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Reaction of •NO Thiolate and Thiol Complexes: Elimination of PhSNO from W(phen)(CO)$_2$(SPh)$_2$, CO from W(phen)(CO)$_2$((−S)$_2$Arene), and HNO from W(phen)(CO)$_3$(RSH)

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Reaction of •NO with W(phen)(CO)$_2$(SPh)$_2$ (phen = 1,10-phenanthroline) results in clean conversion to W(phen)(CO)$_2$(NO)(SPh). Reduction of the W(II) bisthiolates to the W(0) nitrosyl thiolate occurs with simultaneous reductive elimination of PhS−NO, which is unstable but could be detected spectroscopically. Reaction of W(phen)(CO)$_2$(1,2-S$_2$-Arene), however, does not result in reductive elimination of either free or bound nitrosothiol. Carbon monoxide is displaced, forming W(phen)(NO)$_2$(1,2-S$_2$-Arene) (1,2-S$_2$-Arene = 1,2-benzene dithiolate or toluene-3,4-dithiolate). Complexes of butanethiol and thiophenol W(phen)(CO)$_3$(RSH) react with excess •NO to form nitrosyl thiolate complexes W(phen)(CO)$_2$(NO)(SR). These reactions also produce N$_2$O and HNO$_2$, which are attributed to decomposition of initially formed HNO. These observations indicate that •NO may be capable of direct attack on complexed thiols. Crystal structures of W(phen)(CO)$_2$(NO)(SPh) and W(phen)(NO)$_2$(toluene-3,4-dithiolate) are reported.

Introduction

Nitric oxide[1−4] is one of the most powerful π-acid ligands known. Theoretical calculation[5] of the enthalpy of dissociation of NO$^+$ from M(CO)$_5$(NO)$^+$ yielded the following M−NO$^+$ bond strengths: Cr = 105.4, Mo = 103.2, and W = 108.6 kcal/mol, exceptionally high values for a metal−ligand bond.[6] Recently we reported solution calorimetric measurements that yielded an estimated value for the dissociation of •NO from Cr(NO)(CO)$_2$C$_5$Me$_5$ of ~70 kcal/mol.[7] In contrast to its "strong" character as a ligand, nitric oxide can be characterized as a "weak" radical. Two quantitative measures of the "strength" of a radical are its enthalpies of dimerization and of combination with a hydrogen atom. The enthalpies of these reactions (kcal/mole) are summarized in terms of increasing radical strength, •NO[8] < •Cr(CO)$_3$C$_5$Me$_5$[9] < •SPh[10] < •SMe.[11]

			A =	•NO	•Cr	•SPh	•SMe	
A + A	→	A-A	ΔH =	-4	-15	-43	-63	(1)
H + A	→	H-A	ΔH =	-50	-62	-79	-89	(2)

The weak nature of stable radicals such as •NO and •Cr(CO)$_3$C$_5$Me$_5$ can be a source of net third-order reactivity, in which two moles of the radical are needed in concerted attack on a stronger bond. Reaction of thiols with the chromium radical was shown to follow net third-order reactivity[12] according to the mechanism shown in eq 3 below. The nearly zero enthalpy

$$\bullet\mathrm{Cr} + \mathrm{RSH} \rightleftharpoons \mathrm{RSH}\cdots\bullet\mathrm{Cr} + \bullet\mathrm{Cr} \rightarrow \mathrm{CrH} + \mathrm{CrSH} \tag{3}$$

of activation of this reaction shows kinetic resemblance to the well studied reaction of •NO and O$_2$ (eq 4).[13]

$$\bullet\mathrm{NO} + \mathrm{O_2} \rightleftharpoons \mathrm{ONO_2}\bullet + \bullet\mathrm{NO} \rightarrow \mathrm{ONOONO} \rightarrow 2\bullet\mathrm{NO_2} \tag{4}$$

The rate of oxidative addition of butanethiol to the chromium radical was found to be catalyzed by the complex W(phen)(CO)$_3$(BuSH) according to the mechanism shown in eq 5. It has been established that nitric oxide does not directly attack the sulfur−hydrogen bond of free thiols.[14,15] This work was begun to see if the sulfur−hydrogen bond in the complex W(phen)(CO)$_3$(BuSH) would be attacked by •NO.

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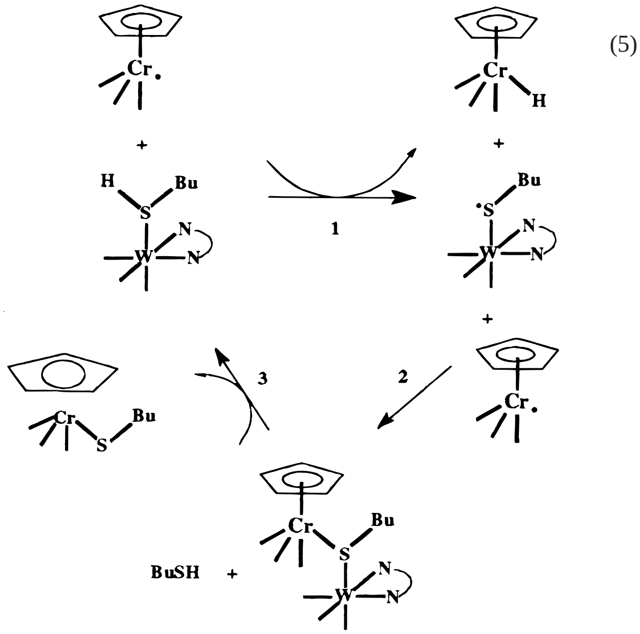


