

Facile Nitrosyl N–O Bond Cleavage upon Thermolysis of $\text{Cp}^*\text{W}(\text{NO})\text{Ph}_2^1$

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Summary: Thermolysis of $\text{Cp}^*\text{W}(\text{NO})\text{Ph}_2$ (1) in C_6H_6 at 60°C for 24 h affords the new nitrosyl N–O bond cleavage products $\text{Cp}^*\text{W}(\eta^2\text{-ONPh})(\text{NPh})\text{Ph}$ (2) and $[\text{Cp}^*\text{W}(\text{O})\text{-Ph}](\mu\text{-N})[\text{Cp}^*\text{W}(\text{NO})\text{Ph}]$ (3), as well as the known $\text{Cp}^*\text{W}(\text{O})_2\text{Ph}$ (4), in isolated yields of 10, 9, and 30%, respectively. Complex 2 has been subjected to a single-crystal X-ray crystallographic analysis. Crystals of 2 are orthorhombic, space group $Pcab$, with $a = 16.538(2)$ Å, $b = 21.803(4)$ Å, $c = 13.492(3)$ Å and $Z = 8$; the structure was solved by conventional heavy-atom methods and was refined by full-matrix least-squares procedures to $R_F = 0.026$ and $R_{wF} = 0.024$ for 2999 reflections having $I \geq 3\sigma(I)$. Also, thermolyses of $\text{Cp}^*\text{W}(\text{NO})\text{Ph}_2$ and $\text{Cp}^*\text{W}(\text{NO})(p\text{-tolyl})_2$ in the presence of PhSSPh result in quantitative conversion to $\text{Cp}^*\text{W}(\text{NO})(\text{Ar})(\text{SPh})$ ($\text{Ar} = \text{Ph}$ (5), $p\text{-tolyl}$ (6), respectively).

Introduction

The principal focus of our research during the past few years has been the development of organometallic nitrosyl complexes of the group 6 elements as unique synthetic reagents.² During these studies we have generally found that the nitrosyl ligands remain intact during the various chemical transformations involving these compounds, thereby permitting the strong π -acidity of the NO groups to be utilized for the regulation of electron density at the metal centers. Recently, however, a new type of chemical reactivity that we are encountering with increasing frequency in these systems is that of nitrosyl N–O bond cleavage under relatively mild conditions. The examples of such cleavage that we have reported to date include (a) exposure of $\text{Cp}^*\text{M}(\text{NO})\text{R}_2$ complexes ($\text{Cp}^* = \text{Cp}^*(\eta^5\text{-C}_5\text{-Me}_5)$, $\text{Cp}^*(\eta^5\text{-C}_5\text{H}_5)$; $\text{M} = \text{Mo}, \text{W}$; $\text{R} = \text{alkyl, aryl}$) to molecular oxygen,³ a process which yields $\text{Cp}^*\text{M}(\text{O})_2\text{R}$ products, and (b) the isomerization of solid $\text{Cp}^*\text{W}(\text{NO})(o\text{-tolyl})_2$ to $\text{Cp}^*\text{W}(\text{O})(\text{N}-o\text{-tolyl})(o\text{-tolyl})$, which is catalyzed by water at room temperature.⁴ In this report we describe facile thermally induced N–O bond cleavage in $\text{Cp}^*\text{W}(\text{NO})\text{Ph}_2$. Our studies of these N–O cleavage processes are designed to contribute to a better understanding of the pathways by which organotransition-metal complexes can degrade or decompose, a mechanistic area that is still relatively poorly understood.⁵

Experimental Section

All reactions and subsequent manipulations involving organometallic reagents were performed under anaerobic and anhydrous

conditions under an atmosphere of purified dinitrogen or argon.⁶ Conventional glovebox and vacuum-line Schlenk techniques were utilized throughout. General procedures routinely employed in these laboratories have been described in detail previously.⁷ Diphenyl sulfide (Aldrich) was used as received. The $\text{Cp}^*\text{W}(\text{NO})\text{Ph}_2$ and $\text{Cp}^*\text{W}(\text{NO})(p\text{-tolyl})_2$ reactants were prepared by the published procedures.⁷

