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Facile Nitrosyl N-O Bond Cleavage upon Thermolysis of $Cp^*W(NO)Ph_2$[1]

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Summary: Thermolysis of $Cp^*W(NO)Ph_2$ (1) in C_6H_6 at 60 °C for 24 h affords the new nitrosyl N-O bond cleavage products $Cp^*W(\eta^2\text{-}ONPh)(NPh)Ph$ (2) and $[Cp^*W(O)Ph](\mu\text{-}N)[Cp^*W(NO)Ph]$ (3), as well as the known $Cp^*W(O)_2Ph$ (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 $Cp^*W(NO)Ph_2$ and $Cp^*W(NO)(p\text{-tolyl})_2$ in the presence of PhSSPh result in quantitative conversion to $Cp^*W(NO)(Ar)(SPh)$ (Ar = Ph (5), p-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 $Cp'M(NO)R_2$ complexes ($Cp' = Cp^*(\eta^5\text{-}C_5Me_5)$, $Cp(\eta^5\text{-}C_5H_5)$; M = Mo, W; R = alkyl, aryl) to molecular oxygen,[3] a process which yields $Cp'M(O)_2R$ products, and (b) the isomerization of solid $CpW(NO)(o\text{-tolyl})_2$ to $CpW(O)(N\text{-}o\text{-tolyl})(o\text{-tolyl})$, which is catalyzed by water at room temperature.[4] In this report we describe facile *thermally* induced N-O bond cleavage in $Cp^*W(NO)Ph_2$. 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 $Cp^*W(NO)Ph_2$ and $Cp^*W(NO)(p\text{-tolyl})_2$ reactants were prepared by the published procedures.[7]

Thermolysis of $Cp^*W(NO)Ph_2$. A sample of $Cp^*W(NO)Ph_2$ (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 $C_{28}H_{30}N_2OW$: C, 56.58; N, 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}. ^1H NMR (C_6D_6): δ 8.08 (d, $^3J_{HH} = 7.9$ Hz, 2H, Ar *H*), 7.47 (d, $^3J_{HH} = 8.5$ 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, $^3J_{HH} = 8.4$ Hz, 2H, Ar *H*), 1.72 (s, 15H, $C_5(CH_3)_5$). 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 $C_{32}H_{40}N_2O_2W_2$: 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}. ^1H NMR (C_6D_6): δ 7.94 (d, $^3J_{HH} = 7.8$ Hz, 2H, Ar *H*), 7.70 (d, $^3J_{HH} = 8.0$ Hz, 2H, Ar *H*), 7.35-7.15 (m, 6H, Ar *H*), 1.69 (s, 15H, $C_5(CH_3)_5$), 1.66 (s, 15H, $C_5(CH_3)_5$). 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 CH_2Cl_2/hexanes at -30 °C to obtain light orange crystals (130 mg, 30% yield) of $Cp^*W(O)_2Ph$, 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)Ph$_2$ in the Presence of PhSSPh. A sample of Cp*W(NO)Ph$_2$ (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 Et$_2$O (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. ^{1}H NMR monitoring of a similarly prepared solution of the reactants in C$_6$D$_6$ showed that the conversion was quantitative (within the detection limits of the technique).

Anal. Calcd for C$_{22}$H$_{25}$NOSW: 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}. ^{1}H NMR (C$_6$D$_6$): 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, C$_5$(C*H*$_3$)$_5$). 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, ^{1}H NMR monitoring of a similarly prepared solution in C$_6$D$_6$ showed that the conversion was quantitative (within the detection limits of the technique).

Anal. Calcd for C$_{23}$H$_{27}$NOSW: 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}. ^{1}H NMR (C$_6$D$_6$): 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, ArC*H*$_3$), 1.61 (s, 15H, C$_5$(C*H*$_3$)$_5$). Low-resolution mass spectrum (probe temperature 120 °C): *m/z* 549 [P$^+$].

