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# Synthesis, Structure, and Reactions of 19-Electron (η^5-C$_5$H$_5$)W(NO)$_2$(PR$_3$) Radicals

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The 18-electron dinitrosyl complexes (η^5-C$_5$H$_5$)W(NO)$_2$(L)$^+$, where L is P(OPh)$_3$, PPh$_3$, or P(OMe)$_3$, undergo a one-electron reduction when reacted with alkoxides, hydrazine, or zinc to yield the purple, air-sensitive, 19-electron, neutral complexes (η^5-C$_5$H$_5$)W(NO)$_2$(L). Cyclic voltammetric studies show these to be quasi-reversible reductions with the reduction potentials becoming more negative with L in the order P(OPh)$_3$ > P(OMe)$_3$ > PPh$_3$. ESR spectra of the (η^5-C$_5$H$_5$)W(NO)$_2$(L) complexes exhibit a 10-line pattern resulting from hyperfine coupling of the unpaired electron with the ^{31}P and two equivalent ^{14}N nuclei. The ν(NO) frequencies of the (η^5-C$_5$H$_5$)W(NO)$_2$(L)$^+$ complexes decrease by 160–175 cm^{-1} upon reduction to (η^5-C$_5$H$_5$)W(NO)$_2$(L); this large decrease is taken to indicate that the electron is added primarily to the NO groups. A single-crystal X-ray diffraction study of (η^5-C$_5$H$_5$)W(NO)$_2$(P(OPh)$_3$) shows that it crystallizes in the monoclinic cell $P2_1/n$ with a = 9.810 (4) Å, b = 14.450 (7) Å, c = 15.45 (1) Å, and β = 91.04 (5)° and four molecules per unit cell. The N–W–N bond angle (102.7°) in this complex is significantly larger than that (92.0°) in the 18-electron analogue CpW(NO)$_2$Cl. Also the 19-electron complex has shorter W–N but longer N–O bonds than in CpW(NO)$_2$Cl, although these differences could be within experimental error. The differences between the 18- and 19-electron structures are readily interpreted in terms of a MO calculation by Hall and co-workers that indicates that the 19th electron will occupy an orbital that has substantial NO 2π character and is antibonding between the two NO ligands and antibonding between the N and O atoms of each NO ligand. The W–N–O angles in (η^5-C$_5$H$_5$)W(NO)$_2$(P(OPh)$_3$) are only slightly bent at 165.7 and 174.9°. The 19-electron complex is readily oxidized back to the (η^5-C$_5$H$_5$)W(NO)$_2$(P(OPh)$_3$)$^+$ cation by a variety of agents such as Ag$^+$, Ph$_3$C$^+$, MeOSO$_2$F, CF$_3$SO$_3$H, and I$_2$.

Introduction

There has been much interest in this laboratory in the reactions of metal carbonyl ligands with nucleophiles such as amines and alkoxides,[2] e.g.

$$M\!-\!C\!\equiv\!O^+ \ + \ OR^- \ \longrightarrow \ M\!-\!C\!\!\begin{smallmatrix}\nearrow O\\[2pt]\searrow OR\end{smallmatrix} \qquad (1)$$
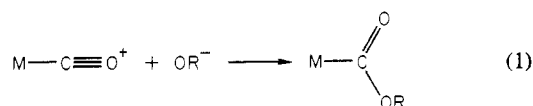
to give carbamoyl and alkoxycarbonyl complexes. While much is known about transition-metal nitrosyl complexes,[3–6] there are, in contrast to the metal carbonyl situation, still relatively few examples of alkoxide attack at nitrosyl ligands to yield alkyl nitrite complexes:[8–10]

$$M\!-\!N\!\equiv\!O^+ \ + \ OR^- \ \longrightarrow \ M\!-\!N\!\!\begin{smallmatrix}\nearrow O\\[2pt]\searrow OR\end{smallmatrix} \qquad (2)$$
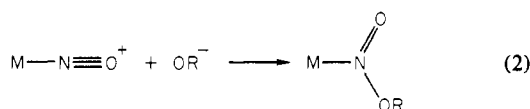
Such reactions appear to occur only in electron-poor complexes in which the ν(NO) frequency is greater than 1850 cm^{-1}.[9]

Although the ν(CO) frequency (2116 cm^{-1})[11] of CpW(NO)$_2$(CO)$^+$ indicates that this complex is sufficiently electron-poor to promote nucleophilic attack at the carbonyl group, its reactions with alkoxides and amines only yielded products resulting from the displacement of the CO group. This result, together with others,[12] suggests that high ν(CO) values not

only indicate enhanced CO susceptibility to nucleophilic attack but also weakened CO bonding to the metal which makes CO displacement more likely.

To probe the possibility that nucleophiles would attack the NO groups in this electron-poor system, we examined the reactions of the phosphite-substituted complexes CpW-(NO)$_2$[P(OR)$_3$]$^+$,[11] where Cp = η^5-C$_5$H$_5$. In reactions with alkoxides, the surprising result was that no products resulting from nucleophilic attack on the NO were identified but instead only one-electron reduction products CpW(NO)$_2$[P(OR)$_3$] were isolated.

