tert-Butylnitroso Complexes. Structural Characterization of W(CO)$_5$(N(O)Bu^t) and [CpFe(CO)(PPh$_3$)(N(O)Bu^t)]$^+$

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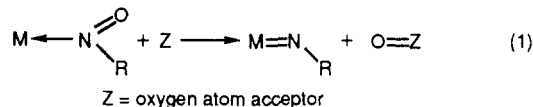*Department of Chemistry, The University of Delaware, Newark, Delaware 19716*

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The new *tert*-butylnitroso complexes W(CO)$_5$(N(O)Bu^t) (1), [CpFe(CO)(PPh$_3$)(N(O)Bu^t)]$^+$ (2), [CpRu(PPh$_3$)$_2$(N(O)Bu^t)]$^+$ (3), and CpMn(CO)$_2$(N(O)Bu^t) (4) have been prepared and spectroscopically characterized. Complexes 1 and 2 have been further defined by crystallographic studies: 1 $P\bar{1}$, a = 6.682 (4) Å, b = 9.510 (5) Å, c = 10.277 (8) Å, α = 96.59 (5)°, β = 94.16 (6)°, γ = 97.83 (5)°, V = 640.1 (7) Å^3, Z = 2, $R(F)$ = 5.12%, $R(wF)$ = 5.53% for 1092 reflections ($5\sigma F_o$); 2 $P\bar{1}$, a = 10.250 (3) Å, b = 10.935 (3) Å, c = 13.665 (3) Å, α = 103.58 (3)°, β = 102.01 (3)°, γ = 103.76 (3)°, V = 1389 (1) Å^3, Z = 2, $R(F)$ = 9.70%, $R(wF)$ = 10.10% for 2606 reflections ($3\sigma F_o$). The nitroso ligands of both complexes are coordinated via the nitrogen atom, and in each case the nitroso ligand is oriented in such a way as to maximize its π bonding to the metal. EHMO calculations on the model complex W(CO)$_5$(N(O)Me) show that the nitroso molecule acts as a σ-donor, π-acceptor ligand with the LUMO being an antibonding combination of a metal d$_{zz}$ orbital and a NO π^* orbital. The LUMO is calculated to lie only ~0.7 eV above the filled, largely nonbonding d$_{xy}$, d$_{yz}$ orbitals, giving rise to a low-energy metal-to-ligand charge-transfer transition in the visible spectral region, which accounts for the intense color of these Bu^{t}N=O complexes. The nitroso ligands in these complexes are not readily displaced by CO, PPh$_3$, or Bu^{t}N≡C, and attempts to form imido complexes via deoxygenation of the coordinated nitroso ligands did not succeed.

Introduction

Transition-metal carbene complexes are useful reagents for a number of important transformations that incorporate the carbene ligand into organic products.[1] In contrast, transition-metal imido (NR, nitrene) complexes have been relatively little explored for their use in organic synthesis.[2] This is in part because imido ligands bound to electron-deficient metals are generally unreactive, and mononuclear imido complexes of electron-rich metals are virtually unknown.[2] Attempts to prepare such species have led either to highly reactive transient imido complexes that rapidly decay to other products[3,4] or to polynuclear clusters possessing relatively inert μ_3- or μ_4-imido ligands.[2] For synthetic applications, a desirable complex would be (CO)$_5$Cr=NR, because of its relationship to the (CO)$_5$Cr=CR$_2$ carbene complexes that have found many synthetic applications.[1] Such imido complexes have never been prepared or observed, although (CO)$_5$Cr=NPh and (CO)$_5$W=NPh have been invoked as transient intermediates in the reaction of (CO)$_5$M=C(OMe)Me (M = Cr, W) with PhN=NPh,[3] and related species appear to form as unstable intermediates in the reaction of (CO)$_5$W=C-(OMe)Ph with a variety of nitroso (RN=O) reagents.[4] Carbonyl-imido complexes have also been invoked as transient intermediates in the reactions of aziridines with Mo(CO)$_6$ and Fe$_2$(CO)$_9$.[5]

One potential way to prepare reactive imido complexes for use in organic synthesis is to employ a stable precursor that can be converted into the desired imido complex by an in situ reaction in the presence of a desired organic substrate. Nitroso complexes are potential imido precursors through deoxygenation of the nitroso ligand (eq 1). Chemistry similar to that of eq 1 presumably occurs

$$M \longleftarrow N\!\!\begin{smallmatrix}\nearrow O \\ \searrow R\end{smallmatrix} \; + \; Z \;\longrightarrow\; M\!\!=\!\!N\!\!\searrow_R \; + \; O\!\!=\!\!Z \qquad (1)$$

Z = oxygen atom acceptor

in the reported reactions of the nitroso complex Ni-(PhNO)(Bu^{t}N≡C)$_2$ with Bu^{t}N≡C and PPh$_3$ to respectively form Bu^{t}N=C=O and Ph$_3$P=O, but the expected imido complex was not detected.[6a] However, stable imido complexes of the form ReCl$_3$(NAr)L$_2$ were formed upon deoxygenation of the nitroso ligand in ReCl$_3$(N(O)Ar)-(OPPh$_3$) by tertiary phosphines and isocyanides.[6b] Metal carbonyls have also been used to induce the deoxygenation of nitroso reagents to form CO$_2$ and polynuclear imido complexes.[2]

Crystallographic and spectroscopic studies have shown that nitroso ligands bind to metals in the six different ways illustrated in I–VI, although by far the most common coordination mode is I.[6b,7–10] We have sought to extend the

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(4) Pilato, R. S.; Williams, G. D.; Geoffroy, G. L.; Rheingold, A. L. *Inorg. Chem.* **1988**, *27*, 3665.