(5)

Experimental Section

General Procedures. All manipulations were carried out with rigorous exclusion of oxygen using standard inert atmosphere techniques. The complexes W(phen)$(CO)_3$(RSH),[16] W(phen)$(CO)_2(SR)_2$,[17] and W(phen)$(CO)_2$(tdt)[18] [tdt = toluene-3,4-dithiolate] were prepared by literature methods. Toluene was distilled from sodium−benzophenone ketyl under argon atmosphere into flame-dried glassware. Methylene chloride was distilled from P_2O_5 under argon. Nitric oxide (98%, Matheson Gas) was passed through KOH pellets and a cold trap (dry ice/acetone, −78 °C) to remove higher nitrogen oxides. FT-IR measurements were made on a Perkin-Elmer Spectrum 2000 FT-IR equipped with an i-series microscope. The crystal structures of W(phen)(NO) $(CO)_2$(SPh) and W(phen)$(NO)_2$(tdt) were determined at the University of Florida. Data were collected at 173 K on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator. The structures were solved by the Direct Methods in SHELXTL5 and refined using full-matrix least squares.

Reaction of Nitric Oxide and M(phen)$(CO)_2(SR)_2$ [M = Mo, W; R = tolyl, Ph]. W(phen)$(CO)_2(SPh)_2$ (36 mg, 0.056 mmol) is dissolved in 10 mL of CH_2Cl_2 in a Schlenk tube under argon. After running an initial spectrum (1944 and 1847 cm^{-1}), the atmosphere is changed to nitric oxide (6 psi), with rapid formation of W(phen)(NO) $(CO)_2$(SPh) as seen by FT-IR with PhSNO at 1560 cm^{-1}. Concentration of the solution to about 2−3 mL followed by addition of heptane afforded the red crystalline complex in 80% yield. W(phen)$(CO)_2$(SPh)(NO) with IR bands: ν_{CO} 2002 and 1911; ν_{NO} 1608 cm^{-1} in CH_2Cl_2. The NMR spectrum of W(phen) (NO)$(CO)_2$(SPh) was recorded in $CDCl_3$ and showed peaks assigned to the phenanthroline ligand (8H), 9.44(d), 8.47(d), 7.86(s), 7.85(dd), and S−C_6H_5 (5H), 6.37(br), 6.12(br). The crystal structure of W(phen)$(CO)_2$(SPh)(NO) is reported below. Strictly analogous procedures yielded the following complexes characterized by infrared spectroscopy: Mo(phen)(NO)$(CO)_2$(SPh), ν_{CO} 2012, 1928 cm^{-1}, ν_{NO} 1633 cm^{-1} in toluene; Mo(phen)(NO)$(CO)_2$(SToluene), ν_{CO} 2014, 1929 cm^{-1}, ν_{NO} 1635 cm^{-1} in CH_2Cl_2; W(phen)(NO)$(CO)_2$(SBu), ν_{CO} 1996, 1913 cm^{-1}, ν_{NO} 1622 cm^{-1} in CH_2Cl_2.

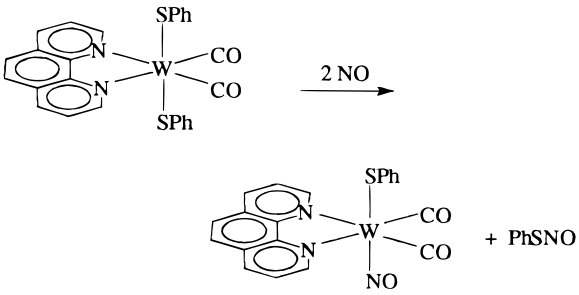
Reaction of Nitric Oxide and W(phen)$(CO)_3$(RSH) [R = Bu, Ph]. A solution of W(phen)$(CO)_3$(EtCN) (200 mg, 0.398 mmol) in 25 mL of CH_2Cl_2 with 0.10 mL of BuSH (about 2 equiv of BuSH) was allowed to stir in the reactor, producing W(phen)$(CO)_3$(BuSH) with FT-IR peaks at 1900 and 1783 cm^{-1}. Using a Hamilton gastight syringe, 50 cm^3 of nitric oxide at 6 psi was added, with rapid formation of W(phen)(NO)$(CO)_2$(SBu) with FT-IR peaks at 1996, 1913, and 1622 cm^{-1}. The presence of HNO was inferred by FT-IR on the basis of detection of its decomposition products N_2O (2220 cm^{-1}) and HNO_2 (3443 cm^{-1}). Reaction of W(phen)$(CO)_3$(PhSH) proceeded in an analogous way and yielded W(phen)(NO)$(CO)_2$(SPh) characterized by observation of IR bands: ν_{CO} 2002 and 1911; ν_{NO} 1608 cm^{-1} in CH_2Cl_2, in agreement with those determined above.