Experimental Section

General Procedures. The complexes [CpW(NO)$_2$(P(OR)$_3$)]PF$_6$ and [CpW(NO)$_2$(PPh$_3$)]PF$_6$ were prepared as described in the literature.[11] The supporting electrolyte [(*n*-Bu)$_4$N]BF$_4$ for the electrochemical studies was prepared by mixing [(*n*-Bu)$_4$N]Br and 48% aqueous HBF$_4$ in water, collecting the precipitate by filtration, recrystallizing it twice from acetone–diethyl ether, and drying it in vacuum. Reagent-grade CH$_2$Cl$_2$ was stored over molecular sieves. Other chemicals were purchased from commercial sources.

ESR spectra of solutions were obtained on a Varian E-3 spectrometer operating at 9.52 GHz. The solutions, prepared with acetone deaerated by freeze-thawing, were studied in flat quartz cells at –28 °C under argon. ESR spectra of solids were measured on a Bruker ER 220D SR at about 9.5 GHz at ambient temperature. Infrared spectra were recorded on a Perkin-Elmer Model 281 spectrophotometer.

Hydrocarbon products were analyzed on a Varian 3700 FID gas chromatograph equipped with a $^1/_8$ in. × 6 ft 5% OV 101 column. Other organic products were analyzed on a Varian 1700 TCD gas chromatograph with a $^1/_4$ in. × 15 ft 10% DC550 column. Electrochemical experiments were carried out on a Princeton Applied Research Model 173 potentiostat and Model 175 universal programmer. Cyclic voltammograms were obtained with a platinum-disk working electrode, a platinum wire counterelectrode, and a saturated (NaCl) calomel (SSCE) reference electrode. The solutions contained approximately 1 × 10^{-3} M complex and 0.1 M [(*n*-Bu)$_4$N]BF$_4$ supporting electrolyte; the scan rate was 20 mV/s.

Synthesis of CpW(NO)$_2$(L) by NaOR Reduction. A 0.035-g (0.66-mmol) sample of NaOMe was suspended in 5 mL of CH$_2$Cl$_2$ under an N$_2$ atmosphere. Subsequently, 0.10 g (0.13 mmol) of [CpW(NO)$_2$(P(OPh)$_3$)]PF$_6$ was added to the solution. The green mixture was stirred for 30 min at room temperature. The solution had then become red-brown and was evaporated at 25 °C under

(1) Operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-ENG-82. This work was supported by the Office of Basic Energy Sciences, Chemical Sciences Division.
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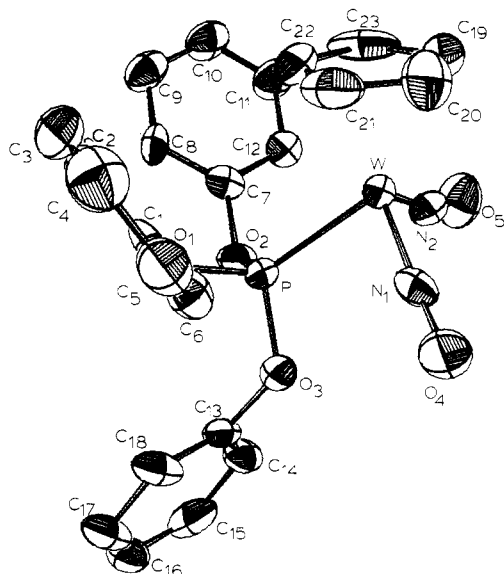(12) Hershberger, S.; Angelici, R. J., unpublished results.

vacuum; the residue was extracted twice with 15 mL of diethyl ether. The solution was filtered through Celite under nitrogen pressure. Pentane (10 mL) was added to the purple ether solution, which was then chilled to -20 °C in a CCl_4–dry ice bath overnight. Analytically pure purple crystals of $CpW(NO)_2(P(OPh)_3)$ were obtained (0.025 g, 31%). Anal. Calcd: C, 44.62; H, 3.23; N, 4.52. Found: C, 44.57; H, 3.29; N, 4.58.

The other complexes $CpW(NO)_2(PR_3)$ were prepared by the same method in similar yields and were characterized by their IR spectra (Table III). The $CpW(NO)_2(PR_3)$ complexes are very sensitive to air and should be stored under argon at -20 °C.

A procedure similar to that used in the NaOMe reaction was also used for the other alkoxide (NaOCH$_2$Ph, NaOEt, NaOCMe$_3$, and NaOCH(CH$_3$)$_2$) reduction reactions.

Reduction of [CpW(NO)$_2$(L)]PF$_6$ with N$_2$H$_4$·H$_2$O. A 0.10-g (0.13-mmol) sample of [CpW(NO)$_2$(P(OPh)$_3$)]PF$_6$ was dissolved in 5 mL of CH_2Cl_2 under an N_2 atmosphere. Subsequently, 17.5 μL (0.66 mmol) of N$_2$H$_4$·H$_2$O (64% in H$_2$O) was injected through a rubber septum into the CH_2Cl_2 solution. The greenish solution turned red within 1 min, and the solvent was removed under vacuum. Using the same workup employed in the previous synthesis, we obtained 0.053 g (65%) of IIa. Complexes IIb and IIc were also obtained in good yields with this method (50–60%).

