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Organometallic Nitrosyl Chemistry. 16.[1,2] Preparation and Properties of the Bimetallic Cations $[(\eta^5\text{-}C_5H_5)_2MM'(NO)_4H]^+$ (M, M′ = Mo or W)

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Treatment of CH_2Cl_2 solutions of the hydrido complexes $(\eta^5\text{-}C_5H_5)M(NO)_2H$ (M = Mo or W) with hydride abstractors such as $(C_6H_5)_3C^+$ or $C_7H_7^+$ in 2:1 stoichiometry results in the precipitation of the bimetallic cations $[(\eta^5\text{-}C_5H_5)_2M_2(NO)_4H]^+$ which are obtained as their BF_4^- or PF_6^- salts in good yields. The mixed-metal cation $[(\eta^5\text{-}C_5H_5)_2MoW(NO)_4H]^+$ can be isolated as its BF_4^- salt in 57% yield from the reaction of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ with an equimolar amount of $[(\eta^5\text{-}C_5H_5)Mo(NO)_2(\eta^2\text{-}C_8H_{14})]^+BF_4^-$ in CH_2Cl_2. Protonation of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ does not afford the analogous dichromium cations, coordinating acids (HX) instead converting the reactant into $(\eta^5\text{-}C_5H_5)Cr(NO)_2X$. The infrared and ^1H NMR spectra of the bimetallic cations are consistent with their possessing the instantaneous molecular structures $[(\eta^5\text{-}C_5H_5)(NO)_2M(H)M'(NO)_2(\eta^5\text{-}C_5H_5)]^+$ (M, M′ = Mo, W) which can be viewed as Lewis acid–base adducts. In solution, the heterometallic species exists in equilibrium with its homometallic analogues. Unlike related carbonyl complexes, the $[(\eta^5\text{-}C_5H_5)_2M_2(NO)_4H]^+$ cations are not deprotonated by a variety of bases (B), undergoing cleavage instead to the monomeric products $(\eta^5\text{-}C_5H_5)M(NO)_2H$ and $[(\eta^5\text{-}C_5H_5)M(NO)_2(B)]^+$ of which only the former can be isolated. A study of the interaction of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ with representative Lewis acids provides some insights into the nature of the metal–metal bond in the bimetallic cations.

Introduction

A most intriguing aspect of the organometallic nitrosyl chemistry of the group 6B elements is that whereas $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ has been known since 1964,[3] the analogous molybdenum and tungsten dimers have yet to be prepared. The chromium complex can be isolated in varying yields from any of the reactions

$$(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl \xrightarrow[\text{or Na/Hg, } C_6H_6{}^5]{\text{Zn/Hg, THF}^4} [(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2 \qquad (1)$$

$$(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO) + \text{excess NO} \xrightarrow[\text{hexanes}]{h\nu^6} [(\eta^5\text{-}C_5H_5)Cr(NO_2)]_2 + (\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2) \qquad (2)$$

$$(\eta^5\text{-}C_5H_5)_2Cr + \text{excess NO} \xrightarrow{\text{hexanes}^6} [(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2 + (\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2) + (\eta^5\text{-}C_5H_5)Cr(NO)_2(\eta^1\text{-}C_5H_5) \qquad (3)$$

$$(\eta^5\text{-}C_5H_5)Cr(NO)_2X \xrightarrow[C_6H_6,\ C_6H_5CH_3,\ \text{or } CH_2Cl_2]{NaAlH_2(OCH_2CH_2OCH_3)_2{}^{7,8}} [(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2 \qquad (4)$$

$$X = Cl,\ I,\ NO_3,\ NO_2,\ \eta^1\text{-}C_5H_5,\ \text{or } BF_4$$

the transformations represented in eq 1 being the synthetic methods of choice. However, when the identical molybdenum- or tungsten-containing reactants are subjected to the experimental conditions indicated above, only intractable products (eq 1–3) or the hydrides, $(\eta^5\text{-}C_5H_5)M(NO)_2H$ (M = Mo or W) (eq 4), result. Furthermore, these hydrido complexes only afford red-brown nitrosyl-free solids when decomposed thermally.[7] Nevertheless, in view of the extensive and varied chemistry of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ that we have developed previously,[8–11] the preparation of the molybdenum and tungsten analogs for comparative purposes remains one of our prime synthetic objectives.

Recently, Graham and Sweet[12] described the successful synthesis of the valence isoelectronic complex $[(\eta^5\text{-}C_5H_5)Re(CO)(NO)]_2$ by the sequential reactions (eq 5 and 6). We therefore decided to attempt the analogous

$$2(\eta^5\text{-}C_5H_5)Re(CO)(NO)H + (C_6H_5)_3CX \xrightarrow{CH_2Cl_2} [(\eta^5\text{-}C_5H_5)_2Re_2(CO)_2(NO)_2H)]^+X^- + (C_6H_5)_3CH \qquad (5)$$

$$[(\eta^5\text{-}C_5H_5)_2Re_2(CO)_2(NO)_2H]^+X^- + (C_2H_5)_3N \xrightarrow{CH_2Cl_2} [(\eta^5\text{-}C_5H_5)Re(CO)(NO)]_2 + (C_2H_5)_3NH^+X^- \qquad (6)$$

$$X = BF_4 \text{ or } PF_6$$

transformations with the $(\eta^5\text{-}C_5H_5)M(NO)_2H$ (M = Mo or W) complexes. In this paper, we present the results of these attempts and report some new related chemistry which bears on the properties of the bimetallic cations isolated during our investigation.

Experimental Section

All manipulations were performed so as to maintain all chemicals under an atmosphere of prepurified nitrogen either on the bench using conventional techniques for the manipulation of air-sensitive compounds[13] or in a Vacuum Atmospheres Corp.

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Dri-Lab Model HE-43-2 drybox. All chemicals used were of reagent grade or comparable purity. All reagents were either purchased from commercial suppliers or prepared according to published procedures, and their purity was ascertained by elemental analyses and/or melting point determinations. Melting points were taken in capillaries by using a Gallenkamp Melting Point apparatus and are uncorrected. All solvents were dried by standard procedures[14] and distilled just prior to use. Unless specified otherwise, the chemical reactions described below were effected at ambient temperatures.

Infrared spectra were recorded on Perkin-Elmer 457 or 598 spectrophotometers and were calibrated with the 1601-cm^{-1} band of polystyrene film. Proton magnetic resonance spectra were obtained on a Varian Associates T-60 spectrometer with tetramethylsilane employed as an internal standard or on Bruker WP-80, WH-400, or Varian Associates XL-100 spectrometers with reference to the solvent used. All ^1H chemical shifts are reported in parts per million downfield from Me_4Si. Mrs. M. M. Tracey and Ms. M. A. Heldman assisted in obtaining these data. Low-resolution mass spectra were recorded at 70 eV on an Atlas CH4B spectrometer using the direct-insertion method with the assistance of Dr. G. K. Eigendorf and Mr. J. W. Nip. Elemental analyses were performed by Mr. P. Borda of this department.

Reactions of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ with $(C_6H_5)_3CX$ (X = BF_4 or PF_6) in CH_2Cl_2. To a stirred, bright green solution containing $(\eta^5\text{-}C_5H_5)W(NO)_2H$[7] (4.53 g, 14.6 mmol) in CH_2Cl_2 (80 mL) was added dropwise an orange CH_2Cl_2 solution (40 mL) of $(C_6H_5)_3CBF_4$[15] (2.41 g, 7.30 mmol). As the addition proceeded, the bright green solution darkened to an olive green color, and a green precipitate formed gradually. Monitoring of the infrared spectrum of the supernatant solution showed complete disappearance of the nitrosyl absorptions due to $(\eta^5\text{-}C_5H_5)W(NO)_2H$ after the 0.5 equiv of $(C_6H_5)_3CBF_4$ had been added. Concentration of the final reaction mixture under reduced pressure to a volume of approximately 20 mL afforded further solid and a pale green solution. The dark green, microcrystalline solid was collected by filtration, washed with CH_2Cl_2 (3 × 5 mL), and dried in vacuo (<0.005 mm) to obtain analytically pure $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]BF_4$ (3.70 g, 72% yield), mp 95 °C dec.

Anal. Calcd for $C_{10}H_{11}W_2N_4O_4BF_4$: C, 17.02; H, 1.57; N, 7.94. Found: C, 16.91; H, 1.48; N, 7.85. IR (Nujol mull): ν_{NO} 1775, 1748, 1707, 1660 (br); also 1432 (w), 1422 (w), 1359 (w), 1290 (w), 1070 (s, br), 1000 (s, br), 852 (s, br) cm^{-1}.

The reaction of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ with $(C_6H_5)_3CPF_6$ in CH_2Cl_2 was performed in an analogous manner to obtain green, microcrystalline $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]PF_6$ in 91.6% yield; mp 122 °C dec.

Anal. Calcd for $C_{10}H_{11}W_2N_4O_4PF_6$: C, 15.72; H, 1.45; N, 7.33. Found: C, 15.70; H, 1.38; N, 7.25. IR (Nujol mull): ν_{NO} 1752 (br), 1685 (br); also 1427 (m), 1068 (w), 1010 (w), 888 (s), 865 (s), 849 (s), 836 (s), 811 (s), 740 (w) cm^{-1}.

The analogous reaction between $(\eta^5\text{-}C_5H_5)W(NO)_2D$[7] and $(C_6H_5)_3CPF_6$ in CH_2Cl_2 afforded $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4D]PF_6$ in comparable yield.