Thermolysis of $\text{Cp}^*\text{W}(\text{NO})\text{Ph}_2$. A sample of $\text{Cp}^*\text{W}(\text{NO})\text{Ph}_2$ (500 mg, 1.0 mmol) was dissolved in benzene (10 mL) in a glass bomb (i.e., thick-walled glass vessel) equipped with a Kontes stopcock. The deep blue solution was subjected to two freeze-pump-thaw cycles and was then placed in an oil bath at 60°C . During the next 24 h the color of the solution darkened to brown. The final solution was taken to dryness in vacuo to obtain a dark brown oil. This oil was redissolved in a minimum of Et_2O and was loaded onto the top of an alumina I column (2×8 cm) made up in Et_2O . Elution of the column with ether resulted in the development of a yellow band which was eluted, collected, and taken to dryness in vacuo. The resulting yellow residue was crystallized from hexanes at -30°C to obtain yellow crystals (60 mg, 10% yield) of complex 2 which were isolated by cannulation.

Anal. Calcd for $\text{C}_{28}\text{H}_{30}\text{N}_2\text{O}_2\text{W}$: C, 56.58; H, 5.09; N, 4.71. Found: C, 56.20; H, 5.25; N, 4.51. IR (Nujol mull): 1588 (w), 1570 (w), 1202 (m), 1152 (m) cm^{-1} . $^1\text{H NMR}$ (C_6D_6): δ 8.08 (d, $^3J_{\text{HH}} = 7.9$ Hz, 2H, Ar H), 7.47 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H, Ar H), 7.37 (m, 2H, Ar H), 7.21 (m, 1H, Ar H), 7.09 (m, 2H, Ar H), 6.86 (m, 2H, Ar H), 6.70 (m, 1H, Ar H), 6.68 (m, 1H, Ar H), 6.14 (d, $^3J_{\text{HH}} = 8.4$ Hz, 2H, Ar H), 1.72 (s, 15H, $\text{C}_5(\text{CH}_3)_5$). Low-resolution mass spectrum (probe temperature 80°C): m/z 594 [P^+].

Further elution of the column with ether/acetone (5:1) produced a green band, which was collected. This eluate was taken to dryness in vacuo to obtain a dark green solid. This solid was crystallized from Et_2O at -30°C to obtain complex 3 as dark green microcrystals (40 mg, 9% yield), which were isolated by cannulation.

Anal. Calcd for $\text{C}_{32}\text{H}_{40}\text{N}_2\text{O}_2\text{W}_2$: C, 45.09; H, 4.73; N, 3.29. Found: C, 43.97; H, 4.68; N, 3.19. IR (Nujol mull): 1598 (s), 969 (m) cm^{-1} . $^1\text{H NMR}$ (C_6D_6): δ 7.94 (d, $^3J_{\text{HH}} = 7.8$ Hz, 2H, Ar H), 7.70 (d, $^3J_{\text{HH}} = 8.0$ Hz, 2H, Ar H), 7.35–7.15 (m, 6H, Ar H), 1.69 (s, 15H, $\text{C}_5(\text{CH}_3)_5$), 1.66 (s, 15H, $\text{C}_5(\text{CH}_3)_5$). Low-resolution mass spectrum (probe temperature 150°C): m/z 852 [P^+].

Finally, an orange band was eluted from the column with acetone. This fraction was taken to dryness under reduced pressure, and the remaining residue was recrystallized from $\text{CH}_2\text{-Cl}_2/\text{hexanes}$ at -30°C to obtain light orange crystals (130 mg, 30% yield) of $\text{Cp}^*\text{W}(\text{O})_2\text{Ph}$, which were identified by comparison of their physical and spectroscopic properties with those exhibited by an authentic sample.⁸