Reaction of Nitric Oxide and W(phen)$(CO)_2$(toluene-3,4-dithiolate). W(phen)$(CO)_2$(tdt) (106 mg, 0.217 mmol) was dissolved in 15 mL of toluene under argon. An initial IR spectrum was taken, with peaks at 1929 and 1853 cm^{-1}. The atmosphere was then switched to nitric oxide (6 psi), with the solution turning from dark purple to dark green. W(phen)$(CO)_2$(tdt) was rapidly converted to W(phen)$(NO)_2$(tdt), as seen by FT-IR, with peaks ν_{NO} at 1721 and 1630 cm^{-1} in toluene.

Crystal Growth of W(phen)$(CO)_2$(SPh)(NO) and W(phen)$(NO)_2$(tdt). Concentrated solutions of the complexes were prepared in the glovebox by dissolving ~250 mg of the solid in ~7 mL of freshly distilled CH_2Cl_2. The solution was filtered through a syringe filter into a 50 mL Schlenk tube and layered with heptane. The solution was left undisturbed for about a week, at which time crystals were collected and used for X-ray diffraction analysis.

Results

Reaction of Nitric Oxide with W(phen)$(CO)_2(SPh)_2$ and W(phen)$(CO)_2$(toluene-3,4-dithiolate). Reaction of •NO and W(phen)$(CO)_2(SPh)_2$ proceeds as shown in eq 6. The metal complex is formulated based on FT-IR, NMR, and (see later section) X-ray structural analysis. The phenyl thiyl radical that is eliminated from the complex forms PhS−NO, which is known to undergo spontaneous decomposition according to eq 7. The presence of PhS−NO was confirmed on the basis of growth and decay of ν_{PhSNO} at 1560 cm^{-1}, in keeping with literature reports.[19] Similar reactivity was observed for the S-tolyl complex and for analogous complexes of molybdenum.



(6)

$$2PhS-NO \rightarrow PhS-SPh + 2{\bullet}NO \qquad (7)$$

Reaction of W(phen)$(CO)_2$(tdt) with nitric oxide under conditions similar to those for reaction of W(phen)$(CO)_2(SPh)_2$

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(14) Measurement of the W−H bond strength in W$(PCy_3)_2(CO)_3$(H)(SPh), which is obtained by oxidative addition of thiophenol to W$(PCy_3)_2(CO)_3$, is very low. This has been attributed to stabilization of the radical W$(PCy_3)_2(CO)_3$(•SPh) due to electronic effects: Lang, R. F.; Ju, T. D.; Kiss, G.; Hoff, C. D.; Bryan, J. C.; Kubas, G. J. *Inorg. Chim. Acta* **1997**, *259*, 317.

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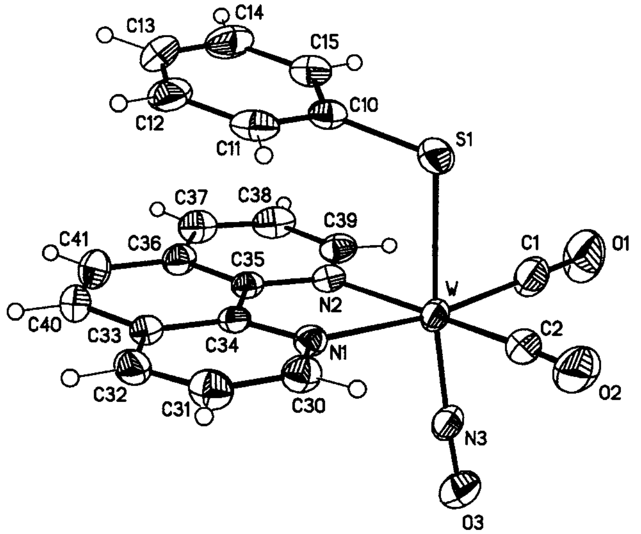
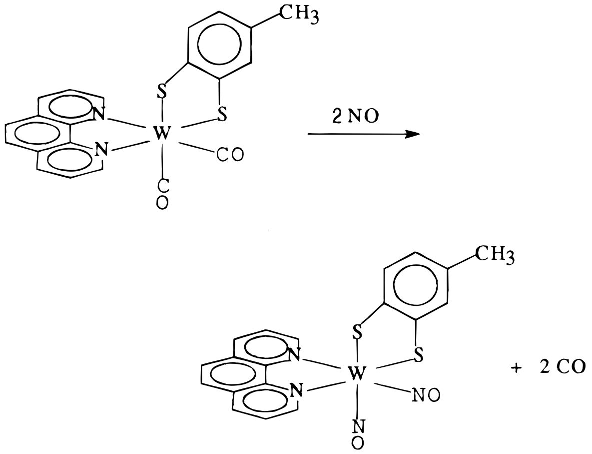


Figure 1. Molecular structure of W(phen)(CO)$_2$(SPh)(NO) (ORTEP, 50% probability ellipsoids). W−NO = 1.825(2) Å and W−N−O = 176.6(2)°.

as shown in eq 6 occurred with elimination of CO rather than a thionitrite (eq 8). No sign of intermediate formation of a bound thionitrite or other metal complex was detected in the infrared spectrum except for the starting dicarbonyl and the product dinitrosyl complex.