Reduction of [CpW(NO)$_2$(P(OPh)$_3$)]PF$_6$ with NaOH. To a suspension of crushed NaOH (0.40 g, 10 mmol) in 5 mL of CH_2Cl_2 under an N_2 atmosphere was added 0.20 g (0.26 mmol) of [CpW(NO)$_2$-(P(OPh)$_3$)]PF$_6$ and 0.1 mL of degassed water. The mixture was allowed to react at room temperature for 30 min. Following the workup procedure described for the NaOR reduction, we isolated 0.042 g (26%) of $CpW(NO)_2(P(OPh)_3)$.

Reduction of [CpW(NO)$_2$(P(OPh)$_3$)]PF$_6$ with Zn. Zinc dust (0.20 g, 3.1 mmol) was added to a solution of [CpW(NO)$_2$(P(OPh)$_3$)]PF$_6$ (0.05 g, 0.07 mmol) in 5 mL of THF. After the mixture was stirred at room temperature for 30 min, $CpW(NO)_2(P(OPh)_3)$ was isolated as given in the NaOR reduction procedure in 24% (0.01 g) yield.

Reaction of CpW(NO)$_2$(P(OPh)$_3$) (IIa) with [Ph$_3$C]BF$_4$. A 0.027-g (0.044-mmol) sample of $CpW(NO)_2(P(OPh)_3)$ was dissolved in 2 mL of CH_2Cl_2 under an N_2 atmosphere, and 0.015 g (0.046 mmol) of [Ph$_3$C]BF$_4$ was added. The purple solution turned green immediately. The solvent was removed under vacuum, and the green residue was extracted with 6 mL of diethyl ether. The extract was filtered through a glass-fiber filter, and the solvent was slowly evaporated from the filtrate in air; a white precipitate was obtained. The solid was washed with acetone and dried under vacuum, leaving 0.002 g (13%) of Ph$_3$COOCPh$_3$, which was identified by its melting point[13] and mass spectrum. The green residue was redissolved in CH_2Cl_2 and was identified as Ia (88%) by the positions and intensities of its ν(NO) IR absorptions.

Reaction of IIa with HSO$_3$CF$_3$. A 0.03-g (0.05-mmol) sample of IIa was dissolved in 2 mL of CH_2Cl_2 under N_2, and 4.4 μL (0.071 mmol) of HSO$_3$CF$_3$ was injected into the solution. A green solution was obtained immediately. It was diluted further with an additional 4 mL of CH_2Cl_2; Ia (75%) was identified in the infrared spectrum of the solution. The same procedure was employed in the reaction of $CpW(NO)_2(P(OPh)_3)$ with CH_3SO_3F. The CH_3SO_3F reaction was complete within 1 min, and Ia (70%) was identified in solution by IR; the gas phase analyzed by GC contained ethane.

Reaction of IIa with AgBF$_4$. A 0.03-g (0.05-mmol) sample of IIa was dissolved in 2 mL of CH_2Cl_2 under N_2, and 0.01 g (0.05 mmol) of AgBF$_4$ was added to the solution. The purple solution became green within 1 min. The resulting solution was analyzed by IR and contained Ia (80%).

Reaction of IIa with I$_2$. A 0.03-g (0.05-mmol) sample of IIa was dissolved in 2 mL of CH_2Cl_2 under N_2, and a small crystal of I$_2$ was added to the solution. The purple solution gradually turned green in a period of 15 min. Ia and $CpW(NO)_2I$ were identified in the reaction mixture by their infrared spectra. Stirring the solution for an additional 15 min resulted in the disappearance of Ia and the increase of $CpW(NO)_2I$ to about 75%.

Crystal Data: $CpW(NO)_2(P(OPh)_3)$, mol wt 618.58, monoclinic, $P2_1/n$, $a = 9.810$ (4) Å, $b = 14.450$ (7) Å, $c = 15.45$ (1) Å, $\beta = 91.04(5)°$, $V = 2189.7$ Å^3, $\rho_{calcd} = 1.876$ g/cm^3, $Z = 4$, and $\mu = 56.9$ cm^{-1}.

(13) Bachmann, W. E. *J. Am. Chem. Soc.* **1931**, *53*, 2758.

Data Acquisition: Automated Syntex $P2_1$ four-circle diffractometer; Mo Kα ($\lambda = 0.71069$ Å); ω scan; 4170 reflections measured in almost four octants; $2\theta \leq 50°$; Lorentz–polarization, absorption,[14a] and decomposition corrections applied; 2581 reflections with $I \geq 3\sigma_I$ after averaging; agreement between equivalent reflections 4%.