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Thermolysis of Cp*W(NO)Ph₂ in the Presence of PhSSPh. A sample of Cp*W(NO)Ph₂ (200 mg, 0.40 mmol) and PhSSPh (86 mg, 0.40 mmol) was dissolved in benzene (10 mL) in a glass bomb equipped with a Kontes stopcock. The deep blue solution was subjected to two freeze-pump-thaw cycles and was then placed in an oil bath at 60 °C. During the next 24 h the color of the solution changed to purple. The final solution was taken to dryness in vacuo to obtain a purple powder. This powder was dissolved in Et₂O (10 mL), and the solution was filtered through Celite (2 × 2 cm) supported on a medium-porosity frit. To the resulting purple solution was added hexanes (5 mL). Cooling of this solution to -30 °C resulted in the deposition of Cp*W(NO)(Ph)(SPh) (5) as a purple solid (150 mg, 71% yield), which was isolated by cannulating away the supernatant solution. ¹H NMR monitoring of a similarly prepared solution of the reactants in C₆D₆ showed that the conversion was quantitative (within the detection limits of the technique).

Anal. Calcd for C₂₂H₂₅NOSW: C, 49.36; H, 4.71; N, 2.62. Found: C, 49.36; H, 4.68; N, 2.49. IR (Nujol mull): 1574 (s) cm⁻¹. ¹H NMR (C₆D₆): δ 7.76 (m, 2H, Ar H), 7.72 (m, 2H, Ar H), 7.17 (m, 2H, Ar H), 7.08 (m, 1H, Ar H), 6.97 (m, 2H, Ar H), 6.81 (m, 1H, Ar H), 1.61 (s, 15H, C₅(CH₃)₅). Low-resolution mass spectrum (probe temperature 120 °C): *m/z* 535 [P⁺].

Thermolysis of Cp*W(NO)(*p*-tolyl)₂ in the Presence of PhSSPh. The thermolysis and workup procedures described above were effected similarly here. Cp*W(NO)(*p*-tolyl)(SPh) (6) was obtained from an ether/hexanes solution (1:1) as a purple solid (79% yield). Again, ¹H NMR monitoring of a similarly prepared solution in C₆D₆ showed that the conversion was quantitative (within the detection limits of the technique).

Anal. Calcd for C₂₃H₂₇NOSW: C, 50.28; H, 4.95; N, 2.55. Found: C, 50.00; H, 4.93; N, 2.53. IR (Nujol mull): 1574 (s) cm⁻¹. ¹H NMR (C₆D₆): δ 7.80 (d, 2H, Ar H), 7.71 (d, 2H, Ar H), 7.0 (m, 4H, Ar H), 6.82 (m, 1H, Ar H), 2.11 (s, 3H, ArCH₃), 1.61 (s, 15H, C₅(CH₃)₅). Low-resolution mass spectrum (probe temperature 120 °C): *m/z* 549 [P⁺].

X-Ray Crystallographic Analysis of Cp*W(NO)(η²-ON-Ph)(NPh)Ph (2). Crystallographic data appear in Table 1. The crystal employed for data collection was sealed in a thin-walled glass capillary tube. The final unit-cell parameters were obtained by least squares on the setting angles for 25 reflections with 2θ = 36.4–42.1°. The intensities of 3 standard reflections, measured every 200 reflections throughout the data collection, showed only small random fluctuations. The data were processed⁹ and corrected for Lorentz and polarization effects and absorption (empirical, based on azimuthal scans for 3 reflections).

The systematic absences uniquely indicate the space group *Pcab* (nonstandard setting of *Pbca* having equivalent positions: ±(*x*, *y*, *z*); ±(*x*, 1/2 - *y*, 1/2 + *z*); ±(1/2 + *x*, -*y*, 1/2 - *z*); ±(1/2 - *x*, 1/2 + *y*, -*z*)). The structure was solved by conventional heavy-atom methods, the coordinates of the W atom being determined from the Patterson function and those of the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were fixed in calculated positions (methyl group orientations based on difference map peaks, C-H = 0.98 Å, B_H = 1.2B_{bonded atom}). A Zachariasen type 2 isotropic secondary extinction correction was applied, the final value of the extinction coefficient being [3.2(2)] × 10⁻⁸. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 10. Final atomic coordinates and equivalent isotropic thermal parameters and selected bond lengths and bond angles appear

(9) 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.

(10) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K. (present distributor Kluwer Academic Publishers: Boston, MA), 1974; Vol. IV, pp 99–102, 149.