(8)

Crystal Structures of W(phen)(CO)$_2$(NO)(SPh) and W(phen)(NO)$_2$(toluene-3,4-dithiolate).

The crystal structure of W(phen)(CO)$_2$(NO)(SPh) has been obtained and is shown in Figure 1. Crystal and experimental data are summarized in Tables 1−3. The key features of this nearly octahedral complex are that the W−N−O angle is essentially linear at 176.6(2)°, with a W−NO bond length of 1.825(2) Å. The W−SPh distances are different in the starting complex[17] versus the final product. The average W−SPh distance in W(phen)(CO)$_2$(SPh)$_2$ is 2.361(2) Å versus 2.5347(7) Å in W(phen)(CO)$_2$(NO)(SPh). Because of the strong π-acidity of NO,[1,4] lengthening of the bond trans to nitric oxide (SPh in this case) is expected. In six-coordinate mononitrosyl complexes[1], the trans M−L bonds appear to be "long and weak" when the ν_{NO} values of the complexes are less than about 1800 cm^{-1}. W(phen)(CO)$_2$(NO)(SPh) is a mononitrosyl complex with M(NO),[6] and according to Enemark−Feltham[20] notation, the MNO link will be essentially linear.

Table 1. Crystal Data and Structure Refinement for W(phen)(CO)$_2$(SPh)(NO) and W(phen)(NO)$_2$(toluene-3,4-dithiolate)

W(phen)(CO)$_2$(SPh)(NO)	
empirical formula	$C_{20}H_{13}N_3O_3SW$
fw	559.24
temp	173(2) K
wavelength	0.71073 Å
cryst syst	orthorhombic
space group	*Pbca*
unit cell dimensions	
a = 14.2099(7) Å	α = 90°
b = 13.8261(7) Å	β = 90°
c = 18.9295(9) Å	γ = 90°
vol	3719.0(3) Å^3
Z	8
density (calcd)	1.998 Mg/m^3
abs coeff	6.351 mm^{-1}
goodness-of-fit on F^2	1.056
final R indices [$I > 2\sigma(I)$]	R1 = 0.0164, wR2 = 0.0358 [3617]
R indices (all data)	R1 = 0.0227, wR2 = 0.0381
W(phen)(NO)$_2$(toluene-3,4-dithiolate)	
empirical formula	$C_{23}H_{22}N_4O_3S_2W$
fw	650.42
temp	173(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	*P*2(1)/*c*
unit cell dimensions	
a = 9.5899(4) Å	α = 90°
b = 16.7921(8) Å	β = 100.359(1)°
c = 15.5309(7) Å	γ = 90°
vol	2460.2(1) Å^3
Z	4
density (calcd)	1.756 Mg/m^3
abs coeff	4.897 mm^{-1}
goodness-of-fit on F^2	1.041
final R indices[a] [$I > 2\sigma(I)$]	R1 = 0.0358, wR2 = 0.0755 [4292]
R indices (all data)	R1 = 0.0577, wR2 = 0.0845

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. $S = [\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$; $w = 1/[s^2(F_o^2) + (0.0370p)^2 + 0.31p]$, $p = [\max(F_o^2,0) + 2F_c^2]/3$.

Table 2. Bond Lengths (Å) for W(phen)(CO)$_2$(SPh)(NO)

W−N3	1.825(2)	C11−C12	1.378(4)
W−C2	1.982(3)	C12−C13	1.369(5)
W−C1	2.004(3)	C13−C14	1.378(4)
W−N2	2.213(2)	C14−C15	1.389(4)
W−N1	2.215(2)	C30−C31	1.399(4)
W−S1	2.5347(7)	C31−C32	1.366(4)
S1−C10	1.769(3)	C32−C33	1.407(4)
O1−C1	1.142(3)	C33−C34	1.407(3)
O2−C2	1.152(3)	C33−C40	1.432(4)
O3−N3	1.199(3)	C34−C35	1.430(3)
N1−C30	1.336(3)	C35−C36	1.403(3)
N1−C34	1.362(3)	C36−C37	1.404(4)
N2−C39	1.328(3)	C36−C41	1.436(4)
N2−C35	1.368(3)	C37−C38	1.360(4)
C10−C15	1.393(3)	C38−C39	1.404(4)
C10−C11	1.403(4)	C40−C41	1.347(4)

Crystals of W(phen)(NO)$_2$(toluene-3,4-dithiolate) were grown, and the structure was solved as shown in Figure 2. The structure of the starting material, W(phen)(CO)$_2$(toluene-3,4-dithiolate), is trigonal prismatic[16,21] compared to the product, which is nearly octahedral as shown in Figure 2. Crystal and experimental data are summarized in Tables 4−5. The complex is cis in regards