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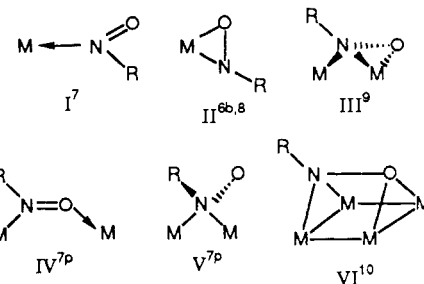
(6) (a) Otsuka, S.; Aotani, Y.; Tatsuno, Y.; Yoshida, T. *Inorg. Chem.* **1976**, *15*, 656. (b) La Monica, G.; Cenini, S. *J. Chem. Soc., Dalton Trans.* **1980**, 1145.
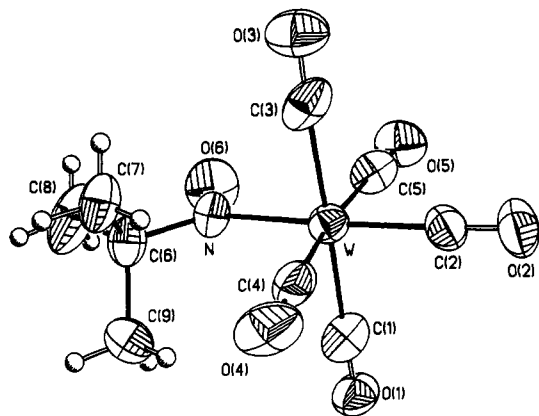
Figure 1. ORTEP drawing of W(CO)$_5$(N(O)Bu^t) (1). Thermal ellipsoids are drawn at the 40% probability level.

Figure 2. ORTEP drawing of [CpFe(CO)(PPh$_3$)(N(O)Bu^t)]$^+$ (2). Thermal ellipsoids are drawn at the 40% probability level.

range of available nitroso complexes with a specific goal of preparing species capable of undergoing in situ deoxygenation to produce reactive imido complexes. Ideal complexes would be those with a nitroso ligand attached to M(CO)$_5$ (M = Cr, Mo, W) and [CpML$_2$]$^+$ (M = Fe, Ru) fragments, since the analogous carbene complexes have proven especially useful in organic synthesis.[1] Herein we report the preparation of several new complexes possessing *tert*-butylnitroso ligands, the crystallographic characterization of W(CO)$_5$(N(O)Bu^t) (1) and [CpFe(CO)(PPh$_3$)(N-(O)Bu^t)]$^+$ (2), and an analysis of the electronic structure of 1 as probed by EHMO calculations and electronic absorption spectral studies.

Results and Discussion

Syntheses. The most useful nitroso ligand for the syntheses reported herein proved to be Bu^{t}N=O, since it consistently gave the cleanest chemistry and the highest yields. This nitroso reagent exists as a dimer in the solid state but is in equilibrium with its monomer in solution.[11] Nearly pure monomer can be formed by warming solid [Bu^{t}NO]$_2$ under vacuum and collecting the distillate as a blue solid in a flask cooled to -78 °C. This solid melts to
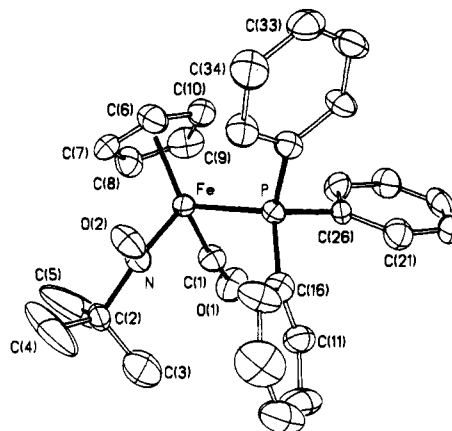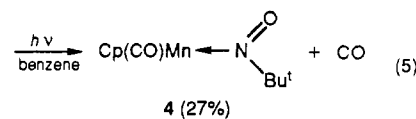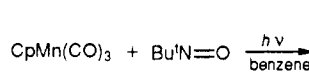
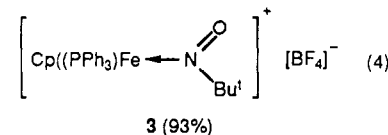a blue liquid upon warming to -30 °C. The monomer is stable at this temperature for several hours, although the white dimer rapidly re-forms upon warming to room temperature. The highest yields in the syntheses described below were generally obtained when monomeric Bu^{t}NO was employed in the reactions.

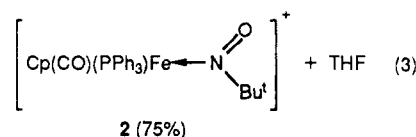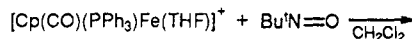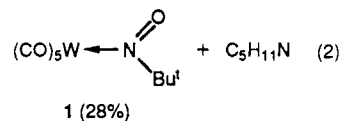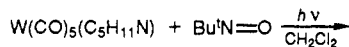The complexes described herein were prepared by the straightforward substitution reactions illustrated in eq 2-5 with use of precursor complexes having a labile ligand or with ligand loss induced by photochemical means. In the

$$W(CO)_5(C_5H_{11}N) + Bu^tN{=}O \xrightarrow[CH_2Cl_2]{h\nu}$$

$$(CO)_5W{\longleftarrow}N{\overset{\displaystyle O}{\diagdown}}_{Bu^t} + C_5H_{11}N \quad (2)$$

1 (28%)

$$[Cp(CO)(PPh_3)Fe(THF)]^+ + Bu^tN{=}O \xrightarrow{CH_2Cl_2}$$

$$\left[Cp(CO)(PPh_3)Fe{\longleftarrow}N{\overset{\displaystyle O}{\diagdown}}_{Bu^t}\right]^+ + THF \quad (3)$$

