Contribution from the Department of Chemistry, The University of Chicago, Chicago, Illinois 60637,
and Central Research Laboratory, Monsanto Company, St. Louis, Missouri 63167

Syntheses and Reactions of $WH(CO)_2(NO)(P(C_6H_5)_3)_2$ and Related Tungsten Nitrosyl Complexes

Gregory L. Hillhouse*[†] and Barry L. Haymore[‡]

Received May 2, 1986

cis-$W(CO)_4(PPh_3)_2$ (**1c**) or *trans*-$W(CO)_4(PR_3)_2$ (**1t**) ($R = C_6H_5$, *p*-$CH_3C_6H_4$) reacted with $NOPF_6$ in methylene chloride to give *cis,mer*-$[W(CO)_3(NO)(PR_3)_2][PF_6]$ (**2**-PF_6); BF_4^- and ClO_4^- salts (**2**-BF_4; **2**-ClO_4) were also prepared. Halide anions ($X = Cl^-, Br^-, I^-$) reacted with **2** first to give *mer*-$WX(CO)_3(NO)(PPh_3)$ (**7a**, X = Cl; **7b**, X = Br; **7c**, X = I) and PPh_3, then *cis,cis*-$WX(CO)_2(NO)(PPh_3)_2$ (**6a**, X = Cl; **6b**, X = Br; **6c**, X = I), and finally *trans,trans*-$WX(CO)_2(NO)(PPh_3)_2$ (**3a**, X = F; **3b**, X = Cl; **3c**, X = Br; **3d**, X = I). Further reaction of **3c** with $NOPF_6$ and *n*-Bu_4NX gave $WXBr(NO)_2(PPh_3)_2$ (**4c**, X = Br; **4f**, X = F). Upon reaction with NO^+, *trans*-$Cr(CO)_4(PPh_3)_2$ gave good yields of *trans*-$[Cr(CO)_4(PPh_3)_2][PF_6]$ (**5**), but *trans*-$Mo(CO)_4(PPh_3)_2$ produced complex mixtures. Acetate reacted with **2** to form *trans,trans*-$W(\eta^1\text{-}CH_3CO_2)(CO)_2(NO)(PPh_3)_2$ (**8**) and then *trans*-$W(\eta^2\text{-}CH_3CO_2)(CO)(NO)(PPh_3)_2$ (**11**) and CO. Dimethyldithiocarbamate reacted with **2** to form *cis*-$W(\eta^2\text{-}S_2CNMe_2)(CO)_2(NO)(PPh_3)$ (**13**) and PPh_3 and then *trans*-$W(\eta^2\text{-}S_2CNMe_2)(CO)(NO)(PPh_3)_2$ (**14**). In the presence of $LiBH_4$ and PPh_3 in tetrahydrofuran, both **3c** and **2** were transformed into the tungsten(0) hydride *trans,trans*-$WH(CO)_2(NO)(PPh_3)_2$ (**15**). This hydride underwent α-insertion reactions with RN_3 and RN_2^+, forming *trans*-$W(\eta^2\text{-}RN_3H)(CO)(NO)(PPh_3)_2$ (**19a**, R = Ph; **19b**, R = To) and *trans,trans*-$[W(RN_2H)(CO)_2(NO)(PPh_3)_2]^+$ (**23**, R = Ph; **24**, R = To), and it underwent β-insertion reactions with RNCNR, CO_2, and CS_2, forming *trans*-$W(\eta^2\text{-}RNCHNR)(CO)(NO)(PPh_3)_2$ (**21**, R = To), *trans,trans*-$W(\eta^1\text{-}HCO_2)(CO)_2(NO)(PPh_3)_2$ (**9**), and *trans,trans*-$W(\eta^1\text{-}HCS_2)(CO)_2(NO)(PPh_3)_2$ (**22**). Heating the hydride with RN=NNHR and RN=CHNHR produced *trans*-$W(\eta^2\text{-}RN_3R)(CO)(NO)(PPh_3)_2$ (**20**) and **21**, respectively. When allowed to react with acids (HX; X = Cl, Br, I, CH_3CO_2, HCO_2, $OClO_3$), **15** gave *trans,trans*-$WX(CO)_2(NO)(PPh_3)_2$ (**3b**, **3c**, **3d**, **8**, **9**, **16** ($X = OClO_3$)). The perchlorato ligand in **16** was rapidly displaced by halide and pseudohalide anions but *not* by CO even at 1000 psi (20-80 °C).

Introduction

We set out to prepare $WH(CO)_2(NO)(PPh_3)_2$ with the intent of comparing its reactivity with those of other third-row transition-metal hydrides such as $ReH(CO)_3(PPh_3)_2$,[1] $ReHCl(CO)(NO)(PPh_3)_2$,[2] $OsHCl(CO)_2(PPh_3)_2$,[3] and $IrHCl_2(CO)(PPh_3)_2$.[4] It was our thought that such a d^6 complex, with a nitrosyl ligand disposed trans to a hydride, might exhibit interesting, unusual reactivity.

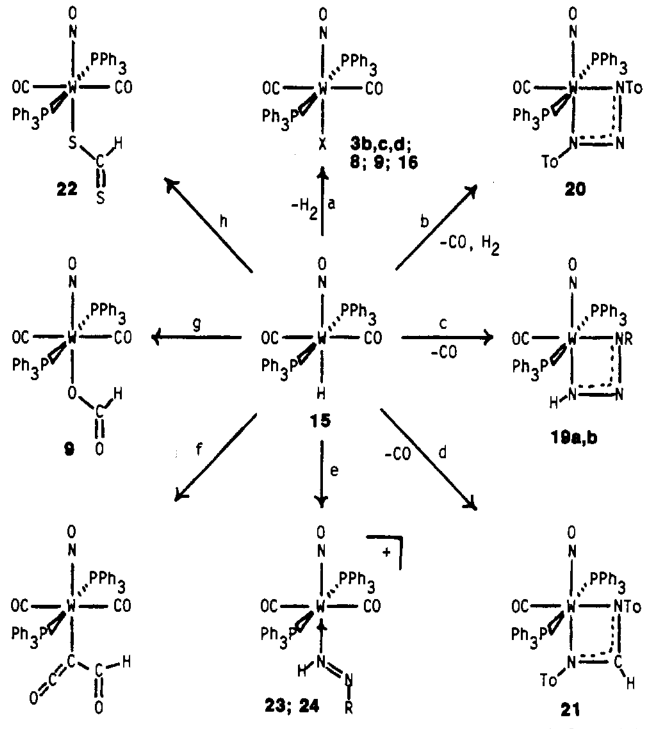
There were few known zerovalent tungsten hydrides when we initiated our work; however, analogous halide complexes were known. The complexes of the type $WX(CO)_2(NO)L_2$ (X = halogen; L = phosphine, arsine, isocyanide) were prepared from $WX(CO)_4(NO)$[5,6] which in turn came from $[WX(CO)_5]^-$ or $HW_2(NO)(CO)_9$. Analogous complexes with chelating ditertiary phosphines, $WX(CO)_2(NO)(LL)$, were similarly prepared from $WX(CO)_4(NO)$[6,7] or from $W(CO)_4(LL)$[8] via sequential carbonyl substitution reactions first by NO^+ followed by X^-.

Starting from the readily prepared complex *trans*-$W(CO)_4(PPh_3)_2$, we devised new syntheses for $WX(CO)_3(NO)(PPh_3)$ and $WX(CO)_2(NO)(PPh_3)_2$ from which $WH(CO)_2(NO)(PPh_3)_2$ was made. The hydride is a convenient precursor (Scheme I) for a variety of new tungsten nitrosyl complexes. Recently, $WX(CO)_3(NO)(PPh_3)$ and $WX(CO)_2(NO)(PPh_3)_2$ have been shown to be effective catalysts for olefin dismutation.[9] Part of this work has appeared in a preliminary form in an earlier publication.[10] The preparation of $WH(NO)(diphos)_2$ has recently appeared,[11a] and the related $WH(CO)_2(NO)[P(O\text{-}i\text{-}Pr)_3]_2$ was recently reported.[11b]

Experimental Section

Unless otherwise noted, all reactions were carried out at room temperature in freshly dried and distilled solvents under a nitrogen atmosphere by using standard Schlenk techniques. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, and by Midwest Microlab, Ltd., Indianapolis, IN. Infrared spectra were measured in Fluorolube S-30 and Nujol mulls by using a Perkin-Elmer 283 or Nicolet 20SXB spectrometer and were calibrated with a polystyrene film. NMR spectra were measured in CD_2Cl_2 or C_6D_6 solution at ambient temperature (unless otherwise noted) by using Varian Associates XL-100 (^1H, ^{31}P) and HR-220 (^1H) spectrometers. The proton spectra are reported by using tetramethylsilane as an internal reference, and the phosphorus spectra were broad-band proton decoupled and calibrated

Scheme I[a]



[a] Key: (a) HX (X = Cl, Br, I, O_2CH, O_2CCH_3, ClO_4); (b) ToNHN=NTo; (c) RN_3 (R = Ph, To); (d) ToN=C=NTo; (e) $[RN_2^+][PF_6^-$ *or* $BF_4^-]$ (R = Ph, To); (f) C_3O_2 (see ref 24); (g) CO_2 (or HOCOH, see part a above); (h) CS_2.

[†] The University of Chicago.

[‡] Monsanto Co.

(1) (a) Freni, M.; Giusto, D.; Valenti, V. *J. Inorg. Nucl. Chem.* **1965**, *27*, 755. (b) Freni, M.; Giusto, D.; Romiti, P. *Ibid.* **1971**, *33*, 4093. (c) Flitcroft, N.; Leach, J. M.; Hopton, F. J. *Ibid.* **1970**, *32*, 137.

(2) Haymore, B. L., unpublished results.

(3) Laing, K. R.; Roper, W. R. *J. Chem. Soc. A* **1969**, 1889.

(4) Hieber, W.; Frey, V. *Chem. Ber.* **1966**, *99*, 2614.

(5) Colton, R.; Commons, C. J. *Aust. J. Chem.* **1973**, *26*, 1487.

(6) King, R. B.; Saran, M. S.; Anand, S. P. *Inorg. Chem.* **1974**, *13*, 3038.

0020-1669/87/1326-1876$01.50/0

with an external 85% phosphoric acid reference. In some cases, quantitative gas evolution studies were carried out by using Toepler vacuum line techniques coupled with high-resolution mass spectrometry to identify and quantify the products.

Most of the starting materials were prepared by standard methods. Aromatic diazonium salts and disubstituted aromatic triazenes were synthesized by standard methods.[12] Aromatic azides were prepared by previously described methods.[13] $NOPF_6$ and $NOBF_4$ were purchased from Ozark-Mahoning Co. (Tulsa, OK), and lithium borodeuteride (98% ^2H) was obtained from Stohler Isotope Chemicals (Rutherford, NJ). *Note*: *Perchlorate compounds are potentially explosive and should be prepared and handled with due care!*[14]

***trans*-$W(CO)_4(PPh_3)_2$ (1t).** This is a modification of the literature method.[15] A total of 10.0 g of $W(CO)_6$, 3.0 g of $NaBH_4$, and 22.0 g of PPh_3 were suspended in 600 mL of 95% ethanol at room temperature. The mixture was refluxed and vigorously stirred for 12 h. The cooled reaction mixture was filtered and the solid washed with water (3 × 75 mL) and then hot EtOH (3 × 75 mL) followed by acetone (2 × 50 mL) and pentane (2 × 50 mL) (washing rids the mixture of $R_3P\cdot BH_3$) to yield 21.2 g (98%) of a yellow, crystalline powder. ***trans*-$Cr(CO)_4(PPh_3)_2$** was prepared as a yellow powder in 76% yield from $Cr(CO)_6$ (6.3 g). ***trans*-$Mo(CO)_4(PPh_3)_2$** was prepared as a yellow, crystalline powder in 82% yield from $Mo(CO)_6$ (7.5 g). ***trans*-$W(CO)_4((p\text{-}CH_3C_6H_4)_3P)_2$** was prepared as yellow crystals in 93% yield from $W(CO)_6$ (10.0 g).