The title compound yielded purple platelike crystals, which were readily indexed with 12 independent reflections and an automatic indexing procedure.[14b] Appreciable (approximately 10%) and accelerating decay was noted approximately midway through data collection; therefore a second crystal was mounted and used for the latter part of data collection, and the two data sets were scaled to a common basis. The standard heavy-atom technique was used for structural solution, and a combination of block-matrix–full-matrix least-squares refinement[15] of all non-hydrogen atoms converged to conventional and weighted residuals of $R = 0.061$ and $R_w = 0.067$, respectively. The scattering factors[16] were modified for anomalous dispersion effects,[17] and hydrogens were included but not refined.

Results and Discussion

Reduction of CpW(NO)$_2$(L)$^+$. If the NO groups are each considered 3-electron donors, the $CpW(NO)_2(L)^+$ complexes are 18-electron systems. They react with a variety of reducing agents to give (eq 3) the 19-electron complexes CpW-

$$CpW(NO)_2(L)^+ \xrightarrow[\text{agent}]{\text{reducing}} CpW(NO)_2(L) \qquad (3)$$
$$\text{Ia–c} \qquad\qquad\qquad \text{IIa–c}$$

$$L = P(OPh)_3 \text{ (Ia), } PPh_3 \text{ (Ib), } P(OMe)_3 \text{ (Ic)}$$
$$\text{reducing agents} = OR^-, OH^-, N_2H_4\cdot H_2O, Zn$$

(NO)$_2$(L). The reaction of $CpW(NO)_2(P(OPh)_3)^+$ (Ia) with excess NaOMe in CH_2Cl_2 produces a purple solution from which an air- and heat-sensitive purple compound (IIa) is isolated in 31% yield. In air, IIa decomposes in solution within 30 min. Even in the solid state under argon at -20 °C, it shows evidence of decomposition within 15 days.

The same purple compound is isolated from reactions of Ia with PhCH$_2$O$^-$, i-PrO$^-$, t-BuO$^-$, EtO$^-$, and OH$^-$. The mechanism of these reductions is not known, but the alkoxide may act as a one-electron donor giving RO· as the initial product. Subsequently, the β-H or alkyl group of RO· could be lost or abstracted by another RO· to give the corresponding aldehyde or ketone and alcohol.[18] In support of this possibility is the GC detection of PhCHO and PhCH$_2$OH as products of the reaction of Ia with PhCH$_2$O$^-$. The complexes $CpW(NO)_2$-$(PPh_3)^+$ (Ib) and $CpW(NO)_2(P(OMe)_3)^+$ (Ic) are also reduced to give similar yields of IIb and IIc, but these products are much less stable to heat and to air than IIa. Due to their instability they were only characterized by their spectra and electrochemistry.

A still better reducing agent is hydrazine hydrate, N_2H_4·H_2O, which converts Ia to IIa in 65% yield. This is also the more effective reducing agent for the preparations of IIb and IIc. Powdered Zn reduces Ia, but the reaction is much slower ($\sim$30 min) and decomposition of the product IIa greatly reduces the yield.

Structure of CpW(NO)$_2$(P(OPh)$_3$). Although the spectroscopic properties of the $CpW(NO)_2(L)$ compounds are consistent with a mononuclear complex, there was some

(14) (a) An empirical absorption correction was made with use of the method described by: Karcher, B. A. Ph.D. Dissertation, Iowa State University, 1981. (b) Jacobson, R. A. *J. Appl. Crystallogr.* **1976**, *9*, 115.

(15) Lapp, R. L.; Jacobson, R. A. "ALLS, A Generalized Crystallographic Least Squares Program", USDOE Report; Iowa State University and Ames Laboratory: Ames, Iowa, 1979.

(16) Cromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A, pp 71–97.

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(18) Kochi, J. K. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, pp 677–692.

Figure 1. ORTEP drawing of CpW(NO)₂(P(OPh)₃) (IIa).

Table I. Final Positional Parameters and Their Estimated Standard Deviations (in Parentheses)[a] for CpW(NO)₂P(OPh)₃

atom	x	y	z
W	0.5938 (0)	0.3837 (0)	0.5978 (0)
P	0.2921 (4)	0.7621 (2)	0.3960 (2)
O1	0.3164 (11)	0.8282 (7)	0.3157 (6)
O2	0.1291 (11)	0.7650 (7)	0.3953 (6)
O3	0.3220 (12)	0.8259 (7)	0.4775 (7)
O4	0.6328 (14)	0.7000 (8)	0.5099 (9)
O5	0.2052 (15)	0.5200 (10)	0.5199 (9)
N1	0.5362 (14)	0.6679 (8)	0.4685 (9)
N2	0.2875 (18)	0.5739 (10)	0.4803 (9)
C1	0.4383 (17)	0.8242 (9)	0.2662 (11)
C2	0.4243 (21)	0.8155 (12)	0.1765 (11)
C3	0.5399 (25)	0.8104 (13)	0.1275 (11)
C4	0.6675 (22)	0.8174 (14)	0.1657 (14)
C5	0.6779 (21)	0.8291 (13)	0.2555 (14)
C6	0.5642 (19)	0.8314 (11)	0.3064 (12)
C7	0.0543 (14)	0.7092 (10)	0.3363 (10)
C8	0.0393 (19)	0.7370 (12)	0.2526 (11)
C9	−0.0287 (20)	0.6794 (14)	0.1938 (12)
C10	−0.0801 (20)	0.5967 (14)	0.2214 (12)
C11	−0.0697 (21)	0.5700 (14)	0.3091 (12)
C12	0.0067 (16)	0.6276 (12)	0.3659 (10)
C13	0.2731 (17)	0.9155 (10)	0.4898 (10)
C14	0.1688 (19)	0.9229 (11)	0.5513 (12)
C15	0.1206 (24)	1.0162 (16)	0.5711 (12)
C16	0.1832 (25)	1.0907 (12)	0.5298 (14)
C17	0.2806 (25)	1.0774 (12)	0.4716 (14)
C18	0.3333 (21)	0.9873 (12)	0.4515 (12)
C19	0.4420 (29)	0.4713 (14)	0.3443 (12)
C20	0.5555 (25)	0.5213 (17)	0.3283 (15)
C21	0.5261 (26)	0.5952 (14)	0.2741 (14)
C22	0.3876 (23)	0.5877 (13)	0.2528 (10)
C23	0.3275 (22)	0.5132 (15)	0.2971 (14)