Reaction of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ with $C_7H_7BF_4$. To a vigorously stirred CH_2Cl_2 solution (70 mL) containing 1.30 g (3.87 mmol) of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ was added 0.23 g (1.29 mmol) of solid, white $C_7H_7BF_4$.[16] The solution gradually darkened as the $C_7H_7BF_4$ was slowly consumed, and then a green precipitate began to form. After 1.5 h, none of the white tropylium salt was evident in the reaction mixture, and an infrared spectrum of the supernatant solution revealed that the nitrosyl absorptions due to $(\eta^5\text{-}C_5H_5)W(NO)_2H$ had diminished to approximately 35% of their initial intensity. Isolation of the green precipitate by filtration afforded 0.60 g (66% yield based on $C_7H_7BF_4$) of analytically pure $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]BF_4$ (vide supra).

Reaction of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ with $(C_6H_5)_3CPF_6$ in CH_3CN. An orange solution of $(C_6H_5)_3CPF_6$ (0.29 g, 0.74 mmol) in CH_3CN (5 mL) was added dropwise to a stirred, green solution of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ (0.23 g, 0.74 mmol) in CH_3CN (18 mL) at −10 °C. Infrared monitoring of the reaction mixture during the addition revealed a diminution of the nitrosyl absorptions of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ (i.e., ν_{NO} = 1715 and 1631 cm^{-1}) and a concomitant increase in the nitrosyl absorbances attributable to $[(\eta^5\text{-}C_5H_5)W(NO)_2(CH_3CN)]^+$ (i.e., ν_{NO} = 1766 and 1689 cm^{-1}).[17] After complete mixing of the two solutions, an infrared spectrum of the resulting blue-green solution indicated that $[(\eta^5\text{-}C_5H_5)W(NO)_2(CH_3CN)]^+$ was the only nitrosyl-containing species present.

Treatment of $[(\eta^5\text{-}C_5H_5)W(NO)_2(CH_3CN)]PF_6$ with $(\eta^5\text{-}C_5H_5)W(NO)_2H$. To a blue-green solution containing 0.37 g (0.74 mmol) of $[(\eta^5\text{-}C_5H_5)W(NO)_2(CH_3CN)]PF_6$ in CH_3CN (35 mL) was added an excess of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ (0.31 g, 1.0 mmol). An infrared spectrum of the resulting solution revealed no interaction between the two organometallic complexes. Removal of the solvent under reduced pressure afforded a brown oil. Dissolution of the oil in CH_2Cl_2 (40 mL) produced a clear green solution whose infrared spectrum displayed nitrosyl absorbances only attributable to $(\eta^5\text{-}C_5H_5)W(NO)_2H$ and $[(\eta^5\text{-}C_5H_5)W(NO)_2(CH_3CN)]PF_6$ (i.e., ν_{NO} = 1718, 1632 and 1770, 1690 cm^{-1}, respectively).

Reaction of $(\eta^5\text{-}C_5H_5)Mo(NO)_2H$ with $(C_6H_5)_3CPF_6$. A solution of $(\eta^5\text{-}C_5H_5)Mo(NO)_2H$ in toluene (190 mL) was prepared in the usual manner[7] from 5.10 g (19.9 mmol) of $(\eta^5\text{-}C_5H_5)Mo(NO)_2Cl$. The green solution was then concentrated in vacuo to a volume of ~30 mL with some attendant decomposition of the hydride occurring as evidenced by the formation of small amounts of a red-brown solid. The final solution was transferred by syringe onto a 4 × 9 cm column of Florisil prepared in CH_2Cl_2. Elution of the column with CH_2Cl_2 provided a green eluate which was concentrated to 105 mL under reduced pressure.

To 70 mL of this solution were added portions of solid $(C_6H_5)_3CPF_6$, the progress of the reaction being monitored by infrared spectroscopy. As each portion of the trityl hexafluorophosphate was added, a green precipitate formed and the nitrosyl absorptions due to $(\eta^5\text{-}C_5H_5)Mo(NO)_2H$ in the infrared spectrum of the supernatant solution diminished in intensity. A total of 0.87 g (2.24 mmol) of $(C_6H_5)_3CPF_6$ was required for complete consumption of the molybdenum reactant. Toluene (10 mL) was added to the final reaction mixture, and solvent was removed in vacuo to give a final volume of ~50 mL. The green solid was collected by filtration, washed with toluene (2 × 5 mL), and dried (<0.005 mm) to obtain 0.75 g (19% yield based on $(\eta^5\text{-}C_5H_5)Mo(NO)_2Cl$; 57% yield based on $(C_6H_5)_3CPF_6$) of analytically pure $[(\eta^5\text{-}C_5H_5)_2Mo_2(NO)_4H]PF_6$, mp 119 °C dec.

Anal. Calcd for $C_{10}H_{11}Mo_2N_4O_4PF_6$: C, 20.42; H, 1.89; N, 9.53. Found: C, 20.24; H, 1.77; N, 9.42. IR (Nujol mull): ν_{NO} 1783 (br), 1675 (br); also 1430 (w), 1070 (w), 1015 (w), 860 (s, br), 820 (s) cm^{-1}. IR (CH_2Cl_2): ν_{NO} 1795, 1768, 1707, 1695 (sh) cm^{-1}.

Preparation of $[(\eta^5\text{-}C_5H_5)_2MoW(NO)_4H]BF_4$. A slight excess of $AgBF_4$ (0.23 g, 1.18 mmol) was added to a stirred CH_2Cl_2 solution (20 mL) containing $(\eta^5\text{-}C_5H_5)Mo(NO)_2Cl$ (0.26 g, 1.0 mmol). Infrared monitoring of the supernatant solution showed the disappearance of the nitrosyl absorptions characteristic of $(\eta^5\text{-}C_5H_5)Mo(NO)_2Cl$ and the appearance of two new bands at ~25-cm^{-1} higher energy (i.e., ν_{NO} = 1783, 1692 cm^{-1}), the conversion being complete within 45 min. The reaction mixture was then filtered to remove the flocculent white precipitate, and the green filtrate was treated with cyclooctene (1 mL) to obtain a stable blue-green solution which displayed ν_{NO} at 1800 and 1717 cm^{-1} in its infrared spectrum. Solid $(\eta^5\text{-}C_5H_5)W(NO)_2H$ (0.31 g, 1.0 mmol) was added to this solution, and the resulting green solution was stirred for 0.5 h. Addition of hexanes (30 mL) induced the formation of a flocculent green precipitate. The mixture was concentrated in vacuo to a volume of ~10 mL, and the colorless supernatant liquid was removed by syringe and discarded. The residue was recrystallized from CH_2Cl_2–hexanes to obtain 0.353 g (57% yield) of analytically pure $[(\eta^5\text{-}C_5H_5)_2MoW(NO)_4H]BF_4$ as a dark green, microcrystalline solid, mp 115 °C dec.

Anal. Calcd for $C_{10}H_{11}MoWN_4O_4BF_4$: C, 19.44; H, 1.79; N, 9.07. Found: C, 19.37; H, 1.89; N, 8.82. IR (Nujol mull): ν_{NO} 1790, 1769 (sh), 1756, 1718, 1660 (br); also 1419 (w), 1287 (w), 1060 (s, br), 1000 (s, br), 850 (s, br) cm^{-1}. IR (CH_2Cl_2): ν_{NO} 1790, 1765

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(sh), 1751, 1706, 1678, 1650 (sh) cm^{-1}.

Reaction of $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]BF_4$ with $(C_2H_5)_3N$. To a stirred suspension of $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]BF_4$ (0.20 g, 0.28 mmol) in CH_2Cl_2 (40 mL) was added a large excess (1 mL) of $(C_2H_5)_3N$. The solid reactant dissolved rapidly to produce a clear, yellow-brown solution whose infrared spectrum exhibited two bands in the nitrosyl region at 1718 and 1632 cm^{-1}. Addition of $(C_2H_5)_2O$ (40 mL) to this solution produced a flocculent, yellow-brown precipitate which was collected by filtration. The filtrate was taken to dryness in vacuo, and the resulting residue was redissolved in a minimum of CH_2Cl_2. An infrared spectrum of this solution showed two strong absorptions at 1718 and 1632 cm^{-1}, the characteristic ν_{NO}'s of $(\eta^5\text{-}C_5H_5)W(NO)_2H$. A Nujol mull of the yellow-brown solid displayed broad infrared absorbances at 1720 and 1600 cm^{-1}.

Reaction of $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]PF_6$ with $(C_6H_5)_3P{=}CH_2$. A stirred suspension containing 0.28 g (0.37 mmol) of $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]PF_6$ in CH_2Cl_2 (15 mL) was treated dropwise with 1 equiv of an orange, diethyl ether solution of 0.3 M $(C_6H_5)_3P{=}CH_2$.[18] The reaction solution darkened to an olive-green color, and the originally suspended solid readily dissolved. To the final solution was added $(C_2H_5)_2O$ (50 mL), whereupon a tan precipitate formed which was isolated by filtration. Extraction of the collected solid with CH_2Cl_2 afforded an orange-brown solution which exhibited strong infrared absorptions at 1728 and 1647 cm^{-1}.

Volatile components were removed from the filtrate under reduced pressure. The remaining residue was dissolved in benzene, and the solution was chromatographed on a Florisil column (2 × 5 cm) with benzene as eluant to obtain $(\eta^5\text{-}C_5H_5)W(NO)_2H$ (~0.1 g) which was identified by its characteristic infrared and ^1H NMR spectra.[7]

Reaction of $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]BF_4$ with $[(CH_3)_2N]_3PO$. To a stirred suspension of $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]BF_4$ (0.30 g, 0.43 mmol) in CH_2Cl_2 (10 mL) was added 1 mL of $[(CH_3)_2N]_3PO$. The solid dissolved immediately to produce a dark green solution whose infrared spectrum displayed three strong absorptions in the nitrosyl region (i.e., ν_{NO} = 1735, 1721, and 1630 cm^{-1}) which were not due to $[(CH_3)_2N]_3PO$. Unfortunately, numerous attempts to separate the excess hexamethylphosphoramide from the nitrosyl-containing species by means such as extraction with H_2O, crystallization from a variety of solvent mixtures (which invariably yielded oils), and chromatography on Florisil were unsuccessful.