2 (75%)

$$Cp(PPh_3)Ru{\longrightarrow}Cl \xrightarrow[\substack{2. +Bu^tN{=}O \\ CH_2Cl_2}]{1. +AgBF_4/-AgCl}$$

$$\left[Cp((PPh_3)Fe{\longleftarrow}N{\overset{\displaystyle O}{\diagdown}}_{Bu^t}\right]^+ [BF_4]^- \quad (4)$$

3 (93%)

$$CpMn(CO)_3 + Bu^tN{=}O \xrightarrow[benzene]{h\nu} Cp(CO)Mn{\longleftarrow}N{\overset{\displaystyle O}{\diagdown}}_{Bu^t} + CO \quad (5)$$

4 (27%)
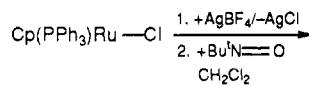
photochemical preparations, the best yields were obtained when band-pass filters (λ = 345–565 nm) were used that minimized light absorption by the highly photosensitive nitroso reagent. Complexes 1–4 were obtained as pure, deeply colored, crystalline solids and were spectroscopically characterized. Routine spectroscopic data are given in the Experimental Section, and only the more important spectral features are summarized below. Complexes 1 and 2 were further defined by X-ray diffraction studies, the results of which are shown in Figures 1 and 2. Complexes 1–4 are stable at room temperature in CH$_2$Cl$_2$ solution under N$_2$, and the nitroso ligands are not readily displaced by CO (1 atm), PPh$_3$ (1 equiv) or Bu^{t}N≡C (5 equiv). However, dissolution of W(CO)$_5$(N(O)Bu^t) in acetone or

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THF results in immediate displacement of the nitroso ligand and formation of $W(CO)_5$(solvent) adducts. In contrast, complexes **2-4** are stable in acetone and THF solutions.

A nitrosobenzene analogue of complex **4** has been prepared by Setkina et al.[7g] via the reaction of PhN=O with $CpMn(CO)_2$(THF), and these same workers described the formation of $W(CO)_5(N(O)Ph)$ from the addition of PhN=O to $W(CO)_5$(THF). However, this latter species was unstable at room temperature and was poorly defined.[7g] It should also be noted that we earlier obtained complex **1** in 35% yield from the reaction of $(CO)_5W$=C-(OMe)Ph with Bu^tN=O.[4]

Spectroscopic Characterization. The crystal structures of complexes **1** and **2** show the nitroso ligands to be bound in an η^1 fashion via the nitrogen atom. The ν_{NO} vibration for nitroso complexes with this type I coordination mode is typically in the 1300–1450-cm^{-1} spectral region[7c,m] (e.g., $CpCo(PPh_3)(N(O)Me)$,[7h] ν_{NO} = 1310 cm^{-1}), and complexes **1** and **4** have corresponding bands at 1415 and 1325 cm^{-1} respectively. The ν_{NO} bands in complexes **2** and **3** were not confidently identified due to overlapping PPh_3 vibrations in this region. As in other studies,[7c,m] IR data indicate that the nitroso ligands are electron withdrawing. This is best illustrated by a comparison of the positions of the most intense ν_{CO} vibration (ν_E) of W-$(CO)_5$(piperidine) (1929 cm^{-1}),[12] $W(CO)_5(PPh_3)$ (1944 cm^{-1}),[12] $(CO)_5W$=C(OMe)Ph (1948 cm^{-1}),[13] and $W(CO)_5$-$(N(O)Bu^t)$ (1966 cm^{-1}), which shows a progressive shift of the ν_{CO} band to higher energy as an increased amount of electron density is removed from the metal center.

Another characteristic feature of all the nitroso complexes prepared in this work is their intense color. For example, solutions of $W(CO)_5(N(O)Bu^t)$ are deep purple, compared to the amine complex $W(CO)_5(NH_3)$, which is yellow. Representative electronic absorption spectra of $W(CO)_5(N(O)Bu^t)$ (**1**) and $CpMn(CO)_2(N(O)Bu^t)$ (**4**) are shown in Figure 3. Both complexes show intense bands in the visible spectral region (**1**, λ = 490 nm (ϵ = 9310 M^{-1} cm^{-1}); **4**, λ = 462 nm (ϵ = 1826 M^{-1} cm^{-1})) that are assigned as metal-to-ligand charge-transfer transitions (MLCT). The latter interpretation is based on the molecular orbital calculations described below and the observation of similar MLCT bands in related carbonyl complexes possessing pyridine ligands that have electron-withdrawing substituents.[14] The spectrum of $W(CO)_5(N(O)Bu^t)$ also shows additional weaker features in the 300–400-nm spectral region (see Figure 3) that are attributed to ligand field transitions since a variety of $W(CO)_5L$ complexes have ligand field bands in this spectral region.[14] The UV–vis spectra of compounds **2** and **3** show only a broad absorption from the UV tailing into the visible region but without well-resolved bands as exhibited by **1** and **4**.

EHMO Calculations. In order to more fully understand the bonding and electronic structures of these type I nitroso complexes, extended Hückel molecular orbital (EHMO) calculations[15] were carried out on the model compound $W(CO)_5(N(O)CH_3)$ and on the fragments W-$(CO)_5$ and CH_3NO. Geometrical parameters used were identical with those found in the X-ray structure of **1**, except that the *tert*-butyl methyl groups were replaced by
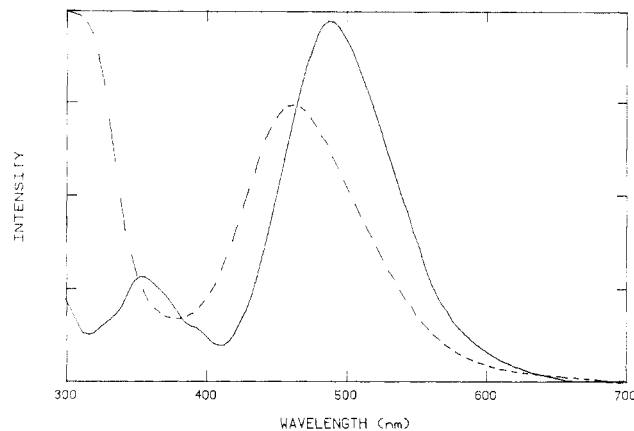

Figure 3. Electronic absorption spectra of $W(CO)_5(N(O)Bu^t)$ (**1**, –) and $Cp(CO)_2Mn(N(O)Bu^t)$ (**4**, - - -) in pentane solutions at 22 °C.