***fac*-$W(CO)_3(PPh_3)_3$.** (Mesitylene)tungsten tricarbonyl[16] (10.0 g) was refluxed in a mixture of 40 mL of cycloheptatriene and 100 mL of *n*-octane for 36 h. The warm solution was filtered and mixed with another warm, filtered solution of 30 g of triphenylphosphine in 240 mL of *n*-octane. The red color of the $(C_7H_8)W(CO)_3$ was immediately discharged, and the light yellow crystalline product came out of solution. The product was filtered, washed with pentane, and dried under vacuum. The product is moderately air-sensitive as a solid and very air-sensitive in solution. Yield was 8.7 g (32%). Anal. Calcd for $C_{57}H_{45}O_3P_3W$: C, 64.91; H, 4.30. Found: C, 65.40; H, 4.49.

***cis*-$W(CO)_4(PPh_3)_2$ (1c).** Carbon monoxide (80 psi) was allowed to react with 7.5 g of *fac*-$W(CO)_3(PPh_3)_3$ in 150 mL of CH_2Cl_2 at room temperature (22 °C) for 90 min. The solution was filtered and reduced in volume under vacuum to about 35 mL. Absolute ethanol (20 mL) was added to precipitate the product as a yellow, crystalline solid. The product was washed with ethanol and pentane and dried under vacuum to give 5.2 g (89%).

***cis,mer*-$[W(CO)_3(NO)(PPh_3)_2][PF_6]$ (2-PF_6).** (a) A 10.0-g sample of *trans*-$W(CO)_4(PPh_3)_2$ was suspended in 50 mL of CH_2Cl_2 and vigorously stirred at room temperature. To the mixture was added 2.20 g of $NOPF_6$, causing vigorous evolution of carbon monoxide. When CO evolution had ceased (about 15 min), another 0.50 g of $NOPF_6$ was added and the solution was stirred until gas evolution was minimal (about another 10 min). The green-yellow solution was filtered, and then 200 mL of benzene was slowly added to the filtrate to induce crystallization of the ionic complex. The mixture was filtered and the precipitate washed sequentially with benzene, ethanol, and pentane to yield 10.35 g (88%) of nicely formed bright yellow prisms. The product can be recrystallized from CH_2Cl_2 by slow addition of Et_2O. Anal. Calcd for $C_{39}H_{30}F_6NO_4P_3W$: C, 48.42; H, 3.13; N, 1.45. Found: C, 48.29; H, 3.22; N, 1.36.

(b) The above procedure was repeated at 50% scale with 5.0 g of *cis*-$W(CO)_4(PPh_3)_2$ used. Except for the shorter reaction time (CO evolution ceased in less than 5 min), this reaction and workup proceeded similarly to give an isolated yield of 5.11 g (87%).

***cis,mer*-$[W(CO)_3(NO)(PPh_3)_2][BF_4]$ (2-BF_4).** This compound was prepared in the same manner as the PF_6^- salt (method a) by using $NOBF_4$ instead of $NOPF_6$. The yield was 8.76 g (79%) of yellow crystals. Anal. Calcd for $C_{39}H_{30}BF_4NO_4P_2W$: C, 51.52; H, 3.33; N, 1.54. Found: C, 50.99; H, 3.30; N, 1.71.

***cis,mer*-$[W(CO)_3(NO)(PPh_3)_2][ClO_4]$ (2-ClO_4).** This compound was prepared in the same manner as the PF_6^- salt (method a) by using *t*-BuONO (1.3 g) and 70% $HClO_4$ (1.8 g) as the nitrosylating agent. Enough absolute methanol (~10 mL) was added to the CH_2Cl_2 solution so that there was only one liquid phase. The yield was 9.01 g (80%) of large yellow prisms. Anal. Calcd for $C_{39}H_{30}ClNO_8P_2W$: C, 50.81; H, 3.28; N, 1.52. Found: C, 50.50; H, 3.49; N, 1.33.

***cis,mer*-$[W(CO)_3(NO)(P(p\text{-}C_6H_4CH_3)_3)_2][PF_6]$.** This compound was prepared in a manner similar to that for the triphenylphosphine analogue (method a) by using $W(CO)_4(p\text{-}To_3P)_2$ (11 g) as the starting complex. The yield was 8.44 g (66%) of bright yellow crystals. Anal. Calcd for $C_{45}H_{42}F_6NO_4P_3W$: C, 51.40; H, 4.03; N, 1.33. Found: C, 51.01; H, 4.44; N, 1.51.

***trans*-$[Cr(CO)_4(PPh_3)_2][PF_6]$ (5).** To 5.0 g of *trans*-$Cr(CO)_4(PPh_3)_2$ suspended in 50 mL of CH_2Cl_2 and vigorously stirred at room temperature was added 1.2 g of $NOPF_6$, and gas evolution was evident. After 40 min, 0.30 g of the nitrosonium salt was added, and the mixture was stirred for another 20 min. The dark purple solution was filtered and then reduced in volume to 25 mL under reduced pressure. Benzene (100 mL) was slowly added to induce crystallization of the ionic complex. The mixture was filtered and washed with benzene and pentane. The solid was carefully recrystallized from CH_2Cl_2/Et_2O and dried under vacuum to yield 4.3 g (71%) of deep purple crystals. Anal. Calcd for $C_{40}H_{30}F_6O_4P_3Cr$: C, 57.64; H, 3.63. Found: C, 57.42; H, 3.40.

$WBr_2(NO)_2(PPh_3)_2$ (4c).[25] (a) Three grams of *trans*-$W(CO)_4(PPh_3)_2$ was added to a stirred mixture of 3.8 g of *n*-Bu_4NBr in 30 mL of CH_2Cl_2. To this slurry was added 0.25 g of $NOBF_4$, and carbon monoxide was rapidly evolved. Within 3–5 min, CO evolution subsided and an additional 0.25 g of $NOBF_4$ was added. The addition of $NOBF_4$ in 0.25-g quantities was continued until no more CO was evolved; this required a total of 1.25–1.50 g of $NOBF_4$. The dark green solution was filtered and reduced in volume to about 10 mL under reduced pressure. To this solution was added, dropwise, 80 mL of absolute ethanol that contained 2.0 g of dissolved PPh_3. The mixture was stirred for 10 min to complete crystallization, and beautiful green crystals separated from solution. The mixture was filtered and washed with ethanol and pentane to yield 2.24 g (66%) of the green crystalline product. Anal. Calcd for $C_{36}H_{30}Br_2N_2O_2P_2W$: C, 46.58; H, 3.26; N, 3.02; Br, 17.22. Found: C, 46.78; H, 3.57; N, 3.21; Br, 17.51. **$MoBr_2(NO)_2(PPh_3)_2$ (4d)** was prepared in 74% yield from 2.5 g of *trans*-$Mo(CO)_4(PPh_3)_2$ as green crystals. Anal. Calcd for $C_{36}H_{30}Br_2N_2O_2P_2Mo$: C, 51.45; H, 3.60; N, 3.33; Br, 19.02. Found: C, 51.06; H, 3.70; N, 3.66; Br, 19.00. **$MoF_2(NO)_2(PPh_3)_2$** was prepared in 31% yield from 2.5 g of *trans*-$Mo(CO)_4(PPh_3)_2$ as green crystals; $NOPF_6$ was the nitrosyl source, but no *n*-Bu_4NBr was used; reaction time was 3 h at 25 °C. Anal. Calcd for $C_{36}H_{30}F_2N_2O_2P_2Mo$: C, 60.18; H, 4.21; N, 3.90. Found: C, 60.47; H, 4.51; N, 3.71. **$CrBr_2(NO)_2(PPh_3)_2$ (4e)** was prepared in 55% yield from 2.0 g of *trans*-$Cr(CO)_4(PPh_3)_2$ as deep orange crystals. Anal. Calcd for $C_{36}H_{30}Br_2N_2O_2P_2Cr$: C, 54.29; H, 3.80; N, 3.52; Br, 20.07. Found: C, 54.01; H, 3.70; N, 3.79; Br, 19.88.

(b) Two grams of *trans,trans*-$WBr(CO)_2(NO)(PPh_3)_2$ was added to a stirred solution of 1.3 g of *n*-Bu_4NBr in 20 mL of CH_2Cl_2. The $NOBF_4$ was added portionwise as described above in part a, and the product was handled similarly to give 1.87 g (88% yield) of $WBr_2(NO)_2(PPh_3)_2$. The same product was obtained in 70% yield from *cis,cis*-$WBr(CO)_2(NO)(PPh_3)_2$.

$WFBr(NO)_2(PPh_3)_2$ (4f). Three grams of *trans,trans*-$WBr(CO)_2(NO)(PPh_3)_2$ and 0.90 g of $NOPF_6$ were stirred together in 30 mL of CH_2Cl_2 at ambient temperature. After 60 min, the green mixture was filtered and the volume of the solution was reduced to about 15 mL under vacuum. The addition of absolute ethanol (80 mL) in a dropwise fashion caused green crystals to form. The mixture was filtered and washed with ethanol and pentane to yield 1.76 g (59%) of the product. Anal. Calcd for $C_{36}H_{30}BrFN_2O_2P_2W$: C, 49.85; H, 3.49; N, 3.23; Br, 9.21. Found: C, 49.49; H, 3.44; N, 3.04; Br, 9.79.

***mer*-$WBr(CO)_3(NO)(PPh_3)$ (7b).** A solution of 5.0 g of *cis,mer*-$[W(CO)_3(NO)(PPh_3)_2][PF_6]$ in 50 mL of CH_2Cl_2 was stirred at room temperature, and then 1.80 g of *n*-Bu_4NBr and 5.00 g of $IrCl(N_2)(PPh_3)_2$[17] were added sequentially. The displacement of the phosphine

---

(7) Colton, R.; Commons, C. J. *Aust. J. Chem.* **1973**, *26*, 1493.

(8) (a) Connelly, N. G. *J. Chem. Soc., Dalton Trans.* **1973**, 2183. (b) For analogous diarsine derivatives, see: Connelly, N. G.; Gardner, C. *Ibid.* **1979**, 609. (c) Connor, J. A.; Riley, P. I.; Rix, C. J. *Ibid.* **1977**, 1317.

(9) Crease, A. E.; Egglestone, H.; Taylor, N. *J. Organomet. Chem.* **1982**, *238*, C5.

(10) Hillhouse, G. L.; Haymore, B. L. *J. Organomet. Chem.* **1978**, *162*, C23.

(11) (a) Kan, C. T.; Hitchcock, P. B.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1982**, 79. No direct evidence for the hydride ligand in this complex was observed. (b) Kundel, P.; Berke, H. *J. Organomet. Chem.* **1986**, *314*, C31.

(12) Vogel, A. I. *Elementary Practical Organic Chemistry, Part I*; Wiley: London, 1965; pp 248, 266.

(13) (a) Noelting, E.; Michel, O. *Ber. Dtsch. Chem. Ges.* **1893**, *26*, 86. (b) Lindsay, R. O.; Allen, C. F. H. *Organic Synthesis*; Horning, E. C., Ed.; Wiley: New York, 1955; Collect. Vol. 3, p 710.

(14) (a) *Chem. Eng. News* **1983**, *61* (Dec 5), 4. (b) *Ibid.* **1963**, *41* (July 8), 47.

(15) Chatt, J.; Leigh, G. J.; Thankarajan, N. *J. Organomet. Chem.* **1971**, *29*, 105.

(16) King, R. B.; Fronzaglia, A. *Inorg. Chem.* **1966**, *5*, 1837.

(17) Collman, J. P.; Hoffman, N. W.; Hosking, J. W. *Inorg. Synth.* **1970**, *12*, 8.

(18) Davis, R.; Johnson, B. F. G.; Al-Obaidi, K. H. *J. Chem. Soc., Dalton Trans.* **1972**, 508.

by the halide was complete on mixing. The iridium complex was conveniently available to us and acted as a phosphine scavenger so that the free phosphine would not react with the product. Any other phosphine scavenger will function well as long as it can be separated from the product and will not react with the tungsten complexes. We successfully used methyl trifluoromethanesulfonate as a phosphine scavenger on one occasion. The solvent (CH_2Cl_2) was completely removed under vacuum at room temperature, and the residue was extracted with 200 mL of *n*-pentane for 30 min. A second extraction with 200 mL of *n*-pentane was carried out, the two portions of pentane were mixed, and the solvent was removed under vacuum, yielding yellow crystals of the product. This material was spectroscopically pure (infrared, ^{31}P NMR) and could be used for most synthetic applications; however, elemental analyses were not entirely satisfactory. The entire amount was further purified by column chromatography (2.5 cm × 100 cm) through alumina using CH_2Cl_2 as the eluent. The yellow fraction was collected, and the solvent was removed. The product was recrystallized from *n*-hexane/methylene chloride (95:5) at −20 °C to give 2.0 g (61%) of the product. Anal. Calcd for $C_{21}H_{15}BrNO_4PW$: C, 39.41; H, 2.36; N, 2.19; Br, 12.48. Found: C, 39.50; H, 2.59; N, 2.47; Br, 12.19. **$WI(CO)_3(NO)(PPh_3)$ (7c**; 69% yield) and **$WCl(CO)_3(NO)(PPh_3)$ (7a**; 54% yield) were analogously prepared on a 50% scale. The iridium residue was dissolved in CH_2Cl_2 and CO was bubbled through the solution for 10 min. The solvent was partially removed, and crystalline $IrCl(CO)(PPh_3)_2$ (4.4 g) was recovered by the addition of absolute ethanol. Thus, most of the iridium was recovered and recycled.