Table 1. Crystallographic Data for Cp*W(NO)(η²-ONPh)(NPh)Ph (2)*

compd	2
formula	C ₂₈ H ₃₀ N ₂ OW
fw	594.41
color, habit	yellow, prism
cryst size, mm	0.20 × 0.25 × 0.45
cryst syst	orthorhombic
space group	<i>Pcab</i> (No. 62)
<i>a</i> , Å	16.538(2)
<i>b</i> , Å	21.803(4)
<i>c</i> , Å	13.492(3)
<i>V</i> , Å ³	4865(1)
<i>Z</i>	8
<i>ρ</i> _{calc} , g/cm ³	1.623
<i>F</i> (000)	2352
μ(Mo Kα), cm ⁻¹	48.70
transmiss factors (relative)	0.61–1.00
scan type	ω-2θ
scan range, deg in ω	1.10 + 0.35 tan θ
scan rate, deg/min	32
data collected	+ <i>h</i> , + <i>k</i> , + <i>l</i>
2θ _{max} , deg	55.0
cryst decay, %	negligible
total no. of unique rflns	6195
no. of rflns with <i>I</i> ≥ 3σ(<i>I</i>)	2999
no. of variables	290
<i>R</i>	0.026
<i>R</i> _w	0.024
GOF	1.39
max Δ/σ (final cycle)	0.03
residual density, e/Å ³	-0.44 to +0.49 (near W)

* Conditions and definitions: temperature 294 K, 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), σ²(*F*²) = [S²(*C* + 4*B*)]/L*p*² (*S* = scan rate, *C* = scan count, *B* = normalized background count, function minimized Σw(|*F*_o - |*F*_c||², where w = 4*F*_o²/σ²(*F*_o²), *R* = Σ||*F*_o - |*F*_c||/Σ|*F*_o|, *R*_w = (Σw(|*F*_o - |*F*_c||²)/Σw|*F*_o|²)^{1/2}, and GOF = [Σw(|*F*_o - |*F*_c||²)/(*m* - *n*)]^{1/2}. Values given for *R*, *R*_w, and GOF are based on those reflections with *I* ≥ 3σ(*I*).

in Tables 2 and 3, respectively. A view of the solid-state molecular structure of complex 2 is displayed in Figure 1.

Results and Discussion

During the course of investigating the insertion of various heterocumulenes into the M-C σ bonds of Cp*M(NO)-(aryl)₂ complexes, we found that the reaction of Cp*W(NO)Ph₂ with CO₂ (1 atm) at 60 °C produced the expected insertion product Cp*W(NO)(η²-O₂CPh)Ph, but in low yield.¹¹ This low yield was attributed, in part, to the concomitant thermal decomposition of Cp*W(NO)Ph₂ at the moderate temperatures required to produce the inserted complex. Consistent with this view was the fact that a CO₂-free product, namely Cp*W(η²-ONPh)(NPh)-Ph (2), was also isolated in low yield from this reaction. It thus became of interest to us to determine the thermolytic properties of Cp*W(NO)Ph₂ in the absence of CO₂ in order to better understand the origins of complex 2.

In general, we have not been able to obtain tractable products from the thermolysis of a variety of dialkyl complexes, Cp*M(NO)(alkyl)₂. An exception to this generalization is the room-temperature thermolysis of CpMo(NO)(CH₂CMe₃)₂, which results in the formation of the unusual dimer [CpMo(NO)](μ-η¹:η²-NO)(μ-CHCMe₃)-

(11) Brouwer, E. B.; Legzdins, P.; Rettig, S. J.; Ross, K. J. *Organometallics* 1993, 11, 4234.