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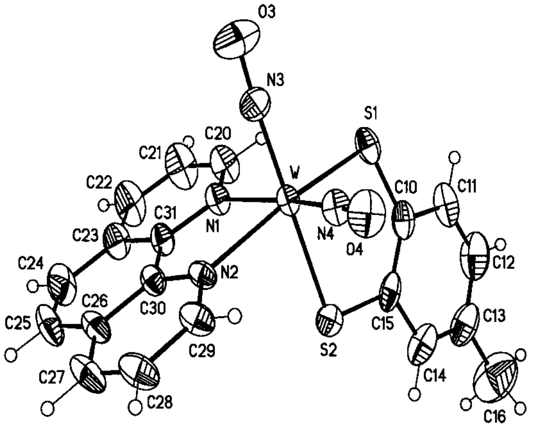

Figure 2. Molecular structure of W(phen)$(NO)_2$(toluene-3,4-dithiolate) (ORTEP, 50% probability ellipsoids). Selected bond distances (Å) and angles (°): W−N3O3 = 1.835(5) Å, W−N3−O3 = 175.7(5)°; W−N4O4 = 1.815(5) Å, W−N4−O4 = 175.5(4)°; N3−W−N4 = 88.8(2)°.

Table 3. Bond Angles (deg) for W(phen)$(CO)_2$(SPh)(NO)

N3−W−C2	89.22(10)	N1−C34−C33	123.1(2)
N3−W−C1	89.47(11)	N1−C34−C35	116.9(2)
C2−W−C1	89.41(12)	C33−C34−C35	119.9(2)
N3−W−N2	96.21(8)	N2−C35−C36	122.8(2)
C2−W−N2	169.40(10)	N2−C35−C34	117.0(2)
C1−W−N2	99.71(10)	C39−N2−W	126.15(17)
N3−W−N1	97.28(8)	C35−N2−W	115.87(15)
C2−W−N1	96.23(10)	O3−N3−W	176.6(2)
C1−W−N1	171.24(9)	O1−C1−W	179.8(4)
N2−W−N1	74.09(7)	O2−C2−W	176.5(2)
N3−W−S1	172.98(7)	C15−C10−C11	117.8(2)
C2−W−S1	88.55(8)	C15−C10−S1	121.3(2)
C1−W−S1	83.86(9)	C11−C10−S1	120.9(2)
N2−W−S1	87.08(5)	C12−C11−C10	120.8(3)
N1−W−S1	89.58(5)	C13−C12−C11	120.5(3)
C10−S1−W	107.66(8)	C12−C13−C14	120.1(3)
C30−N1−C34	117.7(2)	C13−C14−C15	120.0(3)
C30−N1−W	126.21(16)	C36−C35−C34	120.2(2)
C34−N1−W	116.07(15)	C35−C36−C37	117.3(2)
C39−N2−C35	117.8(2)	C35−C36−C41	118.4(2)
C14−C15−C10	120.9(3)	C37−C36−C41	124.3(2)
N1−C30−C31	122.8(2)	C38−C37−C36	119.8(2)
C32−C31−C30	119.6(2)	C37−C38−C39	119.5(2)
C31−C32−C33	119.6(2)	N2−C39−C38	122.7(2)
C34−C33−C32	117.2(2)	C41−C40−C33	120.8(2)
C34−C33−C40	118.9(2)	C40−C41−C36	121.8(2)
C32−C33−C40	123.9(2)		

to the two NO ligands. Given the strong π-acid nature of the NO ligand, the majority of dinitrosyl complexes possess cis geometry. Both NO ligands are essentially linear, as predicted by Enemark−Feltham[20] notation. The W−N3−O3 angle is 175.7(5)° with a W−NO length of 1.835(5) Å, and the W−N4−O4 angle is 175.5(4)° with a W−NO length of 1.815(5) Å. The N−W−N angle of 88.8(2)° ιs in accord with related group VI structures of the form *cis*-$M(NO)_2(chelate)_2$.[21] All other bond distances and angles are within the expected range.

Reaction of Nitric Oxide and Thiols Coordinated to Metal. The complex W(phen)$(CO)_3$(EtCN) has been shown to bind thiols as shown in eq 9. In the case of PhSH, oxidative addition

$$W(phen)(CO)_3(EtCN) + RSH \rightarrow W(phen)(CO)_3(RSH) + EtCN \quad (9)$$

occurs, but for BuSH a thiol complex is formed.[16a] Generation of the thiol adduct (BuSH) or the thiolate hydride[16b] complex (PhSH) in methylene chloride followed by exposure to •NO

Table 4. Bond Lengths (Å) for W(phen)$(NO)_2$(toluene-3,4-dithiolate)