***cis,cis*-$WBr(CO)_2(NO)(PPh_3)_2$ (6b).** (a) To 50 mL of CH_2Cl_2 were added 5.00 g of $[W(CO)_3(NO)(PPh_3)_2][PF_6]$ and 1.80 g of *n*-Bu_4NBr. Within a minute the solution was homogeneous, and the CH_2Cl_2 was completely removed under vacuum at room temperature. *n*-Pentane (200 mL) was added, and the mixture was stirred and refluxed for 20–30 min or until the pentane solution was nearly colorless. The solid was isolated and recrystallized from CH_2Cl_2 by addition of EtOH to give 3.57 g (79%) of yellow crystals. ***cis,cis*-$WCl(CO)_2(NO)(PPh_3)_2$ (6a**; 70% yield) and ***cis,cis*-$WI(CO)_2(NO)(PPh_3)_2$ (6c**; 76% yield) were analogously prepared.

(b) A suspension of 5.00 g of $[W(CO)_3(NO)(PPh_3)_2][PF_6]$ in 75 mL of absolute ethanol was vigorously stirred and cooled to 10 °C by using an ice–water bath. To the mixture was added 0.50 g of anhydrous LiBr followed by 0.50 g of $LiOCH_3$. Upon addition of the lithium methoxide, CO began to evolve and the solution's color changed from yellow to orange. After the gas evolution had stopped (about 5 min), the mixture was stirred for an additional 10 min, and then 1.5 mL of 48% aqueous HBr was added dropwise. This was just enough acid to turn the orange solution yellow again. The mixture was stirred for 5 min during which time yellow crystals began to form. Another 2.0 mL of HBr was added dropwise, the ice bath was removed, and the mixture was stirred for an additional 1 h at ambient temperature to allow more complete precipitation of the product. The reaction mixture was filtered, and the precipitate was washed with ethanol followed by hexane to yield 3.18 g (71%) of yellow crystals. Anal. Calcd for $C_{38}H_{30}BrNO_3P_2W$: C, 52.20; H, 3.46; N, 1.60; Br, 9.14. Found: C, 52.39; H, 3.19; N, 1.66; Br, 9.09.

***trans,trans*-$WBr(CO)_2(NO)(PPh_3)_2$ (3c).** Five grams of $[W(CO)_3(NO)(PPh_3)_2][PF_6]$ and 1.80 g of Bu_4NBr were refluxed in 50 mL of $CHCl_3$ for 1 h. The volume of the solution was reduced to 20 mL, and then 100 mL of warm 1-propanol was added dropwise to the boiling chloroform solution, during which time the product crystallized from solution. The mixture was filtered and the precipitate washed with ethanol and hexane to yield 3.30 g (73%) of lemon yellow crystals. Anal. Found: C, 52.01; H, 3.29; N, 1.77; Br, 9.41 ***trans,trans*-$WCl(CO)_2(NO)(PPh_3)_2$ (3b**; 74% yield) and ***trans,trans*-$WI(CO)_2(NO)(PPh_3)_2$ (3d**; 60% yield) were similarly prepared.

$WBr(CO)_2(NO)(PPh_3)_2$ (Isomer Mixture). A 5.00-g sample of $[W(CO)_3(NO)(PPh_3)_2][PF_6]$ and 1.00 g of anhydrous LiBr were refluxed for 5 min in 75 mL of absolute ethanol. The cooled mixture was filtered, and the precipitate was washed with ethanol and hexane to yield 3.40 g (75%) of yellow crystals.

Isomerization of *cis,cis*-$WBr(CO)_2(NO)(PPh_3)_2$. One gram of *cis,cis*-$WBr(CO)_2(NO)(PPh_3)_2$ was suspended in 25 mL of 1,2-dimethoxyethane and heated and stirred. The mixture was refluxed for 1–2 min and then cooled. Hexane (25 mL) was added, and the cooling mixture was allowed to sit for 15 min to complete the crystallization of the product. The precipitate was filtered and washed with ethanol and hexane to yield 0.85 g (85%) of the trans,trans isomer. If the mixture were refluxed for longer periods, thermal decomposition occurred and the product was contaminated with $WBr_2(NO)_2(PPh_3)_2$.

***trans,trans*-$CrBr(CO)_2(NO)(PPh_3)_2$ (25).** This compound was prepared by a method similar to that used for the analogous iodo complex.[23] Anhydrous lithium bromide (1.0 g) was dissolved in 25 mL of absolute ethanol, and then 2.0 g of $[(C_6Me_6)Cr(CO)_2(NO)][PF_6]$ was added all at once. This mixture was stirred at room temperature for 10 min, and then 4.0 g of PPh_3 was added to the resulting red solution. This mixture was stirred at room temperature for 2 h, then very briefly heated to reflux, and finally cooled to 0 °C. The red precipitate was removed by filtration and washed with ethanol. Finally, the product was recrystallized from CH_2Cl_2 by addition of EtOH and washed with pentane to yield 2.2 g (66%) of solvent-free orange crystals. Anal. Calcd for $C_{38}H_{30}BrNO_3P_2Cr$: C, 61.47; H, 4.07; N, 1.89. Found: C, 59.96; H, 4.01; N, 1.79.

***trans,trans*-$WH(CO)_2(NO)(PPh_3)_2$ (15).** (a) To 75 mL of THF were added 3.00 g of $[W(CO)_3(NO)(PPh_3)_2][PF_6]$, 5.0 g of PPh_3, and 0.25 g of $LiBH_4$. Upon addition of the borohydride, the mixture became homogeneous, began to evolve carbon monoxide, and darkened in color from yellow to orange. The solution was refluxed for 15 min and filtered through Celite, and the volume of the filtrate was reduced to 10 mL by using a rotary evaporator. Absolute ethanol (50 mL) was added dropwise to precipitate orange-yellow crystals of the product. The mixture was heated to boiling and filtered while hot. The precipitate was washed with hot EtOH (2 × 75 mL) followed by pentane to yield 1.96 g (79%) of the product. The complex was conveniently recrystallized from a minimum of CH_2Cl_2 by slow addition of EtOH. Anal. Calcd for $C_{38}H_{31}NO_3P_2W$: C, 57.38; H, 3.93; N, 1.76. Found: C, 57.21; H, 4.02; N, 1.55. **$WD(CO)_2(NO)(PPh_3)_2$ (15-d)** was analogously prepared from $LiBD_4$ (and worked up as above except using EtOD).

(b) To 75 mL of dry THF were added 3.00 g of *trans,trans*-$WBr(CO)_2(NO)(PPh_3)_2$, 6.0 g of triphenylphosphine, and 0.30 g of $LiBH_4$. The solution was refluxed for 1 h and filtered, and the volume of the filtrate was reduced to 10 mL. Absolute ethanol (75 mL) was added to precipitate the yellow product and the mixture was heated and filtered while hot. The precipitate was washed with hot ethanol and then with pentane to yield 1.89 g (77%). If *cis,cis*-$WBr(CO)_2(NO)(PPh_3)_2$ instead of the trans isomer were used, lower yields (41%) of the hydrido complex were obtained.

***cis*-$W(CO)_2(NO)(PPh_3)(\eta^2\text{-}S_2CNMe_2)$ (13).** To a solvent mixture containing 2 mL of dichloromethane and 15 mL of methanol were added 1.00 g of $[W(CO)_3(NO)(PPh_3)_2][PF_6]$ and 0.35 g of $NaS_2CNMe_2\cdot 2H_2O$. The mixture was stirred for 15 min at ambient temperature, during which time an orange precipitate formed. The precipitate was filtered and washed with methanol and then diethyl ether to yield 0.42 g (56%). Anal. Calcd for $C_{23}H_{21}N_2O_3PS_2W$: C, 42.35; H, 3.24; N, 4.29. Found: C, 42.56; H, 3.51; N, 4.27.

***trans*-$W(CO)(NO)(PPh_3)_2(\eta^2\text{-}S_2CNMe_2)\cdot CH_2Cl_2$ (14·CH_2Cl_2).** (a) To a mixture of 5 mL of dichloromethane and 25 mL of 1-propanol were added 1.00 g of $[W(CO)_3(NO)(PPh_3)_2][PF_6]$ and 0.35 g of $NaS_2CNMe_2\cdot 2H_2O$, and the solution was refluxed for 15 min. The solution was cooled, and the red-brown microcrystalline precipitate was filtered and washed with MeOH followed by Et_2O to yield 0.86 g (86%) of the methylene chloride (1:1) solvate. Anal. Calcd for $C_{41}H_{38}Cl_2N_2O_2P_2S_2W$: C, 50.68; H, 3.94; N, 2.88. Found: C, 50.87; H, 3.99; N, 2.98.

(b) To a solvent mixture containing 5 mL of dichloromethane and 25 mL of 1-propanol were added 0.40 g of $W(CO)_2(NO)(PPh_3)(S_2CNMe_2)$ and 0.18 g of triphenylphosphine. The mixture was refluxed for 15 min, and the precipitate was filtered and washed as described in method a to

---

(19) (a) LaMonica, G.; Cenini, S.; Forni, E.; Manassero, M.; Albano, V. G. *J. Organomet. Chem.* **1976**, *112*, 297. (b) Dean, W. K.; Simon, G. L.; Treichel, P. M.; Dahl, L. F. *Ibid.* **1973**, *50*, 193. (c) For related Ru, Rh, and Ir examples, see: Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1973**, 1912.

(20) For related HN_3R and HN_3H complexes, see: (a) Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1025. (b) Burgess, K.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Organomet. Chem.* **1982**, *224*, C40. (c) Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Sankey, S. W. *Ibid.* **1982**, *228*, 135.

(21) Kosower, E. M. *Acc. Chem. Res.* **1971**, *4*, 193.

(22) The ν(NN) of $NH{=}NPh$ complexes are usually only weakly infrared active,[22a] and that is the case for these tungsten derivatives. The values reported are the observed ν(NN) frequencies. They can be mathematically decoupled, as described elsewhere for aryldiazo systems,[22b] to give ν(NN) = 1464, 1442, and 1439 cm^{-1} (for **23**, **23**-α-^{15}N, and **23**-β-^{15}N). (a) Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 5369. (b) Haymore, B. L.; Ibers, J. A.; Meek, D. W. *Inorg. Chem.* **1975**, *14*, 541.

(23) Connelly, N. G.; Kelly, B. A.; Kelly, R. L.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1976**, 699.

(24) Carbon suboxide ($O{=}C{=}C{=}C{=}O$) also undergoes a clean insertion reaction with **15** to give the ketenyl derivative *trans,trans*-$W(\eta^1\text{-}C(CHO)CO)(CO)_2(NO)(PPh_3)_2$: Hillhouse, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 7772.

yield 0.46 g (77%) of brown crystals.

(c) To a solvent mixture containing 5 mL of methylene chloride and 25 mL of 1-propanol was added 0.50 g of $W(CO)_2(NO)(PPh_3)(S_2CNMe_2)$, but no PPh_3. The mixture was refluxed for 2 h and the precipitate filtered and washed as in method a to yield 0.24 g (31%).

***trans,trans*-$W(CO)_2(NO)(PPh_3)_2(\eta^1$-$OC(O)CH_3)$ (8).** (a) A 0.85-g sample of $[W(CO)_3(NO)(PPh_3)_2][PF_6]$ and 0.20 g of sodium acetate were added to a solvent mixture of 20 mL of 2-propanol and 5 mL of dichloromethane. The mixture was stirred for 20 min at ambient temperature and filtered, and the volume of the filtrate was reduced to 10 mL by using a rotary evaporator. The yellow crystals were filtered and washed with methanol followed by pentane to yield 0.54 g (72%). Anal. Calcd for $C_{40}H_{33}NO_5P_2W$: C, 56.29; H, 3.90; N, 1.64. Found: C, 56.39; H, 3.91; N, 1.56.