Reaction of $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]BF_4$ with $KOH\text{–}C_2H_5OH$. A 0.07 M solution of KOH in 95% ethanol was added dropwise to a stirred suspension of $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]BF_4$ (0.30 g, 0.43 mmol) in CH_2Cl_2 (20 mL) with infrared monitoring. Upon addition of the first few drops of the KOH solution, the solid reactant rapidly dissolved to give a light green solution whose infrared spectrum displayed a broad, weak band at ~1900 cm^{-1} and two strong, sharp bands at 1718 and 1632 cm^{-1}, all characteristic of $(\eta^5\text{-}C_5H_5)W(NO)_2H$.[7] As further $KOH\text{–}C_2H_5OH$ was added, to a total of 1 equiv of KOH, the only change in the nitrosyl region of the infrared spectra was a gradual diminution in intensity of these bands as the solution became more dilute. Solvents were removed from the final reaction mixture in vacuo, and the resulting residue was transferred as a suspension in benzene onto a Florisil column (2 × 5 cm). Elution of the column with benzene developed a green band which, when collected, taken to dryness, and redissolved in CH_2Cl_2, exhibited the characteristic infrared absorptions of $(\eta^5\text{-}C_5H_5)W(NO)_2H$. Elution of the column with tetrahydrofuran slowly developed a yellow band which was eluted from the column with H_2O. The eluate was taken to dryness in vacuo, and an infrared spectrum of the residue (~0.1 g) in tetrahydrofuran displayed ν_{NO} at 1718 and 1610 cm^{-1}.

Reaction of $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]PF_6$ with $C_{10}H_6[N(CH_3)_2]_2$. Upon addition of 1 equiv (0.05 g) of $C_{10}H_6[N(CH_3)_2]_2$[19] to a suspension of green $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]PF_6$ (0.18 g, 0.24 mmol) in CH_2Cl_2 (10 mL), the supernatant solution immediately became yellow. However, even after being stirred for 30 min, the green solid did not appear to be dissolving, and the supernatant solution exhibited only weak infrared absorptions at 1718 and 1632 cm^{-1}. A large excess of $C_{10}H_6[N(CH_3)_2]_2$ was therefore added (to a total of 10 equiv), and the progress of the reaction was monitored by infrared spectroscopy. The bands at 1718 and 1632 cm^{-1} gradually increased in intensity as the supernatant solution darkened, but after 3 h of stirring some green solid still remained. After 18 h, the bands were even more intense, and only a brown precipitate was present in the reaction mixture. The solid was isolated by filtration and was extracted with tetrahydrofuran; an infrared spectrum of the extracts showed only weak, broad absorbances at 1720 and 1615 cm^{-1}. The filtrate was concentrated under reduced pressure, and its infrared spectrum displayed strong bands due to $(\eta^5\text{-}C_5H_5)W(NO)_2H$ as the only absorptions in the nitrosyl region not attributable to the $C_{10}H_6[N(CH_3)_2]_2$.

The reaction was repeated in CD_3NO_2, and its progress was monitored by ^1H NMR spectroscopy. The monitoring indicated that the bimetallic cation was cleaved initially to $(\eta^5\text{-}C_5H_5)W(NO)_2H$ (δ 6.13 (s, 5 H), 2.08 (s, 1 H)) and another cyclopentadienyltungsten complex (δ 6.53 (s, 5 H)), but the latter decomposed rapidly to produce a brown, insoluble residue.

Reaction of $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]PF_6$ with $NaBH_4$. A small sample (~0.1 g) of $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]PF_6$ was dissolved in CH_3NO_2 (10 mL) to give a yellow-green solution which exhibited three infrared absorptions (1770, 1718, 1691 cm^{-1}) in the portion of the nitrosyl region not obscured by the solvent (i.e., >1650 cm^{-1}). To this stirred solution was added an excess (~10 equiv) of solid $NaBH_4$; after 48 h only the band at 1718 cm^{-1} remained in the infrared spectrum of the supernatant solution. Solvent removal under reduced pressure afforded a solid which was extracted with CH_2Cl_2. Chromatography of the extracts on Florisil with CH_2Cl_2 as eluant yielded only $(\eta^5\text{-}C_5H_5)W(NO)_2H$ which was identified spectroscopically (vide supra); a trace of impurity remained at the top of the column.

Treatment of $[(\eta^5\text{-}C_5H_5)_2Mo_2(NO)_4H]PF_6$ with Various Lewis Bases. (a) With Acetone. To a CD_3NO_2 solution of $[(\eta^5\text{-}C_5H_5)_2Mo_2(NO)_4H]PF_6$ was added 8 equiv of $(CH_3)_2CO$. The solution remained green, and the ^1H NMR signals due to the bimetallic cation (δ 6.37, −9.78) were unaltered.

(b) With Nitrogen-Containing Bases. Upon the addition of the bases $(C_2H_5)_3N$ or $C_{10}H_6[N(CH_3)_2]_2$, CD_3NO_2 solutions of the cation immediately became brown. In each case, ^1H NMR spectroscopy revealed the absence of the signals due to $[(\eta^5\text{-}C_5H_5)_2Mo_2(NO)_4H]PF_6$ and the presence of several new resonances in the cyclopentadienyl region. Repetition of the experiments in $(CD_3)_2CO$ afforded solutions which again displayed multiple resonances in the region δ 6.2 → 6.7 ppm of their ^1H NMR spectra.

(c) With a Magnesium Silicate. A suspension of $[(\eta^5\text{-}C_5H_5)_2Mo_2(NO)_4H]PF_6$ (0.10 g) in CH_2Cl_2 (10 mL) was transferred to the top of a Florisil column (2 × 4 cm). Elution of the column with CH_2Cl_2 developed a single green band which was collected. Concentration of the eluate under reduced pressure to a volume of ~3 mL gave a solution of $(\eta^5\text{-}C_5H_5)Mo(NO)_2H$ as indicated by its infrared spectrum (i.e., ν_{NO} = 1738, 1647; $\nu_{Mo\text{–}H}$ = 1805 (w) cm^{-1}). Removal of the remaining solvent in vacuo produced a brown residue. Extraction of the residue with $(CD_3)_2CO$ resulted in a green solution whose ^1H NMR spectrum consisted of resonances at δ 6.43 (s, 5 H) and 3.80 (s, 1 H) which were assignable to $(\eta^5\text{-}C_5H_5)Mo(NO)_2H$.

Reaction of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ with $p\text{-}CH_3C_6H_4SO_3H$. To a dark purple CH_2Cl_2 solution (40 mL) containing 0.54 g (1.53 mmol) of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$[5] was added 1 equiv (0.265 g) of anhydrous $p\text{-}CH_3C_6H_4SO_3H$ with vigorous stirring. Infrared spectral monitoring of the reaction mixture revealed the gradual decrease in intensity of the nitrosyl absorptions due to $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ (i.e., at 1667 and 1505 cm^{-1}) and the gradual increase in intensity of two new absorptions at 1829 and 1722 cm^{-1} over a period of ~10 min. However, only half of the chromium dimer was consumed by the p-toluenesulfonic acid, so an additional 1 equiv of the latter was added. This led to a change in color of the solution from purple to dark orange in ~15 min, the final solution having an infrared spectrum from which the characteristic ν_{NO}'s of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ were absent. The

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addition of an equal volume of hexanes and concentration of the mixture under reduced pressure induced the precipitation of a green powder which was collected by filtration. Recrystallization of this solid from CH_2Cl_2–$(C_2H_5)_2O$ afforded $(\eta^5\text{-}C_5H_5)Cr(NO)_2OSO_2C_6H_4CH_3$ (0.48 g, 45% yield) as a fine green powder, mp 64–66 °C.

Anal. Calcd for $C_{12}H_{12}CrN_2O_5S$: C, 41.38; H, 3.47; N, 8.04. Found: C, 40.84; H, 3.68; N, 7.36. IR (CH_2Cl_2): ν_{NO} 1829, 1722 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.72 (d, 2 H, J = 8.0 Hz), 7.21 (d, 2 H, J = 8.0 Hz), 5.75 (s, 5 H), 2.36 (s, 3 H).

Reaction of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ with $Cr(CO)_5(C_4H_8O)$. A solution of $Cr(CO)_5(C_4H_8O)$[22] was generated by irradiating a tetrahydrofuran solution (210 mL) of $Cr(CO)_6$ (0.65 g, 2.9 mmol) for 1 h in a photoreactor [using a medium-pressure mercury lamp (Hanovia L-450W) housed in a water-cooled Pyrex immersion well] while gently purging the solution with N_2 to remove the liberated CO. The orange solution so obtained was then concentrated to a volume of ~25 mL under reduced pressure and cooled to −78 °C. To this stirred solution was added a quantity (0.58 g, 1.87 mmol) of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ which dissolved rapidly to produce an orange-brown solution. After being stirred for 25 min, the solution displayed an infrared spectrum which had four bands in the nitrosyl region (ν_{NO} = 1736, 1718, 1661, and 1629 cm^{-1}) as well as a poorly resolved envelope of bands in the carbonyl region (ν_{CO} = 2085 (w), 1995 (sh), 1975, and 1920 (br) cm^{-1}). The solution was allowed to warm to room temperature after 1 h, its infrared spectrum remaining invariant. Solvent removal in vacuo afforded an orange-brown solid which was only partially soluble in CH_2Cl_2 or tetrahydrofuran, but both orange solutions displayed comparable infrared spectra containing absorptions assignable to carbonyl ($\nu_{CO}(C_4H_8O)$ = 2085 (w), 2003, 1972, and 1928 cm^{-1}) and nitrosyl ($\nu_{NO}(C_4H_8O)$ = 1738 (w), 1718 (w), 1661, and 1634 (w, sh) cm^{-1}) ligands. Fractional sublimation of the solid at 0.005 mm yielded first $Cr(CO)_6$[22] (0.20 g, 31% yield) at 35 °C and then $(\eta^5\text{-}C_5H_5)W(CO)_2(NO)$[23] (0.12 g, 17% yield based on W) at ~55 °C. Each isolated compound was identified by its characteristic infrared and mass spectra. A Nujol mull infrared spectrum of the intractable brown residue which remained after sublimation exhibited broad absorptions at 1920 and 1660 cm^{-1}.

