures. Stirring of the reaction solution at room temperature for 2 days and then cooling to −30 °C results in the deposition of CpW(NO)(*o*-tolyl)(NHCMe$_3$) (**6**) as an orange solid. The ^1H NMR spectrum of **6**

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[24] The fact that the ^{18}O label ends up in **3** after this reaction is not conclusive by itself since we have established previously that such Cp'M(O)$_2$R (M = Mo, W) complexes are prone to undergo oxygen-atom exchange processes; see, Legzdins, P.; Phillips, E. C.; Sánchez, L. Organometallics **1989**, *8*, 940.

[25] Legzdins, P.; Rettig, S. J.; Sánchez, L. *Organometallics* **1988**, *7*, 2394.

[26] Dryden, N. H.; Legzdins, P.; Lundmark, P. J.; Riesen, A.; Einstein, F. W. B. *Organometallics* **1993**, *12*, 2085.

[27] A discussion of the steric and electronic factors operative in complexes of this type has appeared; see: Legzdins, P.; Veltheer, J. E. *Acc. Chem. Res.* **1993**, *26*, 41.

indicates that it exists as two isomers in solution which are most likely rotational isomers resulting from restricted rotation about the W−N multiple bond, a phenomenon previously noted for similar complexes.[28] Complex **6** may result from protonolysis of a W−aryl bond in **1** by the amine.

Complex **1** also reacts with 2-propanol, a protic acid having a pK_a similar to H_2O.[29] Again, however, this reagent does not induce the isomerization conversion 1 but rather forms the alkoxo aryl complex, CpW(NO)(*o*-tolyl)($OCHMe_2$) (**7**). This conversion again most likely involves protonolysis of the aryl ligand; similar reactions with analogous Cp* complexes proceed more slowly and also result in the formation of alkoxo complexes.[30] In summary, the reactions of **1** with reagents that have Lewis basic and weakly Brønsted acidic properties do not result in the isomerization of **1** to **2**.

(C) Other Reactivity of Complex 1. Complex **1** also exhibits reactivity toward elemental sulfur and *p*-tolyl isocyanate. These reactions (Scheme 1) provide the products expected on the basis of comparisons with related dialkyl or diaryl systems. Treatment of **1** with elemental sulfur provides the dithiolate complex, CpW(NO)(S-*o*-tolyl)$_2$ (**8**). Once again, this reaction is much more facile than that for the dialkyl systems. For example, when CpW(NO)(CH_2SiMe_3)$_2$ is treated with elemental sulfur, it proceeds through several isolable intermediates, namely CpW(NO)(SCH_2SiMe_3)(CH_2SiMe_3) and CpW(NO)(η^2-$S_2CH_2SiMe_3$)(CH_2SiMe_3).[31] However, complex **1** reacts with sulfur in less than 1 min at ambient temperatures to produce the dithiolate complex. This facile insertion of elemental sulfur appears to be a simple alkyl vs aryl dependence as evidenced by the fact that CpW(NO)(*p*-tolyl)$_2$ also reacts rapidly with elemental sulfur to form CpW(NO)(S-*p*-tolyl)$_2$ (**9**).

Complex **1** also reacts with *p*-tolyl isocyanate to give CpW(NO)(η^2-N(*p*-tolyl)C{O}-*o*-tolyl)(*o*-tolyl) (**10**). Again, this is the product expected on the basis of the reactivity found for the analogous Cp* systems.[32] Reactions of complex **1** with other heterocumulenes such as CO_2 and CS_2 do not result in any isolable products. These reactions (especially the CO_2 reaction) are slower than that of the isocyanate reaction, and thus the thermal decomposition of **1** and not the insertion of the heterocumulene into a W−C bond is the dominant process.

In summary, the characteristic chemistry of **1** parallels that established for the well-studied dialkyl systems with the exception that the diaryl systems undergo qualitatively more facile reactions. If, however, a reaction does not proceed rapidly (i.e. in a matter of minutes), then the thermal decomposition of complex **1** becomes the dominant process.

Reactivity of Analogues of CpW(NO)(*o*-tolyl)$_2$ with H_2O/D_2O. Since no other species besides water could be found to promote the isomerization outlined in eq 1, it became of interest to us to determine the generality of the water-induced isomerization in terms of the organometallic reactant. The closest analogues to **1** are found by (1) changing the nature of the cyclopentadienyl ligand, (2) changing the metal to another group 6 metal, and (3) changing the nature of the aryl ligands.