(b) One-half gram of $WH(CO)_2(NO)(PPh_3)_2$ and 3 mL of glacial acetic acid were stirred together in a solvent mixture of 20 mL of 2-propanol and 5 mL of dichloromethane for 15 min during which time gas evolution was evident. The volume of the solution was reduced to 10 mL by using a rotary evaporator, and the crystals of the product were filtered and washed with EtOH followed by pentane to yield 0.34 g (64%).

***trans*-$W(CO)(NO)(PPh_3)_2(\eta^2$-$O_2CCH_3)$ (11).** A 1.05-g sample of $W(CO)_2(NO)(PPh_3)_2(\eta^1$-$OC(O)CH_3)$ was refluxed for 30 min in a solvent mixture of 20 mL of 1-propanol and 5 mL of dichloromethane. It was cooled and filtered to yield 0.93 g (92%) of deep red crystals. Anal. Calcd for $C_{39}H_{33}NO_4P_2W$: C, 56.75; H, 4.03; N, 1.70. Found: C, 56.50; H, 4.03; N, 1.61. This red monocarbonyl was *quantitatively reconverted* to the yellow dicarbonyl by bubbling carbon monoxide through CH_2Cl_2 solutions of the complex.

***trans,trans*-$W(CO)_2(NO)(PPh_3)_2(\eta^1$-$OC(O)H)$ (9).** (a) The yellow formato complex was prepared in a manner similar to that used for the acetate complex, method a, except that sodium formate was used instead of sodium acetate to give an 81% yield. Anal. Calcd for $C_{39}H_{31}NO_5P_2W$: C, 55.80; H, 3.72; N, 1.67. Found: C, 56.25; H, 3.98; N, 1.45.

(b) Analogous to the preparation of the acetate complex **8** (method b), dropwise addition of formic acid (97% solution) to a methylene chloride solution of $WH(CO)_2(NO)(PPh_3)_2$ produced the yellow product in 65% yield.

(c) Carbon dioxide gas was bubbled through a stirred solution of $WH(CO)_2(NO)(PPh_3)_2$ (0.50 g in 60 mL of CH_2Cl_2) for 3 h. The solvent was reduced in volume to 5 mL, and 1-propanol was added to precipitate 0.44 g of an approximately equimolar mixture of the starting material and $W(CO)_2(NO)(PPh_3)_2(\eta^1$-$OC(O)H)$ (infrared and ^{31}P NMR spectroscopy). Longer reaction times resulted in the recovery of less of the hydrido starting material, but the dicarbonyl formato complex was contaminated by the monocarbonyl formato complex and by an uncharacterized decomposition product.

***trans*-$W(CO)(NO)(PPh_3)_2(\eta^2$-$O_2CH)$ (12).** The red monocarbonyl complex could be prepared by refluxing 0.86 g of $W(CO)_2(NO)(PPh_3)_2(\eta^1$-$OC(O)H)$ in 25 mL of a 1-propanol/dichloromethane solvent mixture (4:1, v:v) for 30 min to give 0.70 g (84% yield) as an air-sensitive material. Anal. Calcd for $C_{38}H_{31}NO_4P_2W$: C, 56.25; H, 3.85; N, 1.73. Found: C, 56.52; H, 3.91; N, 1.60. This complex was reconverted to the yellow dicarbonyl formato complex by bubbling carbon monoxide through a methylene chloride solution.

***trans,trans*-$W(CO)_2(NO)(PPh_3)_2(\eta^1$-$SC(S)H)$ (22).** To a solution of 0.62 g of $WH(CO)_2(NO)(PPh_3)_2$ in 10 mL of CH_2Cl_2 was added 5 mL of CS_2, and the mixture was stirred for 20 min at ambient temperature. Carbon monoxide was bubbled through the resulting red solution for about 2 min, the volume of the solution was reduced to 2 mL, and methanol was added dropwise to precipitate 0.42 g (62%) of yellow-orange crystals. Anal. Calcd for $C_{39}H_{31}NO_3P_2S_2W$: C, 53.74; H, 3.58; N, 1.61. Found: C, 53.49; H, 3.39; N, 1.43.

***trans*-$W(CO)(NO)(PPh_3)_2(\eta^2$-$NHNNPh)$ (19a).** To a solution of 0.94 g of $WH(CO)_2(NO)(PPh_3)_2$ in 10 mL of CH_2Cl_2 was added 2.5 equiv of phenyl azide. Gas evolution (1.0 equiv of CO/W) was initially vigorous and ceased within 5 min. The volume of the deep red solution was reduced to about 2 mL, and absolute ethanol was added dropwise to precipitate 0.68 g (65% yield) of red-brown prisms. Anal. Calcd for $C_{43}H_{36}N_4O_2P_2W$: C, 58.25; H, 4.09; N, 6.32. Found: C, 57.97; H, 4.14; N, 6.12. ***trans*-$W(CO)(NO)(PPh_3)_2(\eta^2$-$NHNNTo)$ (19b)** was prepared analogously from *p*-tolyl azide, ToN_3, as an orange-red powder in 59% yield. Anal. Calcd for $C_{44}H_{38}N_4O_2P_2W$: C, 58.68; H, 4.25; N, 6.22. Found: C, 58.40; H, 4.30; N, 6.02.

***trans*-$W(CO)(NO)(PPh_3)_2(\eta^2$-$NToNNTo)$ (20).** To 0.85 g of $WH(CO)_2(NO)(PPh_3)_2$ in 5 mL of CH_2Cl_2 was added 0.30 g of di-*p*-tolyltriazene, ToN=N—NHTo, and the solution was stirred for 15 min at reflux. Absolute ethanol was added to precipitate a ruby red powder, the mixture was cooled to −20 °C to insure complete crystallization, and the product was filtered and washed with EtOH to yield 0.72 g (68%) of the bright red complex. Anal. Calcd for $C_{51}H_{44}N_4O_2P_2W$: C, 61.83; H, 4.48; N, 5.60. Found: C, 61.72; H, 4.39; N, 5.69.

***trans*-$W(CO)(NO)(PPh_3)_2(\eta^2$-$NToCHNTo)$ (21).** (a) To 10 mL of CH_2Cl_2 were added 0.88 g of $WH(CO)_2(NO)(PPh_3)_2$ and 0.30 g of *N,N'*-di-*p*-tolylcarbodiimide, ToN=C=NTo. The solution was stirred at reflux for 30 min to give a deep red solution, which was filtered and reduced in volume to 2 mL. Absolute ethanol was added to precipitate 0.80 g (73%) of a red-brown crystalline product. Anal. Calcd for $C_{52}H_{45}N_3O_2P_2W$: C, 63.10; H, 4.58; N, 4.25. Found: C, 62.71; H, 4.66; N, 3.99.

(b) The synthesis for $W(ToN_3To)(CO)(NO)(PPh_3)_2$ was carried out by using 0.30 g of 1,3-di-*p*-tolylformamidine, ToN=CH—NHTo, instead of the triazene. This produced 0.77 g (73%) of product.

***trans,trans*-$[W(NHNPh)(CO)_2(NO)(PPh_3)_2][PF_6]$ (23).** To acetone (5 mL) were added 1.00 g of $WH(CO)_2(NO)(PPh_3)_2$ and 0.32 g of $[PhNN][PF_6]$, and the solution was stirred for 5 min at ambient temperature. Another 0.05 g of the diazonium salt was added, and the mixture was stirred for another 5 min. The deep red solution was filtered, and the product was precipitated by the slow addition of ether and hexane. The precipitate was filtered and washed with hexane to yield 1.11 g (84%) of red-orange prisms. Anal. Calcd for $C_{44}H_{36}F_6N_3O_3P_3W$: C, 50.55; H, 3.47; N, 4.02. Found: C, 50.47; H, 3.40; N, 3.88. The reaction proved to be general for other diazonium hexafluorophosphate and tetrafluoroborate derivatives in similar yields. Nitrogen-15-labeled diazenes (**23**-β-^{15}N; **23**-α-^{15}N) were prepared from Ph–$^{15}NN^+$ and Ph–$N^{15}N^+$, respectively, on a half-scale.

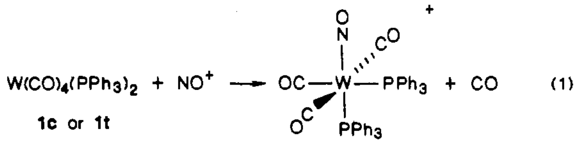
***trans,trans*-$W(\eta^1$-$OClO_3)(CO)_2(NO)(PPh_3)_2$ (16).** A 1-g sample of $WH(CO)_2(NO)(PPh_3)_2$ was suspended in 25 mL of acetone, and 0.5 mL of 70% $HClO_4$ was added dropwise. Hydrogen evolution immediately ensued, and within 5–10 min the vigorously stirred mixture became homogeneous. The solution was filtered, the volume of the solution was reduced to about 5 mL under reduced pressure, and 20 mL of absolute ethanol was added. Crystallization of the product was completed at −10 °C for 20 min. The cold mixture was filtered and washed with ethanol and pentane to give 1.00 g (89%) of well-formed, yellow prisms. Anal. Calcd for $C_{38}H_{30}ClNO_7P_2W$: C, 51.06; H, 3.38; N, 1.57. Found: C, 51.39; H, 3.58; N, 1.76. This reaction was also carried out by using HBr instead of $HClO_4$ to give *trans,trans*-$WBr(CO)_2(NO)(PPh_3)_2$.

Addition of Coordinating Anions to $W(\eta^1$-$OClO_3)(CO)_2(NO)(PPh_3)_2$. A concentrated methanolic solution of a coordinating anion was added in a dropwise fashion to a solution of 0.50 g of $W(OClO_3)(CO)_2(NO)(PPh_3)_2$ in 10 mL of acetone. Within 10 min good yields of the yellow crystalline solid precipitated from solution. The following complexes were prepared in this manner: ***trans,trans*-$WF(CO)_2(NO)(PPh_3)_2$** (**3a**; 71% from Bu_4NF); ***trans,trans*-$WCl(CO)_2(NO)(PPh_3)_2$** (**3b**; 88% from LiCl); ***trans,trans*-$WBr(CO)_2(NO)(PPh_3)_2$** (**3c**; 86% from LiBr); ***trans,trans*-$WI(CO)_2(NO)(PPh_3)_2$** (**3d**; 71% from NaI); ***trans,trans*-$W(NCO)(CO)_2(NO)(PPh_3)_2$** (**17**; 77% from $(Ph_3P)_2NNCO$. Anal. Calcd for $C_{39}H_{30}N_2O_4P_2W$: C, 56.00; H, 3.61; N, 3.35. Found: C, 55.88; H, 3.79; N, 3.22); ***trans,trans*-$W(ONO)(CO)_2(NO)(PPh_3)_2$** (**10**; 75% from 18-crown-6·$NaNO_2$. Anal. Calcd for $C_{38}H_{30}N_2O_5P_2W$: C, 54.31; H, 3.60; N, 3.33. Found: C, 54.14; H, 3.66; N, 3.31).

$[W(CO)(NO)(C_5H_5N)_2(PPh_3)_2][ClO_4]$ (18). Pyridine (1 g) was added to a stirred suspension of 1.00 g of $W(OClO_3)(CO)_2(NO)(PPh_3)_2$ in 10 mL of acetone. After 1 h at ambient temperature, the orange solution was filtered, and the volume of the solution was reduced to 5 mL. Diethyl ether was added dropwise to precipitate the product, which was obtained as an orange crystalline solid after filtration and washing with ether. The yield was 0.97 g (85%). Anal. Calcd for $C_{47}H_{40}ClN_3O_6P_2W$: C, 55.12; H, 3.94; N, 4.10; Cl, 3.46. Found: C, 55.49; H, 3.66; N, 3.86; Cl, 3.50.