The reaction was also carried out in $(CD_3)_2CO$ with ^1H NMR monitoring of its progress. Upon addition of less than 1 equiv of "$Cr(CO)_5(C_4H_8O)$" (prepared as above, but with virtually all of the excess tetrahydrofuran removed) at −80 °C, the resonance attributable to the cyclopentadienyl protons shifted to lower field (i.e., δ 6.38), but the hydride resonance could not be detected. When being warmed to 0 °C, the reaction mixture displayed a ^1H NMR spectrum which consisted of signals attributable to $(\eta^5\text{-}C_5H_5)W(NO)_2H$ [δ 6.24 (s, 5 H), 2.19 (s, 1 H)] and $(\eta^5\text{-}C_5H_5)W(CO)_2(NO)$ (δ 6.49) in a ratio of 5:1. The introduction of additional "$Cr(CO)_5(C_4H_8O)$" at this temperature simply resulted in a decrease in intensity of the signals due to the hydride and an increase in intensity of the signal due to the dicarbonyl nitrosyl complex after the ~2 min required to mix the reactants and obtain the spectrum.

The analogous reaction of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ with $Cr(CO)_5[N(CH_3)_3]$[24] in CH_2Cl_2 gave comparable results.

Reactions of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ with $W(CO)_5(C_4H_8O)$,[22] $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(C_4H_8O)$,[22] and $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(H)[Si(C_6H_5)_3]$.[25] These reactions were performed in a manner identical with that described in the preceding section for $Cr(CO)_5(C_4H_8O)$. Infrared spectral monitoring indicated an interaction between the reactants in each case, but tractable products could not be isolated from the final reaction mixtures at room temperature.

Reaction of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ with $HgCl_2$. To a stirred mixture of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ (0.27 g, 0.87 mmol) and $HgCl_2$ (0.23 g, 0.87 mmol) was added tetrahydrofuran (30 mL). Both solids dissolved rapidly to produce a clear, lime green solution. However, within 1 min the solution became cloudy, and then a white precipitate began to form. The suspension was filtered after 1.5 h to obtain a gray solid and an olive green filtrate. The filtrate was taken to dryness under reduced pressure, and the resulting residue was crystallized from CH_2Cl_2–hexanes to obtain 0.20 g (0.58 mmol, 67% yield) of $(\eta^5\text{-}C_5H_5)W(NO)_2Cl$ which was identified by elemental analysis and its characteristic infrared, ^1H NMR, and mass spectra.[26] The gray solid was identified qualitatively as HgCl (0.11 g, 53% yield) by treating it with NH_4OH to obtain a very dark gray residue (Hg + $Hg(NH_2)Cl$).[27]

The reaction was also performed at −80 °C in $(CD_3)_2CO$ with ^1H NMR monitoring. At this temperature, a sharp peak was observed at δ 6.53 (s, 5 H) [cf. δ 6.23 for $(\eta^5\text{-}C_5H_5)W(NO)_2H$ and δ 6.40 for $(\eta^5\text{-}C_5H_5)W(NO)_2Cl$] along with a broader peak at δ 4.35 (s, 1 H), both attributable to the adduct, $(\eta^5\text{-}C_5H_5)W(NO)_2H\cdot HgCl_2$. When the mixture was warmed to 0 °C, a reaction occurred, and the resonance due to the cyclopentadienyl protons broadened and shifted to δ 6.40.

The reaction of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ with $ZnCl_2$ gave comparable results, but the conversion to $(\eta^5\text{-}C_5H_5)W(NO)_2Cl$ was only 15% complete after 11 h of stirring at ambient temperature.

Reaction of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ with $HBF_4\cdot O(CH_3)_2$. A stirred, green solution of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ (0.30 g, 0.97 mmol) in CH_2Cl_2 (25 mL) was treated dropwise with an emulsion containing 0.5 mL (5.6 mmol) of $HBF_4\cdot O(CH_3)_2$ in CH_2Cl_2 (5 mL), and the progress of the reaction was monitored by infrared spectroscopy. As the addition proceeded, the solution became dark green, and the nitrosyl absorptions due to the hydride reactant diminished in intensity; simultaneously, new bands at higher energy (ν_{NO} = 1778, 1749, 1696, and 1665 cm^{-1}) due to $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]BF_4$ appeared and intensified. Complete consumption of the $(\eta^5\text{-}C_5H_5)W(NO)_2H$ required 0.5 equiv of $HBF_4\cdot O(CH_3)_2$; the addition of excess acid resulted in the destruction of the bimetallic cation.

The reaction was also carried out at −20 °C in CD_3NO_2. This experiment verified the clean conversion of the hydride to the ditungsten cation (δ 6.47 (s, 10 H), −8.33 (s, 1 H)) by 0.5 equiv of the acid. In contrast, addition of H_2SO_4 to a CD_3NO_2 solution of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ produced a green solution whose ^1H NMR spectrum displayed a single new resonance at δ 6.35 attributable to $[(\eta^5\text{-}C_5H_5)W(NO)_2]_2SO_4$.

Reaction of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ with $AlCl_3$. To a $CDCl_3$ solution of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ was added ~1.2 equiv of $AlCl_3$ dissolved in $CDCl_3$. After being mixed well, the resulting green solution was monitored by ^1H NMR spectroscopy. Over a period of ~30 min, the gradual disappearance of the signals at δ 5.99 (s, 5 H) and 2.07 (s, 1 H) (attributable to $(\eta^5\text{-}C_5H_5)W(NO)_2H$) was observed along with the concomitant growth of a new resonance at δ 6.14 (due to $(\eta^5\text{-}C_5H_5)W(NO)_2Cl$). The peak positions for each of the compounds were indistinguishable from those displayed by authentic samples of the complexes in the absence of $AlCl_3$.

In a separate experiment, infrared monitoring of a 1:1 mixture of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ and $AlCl_3$ in CH_2Cl_2 revealed only a gradual shift of the nitrosyl absorbances to higher energy as the hydride (ν_{NO} = 1718, 1632 cm^{-1}) was converted into $(\eta^5\text{-}C_5H_5)W(NO)_2Cl$ (ν_{NO} = 1733, 1650 cm^{-1}).

Results and Discussion

Preparation and Characterization of $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]^+X^-$ (X = BF_4 or PF_6). We have established that in donor solvents such as acetonitrile, $(\eta^5\text{-}C_5H_5)W(NO)_2H$ reacts with an equimolar amount of the hydride abstractor $(C_6H_5)_3C^+$ via loss of H^-, i.e.

$$(\eta^5\text{-}C_5H_5)W(NO)_2H + (C_6H_5)_3C^+X^- \xrightarrow{CH_3CN} [(\eta^5\text{-}C_5H_5)W(NO)_2(CH_3CN)]^+X^- + (C_6H_5)_3CH \quad (7)$$

X = BF_4[7] or PF_6

We have now found that in CH_2Cl_2 with 2:1 stoichiometry, hydride abstraction results in the formation of the spar-

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ingly soluble, dark green solids $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]^+X^-$ (X = BF_4 or PF_6), i.e.

$$2(\eta^5\text{-}C_5H_5)W(NO)_2H + (C_6H_5)_3C^+X^- \xrightarrow{CH_2Cl_2} [(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]^+X^- + (C_6H_5)_3CH \quad (8)$$

$$X = BF_4 \text{ or } PF_6$$

$$2(\eta^5\text{-}C_5H_5)W(NO)_2H + C_7H_7{}^+BF_4{}^- \xrightarrow{CH_2Cl_2} [(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]^+BF_4{}^- + (C_7H_8) \quad (9)$$

transformations which are identical with that depicted for the isoelectronic rhenium complexes in eq 5. The new organometallic products of these conversions precipitate from solution as microcrystalline, analytically pure solids which can be isolated in good to excellent yields.

$[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]BF_4$ is a dark green, diamagnetic solid (mp 95 °C dec) which can be handled in air for short periods of time without the occurrence of noticeable decomposition, and it remains unaltered when stored under N_2 at ambient temperature for periods of at least several months. The compound is insoluble in paraffin or aromatic hydrocarbons and is only sparingly soluble in CH_2Cl_2. It has good solubility in nitromethane and, presumably, other strongly solvating but weakly donating solvents;[28] however, the originally green CH_3NO_2 solutions slowly become brown as the complex decomposes ($\tau_{1/2} \approx$ 3 h) in an as yet undetermined manner. Treatment of the compound with a donor solvent such as $(CH_3)_2CO$ or CH_3CN results in the rapid dissociation of the bimetallic cation into monomeric products, i.e.

$$[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]^+BF_4{}^- + L \rightarrow (\eta^5\text{-}C_5H_5)W(NO)_2H + [(\eta^5\text{-}C_5H_5)W(NO)_2L]^+BF_4{}^- \quad (10)$$

$$L = \text{a 2-e}^- \text{ donor ligand}$$

a feature that is readily discernible by infrared and ^1H NMR spectroscopy. Thus, the infrared spectrum of an acetonitrile solution of $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]^+BF_4{}^-$ displays nitrosyl absorptions at frequencies identical with those of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ (ν_{NO} = 1715, 1631 cm^{-1}) and $[(\eta^5\text{-}C_5H_5)W(NO)_2(CH_3CN)]^+BF_4{}^-$ (ν_{NO} = 1766, 1689 cm^{-1}) as a 1:1 mixture in the same solvent. Furthermore, the addition of donor solvents to CD_3NO_2 solutions of the bimetallic complex results in the disappearance of the ^1H NMR signals due to $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]^+BF_4{}^-$ (δ 6.48 (s, 10 H), −8.33 (s, 1 H)) and the appearance of new resonances (at δ 6.15 (s, 5 H), 1.94 (s, 1 H)) characteristic of $(\eta^5\text{-}C_5H_5)W(NO)_2H$. Signals due to the added solvent also appear along with several new resonances at low field (δ >6.15), presumably due to $[(\eta^5\text{-}C_5H_5)W(NO)_2L]^+$.