W−N4	1.815(5)	C13−C16	1.472(11)
W−N3	1.835(5)	C14−C15	1.405(8)
W−N2	2.185(4)	C20−C21	1.382(9)
W−N1	2.246(4)	C21−C22	1.360(10)
W−S1	2.423(1)	C22−C23	1.416(9)
W−S2	2.461(1)	C23−C31	1.411(8)
S1−C10	1.755(7)	C23−C24	1.427(9)
S2−C15	1.771(6)	C24−C25	1.339(10)
N1−C20	1.338(7)	C25−C26	1.431(9)
N1−C31	1.373(7)	C26−C30	1.403(7)
N2−C29	1.339(7)	C26−C27	1.407(9)
N2−C30	1.355(7)	C27−C28	1.361(10)
N3−O3	1.180(6)	C28−C29	1.380(8)
N4−O4	1.197(6)	C30−C31	1.419(8)
C10−C15	1.197(6)	O1−C1	1.464(14)
C10−C11	1.403(8)	O1−C4	1.479(12)
C11−C12	1.381(10)	C1−C2	1.407(17)
C12−C13	1.386(12)	C2−C3	1.549(18)
C13−C14	1.409(10)	C3−C4	1.418(16)

Table 5. Bond Angles (deg) for W(phen)$(NO)_2$(toluene-3,4-dithiolate)

N4−W−N3	88.8(2)	C12−C13−C16	120.1(8)
N4−W−N2	95.34(19)	C14−C13−C16	120.0(9)
N3−W−N2	99.3(2)	C15−C14−C13	120.5(7)
N4−W−N1	168.75(18)	C10−C15−C14	119.2(6)
N3−W−N1	89.2(2)	C10−C15−S2	122.3(5)
N2−W−N1	74.10(16)	C14−C15−S2	118.4(6)
N4−W−S1	101.58(15)	N1−C20−C21	122.6(6)
N3−W−S1	93.42(16)	C22−C21−C20	120.5(6)
N2−W−S1	159.03(12)	C21−C22−C23	119.3(6)
N1−W−S1	89.59(11)	C31−C23−C22	117.2(6)
N4−W−S2	93.90(16)	C31−C23−C24	118.4(6)
N3−W−S2	177.08(16)	C22−C23−C24	124.4(6)
N2−W−S2	81.70(12)	C25−C24−C23	121.3(6)
N1−W−S2	88.47(13)	C24−C25−C26	121.6(6)
S1−W−S2	84.84(5)	C30−C26−C27	116.6(6)
C10−S1−W	105.6(2)	C30−C26−C25	118.6(6)
C15−S2−W	104.3(2)	C27−C26−C25	124.8(6)
C20−N1−C31	118.0(5)	C28−C27−C26	119.8(6)
C20−N1−W	127.7(4)	C27−C28−C29	120.2(6)
C31−N1−W	114.2(3)	N2−C29−C28	122.0(6)
C29−N2−C30	118.4(5)	N2−C30−C26	122.9(5)
C29−N2−W	124.5(4)	N2−C30−C31	117.2(5)
C30−N2−W	117.1(3)	C26−C30−C31	119.8(5)
O3−N3−W	175.7(5)	N1−C31−C23	122.3(5)
O4−N4−W	175.5(4)	N1−C31−C30	117.4(5)
C15−C10−C11	119.1(6)	C23−C31−C30	120.3(5)
C15−C10−S1	122.7(5)	C1−O1−C4	104.7(10)
C11−C10−S1	118.2(6)	C2−C1−O1	107.2(12)
C12−C11−C10	121.9(7)	C1−C2−C3	104.7(11)
C11−C12−C13	119.3(7)	C4−C3−C2	99.2(11)
C12−C13−C14	119.8(7)	C3−C4−O1	107.8(10)

results in eq 10. The metal-containing products showed spectroscopic parameters identical to those of W(phen)$(CO)_2$(SR)(NO) complexes prepared from bisthiolates as described above. The complex HNO is unstable and known to decompose rapidly.[22] In the presence of •NO, formation of N_2O and HNO_2 would be expected (eq 11). Formation of N_2O and HNO_2 are

$$W(phen)(CO)_3(RSH) + 2NO \rightarrow M(phen)(CO)_2(SR)(NO) + \text{“HNO”} + CO \quad (10)$$

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[22] (a) Gallup, G. A. *Inorg. Chem.* **1975**, *14*, 563. (b) Walch, S. P.; Rohlfing, C. M. *J. Chem Phys.* **1989**, *91*, 2939. (c) Guadagnini, R.; Schatz, G. C.; Walch, S. P. *J. Chem. Phys.* **1995**, *102*, 774. (d) Guadagnini, R.; Schatz, G. C.; Walch, S. P. *J. Chem. Phys.* **1995**, *102*, 784.

$$\mathrm{HNO + 2{\bullet}NO \rightarrow N_2O + HNO_2} \qquad (11)$$

assigned on the basis of FT-IR data that were in agreement with authentic samples prepared and studied under the same conditions.