Results and Discussion

Nitrosonium hexafluorophosphate reacts with *trans*-$W(CO)_4(PPh_3)_2$ (**1t**) in methylene chloride to form $[W(CO)_3(NO)(PPh_3)_2][PF_6]$ (**2**-PF_6) and carbon monoxide, as shown in eq 1. The ligand replacement reaction proceeds rapidly (10–15 min) at room temperature in high yield (80%–90%). The same complex with BF_4^- or ClO_4^- anions was prepared by using $NOBF_4$ or *t*-BuONO/$HClO_4$/MeOH as sources of the nitrosonium ion; however, solutions of the BF_4^- and ClO_4^- salts were less stable. Successful isolation of these salts requires that coordinating anions



1c or **1t**

2

be absent. Under conditions similar to ours, NOCl and $\mathrm{W(CO)_4(PPh_3)_2}$ gave $\mathrm{WCl_3(NO)(OPPh_3)_2}$.[18] When yellow solutions of **2**-$\mathrm{PF_6}$ were heated or when they were allowed to stand for extended periods at room temperature, small amounts of $\mathrm{WF(CO)_2(NO)(PPh_3)_2}$ (**3a**) and $\mathrm{WF_2(NO)_2(PPh_3)_2}$ (**4a**) formed. *trans*-$\mathrm{Mo(CO)_4(PPh_3)_2}$ and *trans*-$\mathrm{Cr(CO)_4(PPh_3)_2}$ behaved differently. From the molybdenum complex we obtained low yields of $\mathrm{MoF_2(NO)_2(PPh_3)_2}$ (**4b**); several intermediates were spectroscopically detected, but these labile Mo species could not be isolated in a pure form (eq 2). From the chromium complex,

$$\mathrm{Mo(CO)_4(PPh_3)_2 + NOPF_6 \rightarrow [intermediates] \rightarrow \underset{\textbf{4b}}{MoF_2(NO)_2(PPh_3)_2}} \qquad (2)$$

we isolated good yields of the purple, paramagnetic oxidation product $\mathrm{[Cr(CO)_4(PPh_3)_2][PF_6]}$ (**5**) (eq 3). $\mathrm{[Cr(CO)_4(diphos)]^+}$

$$\mathrm{Cr(CO)_4(PPh_3)_2 + NOPF_6 \rightarrow \underset{\textbf{5}}{[Cr(CO)_4(PPh_3)_2][PF_6]} + NO} \qquad (3)$$

has been similarly prepared.[8] In the presence of $\mathrm{NOPF_6}$ and $\mathrm{Bu_4NBr}$, all three $\mathrm{M(CO)_4(PPh_3)_2}$ (M = Cr, Mo, W) complexes reacted to give the dinitrosyl complexes $\mathrm{MBr_2(NO)_2(PPh_3)_2}$ (**4c–e**; eq 4).[25]

$$trans\text{-}\mathrm{M(CO)_4(PPh_3)_2} \xrightarrow[n\text{-}\mathrm{Bu_4NBr}]{\mathrm{NOPF_6}} \mathrm{MBr_2(NO)_2(PPh_3)_2 + 4CO} \qquad (4)$$

4c, M = W
4d, M = Mo
4e, M = Cr

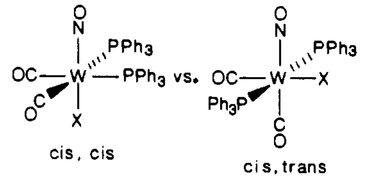
The cis,mer stereochemistry of $\mathrm{[W(CO)_3(NO)(PPh_3)_2]^+}$ was unequivocally ascertained from the ^{31}P NMR spectrum, which displayed a doublet of doublets ($^2J_{\mathrm{PP}}$ = 23 Hz) along with the respective tungsten satellites; see Table I for a listing of spectroscopic data. Using *cis*-$\mathrm{W(CO)_4(PPh_3)_2}$ (**1c**) as the starting material, we found that high yields of the same cis,mer isomer were produced by reaction with $\mathrm{NO^+}$, but the substitution of CO by $\mathrm{NO^+}$ was distinctly faster for **1c** as compared to **1t** (eq 1).

The cation **2** yielded a variety of new nitrosyl complexes upon reaction with coordinating anions (eq 5). Chloride, bromide, and

$$\mathrm{\mathbf{2} + X^- \rightarrow} cis,cis\text{-}\mathrm{WX(CO)_2(NO)(PPh_3)_2 + CO} \qquad (5)$$

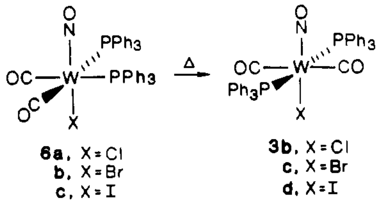
6a, X = Cl
6b, X = Br
6c, X = I

iodide reacted to produce $\mathrm{WX(CO)_2(NO)(PPh_3)_2}$ (**6a–c**), which contained chemically equivalent phosphine ligands and cis carbonyls. The complexes probably possess cis,cis rather than cis,trans geometries as judged by $^1J_{\mathrm{WP}}$ (see Table I). On heating, the cis,cis isomers thermally isomerized to form the more stable trans,trans isomers (eq 6). Prolonged heating of *trans,trans*-$\mathrm{WBr(CO)_2(NO)(PPh_3)_2}$ led to slow decomposition. We identified (^{31}P NMR and infrared spectra) $\mathrm{WBr_2(NO)_2(PPh_3)_2}$ among the decomposition products.



cis, cis

cis,trans

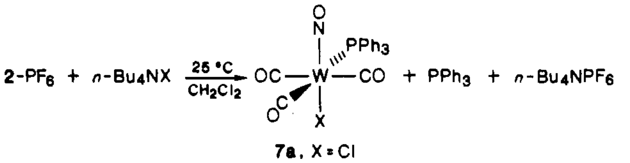


6a, X = Cl
b, X = Br
c, X = I

3b, X = Cl
c, X = Br
d, X = I

Colton and Commons have prepared *mer*-$\mathrm{WBr(CO)_3(NO)(PPh_3)}$ and *cis,cis*-$\mathrm{WBr(CO)_2(NO)(PR_3)_2}$ ($\mathrm{PR_3 = PMe_2Ph, PMePh_2, PPh_3}$) from $\mathrm{WBr(CO)_4(NO)}$; with less bulky phosphines ($\mathrm{PMe_2Ph, PMePh_2}$), the cis to trans isomerization did not occur.[5] Sometimes our *cis,cis*-$\mathrm{WBr(CO)_2(NO)(PPh_3)_2}$, which was prepared directly from $\mathrm{[W(CO)_3(NO)(PPh_3)_2{}^+]}$ and $\mathrm{Br^-}$, contained small amounts of the trans,trans isomer **3c**. We found that this substitution reaction could be conveniently carried out at 10 °C without isomerization to **3c** if we used small amounts of $\mathrm{LiOCH_3}$. This procedure greatly facilitated CO evolution, and the pure cis,cis isomer was obtained in good yield upon acidification with HBr.

Spectroscopic studies indicated that intermediate species were formed in the reaction of halide anions with **2**. This was first discovered while measuring solution spectra of $\mathrm{[W(CO)_3(NO)(PPh_3)_2][ClO_4]}$ (**2**-$\mathrm{ClO_4}$). After 20 min at room temperature, we discovered partial conversion of this complex to a new product. The infrared spectrum showed that the nitrosyl band at 1732 cm^{-1} was replaced by one at 1692 cm^{-1} and that the carbonyl bands changed only slightly in intensity and energy (shifted 5 cm^{-1} to higher energy). Although $\mathrm{[W(CO)_3(NO)(PPh_3)_2][PF_6]}$ was stable in solution, the addition of 1 equiv of n-$\mathrm{Bu_4NClO_4}$ to the solution of the $\mathrm{PF_6^-}$ salt induced the same reaction noted above. Phosphorus NMR spectra showed the disappearance of **2** (two doublets) and the appearance of 1 equiv of free $\mathrm{PPh_3}$ and 1 equiv of a new complex (one singlet, ^{31}P NMR), which we formulated as $\mathrm{W(OClO_3)(CO)_3(NO)(PPh_3)}$. There was no CO evolution observed during this initial reaction. Careful spectroscopic investigation of the reactions of the type shown in eq 5 showed that the addition of coordinating anions (n-$\mathrm{Bu_4NX}$; X = Cl, Br, I) to the methylene chloride solutions of $\mathrm{[W(CO)_3(NO)(PPh_3)_2][PF_6]}$ led to instantaneous and quantitative displacement of one phosphine ligand by the anion, shown in eq 7. That the reaction proceeded so quickly and cleanly even with the weakly coordinating perchlorate anion left little doubt that this reaction would proceed with most common anions. The carbonyl intensity patterns (e.g., 2097 (m), 2049 (w), 2012 (s) cm^{-1} for **7b**) in the infrared spectra were characteristic of a meridional tricarbonyl geometry. The large changes in ν(NO) indicated that the anion probably was trans to the nitrosyl ligand. This same compound with identical spectroscopic properties was prepared previously from $\mathrm{WX(CO)_4(NO)}$ and $\mathrm{PPh_3}$.[5] We could not isolate analytically pure solid samples of $\mathrm{W(OClO_3)(CO)_3(NO)(PPh_3)}$ owing to its lability. However, the halide complexes **7a–c** were isolated as pure solids by working quickly at 25 °C. A phosphine scavenger, $\mathrm{IrCl(N_2)(PPh_3)_2}$, was added to consume the free $\mathrm{PPh_3}$, which prevented formation of the unwanted bis(phosphine) complex; $\mathrm{WX(CO)_3(NO)(PPh_3)}$ was then isolated from solutions of n-pentane in which it is soluble.



7a, X = Cl
b, X = Br
c, X = I
d, X = ClO4

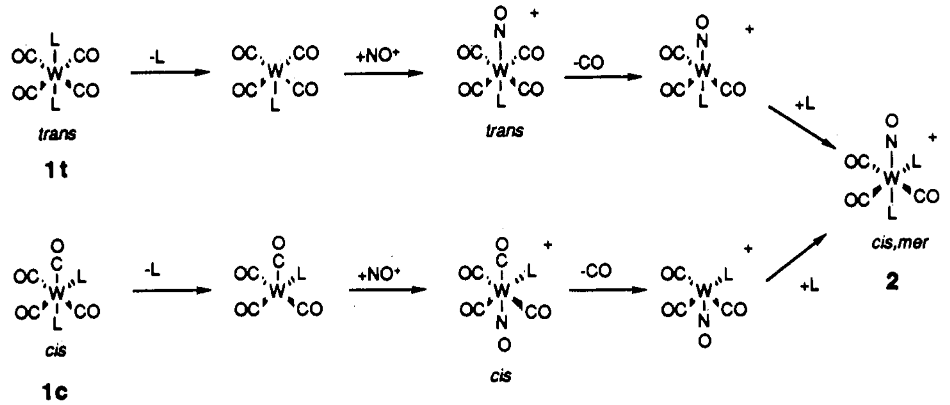
(7)

Acetate ($\mathrm{LiCH_3CO_2}$), formate ($\mathrm{LiHCO_2}$), and nitrite (18-crown-6–$\mathrm{NaNO_2}$) displaced CO from **2** under mild conditions to produce good yields of *trans,trans*-$\mathrm{WX(CO)_2(NO)(PPh_3)_2}$ (**8**, X = OC(O)$\mathrm{CH_3}$; **9**, X = OC(O)H; **10**, X = ONO). The infrared spectra showed that the $\mathrm{NO_2}$, $\mathrm{HCO_2}$, and $\mathrm{CH_3CO_2}$ ligands are unidentate and bound through oxygen and that trans carbonyl ligands are present. We did not study these reactions to determine if intermediate species (see eq 7) were formed. The ^{1}H NMR shows a methyl singlet for the $\mathrm{CH_3CO_2}$ ligand of **8** at δ +1.72; however, the expected proton resonance for the $\mathrm{HCO_2}$ ligand of

---

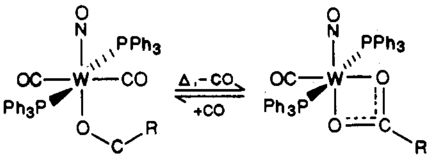
(25) The well-known $\mathrm{MX_2(NO)_2(PPh_3)_2}$ (M = Mo, W; X = halide) derivatives are very conveniently prepared by other routes: (a) Anker, M. W.; Colton, R.; Tomkins, I. B. *Aust. J. Chem.* **1968**, *21*, 1149. (b) Johnson, B. F. G. *J. Chem. Soc. A* **1967**, 475. (c) Hunter, A. D.; Legzdins, P. *Inorg. Chem.* **1984**, *23*, 4198.