X-ray Crystallographic Analysis of Cp*W(NO)(η^2-ONPh)(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 processed[9] 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: $\pm(x, y, z; -x, {}^1/_2 - y, {}^1/_2 + z; {}^1/_2 + x, -y, {}^1/_2 - z; {}^1/_2 - x, {}^1/_2 + y, -z)$). 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, $B_H = 1.2B_{\text{bonded atom}}$). A Zachariasen type 2 isotropic secondary extinction correction was applied, the final value of the extinction coefficient being $[3.2(2)] \times 10^{-8}$. 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 in Tables 2 and 3, respectively. A view of the solid-state molecular structure of complex **2** is displayed in Figure 1.

Table 1. Crystallographic Data for Cp*W(NO)(η^2-ONPh)(NPh)Ph (2)[a]

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	*Pcab* (No. 62)
a, Å	16.538(2)
b, Å	21.803(4)
c, Å	13.492(3)
V, Å^3	4865(1)
Z	8
ρ_{calc}, g/cm^3	1.623
F(000)	2352
μ(Mo Kα), cm^{-1}	48.70
transmissn 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	+*h*,+*k*,+*l*
$2\theta_{max}$, deg	55.0
cryst decay, %	negligible
total no. of unique rflns	6195
no. of rflns with $I \geq 3\sigma(I)$	2999
no. of variables	290
R	0.026
R_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)

[a] 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 backbground 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, function minimized $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, and GOF = $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$. Values given for R, R_w, and GOF are based on those reflections with $I \geq 3\sigma(I)$.

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)Ph$_2$ with CO$_2$ (1 atm) at 60 °C produced the expected insertion product Cp*W(NO)(η^2-O$_2$CPh)Ph, but in low yield.[11] This low yield was attributed, in part, to the concomitant thermal decomposition of Cp*W(NO)Ph$_2$ at the moderate temperatures required to produce the inserted complex. Consistent with this view was the fact that a CO$_2$-free product, namely CP*W(η^2-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)Ph$_2$ in the absence of CO$_2$ 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)(CH$_2$CMe$_3$)$_2$, which results in the formation of the unusual dimer [CpMo(NO)](μ-η^1:η^2-NO)(μ-CHCMe$_3$)-

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(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.

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Table 2. Final Positional and Equivalent Isotropic Thermal Parameters (Å^2) for Cp*W(NO)(η^2-ONPh)(NPh)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] $B_{eq} = {}^8/_3\pi^2\sum\sum U_{ij}a_i{}^*a_j{}^*(\mathbf{a}_i\cdot\mathbf{a}_j)$.

Table 3. Selected Metrical Parameters[a] for Cp*W(NO)(η^2-ONPh)(NPh)Ph (2)

atoms	bond length (Å)	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.

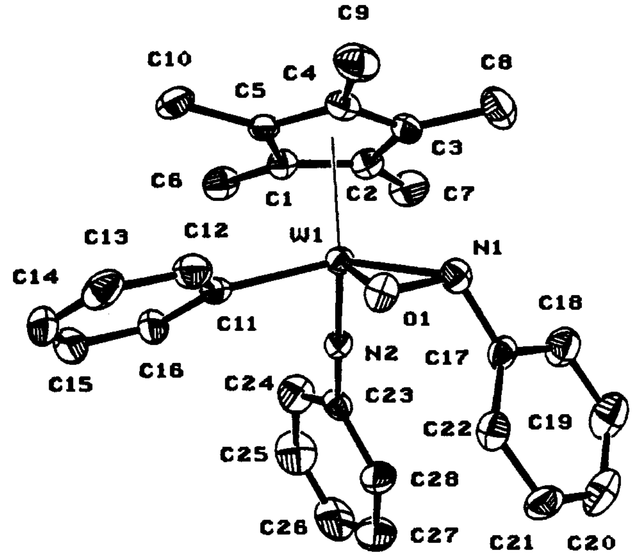
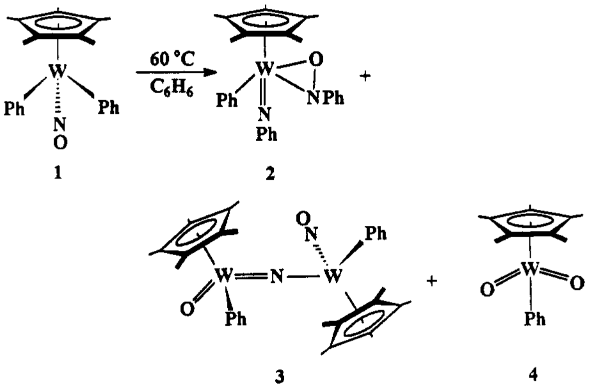