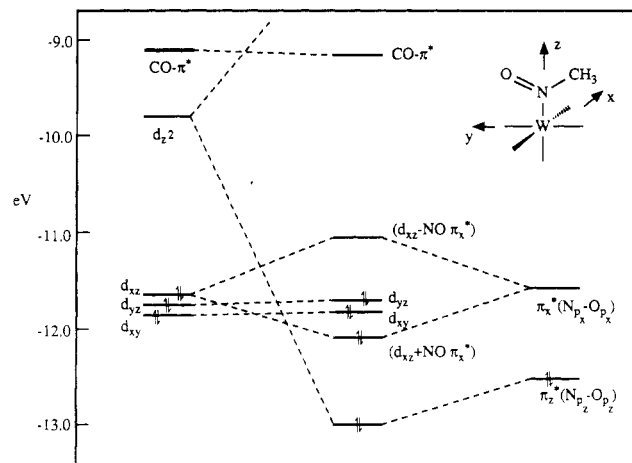**Figure 4.** EHMO diagram of $W(CO)_5(N(O)Me)$.

hydrogen atoms (d_{C-H} = 1.11 Å). The resultant molecular orbital diagram showing only those orbitals that significantly contribute to the tungsten–nitroso bonding is given in Figure 4.

The HOMO of the free nitroso molecule, constrained to the geometrical parameters that it has in complex **1**, is mainly an antibonding combination of the p_z orbitals of the oxygen and nitrogen atoms, with considerable electron density localized on nitrogen. The LUMO of the nitroso ligand is the $\pi^*(x)$ orbital. Free monomeric nitroso molecules are generally highly absorbing in the visible region (e.g., Bu^tN=O, λ = 675 nm[16a]) due to an electronic transition between the HOMO and LUMO. Although not strictly correct, this transition is usually termed an n → π^* transition.[16]

The nitroso ligand interacts with the tungsten atom through its LUMO/HOMO orbitals in a σ-donor, π-acceptor fashion. As illustrated by the drawing in Figure 4, the donor interaction occurs via overlap of the lobe of the occupied HOMO that is localized on the nitrogen atom with the metal d_{z^2} orbital, but with the resultant bonding MO still localized largely on the nitroso ligand. In turn, the occupied metal d_{xz} orbital donates electron density into the nitroso π-system via its overlap with the empty nitroso $\pi^*(x)$ orbital, giving rise to the usual bonding and antibonding combinations. The latter is the LUMO of the complex and lies just slightly (0.64 eV) above the filled, largely nonbonding, and essentially degenerate d_{yx}, d_{xy}

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Table I. Crystallographic Data for W(CO)₅(N(O)Buᵗ) (1) and [CpFe(CO)(PPh₃)(N(O)Buᵗ)][BF₄] (2[BF₄])ᵃ

	1	2[BF₄]
(a) Crystal Parameters		
formula	C₉H₉NO₆W	C₂₈H₂₉NO₂PFeBF₄
cryst syst	triclinic	triclinic
space group	P1̄	P1̄
a, Å	6.682 (4)	10.250 (3)
b, Å	9.510 (5)	10.935 (3)
c, Å	10.277 (8)	13.665 (4)
α, deg	96.59 (5)	103.58 (3)
β, deg	94.16 (6)	102.01 (3)
γ, deg	97.83 (5)	103.76 (3)
V, Å³	640.1 (7)	1389 (1)
Z	2	2
D(calc), g cm⁻³	2.131	1.399
±(Mo Kα), cm⁻¹	95.6	6.49
temp, °C	23	20
size, mm	0.40 × 0.40 × 0.40	0.08 × 0.38 × 0.46
color	black	orange-brown
T(max)/T(min)	3.75	1.24
(b) Data Collection		
diffractometer	Nicolet R3m	
radiation	Mo Kα	
wavelength, Å	0.710 73	
monochromator	graphite	
scan method	Wyckoff	θ/2θ
scan speed, deg min⁻¹	variable, 10–20	variable, 6–20
scan limits, deg	4 ≤ 2θ ≤ 45	4 ≤ 2θ ≤ 45
octants collected	±h,±k,+l	±h,±k,+l
no. of std rflns	3 std/97 rflns	
decay	<1%	<1%
no. of rflns collected	1899	3822
no. of unique data	1711	3638
no. of obs rflns	1092 (5σFₒ)	2606 (3σFₒ)
R(int), %	2.84	2.1
(c) Data Reduction and Refinement		
R(F), %	5.12	9.70
R(wF), %	5.53	10.10
GOF	1.248	1.141
Δ/σ (mean)	0.015	0.063
Nₒ/Nᵥ	7.1	7.12
Δ(ρ), e Å⁻³	0.84	1.03

ᵃ $R(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R(wF) = \sum(w^{1/2}(|F_o| - |F_c|))/(w^{1/2}|F_o|)$; GOF = $[\sum w ||F_o| - |F_c||/(N_o - N_v)]^{1/2}$.

orbitals. The π-donation from tungsten into the ligand π*(x) orbital should weaken the N=O bond, as evidenced by the characteristic decrease in the ν_{NO} stretch from 1546 cm⁻¹ in free BuᵗN=O to 1415 cm⁻¹ when it is complexed in 1. The results of the EHMO calculation also imply that the lowest energy electronic transition in these complexes is from the nonbonding d_{yz}, d_{xy} orbitals to the d_{zz}–π*(x) LUMO, a transition that has substantial tungsten to nitroso charge-transfer character.