Scheme II



9 was observed only at high field (500 MHz) due to its proximity to the phosphine proton resonances (see Table I).

When yellow solutions of 8 or 9 were heated under N_2, 1 equiv of carbon monoxide was lost and red solutions of *trans*-W(η^2-O_2CR)(CO)(NO)(PPh_3)$_2$ (**11**, R = CH_3; **12**, R = H) were formed. As shown in eq 8, the reaction is reversible; when CO was bubbled through the solution of the red monocarbonyl at 25 °C, the yellow dicarbonyl was quantitatively re-formed. In contrast, heating the nitrito complex, **10**, did not cause loss of carbon monoxide. The ^{1}H NMR resonance of the bidentate acetate ligand of **11** at δ +0.55 is shifted upfield by 1.2 ppm relative to that of the monodentate ligand of **8**. Similar upfield shifts in methyl protons resonances have been observed in other phosphine complexes containing bidentate acetate ligands such as $M(CO)_2(O_2CCH_3)(PPh_3)_2$ (M = Mn, Re).[19]

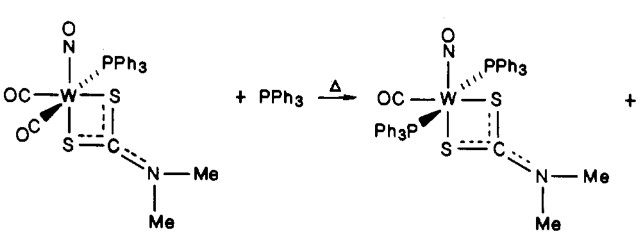


(8)

8, R = CH_3
9, R = H

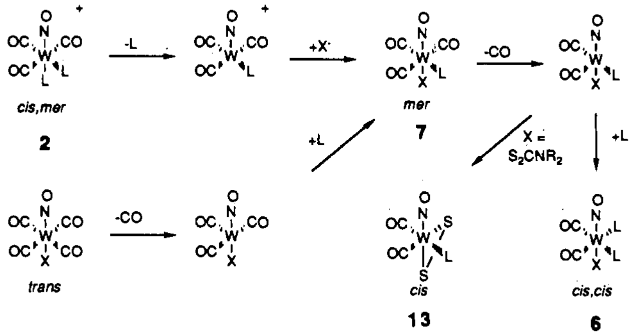
11, R = CH_3
12, R = H

It is noteworthy that dimethyldithiocarbamate reacts with **2** in a different manner than the other anions previously discussed (Scheme III). The initial isolated product is a monophosphine, *cis*-dicarbonyl complex, *cis*-W(CO)$_2$(NO)(PPh_3)(S_2CNMe_2) (**13**). The infrared spectrum and the ^{1}H NMR spectrum, which shows two methyl resonances for the dithiocarbamate ligand, uniquely define the geometry. If the reaction mixture is heated moderately, the displaced PPh_3 ligand reassociates, liberating another equivalent of CO to give *trans*-W(CO)(NO)(PPh_3)$_2$(S_2CNMe_2) (**14**) as a red-brown, crystalline solid (eq 9). The structure of **14** is also uniquely defined by its ^{31}P NMR spectrum (singlet, equivalent phosphorus nuclei) and its ^{1}H NMR spectrum (inequivalent methyl resonances). In addition, isolated samples of **13** can be converted in high yield (77%) to **14** on heating with added phosphine, or this conversion can be effected in low yield (31%) on thermolysis without added phosphine. The complex W(CO)$_2$(NO)(PPh_3)(S_2CNMe_2) could prove to be a useful precursor of complexes of the formula W(CO)(NO)(PPh_3)L(S_2CNMe_2) (L = neutral, 2-electron donor). Unlike the analogous carboxylate complexes, W(S_2CNMe_2)(CO)(NO)(PPh_3)$_2$ will not reversibly add CO. We have no evidence for the presence of unidentate dithiocarbamate ligands in our complexes.



13
14
CO (9)

Scheme III



Lithium borohydride readily reacted with **2** in THF to give pure $WH(CO)_2(NO)(PPh_3)_2$ (**15**), which has a trans,trans geometry. Yields were low, and the product was contaminated with byproducts unless free triphenylphosphine was added (PPh_3:BH_4^- ratio = 1.0–1.5) to the reaction mixture. $LiBH_4/PPh_3$ was a good source of hydride, and the H_3BPPh_3 byproduct was easily separated from the desired product. The infrared spectrum of **15** shows a weak band at 2004 cm^{-1} and a strong absorption at 1921 cm^{-1} corresponding to ν_s and ν_{as} for the C–O stretches of a *trans*-dicarbonyl species. Two strong absorptions at 1681 and 1596 cm^{-1} are assigned to strongly coupled ν(WH) and ν(NO) vibrations. The coupling can be almost completely removed by preparing the isotopically substituted deuteride complex **15**-*d*, which exhibits a strong ν(NO) at 1628 cm^{-1}; the ν(WD) must be very weak because it was not observed in the expected region around 1200 cm^{-1}. The ^{1}H NMR spectrum (CD_2Cl_2) of **15** exhibits the expected triplet for a hydride coupled to two equivalent phosphorus nuclei (δ +0.05, $^2J_{PH}$ = 23 Hz); however, the $^1J_{WH}$ coupling was not observed. This triplet is absent in the ^{1}H NMR spectrum of **15**-*d*. The ^{31}P NMR spectrum of **15** exhibits a sharp singlet flanked by tungsten satellites, implying a trans phosphine configuration. **15** can be alternatively prepared by an exchange reaction on *trans,trans*-WBr(CO)$_2$(NO)(PPh_3)$_2$ using $LiBH_4$/PPh_3. Interestingly, this exchange reaction does not work as well with the cis,cis isomer of WBr(CO)$_2$(NO)(PPh_3)$_2$, and the smaller yield of tungsten hydride that is observed may arise from cis → trans isomerization of the tungsten bromide followed by hydride exchange on the trans isomer.

Protic acids (HX) react with **15** with the liberation of H_2 to form the respective complexes *trans,trans*-WX(CO)$_2$(NO)(PPh_3)$_2$ (X = HCO_2, CH_3CO_2, Cl, Br, I, ClO_4). The perchlorate ligand in W($OClO_3$)(CO)$_2$(NO)(PPh_3)$_2$ (**16**) appears to be coordinated through a single oxygen atom. This complex is a useful precursor for other complexes of the type WX(CO)$_2$(NO)(PPh_3)$_2$; the addition of a coordinating anion in acetone gives good yields of the

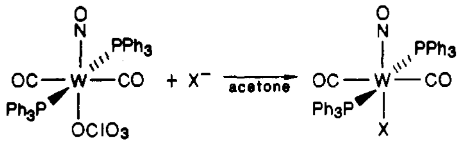
Table I. Physical and Spectroscopic Data

compd	color	ν(CO),[a,b] cm^{-1}	ν(NO),[a,b] cm^{-1}	$^{31}P\{^1H\}$NMR[g] δ, mult ($^1J_{PW}$, Hz)	^1H NMR[i] δ, mult
trans-$W(CO)_4(PPh_3)_2$ (**1t**)	pale yellow	1885		27.3, s (282)	
cis-$W(CO)_4(PPh_3)_2$ (**1c**)	yellow	1880, 1894, 1923, 2022		21.7, s (232)	
fac-$W(CO)_3(PPh_3)_3$	pale yellow	1835, 1931		21.5, s (214)	
cis,mer-$[W(CO)_3(NO)(PPh_3)_2][PF_6]$ (**2-PF_6**)	bright yellow	2016, 2053, 2096[c]	1731	16.6, d (261); $^2J_{PP}$ = 23 Hz 10.3, d (178); $^2J_{PP}$ = 23 Hz	
cis,mer-$[W(CO)_3(NO)(PPh_3)_2][BF_4]$ (**2-BF_4**)	bright yellow	2018, 2054, 2097[c]	1732	same as PF_6 salt	
cis,mer-$[W(CO)_3(NO)(PPh_3)_2][ClO_4]$ (**2-ClO_4**)	bright yellow	2019, 2055, 2099[c]	1732	same as PF_6 salt	
cis,mer-$[W(CO)_3(NO)(PTo_3)_2][PF_6]$	bright yellow	2015, 2055, 2097[c]	1734	14.3, d (261); $^2J_{PP}$ = 23 Hz 8.2, d (178); $^2J_{PP}$ = 23 Hz	
cis,trans-$[W(CO)(NO)(C_5H_5N)_2(PPh_3)_2]$-$[ClO_4]$ (**18**)	orange	1896	1595	[h]	[j]
mer-$WCl(CO)_3(NO)(PPh_3)$ (**7a**)	yellow	1993, 2030, 2103	1655	15.5, s (267)	
mer-$WBr(CO)_3(NO)(PPh_3)$ (**7b**)	yellow	2012, 2049, 2097	1667	11.1, s (267)	
mer-$WI(CO)_3(NO)(PPh_3)$ (**7c**)	yellow	2010, 2048, 2092	1670	4.5, s (251)	
cis,cis-$WCl(CO)_2(NO)(PPh_3)_2$ (**6a**)	yellow	1948, 2021	1618	13.9, s (249)	
cis,cis-$WBr(CO)_2(NO)(PPh_3)_2$ (**6b**)	yellow	1957, 2025	1621	9.8, s (250)	
cis,cis-$WI(CO)_2(NO)(PPh_3)_2$ (**6c**)	bright yellow	1952, 2018	1624	4.7, s (249)	
trans,trans-$WF(CO)_2(NO)(PPh_3)_2$ (**3a**)	yellow	1940, 2033[d]	1606	20.7, d (300); $^2J_{PF}$ = 43 Hz	
trans,trans-$WCl(CO)_2(NO)(PPh_3)_2$ (**3b**)	yellow	1942, 2033[d]	1624	18.9, s (288)	
trans,trans-$WBr(CO)_2(NO)(PPh_3)_2$ (**3c**)	yellow	1942, 2040[d]	1613	14.8, s (286)	
trans,trans-$WI(CO)_2(NO)(PPh_3)_2$ (**3d**)	yellow	1942, 2033[d]	1618	9.9, s (284)	
trans,trans-$WH(CO)_2(NO)(PPh_3)_2$ (**15**)	orange-yellow	1921, 2005[d]	1596;[f] ν(WH) = 1681[f]	27.8, s (288)	0.05, t, $^2J_{PH}$ = 23 Hz
trans,trans-$WD(CO)_2(NO)(PPh_3)_2$ (**15-*d***)	orange-yellow	1921, 2005[d]	1629; ν(WD) = unobsd	27.8, t (288); $^2J_{PD}$ = 3 Hz	
trans,trans-$W(HCO_2)(CO)_2(NO)(PPh_3)_2$ (**9**)	orange-yellow	1949, 2040;[d] ν(OCO) = 1612, 1312	1622	24.6, s (295)	7.08, s, HCO_2
trans,trans-$W(CH_3CO_2)(CO)_2(NO)(PPh_3)_2$ (**8**)	bright yellow	1944, 2040;[d] ν(OCO) = 1604, 1372	1615	25.1, s (296)	1.72, s, CH_3
trans,trans-$W(HCS_2)(CO)_2(NO)(PPh_3)_2$ (**22**)	orange yellow	1954, 2015[d]	1605	22.5, s (290)	[j]
trans,trans-$W(OClO_3)(CO)_2(NO)(PPh_3)_2$ (**16**)	yellow	1973, 2053[d]	1655	25.0, s (293)	
trans,trans-$W(NCO)(CO)_2(NO)(PPh_3)_2$ (**17**)	yellow	1984, 2034;[d] ν(NCO) = 2232	1626	[h]	
trans,trans-$W(ONO)(CO)_2(NO)(PPh_3)_2$ (**10**)	yellow	1947, 2033[d]	1632	[h]	
trans,trans-$[W(HN_2Ph)(CO)_2(NO)(PPh_3)_2]$-$[PF_6]$ (**23**)	red	1974, 2055;[d] ν(NN) = 1483, 1422[e]	1648	25.4, s (287)	11.85, s, NH
trans,trans-$[W(H^{15}NNPh)(CO)_2(NO)(PPh_3)_2]$-$[BF_4]$ (**23-α-^{15}*N***)	red	1968, 2051;[d] ν(NN) = 1465, 1417[e]	1646	25.4, d (287); $^2J_{PN}$ = 2.1 Hz	11.85, d, $^1J_{NH}$ = 65.2 Hz
trans,trans-$[W(HN^{15}NPh)(CO)_2(NO)(PPh_3)_2]$-$[BF_4]$ (**23-β-^{15}*N***)	red	1969, 2052;[d] ν(NN) = 1474, 1407[e]	1647	25.4, s (287)	11.85, d, $^2J_{NH}$ = 2.9 Hz
trans,trans-$[W(HN_2To)(CO)_2(NO)(PPh_3)_2]$-$[PF_6]$ (**24**)	red	1974, 2055[d]	1648	24.7, s (287)	2.25, s, CH_3; 6.30, q, C_6H_4; 11.92, s, NH