[a] Positional parameters are listed in fractional unit cell coordinates.

question whether these 19-electron compounds might be dimers, especially in the solid state. To examine this possibility, as well as to determine whether the added electron causes the expected linear NO in CpW(NO)₂(L)⁺ to bend in the neutral complex, we performed an X-ray structural investigation of CpW(NO)₂(P(OPh)₃) (IIa).

As shown in the ORTEP drawing (Figure 1) of IIa, the complex is clearly mononuclear with a three-legged piano-stool structure. There are no unusually short distances between molecules that would suggest intermolecular interactions. Final positional parameters for the atoms are given in Table I, and selected bond distances and angles are given in Table

Table II. Selected Interatomic Distances (Å) and Bond Angles (Deg) and Their Estimated Standard Deviations (in Parentheses) for CpW(NO)₂P(OPh)₃

A. Bond Distances

W–P	2.386 (4)	N2–O5	1.20 (2)
W–N1	1.78 (1)	P–O1	1.58 (1)
W–N2	1.80 (1)	P–O2	1.59 (1)
W–C19	2.30 (2)	P–O3	1.58 (1)
W–C20	2.32 (2)	C19–C20	1.35 (3)
W–C21	2.33 (2)	C20–C21	1.38 (3)
W–C22	2.34 (1)	C21–C22	1.39 (3)
W–C23	2.32 (2)	C22–C23	1.41 (2)
N1–O4	1.22 (2)	C23–C19	1.46 (3)

B. Bond Angles

W–N1–O4	174.9 (1.2)	W–P–O2	119.4 (4)
W–N2–O5	165.7 (1.3)	W–P–O3	113.7 (4)
N1–W–N2	102.7 (6)	O1–P–O3	104.0 (6)
P–W–N1	89.0 (4)	O1–P–O2	98.2 (6)
P–W–N2	91.0 (5)	O2–P–O3	99.2 (6)
W–P–O1	119.0 (4)		
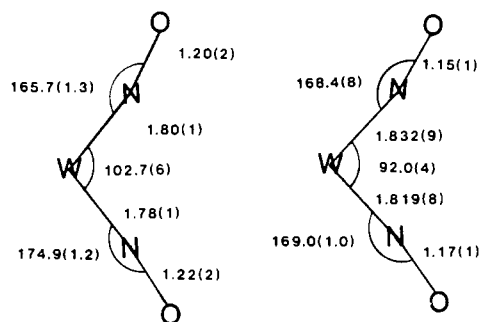
CpW(NO)₂(P(OPh)₃),IIa   **CpW(NO)₂Cl**

Figure 2. Bond distances and angles associated with the NO groups in IIa and CpW(NO)₂Cl.[21]

II. Within experimental error, the W–C(cyclopentadienyl) distances are equal, and the C–C distances in the ring are equal within approximately 3 standard deviations, yet the C23–C19 distance (1.46 Å) is somewhat longer than the average (1.40 Å). Both the W–C and C–C distances of the Cp ring in IIa are comparable to those in the 18-electron complex CpW-(NO)₂Cl.[19]

If one assumes that the 18-electron CpW(NO)₂(P(OPh)₃)⁺ complex has a structure very similar to that of structurally characterized CpW(NO)₂Cl, then any deviation in the structure of IIa from CpW(NO)₂Cl might be attributed to effects of the extra electron in IIa. The major differences between IIa and CpW(NO)₂Cl occur in the distances and angles associated with the NO ligands; these are shown in Figure 2. There is much discussion in the literature[3-8] about the influence of electron density on M–N–O bond angles in metal nitrosyl complexes. In some systems, additional electron density provided to the complex causes a linear M–N–O bond to become bent, even up to 120°. As seen in Figure 2, there is little difference in the average W–N–O bond angles between CpW(NO)₂Cl (168.7° average) and CpW(NO)₂(P(OPh)₃) (170.3° average), although there is a greater variation between the two angles in IIa than in CpW(NO)₂Cl. Differences appear more evident in the W–N–O distances, although standard deviations are too large to prevent their unequivocal interpretation. In the 19-electron IIa the W–N distances (1.79 Å average) are shorter than those in CpW(NO)₂Cl (1.825 Å average), while the N–O distances in IIa (1.21 Å average) are longer than in CpW(NO)₂Cl (1.16 Å average). The major

(19) Greenhough, T. J.; Kolthammer, B. W. S.; Legzdins, P.; Trotter, J. *Acta Crystallogr., Sect. B* **1980**, *B36*, 795.