Attempted Nitroso Deoxygenation Reactions. As noted in the Introduction, one objective of this study was to prepare nitroso complexes that might be capable of in situ deoxygenation to yield reactive imido complexes. Oxygen atom transfers from a nitroso ligand to a phosphine to form a phosphine oxide, to an isocyanide to yield an isocyanate, and to carbon monoxide to form carbon dioxide are possible routes to the desired imido complexes, and deoxygenation reactions like these have been employed for other nitroso complexes.[2,6] However, none of the complexes described herein were found to react with BuᵗNC (5 equiv), PPh₃ (1 equiv), or CO (1 atm), although complex 1 did decompose in solution over a 2-day period to yield a mixture of W(CO)₆ and W(CO)₅(NH₂Buᵗ) (IR 2071 (w), 1936 (s), 1919 (s) cm⁻¹; MS (EI) m/z 397 (M⁺)). The latter product may have arisen via the transient formation of an imido complex or via a free nitrene. This reaction is accelerated by air exposure, by chromatography

Table II. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for W(CO)₅(N(O)Buᵗ) (1)ᵃ

	x	y	z	U
W	2705 (1)	8489 (1)	2618 (1)	62 (1)
N	1105 (25)	6303 (21)	2161 (20)	70 (7)
O(1)	4431 (29)	8256 (26)	−210 (20)	96 (8)
O(2)	4674 (30)	11696 (20)	3227 (21)	98 (8)
O(3)	1058 (29)	8717 (30)	5482 (19)	105 (10)
O(4)	6889 (20)	7801 (28)	3843 (22)	111 (10)
O(5)	−1205 (23)	9628 (25)	1398 (21)	100 (9)
O(6)	−634 (24)	6116 (29)	1603 (29)	124 (12)
C(1)	3813 (33)	8311 (33)	752 (25)	86 (10)
C(2)	3937 (32)	10508 (26)	2963 (24)	73 (8)
C(3)	1650 (24)	8614 (33)	4494 (31)	86 (11)
C(4)	5336 (33)	8101 (28)	3449 (28)	78 (9)
C(5)	169 (31)	9167 (31)	1791 (22)	76 (9)
C(6)	1792 (33)	4900 (25)	2400 (26)	76 (9)
C(7)	2494 (37)	4984 (31)	3835 (26)	93 (10)
C(8)	139 (53)	3669 (36)	1989 (37)	140 (16)
C(9)	3694 (40)	4720 (36)	1566 (33)	99 (12)

ᵃEquivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Distances and Angles for W(CO)₅(N(O)Buᵗ) (1)

Bond Lengths (Å)			
W–N	2.19 (2)	W–C(5)	2.06 (2)
W–C(1)	2.10 (3)	N–O(6)	1.24 (3)
W–C(2)	1.97 (2)	N–C(6)	1.51 (3)
W–C(3)	2.10 (3)	C–O (av)	1.14 (3)
W–C(4)	2.00 (2)	C–C (av)	1.53 (4)

Bond Angles (deg)			
N–W–C(1)	89.3 (9)	C(1)–W–C(5)	89 (1)
N–W–C(2)	175.1 (9)	C(2)–W–C(5)	88 (1)
C(1)–W–C(2)	91 (1)	C(3)–W–C(5)	92.9 (9)
N–W–C(3)	89.9 (9)	C(4)–W–C(5)	172 (1)
C(1)–W–C(3)	178 (1)	W–N–O(6)	119 (2)
C(2)–W–C(3)	90 (1)	W–N–C(6)	130 (1)
N–W–C(4)	100.0 (9)	O(6)–N–C(6)	111 (2)
C(1)–W–C(4)	91 (1)	W–C–O (av)	177 (2)
C(2)–W–C(4)	85 (1)	N–C(6)–C (av)	109 (2)
C(3)–W–C(4)	88 (1)	C–C(6)–C (av)	110 (2)
N–W–C(5)	87.5 (9)		

on wet SiO₂, by addition of less than stoichiometric amounts of HBF₄, or by warming to 40 °C. However, the decomposition is inhibited by a CO atmosphere, suggesting CO dissociation as a key step in the reaction.

Crystallographic Characterization of W(CO)₅(N-(O)Buᵗ) (1) and [CpFe(CO)(PPh₃)(N(O)Buᵗ)][BF₄] (2[BF₄]). Both nitroso complexes crystallize in the triclinic space group P1̄ with one independent molecule per asymmetric unit, although considerable disorder exists in the crystal of 2, accounting for the large residuals reported (see Experimental Section). ORTEP drawings of the two molecules are shown in Figures 1 and 2, and relevant crystallographic parameters are given in Tables I–V. In both molecules the nitroso ligand is bound in an η¹ fashion via the nitrogen atom, and the metric parameters of the nitroso ligands are essentially identical for the two molecules. For 1 and 2, respectively, the metal–N–C bond angles are 130 (1) and 130.3 (6)°, the metal–N–O bond angles are 119 (2) and 117.4 (8)°, and the N–O bond lengths are 1.24 (3) and 1.234 (10) Å. These bond lengths have typical N–O double-bond values[17] and compare well to the N–O bond distances in other structurally characterized N-bound nitroso complexes (e.g., CpCo(PPh)₃(N-(O)Et), 1.282 Å,[7h] Rh(norbornadiene)Cl(N(O)-p-BrC₆H₄), 1.23 (1) Å[7r]).