cis-W(S_2CNMe_2)$(CO)_2$(NO)(PPh_3) (**13**)	orange	1904, 2000	1610	20.8, s (241)	2.67, s, CH_3; 2.83, s, CH_3
trans-W(S_2CNMe_2)(CO)(NO)$(PPh_3)_2$·CH_2Cl_2 (**14**·CH_2Cl_2)	brown	1868	1595	27.3, s (289)	2.30, s, CH_3; 2.49, s, CH_3
trans-W(HN_3Ph)(CO)(NO)$(PPh_3)_2$ (**19a**)	red	1869	1596	36.8, s (299)	8.20, s, NH
trans-W(HN_3To)(CO)(NO)$(PPh_3)_2$ (**19b**)	red	1872	1606	35.0, s (299)	2.23, s, CH_3; 6.43, q, C_6H_4; 7.93, s, NH
trans-W(ToN_3To)(CO)(NO)$(PPh_3)_2$ (**20**)	red	1889	1600	32.7, s (294)	2.10, s, CH_3; 2.23, s, CH_3; 6.30, q, C_6H_4; 6.70, q, C_6H_4
trans-W(ToNCHNTo)(CO)(NO)$(PPh_3)_2$ (**21**)	red	1870	1590	31.6, s (295)	2.20, s, CH_3; 2.27, s, CH_3; 6.23, q, C_6H_4; 6.53, q, C_6H_4; 8.23, t, CH, $^4J_{PH}$ = 4 Hz
trans-W(HCO_2)(CO)(NO)$(PPh_3)_2$ (**12**)	red	1879; ν(OCO) = 1522, 1412	1597	36.3, s (307)	*j*
trans-W(CH_3CO_2)(CO)(NO)$(PPh_3)_2$ (**11**)	red	1892; ν(OCO) = 1512, 1464	1610	36.7, s (309)	0.55, s, CH_3
cis,trans-$WBr_2(NO)_2(PPh_3)_2$ (**4c**)	green		1656, 1769	7.1, s (277)	
cis,trans-$MoBr_2(NO)_2(PPh_3)_2$ (**4d**)	green		1666, 1784	43.8, s	
cis,trans-$CrBr_2(NO)_2(PPh_3)_2$ (**4e**)	dark orange		1699, 1833	20.8, s	
cis,trans-WFBr$(NO)_2(PPh_3)_2$ (**4f**)	green		1642, 1754	13.9, d (296); $^2J_{PF}$ = 42 Hz	
trans,trans-CrBr$(CO)_2$(NO)$(PPh_3)_2$ (**25**)	orange	1968, 2040^d	1688	*h*	
trans-[$Cr(CO)_4(PPh_3)_2$][PF_6] (**5**)	violet	1990		paramagnetic	

[a] Fluorolube mull. [b] Bands are of strong intensity unless otherwise specified. [c] CH_2Cl_2 solution with vs, w, s, intensities. [d] vs, w intensities. [e] Weak bands; see ref 22. [f] These bands are strongly coupled ν(NO) and ν(WH) modes. [g] CH_2Cl_2 solution, external 85% H_3PO_4 reference. [h] Not measured. [i] CD_2Cl_2 solution, phosphine resonances omitted. [j] Obscured by phosphine multiplets.

substitution products (eq 10). The addition of excess pyridine

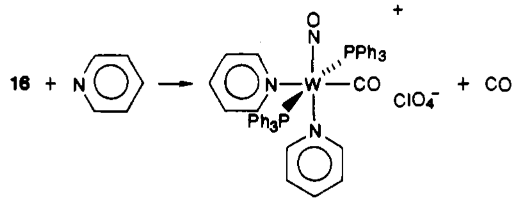


(10)

16

3a, X = F
b, X = Cl
c, X = Br
d, X = I
8, X = CH_3CO_2
10, X = NO_2
17, X = NCO

resulted in the displacement of the ClO_4^- ligand and one molecule of CO to give *cis,trans*-[W$(NC_5H_5)_2$(CO)(NO)$(PPh_3)_2$][ClO_4] (**18**) (eq 11). Every attempt to displace the ClO_4^- by CO, even

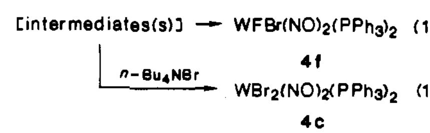


(11)

18

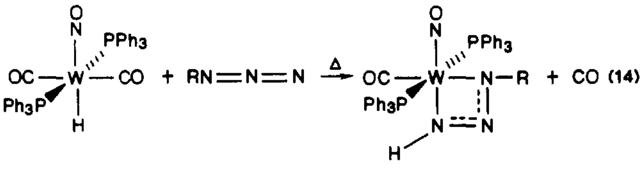
under pressure, failed. Infrared spectra measured in situ in a high-pressure cell showed that there was no reaction of W$(OClO_3)(CO)_2(NO)(PPh_3)_2$ (in THF solution) with CO (1000 psi) at 25–80 °C within a period of 1 h. We know the reactivity barrier is not kinetic because ClO_4^- is rapidly lost in other reactions; thus, the barrier must be thermodynamic. The entering CO ligand does not want to be located trans to the NO ligand, which is a powerful π-acceptor. Thus, if *cis,mer*-[$W(CO)_3(NO)(PPh_3)_2$][ClO_4] ever isomerized under mild conditions to the trans,mer isomer, the CO ligand trans to the NO would certainly dissociate, and the weakly binding perchlorate anion would occupy the vacant coordination site. Thermolysis of **2**-ClO_4 in refluxing CH_2Cl_2 *did not*, however, lead to the expected **16**. Rather, *mer*-$W(OClO_3)(CO)_3(NO)(PPh_3)$ was first formed followed by formation of an unidentified intermediate. Finally, *cis,cis*-$WCl(CO)_2(NO)(PPh_3)_2$ was isolated in about 35% yield! Similarly, thermolysis of **16** in refluxing acetone rapidly led to the formation of a red solution. This was followed by a second reaction, which produced a yellow-brown solution from which a 6% yield of *trans,trans*-$WCl(CO)_2(NO)(PPh_3)_2$ was isolated. A red solid obtained from the red solution was not pure, but strong infrared bands at 1902 and 1642 cm^{-1} suggested the presence of W(η^2-O_2ClO_2)(CO)(NO)$(PPh_3)_2$. It seems that the perchlorato ligand is converted to a chloro ligand at the expense of the phosphine and low-valent tungsten.

The cis,cis and trans,trans isomers of WBr$(CO)_2(NO)(PPh_3)_2$ reacted rapidly with $NOPF_6$ in CH_2Cl_2 with CO evolution to form green solutions. The green solutions, which contain two species (^{31}P NMR), were unstable and decomposed in minutes to form a third compound (also green), which was isolated in modest yield and characterized as WBrF$(NO)_2(PPh_3)_2$ (**4f**, trans PPh_3, cis NO) (eq 12). The same product and intermediates were observed from



both cis,cis and trans,trans isomers. The addition of bromide ion along with the $NOPF_6$ produced good yields of $WBr_2(NO)_2(PPh_3)_2$ (^{31}P NMR, singlet) with no contamination from the fluorobromo complex (^{31}P NMR, doublet), shown in eq 13.[25]

Insertion Reactions. The tungsten(0) hydride $WH(CO)_2(NO)(PPh_3)_2$ undergoes a series of interesting insertion reactions with a variety of small molecules. Aryl azides (PhN_3 or ToN_3) undergo α-insertion into the W–H bond with concomitant elimination of exactly 1 equiv of carbon monoxide to give novel monosubstituted aryltriazene complexes, which probably have the structures depicted in eq 14. These complexes are unique as they



19a, R=Ph
b, R=To

represented the first examples of monosubstituted triazenido complexes when they were first reported.[10,20] The infrared spectrum of **19b** exhibits strong absorptions for the carbonyl and nitrosyl ligands, but the triazenido bands have not been located with certainty. The triazene ligand is probably chelating on the basis of spectroscopic similarities with other complexes of this type known to be chelating. The ^{31}P NMR spectrum indicates equivalent phosphorus nuclei. The resonance of the unique triazenido proton can be clearly seen in the ^1H NMR spectrum of the complex as a broadened singlet (δ +7.93). The complex *trans*-$W(CO)(NO)(PPh_3)_2(ToN_3To)$ (**20**, eq 15) was prepared

$$\mathbf{15} + ToNHN{=}NTo \xrightarrow{\Delta} \underset{\mathbf{20}}{W(CO)(NO)(PPh_3)_2(ToN_3To)} + H_2 + CO \quad (15)$$

in good yield by the action of 1,3-di-*p*-tolyltriazene on the tungsten hydride. This bright red complex has spectroscopic properties similar to those of **19a** and **19b**, which gives further confirmation that a monosubstituted triazenido ligand has indeed been prepared by insertion of an organic azide into the tungsten–hydride bond. None of these triazene complexes will add CO at 1 atm to give η^1-triazenido dicarbonyl complexes.

Di-*p*-tolylcarbodiimide (ToN=C=NTo) also inserts into the W–H bond of **15** to form the deep red $W(CO)(NO)(PPh_3)_2(ToNCHNTo)$ (**21**). In this case, however, a β-insertion with CO loss is observed to form the analogous di-*p*-tolylformamidinato ligand. Two tolyl resonances are observed in the ^1H NMR spectrum of this complex because one of the coordinated nitrogen atoms is trans to NO while the other nitrogen atom of the chelate is trans to CO. This information, coupled with the observation of a single signal in the ^{31}P NMR spectrum, defines the geometry. The unique proton of the $ToNCHNTo^-$ ligand is observed as a triplet in the ^1H NMR spectrum ($^4J_{PH}$ = 4 Hz). This complex is also immune to CO addition under 1 atm of carbon monoxide.

A solution of **15** stirred under 1 atm of carbon dioxide slowly darkened in color from yellow to orange and finally red. After 2 h of stirring, the ^{31}P NMR of this solution showed approximately equimolar amounts of the starting tungsten hydride complex and $W(\eta^1\text{-}OC(O)H)(CO)_2(NO)(PPh_3)_2$ (**9**). Prolonged reaction times (24 h) were used in an effort to consume all of the hydrido complex; however, some **12** was formed under these conditions, along with substantial amounts of a third, brown product that could not be conveniently separated from **9** and **12**.

Carbon disulfide reacted rapidly (20 min) with **15** to form an orange solution from which we isolated pure $W(\eta^1\text{-}SC(S)H)(CO)_2(NO)(PPh_3)_2$ (**22**). The spectroscopic data of this dithioformate complex indicate that it has the same structure as the monodentate formate complex **9**. The monocarbonyl η^2-dithioformate complex (the analogue of **12**) could not be prepared in a pure form, apparently due to its instability, but infrared evidence (ν(CO) = 1888, ν(NO) = 1595 cm^{-1}) suggests that it is formed in solution upon heating **22**. The proton resonance of the unique hydrogen of the dithioformate complex was not observed in the ^1H NMR spectrum.