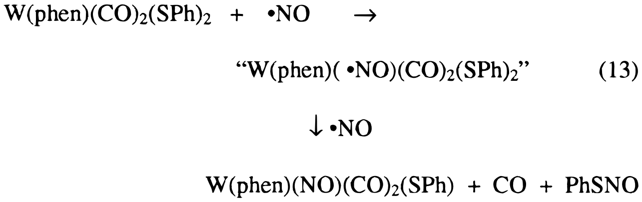
Discussion

The main goal of this work was to determine if •NO would be able to attack the sulfur−hydrogen bond in the complex W(phen)$(CO)_3$(BuSH), as was shown to occur for the transition-metal-based radical •$Cr(CO)_3C_5Me_5$ as shown in eq 5. To be able to characterize the metal-containing products, the reaction of •NO with W(phen)$(CO)_2(SR)_2$ complexes was investigated first. As shown in eq 6, the W(II) bisthiolate undergoes reductive elimination of PhSNO and formation of the W(0) nitrosyl thiyl complex, the crystal structure of which is shown in Figure 1.

The net driving force for elimination of RSNO is no doubt formation of the strong W−NO bond in the complex. It has been shown that CO rapidly adds to the 16 e^- complex and that the equilibrium[17,18] shown in eq 12 is rapidly established.

$$\mathrm{W(phen)(CO)_2(SPh)_2 + CO \rightleftharpoons W(phen)(CO)_3(SPh)_2} \qquad (12)$$

It is reasonable to predict that, because the M−NO bond appears to be stronger than the M−CO bond,[5,7] •NO would also rapidly bind as shown in eq 13.[12] A mechanistic study of whether the proposed second step of reaction 13 is dissociative (loss of CO or •SPh) or associative (attack by a second mole of •NO) is planned.



$$\begin{array}{l} \mathrm{W(phen)(CO)_2(SPh)_2 + {\bullet}NO \rightarrow} \\ \qquad\qquad \text{“}\mathrm{W(phen)({\bullet}NO)(CO)_2(SPh)_2}\text{”} \qquad (13) \\ \qquad\qquad\qquad \downarrow \mathrm{{\bullet}NO} \\ \qquad\qquad \mathrm{W(phen)(NO)(CO)_2(SPh) + CO + PhSNO} \end{array}$$

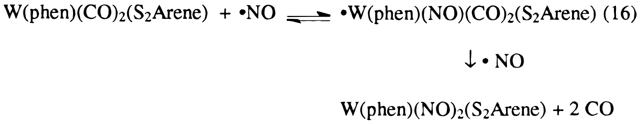
In apparent contrast to our observed reductive elimination of RSNO, Richter-Addo[23] has recently reported oxidative addition of thionitrosyls. Trans addition of RSNO compounds to the metal center in ruthenium and osmium porphyrins of the form (por)M(CO) [por = octaethylporphyrinato dianion (OEP), tetratolyporphyrinato dianion (TTP)] gives (por)M(NO)(SR) as shown in eq 14. For the organochromium complexes shown in eq 15, however, reductive elimination of RSNO has been shown[7]

$$\mathrm{(por)M(CO) + RSNO \rightarrow (por)M(SR)(NO) + CO} \qquad (14)$$

$$\mathrm{RS{-}Cr(CO)_3C_5Me_5 + 2{\bullet}NO \rightarrow RSNO + Cr(NO)(CO)_2C_5Me_5} \qquad (15)$$

to occur for R = H, Me, Ph. It is clear that oxidative addition/reductive elimination of RSNO depends critically on the complex and conditions. It should be pointed out that the reactions in which reductive elimination of RSNO was observed (eqs 6 and 15) a metal−nitrosyl bond is formed during the reaction. This may simply be the result of trapping an ejected thiyl radical.[24]

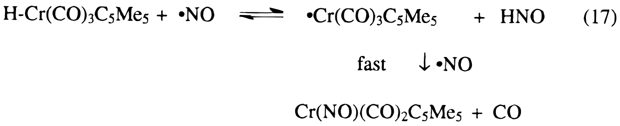
Reaction 8 was investigated in hopes of trapping a bound nitrosothiol. The complex W(phen)(benzene-3,4-dithiolate)$(CO)_2$ has been prepared and structurally characterized.[16,21] Reaction in a fashion similar to that shown in eq 6 would be expected to produce the complex W(phen)(NO)$(CO)_2$(−S−Arene-S−NO). No evidence for formation of such a complex, even as an intermediate has been found. As shown in reaction 8, as well as the crystal structure in Figure 2, it is CO and not a thiyl radical or its nitrosylated derivative that are ejected from the metal (eq 16).[15] Disruption of the chelate system may provide resistance to reductive elimination of nitrosothiol in this system.



$$\begin{array}{l} \mathrm{W(phen)(CO)_2(S_2Arene) + {\bullet}NO \rightleftharpoons {\bullet}W(phen)(NO)(CO)_2(S_2Arene)} \quad (16) \\ \qquad\qquad\qquad\qquad\qquad \downarrow \mathrm{{\bullet}\ NO} \\ \qquad\qquad\qquad\qquad \mathrm{W(phen)(NO)_2(S_2Arene) + 2\ CO} \end{array}$$