(17) See, for example, data given in: Palopoli, S. F.; Geib, S. J.; Rheingold, A. L.; Brill, T. B. *Inorg. Chem.* 1988, 27, 2963.

Table IV. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for [CpFe(CO)(PPh₃)(N(O)Buᵗ)][BF₄] (2[BF₄])ᵃ

	x	y	z	U
Fe	1263 (1)	2612 (1)	3323 (1)	43 (1)
Fe′	2735 (16)	3219 (14)	1511 (12)	39 (5)
P	843 (2)	3567 (2)	2021 (2)	43 (1)
N	3203 (9)	3054 (9)	3465 (6)	60 (4)
O(1)	184 (10)	22 (7)	1784 (6)	93 (4)
O(2)	3866 (7)	4236 (6)	3746 (7)	76 (4)
C(1)	696 (11)	1029 (9)	2378 (8)	62 (4)
C(2)	4198 (10)	2181 (9)	3473 (7)	58 (4)
C(3)	4113 (30)	1599 (30)	2393 (15)	269 (23)
C(4)	5553 (18)	2986 (18)	4007 (21)	227 (15)
C(5)	3731 (30)	1151 (29)	3924 (28)	294 (26)
C(6)	1176 (12)	4058 (11)	4573 (9)	74 (5)
C(7)	1754 (13)	3248 (12)	4989 (8)	76 (6)
C(8)	743 (13)	1947 (12)	4583 (9)	78 (6)
C(9)	-438 (14)	2040 (12)	3927 (11)	86 (6)
C(10)	-193 (12)	3382 (11)	3963 (8)	71 (5)
C(11)	1953 (9)	2419 (6)	517 (6)	73 (6)
C(12)	2975	2333	-7	115 (10)
C(13)	4182	3397	259	111 (9)
C(14)	4368	4547	1049	126 (10)
C(15)	3346	4633	1574	88 (7)
C(16)	2139	3569	1307	62 (5)
C(21)	-988 (8)	2967 (7)	35 (5)	79 (6)
C(22)	-2282	2416	-720	81 (6)
C(23)	-3402	1615	-509	93 (7)
C(24)	-3227	1364	457	81 (5)
C(25)	-1933	1914	1212	71 (5)
C(26)	-813	2716	1001	48 (4)
C(31)	-444 (6)	5577 (6)	2128 (5)	66 (5)
C(32)	-517	6846	2533	89 (7)
C(33)	636	7806	3281	87 (7)
C(34)	1862	7496	3624	88 (6)
C(35)	1935	6226	3218	69 (5)
C(36)	782	5267	2470	55 (4)
B	3460 (9)	1034 (10)	6882 (7)	78 (7)
F(1)	3468 (10)	448 (11)	7573 (7)	176 (7)
F(2)	4481 (12)	2012 (12)	7166 (10)	385 (15)
F(3)	3509 (15)	250 (12)	6071 (8)	272 (14)
F(4)	2358 (12)	1295 (14)	6677 (13)	290 (16)

ᵃ Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table V. Selected Bond Distances and Angles for [CpFe(CO)(PPh₃)(N(O)Buᵗ)][BF₄] (2[BF₄])

Bond Lengths (Å)			
Fe–P	2.283 (3)	Fe–N	1.888 (9)
Fe–C(1)	1.778 (9)	O(1)–C(1)	1.129 (10)
N–O(2)	1.234 (10)	N–C(2)	1.554 (15)
Fe–CNTᵃ	1.75 (2)		

Bond Angles (deg)			
P–Fe–CNT	121.7 (4)	N–Fe–CNT	121.7 (4)
C(1)–Fe–CNT	122.7 (5)	P–Fe–N	93.1 (3)
P–Fe–C(1)	90.4 (4)	N–Fe–C(1)	99.8 (5)
Fe–N–O(2)	117.4 (8)	Fe–N–C(2)	130.3 (6)
O(2)–N–C(2)	111.4 (8)	Fe–C(1)–O(1)	172.0 (11)

ᵃ CNT = center of the cyclopentadienyl ring.

Complex 1 is a typical octahedral W(CO)₅L complex with the nitrogen atom of the nitroso ligand occupying one octahedral coordination site. A significant feature is the orientation of the nitroso ligand. As Figure 1 shows, the plane of the nitroso ligand defined by C(6)–N–O(6) lies essentially within the plane containing the three carbonyl groups C(4)–O(4), C(5)–O(5), and C(2)–O(2) (dihedral angle 0.5° between the planes defined by C(6)–N–O(6) and C(4)–C(5)–C(2)), even though a sterically more favorable orientation would have the nitroso ligand bisecting the angle between two of the equatorial carbonyls. The adopted orientation is clearly dictated by the electronic considerations discussed above and illustrated in the

EHMO diagram shown in Figure 4. The W–N bond length of 2.19 (2) Å compares well to W–N bond distances in other molecules possessing a dative-bound N-donor ligand (W-(CO)₅(RNN(O)R), R = biphenyl, W–N = 2.258 (10), 2.232 (6) Å;[4] WBr(η³-C₃H₅)(CO)₂(CyNCH=CHNCy), 2.219 (10) Å[18]).