Benzenediazonium salts reacted rapidly with $WH(CO)_2(NO)(PPh_3)_2$ to form the monosubstituted phenyldiazene complex $[W(CO)_2(NO)(PPh_3)_2(HNNPh)^+]$ (**23**), which can be readily crystallized as the BF_4^- or PF_6^- salt, shown in eq 16. Spectroscopic

$$\mathbf{15} + PhN_2PF_6 \rightarrow \underset{\mathbf{23\text{-}PF_6}}{[W(HN{=}NPh)(CO)_2(NO)(PPh_3)_2][PF_6]} \xrightarrow{Bu_4NBr} \mathbf{3c} + \text{“}PhN{=}NH\text{”} \quad (16)$$

data suggest the complex contains trans carbonyl ligands and trans phosphine ligands with the nitrosyl and the diazene groups mutually trans. Repeated attempts to deprotonate the diazene ligand to give an aryldiazo (PhN_2) complex were all unsuccessful. Bromide ions quantitatively converted the diazene complex to *trans,trans*-$WBr(CO)_2(NO)(PPh_3)_2$, and the *cis*-PhN=NH ligand was displaced from the metal. Both N_2 and C_6H_6 were detected as byproducts presumably from the decomposition of the phenyldiazene. The ease of the PhN=NH displacement from the metal by Br^- suggests that this may be a good way to generate and subsequently trap this reactive molecule.[21] We allowed PhN_2^+ to react with *trans*-$W(CO)_4(PPh_3)_2$ and *trans,trans*-$WBr(CO)_2(NO)(PPh_3)_2$ but obtained no appreciable reaction after 60 min at 25 °C.

In the insertion reactions discussed above, CO_2, CS_2, and RNCNR underwent β-insertions (hydride located on atom β to the metal), and RN_3 and RN_2^+ underwent α-insertions (hydride located on atom attached to the metal). One can account for the α-insertions by considering that the terminal nitrogen atoms in $R{-}N{\equiv}N{:}^+$ and $R{-}N{=}N{-}\ddot{N}{:}$ are electron deficient. Nitrous oxide (N_2O), diazotoluene ($PhCHN_2$) and *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (*p*-$ToSO_2N(CH_3)NO$) showed no reactivity toward $WH(CO)_2(NO)(PPh_3)_2$. We found that tolyl isocyanate (*p*-ToNCO) and tolyl isothiocyanate (*p*-ToNCS) reacted on mixing with **15** with CO evolution to give deep red solutions. Although these reactions seemed to proceed well, they were not clean; both the solution and the solids obtained from the solutions were shown by spectroscopic means to be mixtures of several products or isomers. We were unable to obtain a single purified product from the mixtures.[24]

Mechanistic Speculations. Three characteristics of the foregoing carbonyl substitution reactions are noteworthy. When optimal reaction conditions were achieved, (1) the yields were high, (2) the stereoselectivities to a single isomer were excellent, and (3) the coordination sphere frequently rearranged upon CO substitution. This led us to consider that simple multiple substitution mechanisms were operative. By the use of established principles and a few assumptions, the stereochemistries of the above compounds can be conveniently rationalized (schematically shown in Scheme II and Scheme III):

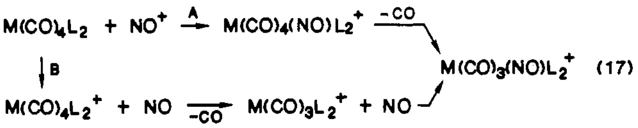
1. In bis(triphenylphosphine) complexes, the most labile ligand is one of the phosphine ligands except when especially labile ligands are present such as $OClO_3$ or CO when trans to NO.
2. Substitution reactions are dissociative, with rigid square-pyramidal intermediates.
3. The labilizing ability of a trans ligand for both CO loss and phosphine loss is NO > CO > PR_3 (L).

The initial substitution of CO by NO^+ would thus produce only the cis,mer isomer $W(CO)_3(NO)L_2^+$ from either isomer of $W(CO)_4L_2$. Note, however, that, for *cis*-$W(CO)_4L_2$, the phosphine cis to NO remains on the metal but, for *trans*-$W(CO)_4L_2$, the phosphine trans to NO remains on the metal. The cis isomer of the intermediate, $W(CO)_4(NO)L^+$, should lose CO faster than the trans isomer.

The second substitution of CO by halide (X^-) would thus produce only *cis,cis*-$WX(CO)_2(NO)L_2$ (NO trans to X) from *cis,mer*-$W(CO)_3(NO)L_2^+$ via the intermediate *mer*-$WX(CO)_3(NO)L$ (L trans to CO), which can also be isolated from the reaction of PPh_3 with $WX(CO)_4(NO)$. When the anion (X^-) is dithiocarbamate, another intermediate, *cis*-$W(S_2CNR_2)(CO)_2(NO)L$ (NO trans to X), should be formed.

The third substitution of CO by NO^+ should produce *cis,cis*-$WX(CO)(NO)_2L_2^+$ (X trans to NO) from both isomers of $WX(CO)_2(NO)L_2$ via different intermediates. However, the presence of a positive charge and two nitrosyl ligands in this complex so labilize the remaining carbonyl that it is not stable enough to be isolated when reactions are carried out at room temperature.

We are aware that the substitution of CO in nitrosyl complexes by phosphine or halide ligands can be associative but we believe that (1) probable reluctance of tungsten to allow the nitrosyl ligand to bend and (2) the steric crowding of the seven-coordinate intermediate might hinder this pathway. The fast rate of CO substitution by NO^+ has been noted and discussed in the above context. With our present information, however, we cannot rule out two other commonly cited substitution mechanisms,[8] acid–base adduct formation (pathway A) and electron transfer (pathway B) shown in eq 17.



$$\begin{tikzcd}
M(CO)_4L_2 + NO^+ \arrow[r, "A"] \arrow[d, "B"] & M(CO)_4(NO)L_2^+ \arrow[r, "-CO"] & M(CO)_3(NO)L_2^+ \\
M(CO)_4L_2^+ + NO \arrow[r, "-CO"'] & M(CO)_3L_2^+ + NO \arrow[ru] &
\end{tikzcd} \qquad (17)$$

Acknowledgment. Financial support from the National Science Foundation (Grant CHE-8520329) and the Research Corp. is sincerely appreciated. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The NMR facilities were supported in part through The University of Chicago Cancer Center Grant NIH-CA-14599.

Contribution from the Lehrstuhl für Anorganische Chemie I,
Ruhr-Universität, D-4630 Bochum, Federal Republic of Germany

Ligating Properties of Monomeric *cis*-Trioxometal(VI) Complexes of Molybdenum(VI) and Tungsten(VI). Preparation and Spectroscopic Characterization of LMO_3 and $[(LMO_3)_4Co^{II}](ClO_4)_2$ (M = Mo, W; L = Cyclic Triamine)

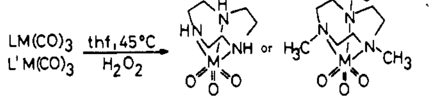
Partha S. Roy and Karl Wieghardt*

Received December 5, 1986

Oxidative decarbonylation of $LM(CO)_3$ and $L'M(CO)_3$, where L represents 1,4,7-triazacyclononane, L′ is *N,N′,N″*-trimethyl-1,4,7-triazacyclononane, and M = Mo, W, with 30% H_2O_2 in tetrahydrofuran afforded essentially quantitatively monomeric LMO_3 and $L'MO_3$ complexes containing a *fac*-trioxometal(VI) unit. The ligating properties of these complexes have been investigated, and the complexes $[(L'MoO_3)_4Co](ClO_4)_2$, $[(L'MoO_3)_2Fe](ClO_4)_2$, and $[(L'MoO_3)_4Fe](ClO_4)_3$ have been isolated. ^{95}Mo, ^{183}W, and ^{17}O, NMR spectra were recorded; magnetic properties and electronic as well as infrared spectra are reported.

Introduction

Recently we have reported that the low-valent carbonylnitrosylrhenium complex $[LRe(CO)_2NO]^{2+}$ is readily oxidatively decarbonylated with H_2O_2 in aqueous solution, yielding the *fac*-trioxorhenium(VII) complex $[LReO_3]^+$ in excellent yields[1] (L represents the cyclic triamine 1,4,7-triazacyclononane). This type of chemistry has attracted considerable interest, since Herrmann and co-workers have shown that the reaction of $Me_5CpRe(CO)_3$ with H_2O_2 yields the organometallic rhenium(VII) species Me_5CpReO_3.[2] The formal oxidation state of the metal center changes in both cases by six units without apparent loss of the coordinated cyclic triamine or Me_5Cp^-. We have now extended this scheme to complexes of molybdenum and tungsten. Thus the reaction of $LM(CO)_3$ or $L'M(CO)_3$ (M = Mo, W; L = 1,4,7-triazacyclononane; L′ = *N,N′,N″*-trimethyl-1,4,7-triazacyclononane)[3–6] with H_2O_2 in tetrahydrofuran (thf) yields essentially quantitatively LMO_3 and $L'MO_3$ (M = Mo, W):

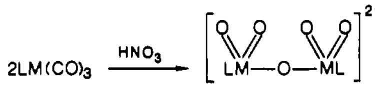


(1)

M = Mo, W

The complexes $LMoO_3$[7] and $L'MoO_3$[8] have been prepared previously from MoO_3 and the respective cyclic triamine in analogy to the preparation of (dien)MoO_3[9] (dien = diethylenetriamine) although in lower yields. Complexes containing a *fac*-WO_3 unit have not been extensively studied in the past[10] —the only reported examples appear to be (dien)WO_3[11] and $[WO_3(nta)]^{3-}$[12] (nta = nitrilotriacetate), where the former is labile in solution and the latter has not been isolated.

Since we have shown that $LMoO_3$ and $L'MoO_3$ are stable both in solution and in the solid state, it was interesting to study the chemistry of these LMO_3 species in more detail. The electrochemistry of $LMoO_3$ and $L'MoO_3$ has been described.[8] We report here on their ligating properties toward Co(II), Fe(II), and Fe(III). This was initiated by the observation that decarbonylation of $LM(CO)_3$ with 2 M nitric acid yielded dimers with a (μ-oxo)bis[dioxometal(VI)] moiety (eq 2).[6,13] Thus at least one terminal



$$2LM(CO)_3 \xrightarrow{HNO_3} [(O)_2LM{-}O{-}ML(O)_2]^{2+} \qquad (2)$$

oxo group in LMO_3 may bind to other centers, forming LO_2M–O–M′ units.

Experimental Section

The macrocyclic ligands 1,4,7-triazacyclononane (L) and *N,N′,N″*-trimethyl-1,4,7-triazacyclononane (L′) have been prepared according to published procedures.[14,15]

---

(1) Wieghardt, K.; Pomp, C.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 1659.

(2) (a) Herrmann, W. A.; Serrano, R.; Bock, H. *Angew. Chem.* **1984**, *96*, 364; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 383. (b) Herrmann, W. A.; Serrano, R.; Schäfer, A.; Küsthardt, U. *J. Organomet. Chem.* **1984**, *272*, 55.

(3) Chaudhuri, P.; Wieghardt, K.; Tsay, Y. H.; Krüger, C. *Inorg. Chem.* **1984**, *23*, 427.

(4) Backes-Dahmann, g.; Herrmann, W.; Wieghardt, K.; Weiss, J. *Inorg. Chem.* **1985**, *24*, 485.

(5) Chaudhuri, P.; Wieghardt, K.; Gebert, W.; Jibril, I.; Huttner, G. *Z. Anorg. Allg. Chem.* **1985**, *521*, 23.

(6) Wieghardt, K.; Backes-Dahmann, G.; Herrmann, W.; Weiss, J. *Angew. Chem.* **1984**, *96*, 890; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 899.

(7) Wieghardt, K.; Hahn, M.; Swiridoff, W.; Weiss, J. *Inorg. Chem.* **1984**, *23*, 94.

(8) Herrmann, W.; Wieghardt, K. *Polyhedron* **1986**, *5*, 513.

(9) (a) Marzluff, W. F. *Inorg. Chem.* **1964**, *3*, 395. (b) Cotton, F. A.; Elder, R. C. *Inorg. Chem.* **1964**, *3*, 397.

(10) Dori, Z. *Prog. Inorg. Chem.* **1981**, *28*, 239.

(11) Taylor, R. S.; Gans, P.; Knowles, P. F.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1972**, 24.

(12) Ben-Shosham, R.; Chatt, J.; Hussain, W.; Leigh, G. J. *J. Organomet. Chem.* **1976**, *112*, C9.

(13) Backes-Dahmann, G.; Wieghardt, K. *Inorg. Chem.* **1985**, *24*, 4049.

(14) (a) Atkins, T. J.; Richman, J. E.; Oettle, W. F. *Org. Synth.* **1978**, *58*, 86. (b) Wieghardt, K.; Schmidt, K.; Nuber, B.; Weiss, J. *Chem. Ber.* **1979**, *112*, 2220.

0020-1669/87/1326-1885$01.50/0