Table III. IR and ESR Data for I and II

complex	$\nu(NO),^a$ cm^{-1}	EPR data^b
$[CpW(NO)_2(P(OPh)_3)]PF_6$	1788 (s), 1712 (vs)	
$CpW(NO)_2(P(OPh)_3)$	1613 (s), 1553 (s)	$a_N = 7.0$ G, $a_P = 5.0$ G^c
$[CpW(NO)_2(P(Ph)_3)]PF_6$	1770 (vs), 1690 (s)	
$CpW(NO)_2(P(Ph)_3)$	1595 (s), 1526 (vs)	$a_N = 7.0$ G, $a_P = 4.4$ G^c
$[CpW(NO)_2(P(OCH_3)_3)]PF_6$	1777 (s), 1702 (vs)	
$CpW(NO)_2P(OCH_3)_3$	1605 (s), 1533 (vs)	d

^{a} Solvent CH_2Cl_2. ^{b} Solvent acetone, temperature -28 °C. ^{c} The g value is 2.02, obtained at room temperature in the solid state with DPPH as the internal reference. ^{d} Decomposed too rapidly for ESR measurement.

difference in structure is the substantially larger N–W–N angle in IIa (102.7°) as compared to that in $CpW(NO)_2Cl$ (92.0°).

These structural differences in the 18- and 19-electron complexes may be readily understood in terms of a recent molecular orbital calculation[20] for complexes of the type $CpM(NO)_2X$, where M = Cr, W and X = Cl, Br, I. The lowest unoccupied MO (13a″ in Figure 2 of ref 20) of $CpCr(NO)_2Cl$, which is separated from higher energy MO's and would accept the 19th electron, has 89% NO 2π character and is antibonding between the two NO ligands and antibonding between the N and O atoms of each NO ligand.[21] Thus, occupation of this level would lead to an increase in the N–W–N bond angle and an increase in the N–O bond distances, which are the observed major structural differences between IIa and $CpW(NO)_2Cl$. Although 13a″ is 89% NO 2π in $CpCr(NO)_2Cl$, the phosphite will contribute some phosphorus character to this MO in $CpW(NO)_2(P(OPh)_3)$ and reduce the NO 2π character.[21] The lengthening of the NO bond distance lowers the energy of the 2π orbital, thereby increasing the W–N π bonding. This effect is reflected in the shorter W–N bond distance.

Infrared and ESR Spectra and Electrochemistry of the $CpW(NO)_2(L)$ Complexes. The $\nu(NO)$ frequencies in the infrared region of Ia (1788, 1712 cm^{-1}) are 160–175 cm^{-1} higher than those (1613, 1553 cm^{-1}) in the 19-electron reduced complex IIa. Similar changes in $\nu(NO)$ values in complexes Ib and Ic are also observed (Table III). These decreases of $\nu(NO)$ values upon one-electron reduction are substantially larger than those observed (50 cm^{-1}) in the pair $Fe(NO)$-$(das)_2^{2+}$ (1760 cm^{-1}) and $Fe(NO)(das)_2^+$ (1710 cm^{-1}), which are 17- and 18-electron species, respectively (das = o-phenylenebis(dimethylarsine)).[22] Much larger decreases (~ 300 cm^{-1}) in $\nu(NO)$ are observed upon reduction of 18-electron complexes such as $Ru(bpy)_2(NO)Cl^{2+}$ (1940 cm^{-1}) to 19-electron $Ru(bpy)_2(NO)Cl^+$ (1640 cm^{-1}).[23] These IR and other studies were interpreted to indicate that the additional electron in the 19-electron ruthenium complex is primarily localized on the NO group. In the present CpW-$(NO)_2(L)$ complexes, the 160–175-cm^{-1} shift in $\nu(NO)$ suggests that the additional electron is substantially on the two NO ligands, as was also inferred from the X-ray structural results.