Table 2. Final Positional and Equivalent Isotropic Thermal Parameters (\AA^2) for $\text{Cp}^*\text{W}(\text{NO})(\eta^2\text{-ONPh})(\text{NPh})\text{Ph}$ (**2**)

atom	x	y	z	B_{eq}^a
W(1)	0.35446(1)	0.36028(1)	0.38365(1)	2.426(8)
O(1)	0.3803(2)	0.3068(2)	0.2699(3)	3.4(2)
N(1)	0.4550(3)	0.3303(2)	0.3076(3)	3.2(2)
N(2)	0.3484(3)	0.4378(2)	0.3485(3)	2.8(2)
C(1)	0.3159(4)	0.3709(3)	0.5505(4)	2.8(3)
C(2)	0.4006(4)	0.3790(3)	0.5469(4)	3.1(3)
C(3)	0.4352(4)	0.3218(3)	0.5195(4)	3.3(3)
C(4)	0.3716(4)	0.2785(3)	0.5071(4)	3.2(3)
C(5)	0.2974(3)	0.3091(3)	0.5284(4)	2.9(3)
C(6)	0.2550(4)	0.4159(3)	0.5887(4)	4.1(3)
C(7)	0.4472(4)	0.4351(3)	0.5717(5)	4.9(4)
C(8)	0.5238(4)	0.3053(4)	0.5135(5)	5.1(4)
C(9)	0.3813(4)	0.2124(3)	0.4777(5)	4.9(4)
C(10)	0.2159(4)	0.2792(3)	0.5397(4)	4.0(3)
C(11)	0.2324(3)	0.3390(3)	0.3359(4)	2.7(3)
C(12)	0.2119(4)	0.2811(3)	0.2984(4)	3.9(3)
C(13)	0.1321(4)	0.2673(3)	0.2713(4)	4.5(4)
C(14)	0.0738(4)	0.3108(4)	0.2811(5)	5.3(4)
C(15)	0.0931(4)	0.3680(4)	0.3143(5)	4.3(4)
C(16)	0.1709(3)	0.3814(3)	0.3426(5)	3.6(3)
C(17)	0.4913(3)	0.3723(3)	0.2388(4)	3.1(3)
C(18)	0.5574(4)	0.4069(3)	0.2737(5)	4.6(4)
C(19)	0.5962(4)	0.4450(4)	0.2098(6)	5.7(4)
C(20)	0.5733(4)	0.4502(3)	0.1132(6)	5.3(4)
C(21)	0.5093(4)	0.4158(3)	0.0777(5)	4.4(3)
C(22)	0.4687(3)	0.3765(3)	0.1414(4)	3.7(3)
C(23)	0.3444(3)	0.5001(2)	0.3272(4)	3.0(3)
C(24)	0.3083(4)	0.5413(3)	0.3928(5)	4.7(3)
C(25)	0.3037(5)	0.6023(3)	0.3676(7)	5.8(4)
C(26)	0.3354(5)	0.6231(3)	0.2812(7)	6.3(5)
C(27)	0.3709(5)	0.5836(4)	0.2165(6)	5.8(4)
C(28)	0.3754(4)	0.5218(3)	0.2382(5)	4.4(3)

$$^a B_{\text{eq}} = \frac{8}{3}\pi^2 \sum U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j)$$

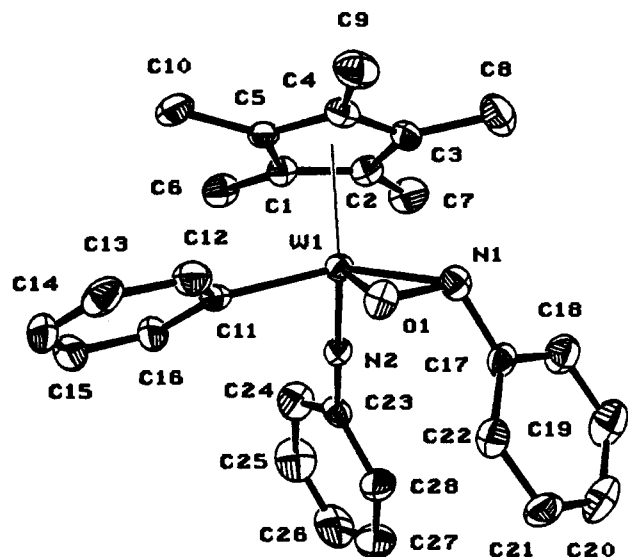
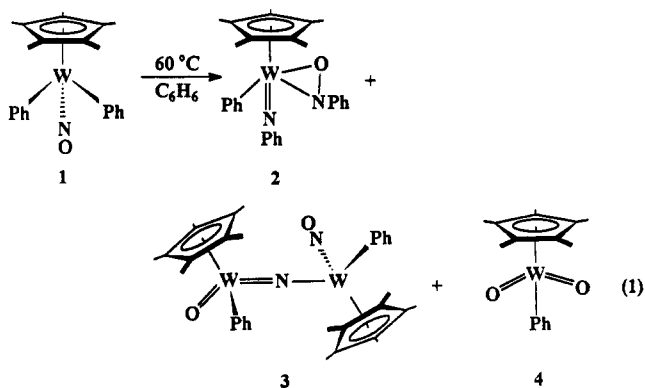
Table 3. Selected Metrical Parameters^a for $\text{Cp}^*\text{W}(\text{NO})(\eta^2\text{-ONPh})(\text{NPh})\text{Ph}$ (**2**)