To investigate the dependence of this conversion on the Cp′ group, the reactivity of Cp*W(NO)(*o*-tolyl)$_2$ with D_2O was examined. Monitoring of this reaction by ^1H NMR spectroscopy reveals one major Cp*-containing product in approximately 90% yield (based on integration). This peak, along with other resonances further downfield, is attributable to the dioxo complex, Cp*W(O)$_2$(*o*-tolyl) (eq 3). Consistently, the EI mass spectrum

$$\text{Cp*W(NO)(}o\text{-tolyl)}_2 \xrightarrow{\text{xs } D_2O} \text{Cp*W(O)}_2(o\text{-tolyl}) \quad (3)$$

of the powder resulting from this reaction reveals a parent envelope centered at *m/z* 442 assignable to Cp*W(O)$_2$(*o*-tolyl). It thus appears that isomerization 1 is dependent on the nature of the cyclopentadienyl ligand such that upon changing this ligand from Cp to Cp* the isomerization does not take place.

A solution of the molybdenum analogue of **1**, CpMo(NO)(*o*-tolyl)$_2$, can be generated in THF at low temperatures. This complex has eluded isolation, but solutions of CpMo(NO)(*o*-tolyl)$_2$ can be generated that exhibit IR properties (ν_{NO} 1624 cm^{-1}) and color (purple) that are consistent with this formulation. Attempts to isolate this complex by cooling solutions containing it result in the deposition of a brown, intractable solid. When the solutions of CpMo(NO)(*o*-tolyl)$_2$ generated in situ are treated with H_2O, workup provides a dark red powder which is identified as [CpMo(NO)(*o*-tolyl)]$_2$-μ-O (eq 4). This finding is not surprising considering that similar molybdenum dialkyl and diaryl complexes generally react with water to form similar bridging oxo complexes.[9]

$$\text{CpMo(NO)(o-tolyl)}_2 \xrightarrow{\text{xs } H_2O} [\text{CpMo(NO)(o-tolyl)}]_2\text{-}\mu\text{-O} \quad (4)$$

The dependence of the isomerization of **1** to **2** on the nature of the aryl ligands can be investigated by preparing solutions of CpW(NO)Ph$_2$ (ν_{NO} 1601 cm^{-1}) and CpW(NO)(*p*-tolyl)$_2$ (ν_{NO} 1599 cm^{-1}) and treating them with H_2O. When CpW(NO)(*p*-tolyl)$_2$ is treated with H_2O, an immediate reaction takes place, but the only product isolable is 4,4′-dimethylbiphenyl. This organic product is most likely the result of reductive elimination of the aryl groups from the metal center. This type of reactivity has been observed during the thermolysis of a related arylnitrosylruthenium compound, Cp*Ru(NO)Ph$_2$.[33] The reaction of CpW(NO)Ph$_2$ with H_2O provides the corresponding dioxo complex CpW(O)$_2$Ph. Again, in these cases there is no evidence for the isomerization of these diaryl complexes upon changing the aryl ligands to groups other than *o*-tolyl ligands.

X-ray Crystallographic Analysis of Complex 2. The solid-state molecular structure of **2** has been established by a single-crystal X-ray crystallographic analysis, and an ORTEP plot of the structure is shown in Figure 2. The intramolecular metrical parameters of **2** (Table 3) indicate that the aryl and oxo ligands

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(28) (a) Legzdins, P.; Young, M. A.; Veltheer, J. E.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1995**, *14*, 407. (b) Legzdins, P.; Rettig, S. J.; Ross, K. J. *Organometallics* **1993**, *12*, 2103.

(29) The pK_a values of water and 2-propanol are both approximately 16. See, for example: Streitweiser, A., Jr.; Heathcock, C. H. *Introduction to Organic Chemistry*; Macmillan: New York, 1985; Chapter 10.

(30) Lundmark, P. J. Ph.D. Dissertation, University of British Columbia, 1993.

(31) See ref 25 and: Legzdins, P.; Sánchez, L. *J. Am. Chem. Soc.* **1985**, *107*, 5525.

(32) Brouwer, E. B.; Legzdins, P.; Rettig, S. J.; Ross, K. J. *Organometallics* **1993**, *12*, 4234.