As indicated in passing in the previous paragraph, the typical ^1H NMR spectrum of $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]^+BF_4{}^-$ at ambient temperature in CD_3NO_2 (Figure 1) consists of a sharp singlet at δ 6.48 attributable to the ten equivalent cyclopentadienyl protons and a high-field singlet due to one hydrogen at δ −8.33, the latter being in the region typical of metal-bound protons.[29] Unfortunately, the large shift of the hydride resonance to higher field ($\Delta\delta$ = 10.27 ppm) upon conversion of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ ($\delta_{W\text{-}H}(CD_3NO_2)$ 1.94) to $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]^+$ ($\delta_{W\text{-}H}(CD_3NO_2)$ −8.33) is not definitive as to whether the H ligand is bonded in a bridging or a terminal fashion in the bimetallic species.[30] A spectrum of the cationic complex having a very large signal-to-noise ratio (~1000:1 for the hydride signal) exhibits six satellite peaks associated with the principal hydride resonance (Figure 1c). At first glance, this seven-peak pattern, having experimental peak intensities of 0.5:11.4:0.5:74.5:0.5:11.8:0.5, appears to be completely consistent with previously reported analyses of the

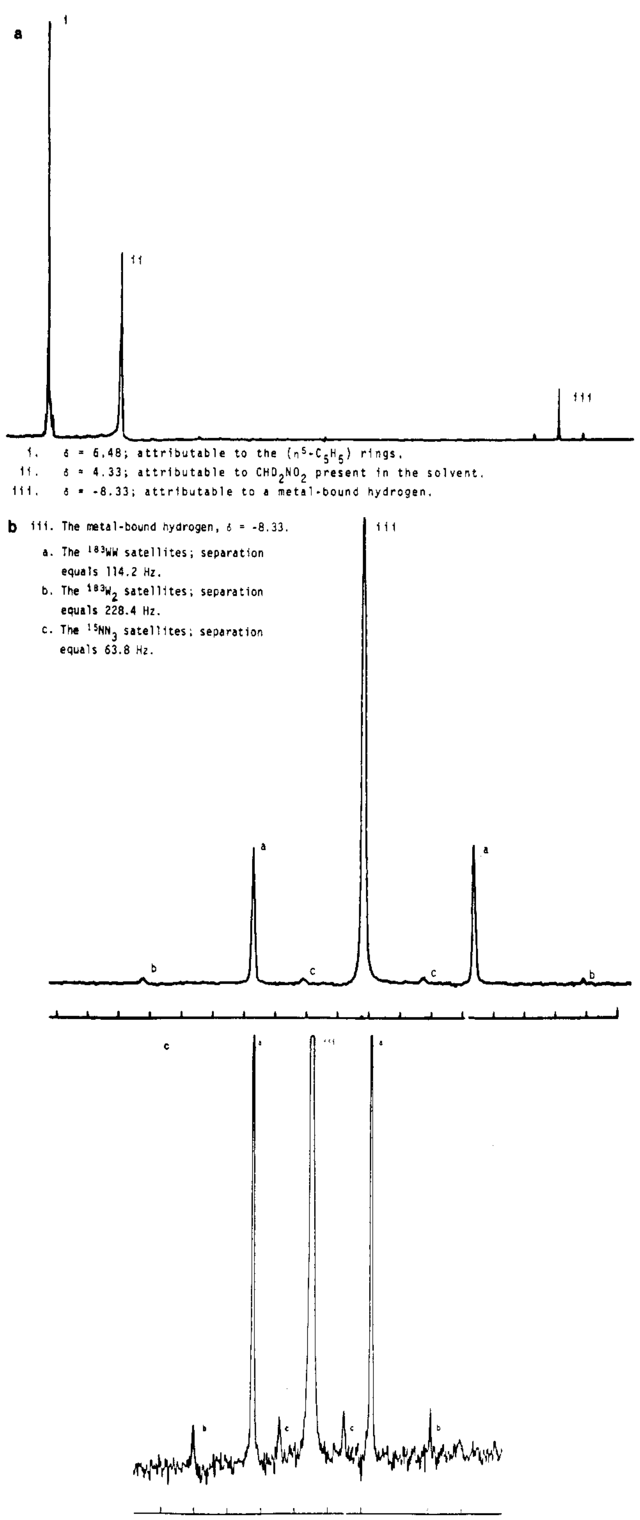

Figure 1. The ^1H NMR spectrum of $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]^+BF_4{}^-$ in CD_3NO_2: (a) the complete spectrum; (b) the hydride region (amplitude ×8) showing the ^{183}WW satellites; (c) the hydride region (amplitude ×128) showing the $^{183}W_2$ and $^{15}NN_3$ satellites.

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(30) In some cases, the ^1H NMR resonance of a bridging hydrogen in hydridometal clusters occurs at higher field than that due to a terminally bound H atom; no such correlation exists for hydridotungsten complexes.[29]

Table I. Characteristic Infrared Absorptions of $(\eta^5\text{-}C_5H_5)M(NO)_2H$ (M = Mo or W) Derivatives[a]

complex	medium	ν_{NO}, cm^{-1}	$\nu_{M\text{-}H}$, cm^{-1}
$(\eta^5\text{-}C_5H_5)Mo(NO)_2H$	toluene	1732, 1642[7]	
	CH_2Cl_2	1738, 1647	1805 (w)
$(\eta^5\text{-}C_5H_5)W(NO)_2H$	CH_2Cl_2	1718, 1632[7]	1900 (w)
	CH_3CN	1715, 1631	
$(\eta^5\text{-}C_5H_5)Mo(NO)_2Cl$	CH_2Cl_2	1759, 1665[26]	
$(\eta^5\text{-}C_5H_5)W(NO)_2Cl$	CH_2Cl_2	1733, 1650[26]	
$[(\eta^5\text{-}C_5H_5)W(NO)_2(CH_3CN)]BF_4$	CH_3CN	1766, 1689	
$[(\eta^5\text{-}C_5H_5)W(NO)_2(CH_3CN)]PF_6$	CH_3CN	1766, 1689	
	CH_2Cl_2	1770, 1690	
$[(\eta^5\text{-}C_5H_5)_2Mo_2(NO)_4H]PF_6$	Nujol mull	1783 (br), 1675 (br)	
	CH_2Cl_2	1795, 1768, 1707, 1695 (sh)	
$[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]BF_4$	Nujol mull	1775, 1748, 1707, 1660 (br)	
	CH_2Cl_2	1778, 1749, 1696, 1665 (sh)	
	CH_3NO_2	1770, 1719, 1689	
$[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]PF_6$	Nujol mull	1752 (br), 1685 (br)	
	CH_3NO_2	1770, 1718, 1691	
	CH_3CN	1769, 1719, 1690, 1633	
$[(\eta^5\text{-}C_5H_5)_2MoW(NO)_4H]BF_4$	Nujol mull	1790, 1769 (sh), 1756, 1718, 1660 (br)	
	CH_2Cl_2	1790, 1765 (sh), 1751, 1706, 1678, 1650 (sh)	

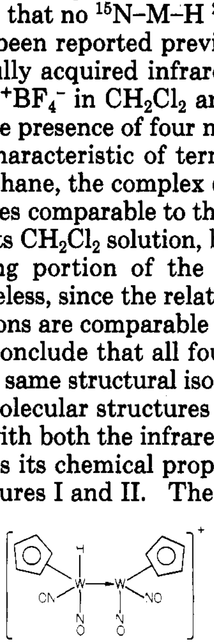
[a] The solution spectra of the cationic complexes were obtained by employing KRS-5 windows since the complexes react rapidly with NaCl.

peak patterns expected for a W_2H spin system.[31] Specifically, it seems to be in excellent agreement with the model in which the hydrogen atom is terminally bound (spin coupling to the remote tungsten being observable) and is undergoing rapid intramolecular site exchange on the NMR time scale between the two metal centers, the predicted peak intensities being 0.51:12.24:0.51:73.48:0-.51:12.24:0.51. However, the theoretical spectrum reported for this particular model is incorrect.[32]