atoms	bond length (\AA)	atoms	bond angles (deg)
W(1)–Cp ^b	2.08	O(1)–W(1)–N(1)	41.5(2)
W(1)–N(1)	2.060(4)	O(1)–W(1)–N(2)	111.08(2)
W(1)–N(2)	1.758(4)	W(1)–N(2)–C(23)	176.3(4)
W(1)–O(1)	1.975(4)	O(1)–N(1)–C(17)	111.0(4)
W(1)–C(11)	2.170(5)	O(1)–W(1)–C(11)	81.1(2)
N(1)–O(1)	1.432(6)	N(2)–W(1)–C(11)	94.1(2)
N(1)–C(17)	1.435(7)	N(1)–W(1)–N(2)	102.5(2)

^a Esd's in parentheses. ^b CP refers to the unweighted centroid of the cyclopentadienyl ring.

$[\text{CpMo}(\text{=CHCMe}_3)]$.¹² In this case, the most accessible pathway of thermal decomposition is α -hydrogen abstraction to generate the transient alkylidene complex $\text{CpMo}(\text{NO})(\text{=CHCMe}_3)$, which then reacts with another 1 equiv of $\text{CpMo}(\text{NO})(\text{CH}_2\text{CMe}_3)_2$ to produce the dimeric product. In contrast, we now find that the thermolysis of $\text{Cp}^*\text{W}(\text{NO})\text{Ph}_2$ at 60 °C affords three isolable products, namely complexes **2**–**4**, each of which formally results from nitrosyl N–O bond cleavage (eq 1).

Suitable crystals of **2** were obtained by cooling of a saturated benzene solution of the complex, and an X-ray crystallographic analysis was performed to establish definitively its solid-state molecular structure. An ORTEP view of complex **2** is displayed in Figure 1. The W–N(2) bond length of the imido moiety (1.758(4) \AA) falls within the range of W–N distances found for other tungsten-arylimido complexes (1.73–1.77 \AA).¹³ The tungsten–imido

**Figure 1.** Solid-state molecular structure of $\text{Cp}^*\text{W}(\text{NO})(\eta^2\text{-ONPh})(\text{NPh})\text{Ph}$ (**2**). The hydrogen atoms have been omitted for clarity.

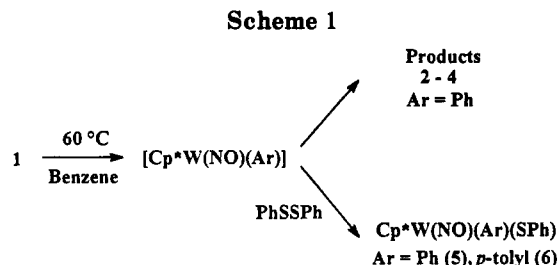
linkage is nearly linear ($\text{W}–\text{N}(1)–\text{C}(23) = 176.3(4)^\circ$), and its metrical parameters are consistent with the imido ligand functioning as a formal four-electron donor to the tungsten center. The W–N(1) bond (2.060(4) \AA) is considerably longer than the W–N(2) bond and is indicative of a bond order of 1. At 1.975(4) \AA , the W–O distance is also best characterized as a single bond. The N(1)–O bond length (1.432(6) \AA) is also consistent with the existence of a single bond, thereby indicating that the η^2 linkage to tungsten is best described as a metallaoxaziridine.¹⁴