Complex **2** is similar to other compounds within the CpFe(CO)(PR₃)(L) family and adopts the usual pseudooctahedral geometry with the Cp ligand formally occupying three coordination sites. The plane of the nitroso ligand defined by C(2)–N–O(2) is nearly aligned with the plane containing the carbonyl ligand (dihedral angle 32.1° between the planes defined by C(2)–N–O(2) and C(1)–Fe–N). This is the orientation that would be predicted to minimize competition between the strongly π-accepting carbonyl and nitroso ligands for the metal d electrons. As illustrated in Newman projections, the *tert*-butyl group nearly eclipses the carbonyl ligand (A) rather than bisects
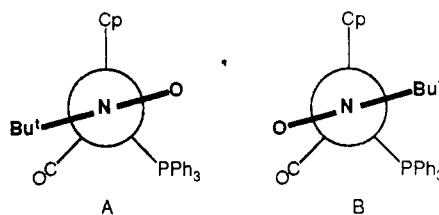
the angle between the Cp and PPh₃ ligands (B). This orientation obviously must be preferred for steric reasons. The Fe–N bond distance of 1.888 (9) Å is similar to Fe–N bond lengths in other compounds possessing dative-bound N-donor ligands (Fe(tetraphenylporphyrin)(PrⁱNO)-(PrⁱNH₂), Fe–N$_{PrNO}$ = 1.86 Å,[7b] [NH₄][Fe(C₄H₂N₃O₄)₃], average Fe–N = 1.87 Å[19]).

Experimental Section

Preparation of Monomeric BuᵗNO from [BuᵗNO]₂. An apparatus was assembled consisting of two Schlenk flasks connected with a glass U-tube. The glassware was flame-dried, and solid [BuᵗNO]₂ was added to one of the Schlenk flasks. The apparatus was evacuated, and the empty flask was cooled to -78 °C while the flask containing solid [BuᵗNO]₂ was warmed with a water bath. Monomeric BuᵗNO was distilled into the cooled vessel and was collected over a 10-min period as a blue solid, which melted into a blue liquid upon warming to -30 °C.

Preparation of W(CO)₅(N(O)Buᵗ) (1). A CH₂Cl₂ (750 mL) solution of W(CO)₅(piperidine) (0.200 g, 0.49 mmol) and [BuᵗNO]₂ (0.050 g, 0.29 mmol) was irradiated at room temperature for 1.5 h, during which time the color changed from yellow to deep red. The solvent was then removed in vacuo at -25 °C, and the residue was extracted with pentane that had been precooled to -30 °C.

(18) Graham, A. J.; Akrigg, D.; Sheldrick, B. *Cryst. Struct. Commun.* 1977, *6*, 253.
(19) Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* 1976, 1915.
(20) Davies, S. G. *J. Organomet. Chem.* 1979, *179*, C5.
(21) Reger, D. L.; Coleman, C. *J. Organomet. Chem.* 1977, *131*, 153.

The dark red extract was chromatographed on SiO_2 at -30 °C with pentane as eluent. A single dark red band eluted, which gave 1 as a black solid in 28% yield (0.056 g) when the solvent was removed in vacuo at -20 °C. Further purification was accomplished by sublimation at 30 °C under vacuum (0.01 mmHg).

Anal. Calcd for $C_9H_9NO_6W$: C, 26.31; H, 2.19; N, 3.41. Found (SML): C, 26.16; H, 1.97; N, 3.23. IR (pentane): ν_{CO} = 2081 (w), 1966 (vs), 1939 (s) cm^{-1}. IR (Fluorolube GR-90): ν_{CO} = 2078 (w), 2001 (w), 1960 (vs), 1937 (s) cm^{-1}; ν_{NO} = 1415 (m) cm^{-1}. ^{1}H NMR (25 °C, CDCl$_3$): δ 1.45 (s). ^{13}C NMR (25 °C, CD$_2$Cl$_2$): δ 205, 197 (CO), 101 (C(CH$_3$)$_3$), 28.8 (C(CH$_3$)$_3$). MS (EI): m/z 411 (M$^+$), and peaks corresponding to loss of five CO's.

Preparation of [CpFe(CO)(PPh$_3$)(N(O)Bu^t)][BF$_4$] (2[B-F$_4$]). A solution of [CpFe(CO)(PPh$_3$)(THF)][BF$_4$] (0.10 g, 0.175 mmol) in CH$_2$Cl$_2$ (50 mL) was cooled to -78 °C and added via cannula to a flask containing Bu^{t}NO monomer at -78 °C prepared as described above from [Bu^{t}NO]$_2$ (0.017 g, 0.096 mmol). The resulting solution was warmed to -30 °C and stirred for 1 h, followed by slow warmup to room temperature. The solvent and unreacted [Bu^{t}NO]$_2$ were removed under vacuum to leave a brown solid that was dissolved in CH$_2$Cl$_2$ (10 mL). After filtration, 50 mL of pentane was added to give a brown precipitate of 2 in 78% yield (0.080 g). Anal. Calcd for $C_{28}H_{29}BF_4FeNO_2P$: C, 57.49; H, 4.96. Found (GL): C, 57.16; H, 5.04. IR (KBr): ν_{CO} = 1991 (s) cm^{-1}. IR (CH$_2$Cl$_2$): ν_{CO} = 1990 (s) cm^{-1}. ^{1}H NMR (25 °C, CDCl$_3$): δ 7.4–7.0 (m, 15 H, Ph), 4.93 (s, 5 H, Cp), 1.40 (s, 9 H, Bu^t). ^{13}C NMR (CD$_2$Cl$_2$): δ 215.4 (d, CO, J_{C-P} = 28 Hz), 134–128 (Ph), 107.2 (C(CH$_3$)$_3$), 88.4 (Cp), 28.8 (C(CH$_3$)$_3$). ^{31}P{^{1}H} NMR (25 °C, CD$_2$Cl$_2$): δ 56.6.