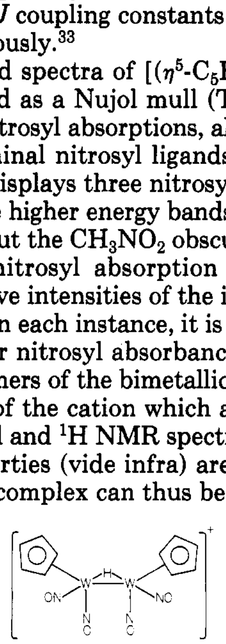
For the case in which ^2J is resolved and rapid intramolecular exchange of the proton between the two tungsten nuclei occurs, the calculated ^1H NMR spectrum consists of a superposition of the following components: (1) a singlet due to W_2H of relative intensity 73.48%; (2) a doublet of separation $(^1J + {}^2J)/2$ due to ^{183}WWH of relative intensity 24.48%; (3) a 1:2:1 triplet (not a doublet of doublets as originally predicted)[31a] due to $^{183}W_2H$ of relative intensity 2.04%, the outermost peaks having a separation of $^1J + {}^2J$. Peaks of separation $^1J - {}^2J$ are not expected to be observable (i.e., with rapid site exchange, the difference between the two sites vanishes and the observed coupling becomes $(^1J + {}^2J)/2$), and so the central component of the triplet will be coincident with the singlet from 1.[32] Hence, an equally spaced, five-peak pattern having peak intensities of 0.51:12.24:74.5:12.24:0.51 is predicted. Of course, an identical pattern is expected for the case in which no intramolecular exchange occurs, the proton being associated with both tungsten atoms symmetrically.[31] The actual spectrum of $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]^+BF_4^-$ in CD_3NO_2 (Figure 1) is invariant when acquired at a variety of sample spinning speeds and exhibits just these intensity features and peak separations (i.e., peaks labeled a, b, and iii). We attribute the two additional resonances (designated by c in Figure 1) to ^{15}N spin–spin coupling in complexes having $^{15}NW_2H$ groupings. With four equivalent nitrosyl ligands each having 0.37% of the ^{15}N isotopomer present, the calculated intensity of each of these signals is 0.54%, as is indeed observed. Further support for this latter assignment comes from the fact that in a separate experiment we were able to observe at the expected positions the outer resonances arising from the combined ^{183}W–H and ^{15}N–H spin–spin couplings in $^{15}N^{183}WWH$ groups of predicted intensity 0.091%. However, we could not locate the peaks arising from the difference of these couplings due to their proximity to the central hydride resonance and the limited stability of the complex in CD_3NO_2.

This analysis of the ^1H NMR data leads to the conclusion that it is not possible on this basis to ascertain definitively the mode of attachment of the H atom in the bimetallic cation. The fact that the data are consistent with both a terminally bound hydrogen rapidly exchanging between the metal centers and one which symmetrically bridges these centers also means that the observed coupling constants (i.e., $J_{^{183}W-^1H}$ = 114.2 Hz and $J_{^{15}N-^1H}$ = 63.8 Hz) cannot be assigned unambiguously. It can be noted, however, that no ^{15}N–M–H ^2J coupling constants appear to have been reported previously.[33]

Carefully acquired infrared spectra of $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]^+BF_4^-$ in CH_2Cl_2 and as a Nujol mull (Table I) reveal the presence of four nitrosyl absorptions, all in the region characteristic of terminal nitrosyl ligands.[34] In nitromethane, the complex displays three nitrosyl bands at energies comparable to the higher energy bands exhibited by its CH_2Cl_2 solution, but the CH_3NO_2 obscures the remaining portion of the nitrosyl absorption region. Nevertheless, since the relative intensities of the infrared absorptions are comparable in each instance, it is reasonable to conclude that all four nitrosyl absorbances arise from the same structural isomers of the bimetallic cation. Static molecular structures of the cation which are consistent with both the infrared and ^1H NMR spectral data as well as its chemical properties (vide infra) are shown in structures I and II. The complex can thus be viewed



I



II

as a Lewis acid–base adduct. In the first structure, the 18-e$^-$ unit, $(\eta^5\text{-}C_5H_5)W(NO)_2H$, provides a pair of electrons from a filled metal-centered orbital to a vacant metal orbital of the 16-e$^-$ unit, $(\eta^5\text{-}C_5H_5)W(NO)_2^+$, both tungsten

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[31] (a) Davison, A.; McFarlane, W.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 3653. (b) Hayter, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 4376.

[32] Bloom, M.; Burnell, E. E., personal communication.

[33] Levy, G. C.; Lichter, R. L. "Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy"; Wiley: Toronto, 1979.

[34] Connelly, N. G. *Inorg. Chim. Acta Rev.* **1972**, *6*, 47.

atoms thus attaining the favored 18-electron configuration. The alternate structure for the cation involves a 3-center 2-electron W_2H linkage between the acid and base entities.

The related complex $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]^+PF_6^-$ is a green solid (mp 122 °C dec) which has stability and solubility properties similar to those of the BF_4^- salt. Its CD_3NO_2 solution displays a ^1H NMR spectrum which is indistinguishable from that of the BF_4^- analogue, thereby ruling out any significant cation–anion interactions in solution. Furthermore, its Nujol mull infrared spectrum exhibits nitrosyl stretching frequencies comparable to those of $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]^+BF_4^-$ (Table I). The deuterio analogue $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4D]^+PF_6^-$, can be readily prepared from $(\eta^5\text{-}C_5H_5)W(NO)_2D$ via reaction 8. Unfortunately, comparison of its concentrated mull infrared spectra with those of $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]^+X^-$ (X = BF_4 or PF_6) gives no indication of any absorptions attributable to a tungsten–hydrogen linkage. ^1H NMR spectra of the deuterated cation in CD_3NO_2 show a decrease in intensity of the high-field resonance to <5% of its original value, thus confirming the successful incorporation of deuterium in the desired position.

Preparation and Characterization of $[(\eta^5\text{-}C_5H_5)_2Mo_2(NO)_4H]^+PF_6^-$. Pale green $[(\eta^5\text{-}C_5H_5)_2Mo_2(NO)_4H]^+PF_6^-$ (mp 119 °C dec) can be readily synthesized in a manner analogous to that employed for its tungsten congener (cf. eq. 8), namely, by treating CH_2Cl_2–toluene solutions of $(\eta^5\text{-}C_5H_5)Mo(NO)_2H$[7] with $(C_6H_5)_3C^+PF_6^-$, i.e.

$$2(\eta^5\text{-}C_5H_5)Mo(NO)_2H + (C_6H_5)_3C^+PF_6^- \xrightarrow[\text{toluene}]{CH_2Cl_2} [(\eta^5\text{-}C_5H_5)_2Mo_2(NO)_4H]^+PF_6^- + (C_6H_5)_3CH \quad (11)$$

Again, the organometallic product precipitates in an analytically pure state and can be isolated in reasonable yields. Its physical properties resemble those displayed by its tungsten analogue (vide supra). In addition, the infrared spectra of the two bimetallic cations are comparable (Table I), thereby suggesting that they are probably isostructural. This inference is supported by the ^1H NMR spectrum of $[(\eta^5\text{-}C_5H_5)_2Mo_2(NO)_4H]^+PF_6^-$ in CD_3NO_2 which consists of two sharp singlets (δ 6.37 (10 H), –9.78 (1 H)). No Mo–H spin–spin coupling is observable because of rapid quadrupolar relaxation of those molybdenum isotopes which have nuclear spin magnetic moments (i.e., ^{95}Mo and ^{97}Mo, both having $I = {}^5/_2$).

Preparation and Characterization of $[(\eta^5\text{-}C_5H_5)_2MoW(NO)_4H]^+BF_4^-$. Since both $(\eta^5\text{-}C_5H_5)Mo(NO)_2H$ and $(\eta^5\text{-}C_5H_5)W(NO)_2H$ react immediately with the trityl cation, it seemed unlikely that either hydride would react preferentially with $(C_6H_5)_3C^+$ if the cation were added to a 1:1 mixture of the two compounds with the hope of forming $[(\eta^5\text{-}C_5H_5)_2MoW(NO)_4H]^+$ (cf. eq 8 and 11). A more rational synthetic route to the mixed-metal bimetallic cation appeared to be the one involving the conversions

$$[(\eta^5\text{-}C_5H_5)M(NO)_2(\eta^2\text{-}C_8H_{14})]^+BF_4^- + (\eta^5\text{-}C_5H_5)M'(NO)_2H \xrightarrow{CH_2Cl_2} [(\eta^5\text{-}C_5H_5)_2MM'(NO)_4H]^+BF_4^- + C_8H_{14} \quad (12)$$

M = Mo, M′ = W or vice versa; C_8H_{14} = cyclooctene

which exploit the known lability of the cyclooctene ligand in the $[(\eta^5\text{-}C_5H_5)M(NO)_2(\eta^2\text{-}C_8H_{14})]^+$ (M = Mo or W) cations.[35] Because $(\eta^5\text{-}C_5H_5)Mo(NO)_2H$ is thermally unstable,[7] we attempted reaction 12 stoichiometrically with $(\eta^5\text{-}C_5H_5)W(NO)_2H$ as the hydride source and were gratified by its successful progress to afford the desired product in 57% isolated yield.

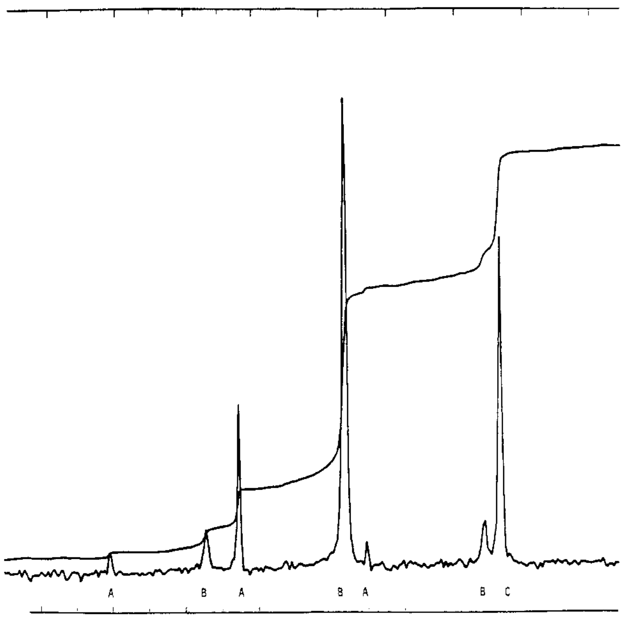
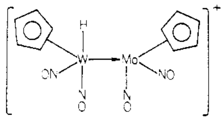


Figure 2. The hydride region of the ^1H NMR spectrum of a $[(\eta^5\text{-}C_5H_5)_2M_2(NO)_4H]^+PF_6^-$ (Mo:W ratio = 1.5:1) mixture in CD_3NO_2: (A) peaks attributable to $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]^+$ (δ –8.33 ($J_{^{183}W-^1H}$ = 114.2 Hz)); (B) peaks attributable to $[(\eta^5\text{-}C_5H_5)_2MoW(NO)_4H]^+$ (δ –8.92 ($J_{^{183}W-^1H}$ = 123.6 Hz)); (C) peak attributable to $[(\eta^5\text{-}C_5H_5)_2Mo_2(NO)_4H]^+$ (δ –9.78).