(33) Chang, J.; Bergman, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4298.

function as one- and two-electron donors, respectively, to the tungsten center. Also, according to the criteria developed by Parkin and Bercaw,[34] the $\nu_{W=O}$ of 897 cm^{-1} displayed by **2** in its Nujol mull IR spectrum indicates that the tungsten–oxygen linkage is principally a double bond. The relatively short W–N bond length (1.764(5) Å) and the essentially linear W–N–C grouping (the angle at N being 178.2(5)°) is consistent with the view that this ligand formally provides four electrons to the W≡N bond.[35]

The transformation in eq 1 thus results in the conversion of the 16-valence-electron reactant to its thermodynamically more stable 18-valence-electron structural isomer. For the simplified conversion shown in eq 5, a crude thermodynamic analysis can be instructive.

$$O{=}N{-}[W]{-}R \longrightarrow O{=}[W]{=}N{-}R \qquad (5)$$

(R = *o*-tolyl; [W] = CpW(*o*-tolyl))

In complex **1**, both the M–C(aryl) and W–N bond strengths can be approximated at 210 kJ/mol,[36] while the minimum N=O bond strength can be estimated as 420 kJ/mol.[37] Little is known with regard to the strengths of transition-metal multiple bonds. However, Mayer and co-workers have estimated that the W=O and W=NR bonds are ≥577 and ≥420 kJ/mol, respectively, in complexes of the type $L_3Cl_2W{=}X$ (L = phosphine; X = O, NR).[38] Assuming these values for the W=O and W=NR bond strengths of complex **2** as well as a value of 290 kJ/mol for the N–R linkage,[29] an approximate value for ΔH of −400 kJ/mol is calculated for the conversion shown in eq 5. It thus appears that this reaction is thermodynamically driven by the propensity of the tungsten center to form strong multiple bonds with oxygen and nitrogen.

X-ray Crystallographic Analysis of Complex 1. It was also of interest to determine if the solid-state molecular structure of complex **1** could provide any insight into conversion 1. It was thought possible that some type of interaction of the *o*-methyl groups with the metal center which allows this conversion might be observed in the solid-state structure of **1**. After considerable effort, crystals of complex **1** suitable for an X-ray analysis were obtained, and the subsequently determined solid-state structure of **1** is shown in Figure 2. This structure can be compared to that of the Cp* analogue, Cp*W(NO)(*o*-tolyl)$_2$, which has been previously characterized crystallographically.[7] Somewhat disappointingly, the Cp complex, **1**, is essentially isostructural with the Cp* complex. The only major difference between the two structures is the fact that the Cp ligand is slightly further away from the metal center than is the Cp* ligand. The only feature of note in the Cp complex is that one of the W–C bonds (W–C(11) 2.160(5) Å) is slightly longer than the other (W–C(21) 2.120(5) Å). Thus, the comparison of these structures does not provide an explanation for the anomalous behavior of complex **1** with water.

Epilogue

To summarize, no complex other than CpW(NO)(*o*-tolyl)$_2$ (**1**) has been found to undergo isomerization to its arylimido oxo analogue upon treatment with water. Also, no other tested reagent induces the conversion of **1** to **2**. However, since our original communication in 1991 of this first example of N–O bond cleavage, we have discovered other systems that exhibit N–O bond cleavage.[2] These examples of nitrosyl N–O bond cleavage are quite varied both in the nature of the conditions used to promote this process and in the nature of the resulting organometallic complexes. However, attempts are being made to understand the factors involved in promoting and controlling N–O bond cleavage in these and other reactions. Many of these N–O bond cleavage reactions may be explained by the initial formation of an η^2-NO linkage which can eventually form oxo and imido/nitrido functionalities. For instance, we recently discovered a cationic nitrosyl complex that adds water to generate an η^2-hydroxylamido ligand.[39] Further studies to test the metal–η^2-NO linkage hypothesis are currently in progress.

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Supporting Information Available: Tables of hydrogen atom parameters, anisotropic thermal parameters, complete bond lengths and bond angles, torsion angles, intermolecular contacts, and least-squares planes for complexes **1** and **2** (17 pages). Ordering information is given on any current masthead page.

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[34] Parkin, G.; Bercaw, J. E. *J. Am. Chem. Soc.* **1989**, *111*, 391.

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[37] It is expected that this bond strength would be lower than the bond strength of 630 kJ/mol for NO(g); see: *Handbook of Chemistry and Physics*; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1984; p F-180.

[38] Hall, K. A.; Mayer, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 10402 and references cited therein.

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