Complex **3** must be the result of a bimolecular process which results in the formation of a nitrido bridge. This complex is formally a dimer of the $\text{Cp}^*\text{W}(\text{NO})\text{Ph}$ fragment, a fact which is consistent with the initial formation of that fragment via W–C bond homolysis. It is possible that the generation of complexes **2**–**4** proceeds through a similar $\text{Cp}^*\text{W}(\text{NO})\text{Ph}$ intermediate (Scheme 1). This intermediate may then undergo intramolecular N–O bond cleavage and be trapped by another $\text{Cp}^*\text{W}(\text{NO})\text{Ph}$ fragment to produce the bridging nitrido dimer **3**. Complexes similar to **3** have been prepared previously in our laboratories by zinc reduction of $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{CMe}_3)\text{Cl}$ and by treatment of $\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2$ with molecular H_2 to obtain complexes of the type $[\text{Cp}^*\text{M}(\text{O})\text{R}](\mu\text{-N})[\text{Cp}^*\text{M}(\text{O})\text{R}]$.

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$\text{M}(\text{NO})\text{R}]$ ($\text{R} = \text{CH}_2\text{CMe}_3, \text{CH}_2\text{SiMe}_3$), the latter having been subjected to an X-ray crystallographic analysis.¹⁵

Complex 4 is a member of a large class of dioxo compounds, $\text{Cp}^*\text{M}(\text{O})_2\text{R}$, many examples of which have been synthesized in these laboratories. These dioxo complexes are usually made by simple oxidation of the parent dialkyl or diaryl complexes (vide supra).¹⁶ However, we have also shown that treatment of the dialkyl complexes with RNO generates some of the corresponding dioxo complexes.¹⁶ Thus, the formation of complex 4 by thermolysis of the diphenyl complex is not surprising if RNO is produced by reductive elimination during the thermolysis of 1.

Our present view is that complexes 2-4 are the thermodynamically more stable products with respect to 1, which result via competing decomposition pathways originating with 1. As noted above, these pathways most likely involve initial $\text{M}-\text{C}$ bond homolysis followed by subsequent intramolecular rearrangements and trapping (Scheme 1). Evidence for the transient formation of the

$\text{Cp}^*\text{W}(\text{NO})\text{Ph}$ radical comes from the fact that when these thermolyses of $\text{Cp}^*\text{W}(\text{NO})\text{Ar}_2$ ($\text{Ar} = \text{Ph}, p\text{-tolyl}$) complexes are effected in the presence of PhSSPh , virtually quantitative yields of $\text{Cp}^*\text{W}(\text{NO})(\text{Ar})(\text{SPh})$ ($\text{Ar} = \text{Ph}$ (5), *p*-tolyl (6)) are obtained (Scheme 1). One possible rearrangement of the $\text{Cp}^*\text{W}(\text{NO})\text{Ph}$ intermediate on the way to complexes 2-4 may well involve intramolecular insertion of NO into the $\text{W}-\text{Ph}$ bond, the resulting PhNO ligand being attached to the metal center in a η^2 fashion (as eventually occurs in 2) in order to satisfy the tungsten's electronic requirements. To date we have not yet succeeded in detecting or isolating such a side-bound NO intermediate complex. Nevertheless, it is clear that the nitrosyl ligand in the reactant complex plays a pivotal and dominant role in its thermal decomposition. Thus, there is no evidence in the nitrosyl system for the formation of benzyne complexes of the type $\text{Cp}^*\text{W}(\text{NO})(\eta^2\text{-C}_6\text{H}_4)$, even though the valence-isoelectronic zirconium analogues $\text{Cp}_2\text{Zr}(\eta^2\text{-C}_6\text{H}_4)$ are the primary products formed during the similar thermolysis of Cp_2ZrPh_2 .¹⁷

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Supplementary Material Available: Tables of hydrogen atom parameters, anisotropic thermal parameters, all bond lengths and bond angles, torsion angles, intermolecular contacts, and least-squares planes for complex 2 (16 pages). Ordering information is given on any current masthead page.

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