Preparation of [CpRu(PPh$_3$)$_2$(N(O)Bu^t)][BF$_4$] (3[BF$_4$]). To a -78 °C CH$_2$Cl$_2$ (25 mL) solution of CpRu(PPh$_3$)$_2$Cl (0.10 g, 0.138 mmol) was added a -78 °C CH$_2$Cl$_2$ (25 mL) solution of AgBF$_4$ (0.030 g, 0.150 mmol). The resulting mixture was slowly warmed to room temperature over a 1-h period and then filtered to remove the precipitated AgCl. The filtrate was cooled to -30 °C and added to a flask containing Bu^{t}NO monomer at -30 °C, which was prepared as described above from [Bu^{t}NO]$_2$ (0.013 g, 0.077 mmol). The solution was stirred for 1 h at -30 °C and then slowly warmed to room temperature. After the solution volume was reduced to 10 mL, it was filtered, and 50 mL of pentane was added to give a brown precipitate of 3 in 93% yield (0.110 g).

Anal. Calcd for $C_{45}H_{44}BF_4NOP_2Ru$: C, 62.50; H, 5.09. Found (SML): C, 62.51; H, 4.98. ^{1}H NMR (25 °C, CDCl$_3$): δ 7.4–7.0 (m, 30 H, Ph), 5.05 (s, 5 H, Cp), 1.12 (s, 9 H, Bu^t). ^{13}C NMR (CD$_2$Cl$_2$): δ 135–128 (Ph), 100.3 (C(CH$_3$)$_3$), 88.7 (Cp), 29.7 (C(CH$_3$)$_3$). ^{31}P{^{1}H} NMR (25 °C, CDCl$_3$): δ 37.8 (s).

Preparation of CpMn(CO)$_2$(N(O)Bu^t) (4). A benzene (20 mL) solution of CpMn(CO)$_3$ (102 mg, 0.50 mmol) and [Bu^{t}NO]$_2$ (174 mg, 0.50 mmol) was irradiated at room temperature for 0.5 h, during which time the initial yellow solution became dark brown. The benzene was removed by evaporation under a flow of N$_2$, and the residue was extracted with a minimum of CH$_2$Cl$_2$. The CH$_2$Cl$_2$ extract was chromatographed on SiO$_2$ at -30 °C by beginning with neat pentane as eluent and adding increasing amounts of CH$_2$Cl$_2$ up to a 1:1 pentane–CH$_2$Cl$_2$ mixture.

Complex 4 was collected as a brown band, and the solvent was evaporated under a flow of N$_2$ to yield 4 in 27% yield (36 mg, 0.14 mmol) as a dark brown waxy solid. Further purification was accomplished by sublimation at 50 °C under vacuum (0.01 mmHg).

Anal. Calcd for $C_{11}H_{14}MnNO_3$: C, 50.22; H, 5.32. Found (GL): C, 50.04; H, 5.39. IR (CH$_2$Cl$_2$): ν_{CO} = 1972 (s), 1902 (s) cm^{-1}. IR (CH$_2$Cl$_2$): ν_{CO} = 1970 (s), 1892 (s) cm^{-1}; ν_{NO} = 1325 (m) cm^{-1}. ^{1}H NMR (25 °C, CDCl$_3$): δ 4.83 (s, 5 H, Cp), 1.31 (s, 9 H, Bu^t). MS (EI): m/z 263 (M$^+$), and peaks corresponding to loss of two CO's.

Crystallographic Characterization of W(CO)$_5$(N(O)Bu^t) (1). Data collection parameters are given in Table I. Computer programs used in the data collection and refinement for this and the following structure are contained in the Nicolet (Madison, WI) program packages P3, SHELXTL (version 5.1), and XP. Crystals

of W(CO)$_5$(N(O)Bu^t) were attached to fine glass fibers with epoxy cement, and unit-cell dimensions were derived from the least-squares fit of the angular settings of 25 reflections with 20° < 2θ < 26°. A profile-fitting procedure was applied to all intensity data to improve the precision of the measurement of weak reflections. Absorption effects were corrected by using the empirical procedure which employs a pseudoellipsoid to define the crystal. Data were collected to the limits of availability.

The structure was solved by using the direct-methods program SOLV, which located the W atom. Remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically, and hydrogen atom positions were calculated (d(C–H) = 0.96 Å with thermal parameters set equal to 1.2 times the isotropic equivalent for the carbon to which it was attached). Atomic positional parameters are listed in Table II, and important bond distances and angles are set out in Table III.

Crystallographic Characterization of [CpFe(CO)-(PPh$_3$)(N(O)Bu^t)][BF$_4$] (2[BF$_4$]). Table I provides a summary of the crystallographic parameters for 2, all samples of which diffracted weakly. A rather large thin plate of 2 was mounted on a glass fiber with epoxy cement. Photographic characterization and the program TRACER revealed that these crystals had no symmetry higher than triclinic. The centrosymmetric alternative was chosen on the basis of E-value statistics and confirmed by the presence of inversional symmetry in the unit cell. Corrections for absorption were made by using a program (XABS) that obtains an empirical absorption tensor from an expression relating F_o and F_c (H. Hope and B. Moezzi, University of California—Davis).

The structure was solved by direct methods. After all of the atoms in the reported structure were accounted for, a persistent peak in the difference map located near C(16), equivalent in electron density to about half of a typical carbon atom, was interpreted as an alternative Fe atom site. The two Fe sites are equidistant from the phosphorus atom; incorporation of this model reduced $R(F)$ from 11.1 to 9.7%. The next highest peak was less than half as large. Occupancy refinement for the two Fe atom sites produced an Fe:Fe' ratio of 92:8. Of necessity, the remaining light atoms must also be disordered to this extent, but their sites could not be found on subsequent maps. This packing disorder and the consequent disorder in the BF$_4^-$ anion account for the unusually large residuals reported.

All non-hydrogen atoms (except Fe') were refined anisotropically, and all hydrogen atoms were treated as idealized isotropic contributions (d(C–H) = 0.96 Å). The phenyl rings were constrained to regular hexagons (d(C–C) = 1.395 Å). Atomic positional parameters are given in Table IV, and important bond distances and angles are set out in Table IV.