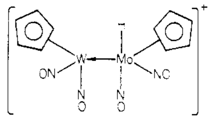
Dark green $[(\eta^5\text{-}C_5H_5)_2MoW(NO)_4H]^+BF_4^-$ (mp 115 °C dec) exhibits stability and solubility properties similar to those of its homometallic analogues (vide supra). Its mull and solution infrared spectra display numerous poorly resolved nitrosyl stretching absorptions (Table I), a feature which is consistent with the total of eight such absorptions expected for the two isomers of the heteronuclear cation containing a terminal H ligand, i.e., III and IV. Nevertheless, the spectral data do not rule out definitively isomeric structures of type V. A ^1H NMR spectrum of $[(\eta^5\text{-}C_5H_5)_2MoW(NO)_4H]^+BF_4^-$ in CD_3NO_2, however, reveals the presence of both of the homonuclear cations (δ_{W_2} 6.47, –8.33; δ_{Mo_2} 6.37, –9.78) in addition to the heteronuclear cation (δ_{MoW} 6.47, 6.37, –8.92), thus indicating the existence of the equilibrium shown in eq 13. As expected, the same

$$[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]^+ + [(\eta^5\text{-}C_5H_5)_2Mo_2(NO)_4H]^+ \rightleftharpoons 2[(\eta^5\text{-}C_5H_5)_2MoW(NO)_4H]^+ \quad (13)$$

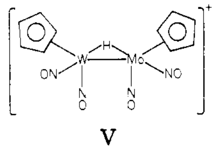
equilibrium is attained when a mixture of the homometallic cations is dissolved in CD_3NO_2 (Figure 2), the value of the equilibrium constant being ~10 at ambient temperature.



III



IV



V

Other features of interest to emerge from the ^1H NMR spectrum of the mixture of bimetallic cations are as follows.

(1) The fact that only two peaks are observable in the region characteristic of cyclopentadienyl protons indicates

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(35) Legzdins, P.; Martin, D. T., unpublished observations.

that a change in identity of the remote metal does not significantly alter the environment of the cyclopentadienyl ring attached to the near metal center. The two peaks do exhibit the expected relative intensities.

(2) The occurrence of the hydride resonance due to the heterometallic cation at a chemical shift position intermediate to those of the ditungsten and dimolybdenum species is not surprising. The fact that only one such resonance is observed again leaves unresolved the mode of attachment of the hydrogen ligand (vide supra), although the number of ν_{NO}'s in the mull infrared spectrum is most consistent with the static structure involving a terminally bound hydride.

(3) The magnitude of the observed spin–spin coupling with the ^{183}W nuclei indicates that the heteronuclear cation ($J_{^{183}W-^1H}$ = 123.6 Hz) has a molecular structure analogous to that of the ditungsten species ($J_{^{183}W-^1H}$ = 114.2 Hz), but again these coupling constants cannot be assigned unambiguously.

It is clear, though, that these bimetallic nitrosyl cations display markedly different behavior than the related carbonyl cations $[(\eta^5\text{-}C_5H_5)_2MM'(CO)_6H]^+$ (M, M′ = Mo or W) which do not equilibrate in solution.[31a] The rapid equilibration of the nitrosyl cations (possibly via initial dissociation of the various Lewis acid–base adducts) means, of course, that our originally envisaged synthetic route to the mixed-metal cation, i.e.

$$(\eta^5\text{-}C_5H_5)Mo(NO)_2H + (\eta^5\text{-}C_5H_5)W(NO)_2H + (C_6H_5)_3C^+BF_4^- \xrightarrow{CH_2Cl_2} [(\eta^5\text{-}C_5H_5)_2MoW(NO)_4H]^+BF_4^- + (C_6H_5)_3CH \quad (14)$$

would have been successful.

Attempted Deprotonation of $[(\eta^5\text{-}C_5H_5)_2M_2(NO)_4H]^+$ (M = Mo or W) The preparation of the bimetallic cations having been achieved, the final step in the anticipated synthesis of the long-sought $[(\eta^5\text{-}C_5H_5)M(NO)_2]_2$ (M = Mo or W) dimers involves the deprotonation of the cations, i.e.

$$[(\eta^5\text{-}C_5H_5)_2M_2(NO)_4H]^+ + B \rightarrow [(\eta^5\text{-}C_5H_5)M(NO)_2]_2 + BH^+ \quad (15)$$

B = a Lowry–Brønsted base

in a manner previously demonstrated for $[(\eta^5\text{-}C_5H_5)_2Re_2(CO)_2(NO)_2H]^+$,[12] $[(\eta^5\text{-}C_5H_5)_2MM'(CO)_6H]^+$ (M, M′ = Mo or W),[36] and $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4H]^+$.[31a] However, unlike the carbonyl species, the nitrosyl cations do not undergo reaction 15 when treated with a variety of bases, but rather cleave to afford monomeric products, e.g.

$$[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]^+ + B \xrightarrow[\text{or } CH_3NO_2]{CH_2Cl_2} (\eta^5\text{-}C_5H_5)W(NO)_2H + [(\eta^5\text{-}C_5H_5)W(NO)_2B]^+ \quad (10)$$

where B equals a Lewis base such as $(C_2H_5)_3N$, $(C_6H_5)_3P{=}CH_2$, $[(CH_3)_2N]_3PO$, OH^-, and H^-. Evidently, the strength of the metal–metal linkage combined with the Lowry–Brønsted acidity of the bimetallic reactant is insufficient to permit deprotonation in the desired manner. The formation of the products in reactions 10 can be inferred on the basis of spectral monitoring of their progress. In most cases, the ubiquitous $(\eta^5\text{-}C_5H_5)W(NO)_2H$ can be isolated, but no attempt was made to isolate the $[(\eta^5\text{-}C_5H_5)W(NO)_2B]^+$ cations since they have defied such attempts previously.[17] Treatment of $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]^+$ with $(\eta^5\text{-}C_5H_5)_2MoH_2$[20] or sodium naphthalene[21] simply results in the deposition of a red-brown nitrosyl-free solid as the major product.

The dimolybdenum cation is somewhat more resistant to cleavage by bases than is its tungsten congener, remaining unchanged when treated with acetone in CD_3NO_2. However, bases such as $(C_2H_5)_3N$ and $C_{10}H_6[N(CH_3)_2]_2$ appear to effect conversions analogous to reaction 10. This proclivity of $[(\eta^5\text{-}C_5H_5)_2Mo_2(NO)_4H]^+$ to cleave can be exploited by using a CH_2Cl_2 column of Florisil as the base, a procedure which leads to direct chromatographic separation of a sample of $(\eta^5\text{-}C_5H_5)Mo(NO)_2H$. The monomeric hydride can then be characterized spectroscopically (i.e., IR (CH_2Cl_2) ν_{Mo-H} 1805 cm^{-1}, ν_{NO} 1738, 1647 cm^{-1}; ^1H NMR ($(CD_3)_2CO$) δ 6.43 (s, 5 H), 3.80 (s, 1 H)) more fully than was possible previously[7] when only the ν_{NO} values for the complex in toluene were accessible. As in the case of $(\eta^5\text{-}C_5H_5)W(NO)_2H$,[7] the ^1H NMR signal of the hydride in the molybdenum analogue occurs at low field.

Protonation of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$. Since the bimetallic molybdenum and tungsten cations could not be deprotonated to obtain the corresponding neutral dimers, the following two questions naturally come to mind. (1) Can the analogous $[(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_4H]^+$ cation be prepared by protonation of the well-known dimer, $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$? (2) Is the protonation of the neutral chromium dimer a reversible process? Our initial experiments in this regard indicate that both questions can be answered in the negative. Treatment of CH_2Cl_2 solutions of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ with aqueous solutions of HPF_6 or $HBF_4{\cdot}O(CH_3)_2$ followed by anion metathesis with $Na^+[B(C_6H_5)_4]^-$ affords a green, microcrystalline solid (mp 119–120 °C). While the exact nature of this complex remains to be ascertained, it is readily apparent that it is *not* $[(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_4H]^+[B(C_6H_5)_4]^-$. An infrared spectrum of the compound in CH_2Cl_2 displays strong nitrosyl absorptions at 1828 and 1721 cm^{-1}. A ^1H NMR spectrum of the complex in $(CD_3)_2CO$ indicates the presence of (a) two inequivalent cyclopentadienyl rings (δ 6.06 (s, 5 H) and 5.68 (s, 5 H)), (b) a metal-bound hydrogen (δ −5.35 (s, 1 H)), and (c) two tetraphenylborate anions (δ 6.8→7.6 (m, 40 H)) per pair of cyclopentadienyl ligands. Once formed, the complex cannot be readily deprotonated, its CH_2Cl_2 solutions being unaffected by $(C_2H_5)_3N$ and $(C_6H_5)_3P{=}CH_2$.