The structures in Figures 1 and 2 warrant additional comment. Few complexes of the form M(NO)(SPh) have been isolated, with even fewer being characterized by X-ray analysis. Richter-Addo[23] has synthesized (OEP)Os(NO)(SPh) by trans addition of RSNO to (OEP)Os(CO), and Bohle[25] has synthesized a related complex, (TTP)Ru(NO)(S-*p*-tolyl), by a thiol exchange reaction of the precursor methoxide, (TTP)Ru(NO)(OMe); however, the crystal structure of neither has been reported. For group VI metals, most M(NO)(SR) complexes are of the form of the five-coordinate neutral $M(NO)(SR)_3(NH_3)$ or anionic $[M(NO)(SR)_4]^-$ and $M(NO)(SR)_3Cl]^-$ complexes (M = Mo, W; R = alkyl, aryl).[26]

The most interesting result of this work is the observation that stable products (N_2O and HNO_2), which can be attributed to decomposition of HNO, are formed when either W(phen)$(CO)_3$(SPh)(H) or W(phen)$(CO)_3$(HSBu) are exposed to •NO. We have recently completed detailed mechanistic study of reaction of H−$Cr(CO)_3C_5Me_5$ and •NO proposed to proceed by the mechanism shown in eq 17.[16] The decomposition products (N_2O and HNO_2) were again taken as sign of initial formation of HNO. The enthalpy of activation for reaction 17 (∼12 kcal/mol[7]) is in keeping with thermochemical estimates for the uphill H atom transfer in the first step. Because according to eq 17 NO• is capable of slow abstraction of an H atom from H−Cr and in eq 5 •Cr is capable of rapid abstraction of an H atom from the W(phen)$(CO)_3$(BuSH), it is proposed that reaction 10 may proceed in as shown in Scheme 1. The principle difference between reaction 5 and Scheme 1 is the irreversible oxidative addition of RSNO to form the metal nitrosyl complex (Scheme 1) versus ligand displacement of bound BuS−Cr-$(CO)_3C_5Me_5$ by free BuSH in eq 5.



$$\begin{array}{l} \mathrm{H{-}Cr(CO)_3C_5Me_5 + {\bullet}NO \rightleftharpoons {\bullet}Cr(CO)_3C_5Me_5 \quad + \quad HNO} \qquad (17) \\ \qquad\qquad\qquad\qquad \text{fast} \quad \downarrow \mathrm{{\bullet}NO} \\ \qquad\qquad\qquad \mathrm{Cr(NO)(CO)_2C_5Me_5 + CO} \end{array}$$

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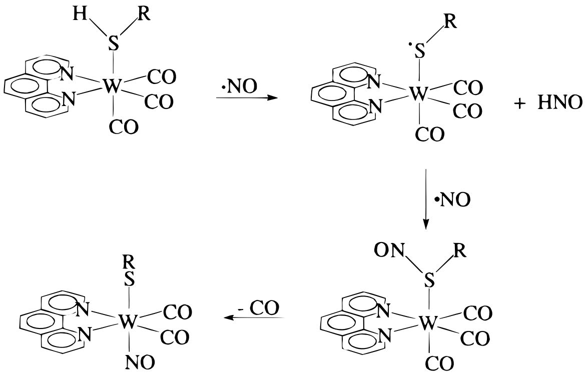
[23] (a) Yi, G. B.; Chen, L.; Khan, M. A.; Richter-Addo, G. B. *Inorg. Chem.* **1997**, *36*, 3876. (b) Yi, G. B.; Khan, M. A.; Richter-Addo, G. B. *Chem. Commun.* **1996**, 2045. (c) Chen, L.; Khan, M. A.; Richter-Addo, G. B. *Inorg. Chem.* **1998**, *37*, 533. (d) Yi, G. B.; Khan, M. A.; Powell, D. R.; Richter-Addo, G. B. *Inorg. Chem.* **1998**, *37*, 208.

[24] Although it seems reasonable that RSNO should be eliminated from the metal center, the strength of nitric oxide as a ligand may allow direct elimination and subsequent trapping of a thiyl radical. See ref 7 for further discussion.

[25] Bohle, D. S.; Goodson, P. A.; Smith, B. D. *Polyhedron* **1996**, *15*, 3147.

[26] Bishop, P. T.; Dilworth, M. J. R.; Hutchinson, J.; Zubieta, J. *J. Chem. Soc., Dalton Trans.* **1986**, 967.

Scheme 1



Conclusion

This work began to investigate if the "weak" main group radical •NO would react in a way analogous to what was found for the "weak" transiton metal radical •Cr(CO)$_3$C$_5$Me$_5$. For the complexes W(phen)(CO)$_3$(HSBu) and W(phen)(CO)$_3$(SPh)(H),[16] transfer of hydrogen to •NO gave products consistent with decomposition of HNO. This says more about the ability of coordination or oxidative addition of a thiol to decrease the effective sulfur−hydrogen bond strength than about any perceived similarity of two such different radicals. The authors view Scheme 1 as the most reasonable explanation of the observed reactions reported here. Detailed additional work will be required before the rates and mechanisms of so complicated a reaction as shown in eq 10 can be established. Such work is in progress.[27]

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Supporting Information Available: Two X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC990830H

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[27] Sukcharoenphon, K.; Capps, K. B.; Hoff, C. D. Work in progress.