ESR spectra of IIa and IIb in acetone solution at -28 °C show a 10-line pattern with approximate peak intensities of 1:1:2:2:3:3:2:2:1:1 (Figure 3). This pattern results from hyperfine coupling of the unpaired electron with the two equivalent ^{14}N ($I = 1$) and ^{31}P ($I = {}^1\!/_2$) nuclei. Coupling
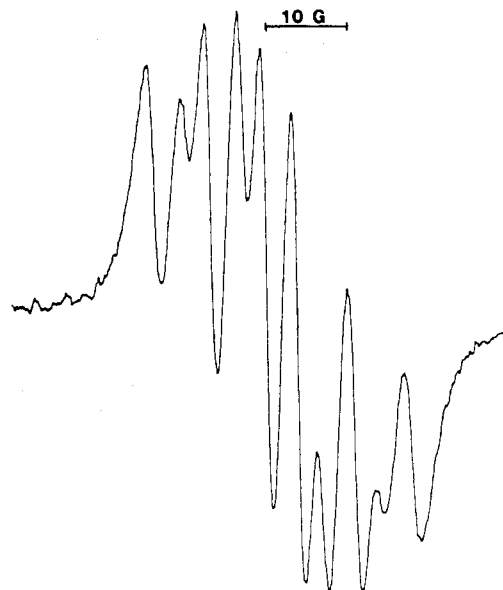
Figure 3. ESR spectrum of $CpW(NO)_2(PPh_3)$ in acetone at -28 °C.

Table IV. Reduction Potentials for the $[CpW(NO)_2L]PF_6$ Complexes

complexes^b	$E_{1/2}(1)$, V	$E_{1/2}(2)$, V
$[CpW(NO)_2(P(OPh)_3)]PF_6$	-0.09	-1.58
$[CpW(NO)_2(P(OCH_3)_3)]PF_6$	-0.16	-1.60
$[CpW(NO)_2(P(Ph)_3)]PF_6$	-0.18	-1.68

^{a} Carried out in CH_2Cl_2 (0.1 M $[Bu_4N]BF_4$) solution with a scan rate of 20 mV/s. The potentials are measured against a SSCE reference electrode. ^{b} Concentrations of the complexes are 1×10^{-3} M.

Scheme I
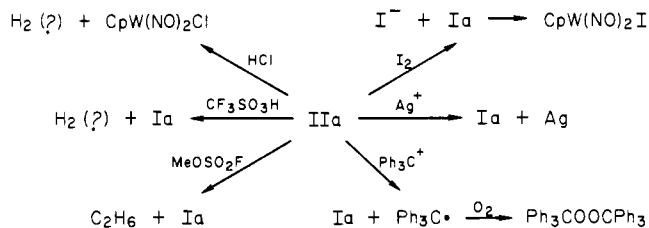
constants to ^{14}N are 7.0 G in both IIa and IIb; the coupling constant to ^{31}P is 5.0 G in IIa and 4.4 G in IIb. Both compounds in the solid state have G values of 2.02 (Table III).

ESR spectra of two other 19-electron dinitrosyl species, $Fe(CO)_2(NO)_2^-$ and $Co(NO)_2(CO)_2$,[24,25] generated in situ by irradiation, were interpreted to indicate that the unpaired electron is largely confined to the NO ligands. It appears therefore that the addition of another electron to an 18-electron dinitrosyl complex occurs predominantly into the NO ligands.

Reduction potentials of the $CpW(NO)_2(L)^+$ complexes in CH_2Cl_2 solution were determined by cyclic voltammetry (Table IV). All complexes undergo reduction in two steps. The first wave is quasi-reversible and occurs at -0.09 to 0.18 V. The small potentials for these reductions account for the easy chemical reductions of I to II. The second wave is nonreversible showing no corresponding oxidation peak on the reverse scan. Although the product of the second reduction step is not clear, a possible species is the 20-electron anion $CpW(NO)_2(L)^-$. An attempt to prepare this anion of IIa in

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THF solution was made by reduction of IIa with 3% sodium amalgam. This reaction yielded only a clear solution that showed no $\nu(NO)$ absorptions. Both the first and the second reduction potentials become more negative with changes in L in the order $P(OPh)_3 > P(OMe)_3 > PPh_3$. This is also the order of decreasing π-acceptor:σ-donor ratios for these ligands, which is consistent with the most strongly electron-withdrawing phosphorus ligands giving the most easily reduced species.

Reactions of $CpW(NO)_2(P(OPh)_3)$. The $CpW(NO)_2(P-(OPh)_3)$ complex (IIa) is easily oxidized to the cation $CpW-(NO)_2(P(OPh)_3)^+$ (Ia) by a variety of oxidizing agents (Scheme I). The purple CH_2Cl_2 solution of IIa becomes the characteristic green of Ia within 1 min upon treatment with $AgBF_4$. Oxidation of IIa by $Ph_3C^+BF_4^-$ occurs immediately; the organic product, $Ph_3COOCPh_3$, is isolated in 13% yield, presumably formed from $Ph_3C\cdot$ during workup of the reaction mixture in air.[13]

The reaction of IIa with CH_3OSO_2F is complete within 1 min and yields Ia and the reduction product ethane, which was detected by gas chromatography. An immediate reaction occurs between IIa and CF_3SO_3H to give 75% Ia; the other product is presumably H_2. When HCl gas is slowly bubbled into a CH_2Cl_2 solution of IIa, $CpW(NO)_2Cl$ is the only NO-containing product identified by IR in the reaction solution. The formation of $CpW(NO)_2Cl$ presumably occurs by Cl^- substitution of $P(OPh)_3$ in Ia generated by acid oxidation.