When $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ is reacted with 2 equiv of the coordinating acid $p\text{-}CH_3C_6H_4SO_3H$, it is rapidly converted to the monomeric complex $(\eta^5\text{-}C_5H_5)Cr(NO)_2OSO_2C_6H_4CH_3$, the tungsten analogue of which has been previously reported.[7] If less than 2 equiv of acid are employed, only the unreacted dimer and the final product are detectable in the reaction mixture by infrared spectroscopy. $(\eta^5\text{-}C_5H_5)Cr(NO)_2OSO_2C_6H_4CH_3$ is an air-stable green solid (mp 64–6 °C) whose solution infrared spectrum ($\nu_{NO}(CH_2Cl_2)$ = 1829, 1722 cm^{-1}) indicates the presence of terminal nitrosyl ligands. Its ^1H NMR spectrum verifies the presence of a η^5-cyclopentadienyl ring ($\delta(CDCl_3)$ 5.75 (s, 5 H)) and a *p*-toluenesulfonate ligand (δ 7.72 (d, 2 H), 7.21 (d, 2 H), and 2.36 (s, 3 H)). The monomeric nature of the complex is confirmed by its mass spectrum (base peak $[P - 2NO]^+$) which is similar to that of other $(\eta^5\text{-}C_5H_5)Cr(NO)_2X$ complexes.[26]

Interaction of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ with Lewis Acids. With a view toward gaining more insight into the apparent donor–acceptor character of the metal–metal interaction in the $[(\eta^5\text{-}C_5H_5)_2M_2(NO)_4H]^+$ cations, we decided to survey briefly the Lewis acid and base properties of the constituent parts. We chose to investigate the tungsten system because of the greater thermal stability of $(\eta^5\text{-}C_5H_5)W(NO)_2H$, and first looked at the interaction of the

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(36) Beck, W.; Schloter, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1214.

monomeric hydride with representative Lewis acids.

(a) With $M(CO)_5(C_4H_8O)$ (M = Cr or W) and $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(C_4H_8O)$. The carbonyl compounds selected are convenient soft Lewis acids since they possess a labile tetrahydrofuran ligand; extensive use has been made of these and related electrophiles to demonstrate the presence of base sites in a variety of transition metal complexes.[37]

The addition of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ to a tetrahydrofuran solution of $Cr(CO)_5(C_4H_8O)$ at -78 °C produces an orange solution whose infrared spectrum displays nitrosyl absorptions attributable to the free hydride (ν_{NO} = 1718, 1629 cm^{-1}) and to the adduct $(\eta^5\text{-}C_5H_5)(NO)_2WH{\cdot}Cr(CO)_5$ (ν_{NO} = 1736, 1661 cm^{-1}).[38] That the two compounds are rapidly equilibrating in solution, i.e.

$$(\eta^5\text{-}C_5H_5)W(NO)_2H + Cr(CO)_5(C_4H_8O) \rightleftharpoons (\eta^5\text{-}C_5H_5)(NO)_2WH{\cdot}Cr(CO)_5 + C_4H_8O \quad (16)$$

is indicated by the ^1H NMR spectrum of the mixture at -80 °C in $(CD_3)_2CO$ which displays just one resonance due to the C_5H_5 protons shifted to a lower field (δ 6.38) than observed for the free hydride. Furthermore, the magnitude of the shift is dependent on the amount of $Cr(CO)_5(C_4H_8O)$ added. Attempts to isolate the adduct at room temperature result in further reaction, $Cr(CO)_6$ and $(\eta^5\text{-}C_5H_5)W(CO)_2(NO)$ being the only isolable products.

The interaction of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ with $W(CO)_5(C_4H_8O)$ and $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(C_4H_8O)$ in tetrahydrofuran resembles that with $Cr(CO)_5(C_4H_8O)$, described above. Spectroscopic monitoring indicates the existence of equilibria of type 16 in both cases, the respective adducts being identifiable in solution. However, $(\eta^5\text{-}C_5H_5)(NO)_2WH{\cdot}W(CO)_5$ ($\nu_{NO}(C_4H_8O)$ = 1738, 1663 cm^{-1}) is thermally unstable at ambient temperature and slowly decomposes to an intractable brown solid. Similarly, $(\eta^5\text{-}C_5H_5)(NO)_2WH{\cdot}Mn(CO)_2(\eta^5\text{-}CH_3C_5H_4)$ ($\nu_{NO}(C_4H_8O)$ = 1725, 1661 cm^{-1}) converts to a carbonyl nitrosyl complex which has so far defied all attempts at isolation.

It has recently been noted[39] that in some instances solutions of photogenerated species such as $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(C_4H_8O)$ may contain traces of impurities which can catalyze the decomposition of eventual products. This potential complication can be avoided by using the isolable complexes $Cr(CO)_5[N(CH_3)_3]$ and $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2[Si(C_6H_5)_3](H)$ in place of their tetrahydrofuran analogues in the reactions with $(\eta^5\text{-}C_5H_5)W(NO)_2H$. When this is done, results identical with those described above are obtained.

(b) With MCl_2 (M = Zn, Cd, or Hg). Numerous instances of the group 2B metal halides forming adducts with transition-metal complexes are known.[37] A particularly pertinent example involves the reactions[40]

$$(\eta^5\text{-}C_5H_5)_2MH_2 + EX_2 \xrightarrow{C_4H_8O} (\eta^5\text{-}C_5H_5)_2(H)_2M{\rightarrow}EX_2{\cdot}C_4H_8O\downarrow \quad (17)$$

$$M = Mo, W;\ E = Zn, Cd, Hg;\ X = Cl, Br$$

However, when $(\eta^5\text{-}C_5H_5)W(NO)_2H$ is treated with these electrophiles, isolable adducts are not formed. Instead, no reaction occurs with $CdCl_2$ in tetrahydrofuran, and the other MCl_2 compounds react in the manner

$$(\eta^5\text{-}C_5H_5)W(NO)_2H + MCl_2 \underset{(CD_3)_2CO}{\overset{C_4H_8O\ \text{or}}{\rightleftharpoons}} (\eta^5\text{-}C_5H_5)(NO)_2WH{\cdot}MCl_2 \rightarrow (\eta^5\text{-}C_5H_5)W(NO)_2Cl + (MCl + {}^1/{}_2H_2) \quad (18)$$

$$M = Zn\ \text{or}\ Hg$$

the conversion being much more rapid when M = Hg. The intermediate adducts can be detected by ^1H NMR spectroscopy, but they do not persist in solution at ambient temperature. The final organometallic product is isolable in 67% yield from the reaction involving $HgCl_2$.

(c) With H^+ and $AlCl_3$. Unlike $(\eta^5\text{-}C_5H_5)W(CO)_3H$ which upon protonation is converted into $[(\eta^5\text{-}C_5H_5)W(CO)_3H_2]^+$,[31a] $(\eta^5\text{-}C_5H_5)W(NO)_2H$ undergoes the transformation when treated with strong, noncoordinating acids

$$2(\eta^5\text{-}C_5H_5)W(NO)_2H + H^+ \xrightarrow[\text{or}\ CD_3NO_2]{CH_2Cl_2} [(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]^+ + (H_2) \quad (19)$$

thereby reflecting its hydridic character.[7] Thus, if reaction 19 is performed with $HBF_4{\cdot}O(CH_3)_2$ as the source of H^+ in CD_3NO_2 at -20 °C, the bimetallic cation can be readily identified by its characteristic ^1H NMR spectrum (vide supra). However, the addition of excess acid results in its destruction.

It has previously been established[7] that coordinating acids, HX, react with $(\eta^5\text{-}C_5H_5)W(NO)_2H$ to form the corresponding $(\eta^5\text{-}C_5H_5)W(NO)_2X$ derivatives in good yields. It is thus not surprising to find now that $AlCl_3$ (a strong, hard Lewis acid) also effects the same conversion of the tungsten hydride in CH_2Cl_2 or $CDCl_3$. Infrared or ^1H NMR monitoring of the latter two reactions provides no evidence for the formation of an intermediate adduct.

The results of these acid–base interaction studies, coupled with the properties of the bimetallic nitrosyl cations presented earlier, indicate that $(\eta^5\text{-}C_5H_5)W(NO)_2H$ functions as a fairly weak and soft Lewis base. $[(\eta^5\text{-}C_5H_5)W(NO)_2]^+$, on the other hand, interacts strongly only with bases capable of good σ donation,[17,35] thereby suggesting that it is a fairly weak Lewis acid. It thus seems reasonable to view the tendency of the $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]^+$ unit to undergo base cleavage as a manifestation of the intrinsic weakness of the metal–metal linkage. Viewed in this light, our failure to obtain the $[(\eta^5\text{-}C_5H_5)M(NO)_2]_2$ (M = Mo or W) dimers by deprotonation of their cationic precursors does not reflect any inherent instability of these desired compounds. They remain prime synthetic targets.

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Registry No. $(\eta^5\text{-}C_5H_5)Mo(NO)_2H$, 69532-05-4; $(\eta^5\text{-}C_5H_5)W(NO)_2H$, 69532-01-0; $(\eta^5\text{-}C_5H_5)Mo(NO)_2Cl$, 12305-00-9; $(\eta^5\text{-}C_5H_5)W(NO)_2Cl$, 53419-14-0; $[(\eta^5\text{-}C_5H_5)W(NO)_2(CH_3CN)]BF_4$, 69532-04-3; $[(\eta^5\text{-}C_5H_5)W(NO)_2(CH_3CN)]PF_6$, 56404-06-9; $[(\eta^5\text{-}C_5H_5)_2Mo_2(NO)_4H]PF_6$, 79329-48-9; $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]BF_4$, 79329-50-3; $[(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]PF_6$, 79329-51-4; $[(\eta^5\text{-}C_5H_5)_2MoW(NO)_4H]BF_4$, 79329-53-6; $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$, 36607-01-9; $(\eta^5\text{-}C_5H_5)Cr(NO)_2OSO_2C_6H_4CH_3$, 79329-54-7; $Cr(CO)_5(C_4H_8O)$, 15038-41-2.

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