Figure 1. Solid-state molecular structure of Cp*W(NO)(η^2-ONPh)(NPh)Ph (2). The hydrogen atoms have been omitted for clarity.



(1)

[CpMo(=CHCMe$_3$)].[12] In this case, the most accessible pathway of thermal decomposition is α-hydrogen abstraction to generate the transient alkylidene complex CpMo(NO)(=CHCMe$_3$), which then reacts with another 1 equiv of CpMo(NO)(CH$_2$CMe$_3$)$_2$ to produce the dimeric product. In contrast, we now find that the thermolysis of Cp*W(NO)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) Å) falls within the range of W–N distances found for other tungsten–arylimido complexes (1.73–1.77 Å).[13] The tungsten-imido linkage is nearly linear (W–N(1)–C(23) = 176.3(4)°), 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) Å) is considerably longer than the W–N(2) bond and is indicative of a bond order of 1. At 1.975(4) Å, the W–O distance is also best characterized as a single bond. The N(1)–O bond length (1.432(6) Å) 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 Cp*W(NO)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 Cp*W(NO)Ph intermediate (Scheme 1). This intermediate may then undergo intramolecular N–O bond cleavage and be trapped by another Cp*W(NO)Ph fragment to produce the bridging nitrido dimer 3. Complexes similar to 3 have been prepared previously in our laboratories by zinc reduction of Cp*W(NO)(CH$_2$CMe$_3$)Cl and by treatment of Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$ with molecular H$_2$ to obtain complexes of the type [Cp*M(O)R](μ-N)[Cp*-

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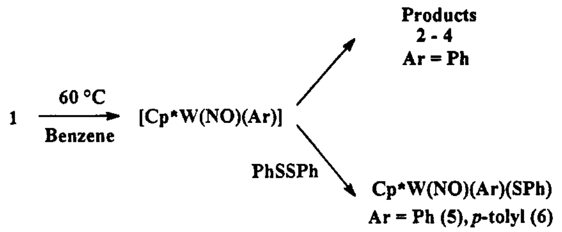
Scheme 1



M(NO)R] (R = CH_2CMe_3, CH_2SiMe_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, $Cp'M(O)_2R$, 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 M–C bond homolysis followed by subsequent intramolecular rearrangements and trapping (Scheme 1). Evidence for the transient formation of the Cp*W(NO)Ph radical comes from the fact that when these thermolyses of $Cp^*W(NO)Ar_2$ (Ar = Ph, *p*-tolyl) complexes are effected in the presence of PhSSPh, virtually quantitative yields of Cp*W(NO)(Ar)(SPh) (Ar = Ph (**5**), *p*-tolyl (**6**)) are obtained (Scheme 1). One possible rearrangement of the Cp*W(NO)Ph intermediate on the way to complexes **2**-**4** may well involve intramolecular insertion of NO into the W–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 $Cp^*W(NO)(\eta^2\text{-}C_6H_4)$, even though the valence-isoelectronic zirconium analogues $Cp_2Zr(\eta^2\text{-}C_6H_4)$ 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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