When I_2 is added to a CH_2Cl_2 solution of IIa, the purple solution gradually turns green over a 15-min period; at this stage both Ia and $CpW(NO)_2I$ are present. When the solution stands an additional 15 min, only $CpW(NO)_2I$ is present in 75% yield; presumably Ia is converted to the iodo complex by substituion of the $P(OPh)_3$ in Ia.

To examine the possibility that the $CpW(NO)_2(P(OPh)_3)$ radical initiates the polymerization of styrene, we added IIa to a CH_2Cl_2 solution of styrene; no reaction occurred.

Note Added in Proof. The extra electron in the dithiocarbamato complexes $M(R_2dtc)_2(NO)_2^-$, M = Mo or W, is also delocalized over both NO groups: Budge, J. R.; Broomhead, J. A.; Boyd, P. D. *Inorg. Chem.* **1982,** *21,* 1031.

Registry No. Ia, 53419-13-9; Ib, 53419-05-9; Ic, 53419-11-7; IIa, 82044-72-2; IIb, 82044-73-3; IIc, 82044-74-4; $CpW(NO)_2I$, 53419-16-2; $Ph_3COOCPh_3$, 596-30-5; $[Ph_3C]BF_4$, 341-02-6.

Supplementary Material Available: Tables of calculated hydrogen atom positions, additional bond distances and angles, thermal parameters, and observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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Organometallic Nitrosyl Chemistry. 17.[1] Solvent Control of the Reactions of Dicyclopentadienyliodonitrosylmolybdenum with Some Silver(I) Salts

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Stoichiometric reactions between $(C_5H_5)_2Mo(NO)I$ and equimolar amounts of AgY ($Y = BF_4$ or SbF_6) produce different organometallic nitrosyl complexes depending upon the solvent employed. In acetonitrile, the monomeric cation $[(C_5H_5)_2Mo(NO)(CH_3CN)]^+$ results and can be isolated as its Y^- salt in good yields. In aqueous acetone, the final isolable products are the trimetallooxonium salts, $[((\eta^5-C_5H_5)Mo(NO)(OH))_3O]Y$, which probably result from initial formation of the aquo cation $[(C_5H_5)_2Mo(NO)(OH_2)]^+$. [The iodo analogue of the trimetallic hydroxo species can be prepared by treatment of an aqueous acetone solution of $[(\eta^5-C_5H_5)Mo(NO)I_2]_2$ with AgY in 1:2 stoichiometry.] In dichloromethane, the Lewis acid–base adducts $(C_5H_5)_2M(NO)I\cdot AgY$ form and precipitate in high yields for both M = Mo or W. These adducts react with the donor solvents in which they dissolve, converting in acetonitrile to the $[(C_5H_5)_2M(NO)(CH_3CN)]^+$ cations and in aqueous acetone to the trimetallooxonium salts. In none of the solvents investigated do the AgY salts transform $(C_5H_5)_2Mo(NO)I$ to $[(\eta^5-C_5H_5)_2Mo(NO)]^+$, this novel cation only being formed in low yield when an excess of $AlCl_3$ in CH_2Cl_2 is used as the iodide-abstracting reagent. The physical properties of all new compounds prepared are presented and discussed in relation to possible molecular structures.

Introduction

Since the first report of its existence in 1968,[2] $(C_5H_5)_2Mo(NO)I$ has attracted considerable attention.[3,4] In particular, the molecular structure of the complex in solutions and the mode of attachment of the cyclopentadienyl rings to the metal center have been the subjects of much speculation. Static structures such as $(\eta^5-C_5H_5)(\eta^3-C_5H_5)Mo(NO)I^2$ and $(\eta^4-C_5H_5)_2Mo(NO)I^3$ have been proposed for this stereochemically nonrigid compound, and it has also been suggested that the complex might exist transitionally as $(\eta^5-C_5H_5)(\eta^1-C_5H_5)Mo(NO)I$ (possibly solvated) with the η^1- and

$\eta^5-C_5H_5$ rings rapidly exchanging their electronic roles.[4] In any event, it is clear from the previous studies that not all of the available electron density on the cyclopentadienyl ligands is being utilized by the metal. Consequently, it should be possible to effect the iodide-abstraction reaction

$$(C_5H_5)_2Mo(NO)I \xrightarrow{-I^-} [(\eta^5-C_5H_5)_2Mo(NO)]^+ \quad (1)$$
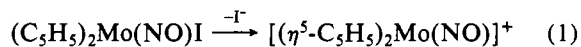
a process that would be facilitated by the concomitant linkage of both C_5H_5 rings to the molybdenum atom in an η^5 fashion in order that the metal center may retain the favored 18-electron configuration.

One of the principal methods for accomplishing conversions of the type (1) involves treatment of the organometallic halide with various silver(I) salts. Generally, the cationic complexes thus produced are 18-electron species in which either a donor solvent (e.g., CH_3CN, THF, acetone, etc.) or a ligated counterion (e.g., BF_4^-, PF_6^-, SbF_6^-, etc.) has replaced the halide in the metal's coordination sphere, the latter situation occurring

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