Three standard reflections measured every hour during the entire data collection period showed no significant trend in intensity. The raw step-scan data were converted to intensities using the Lehmann–Larsen method[19] and then corrected for Lorentz, polarization, and absorption factors, the latter computed by interpolation in the tabulated tables[20] (transmission factors between 0.25 and 0.87). A unique data set of 1326 reflections having $I > 3\sigma(I)$ was used for determining and refining the structure.

The structure was solved by using the heavy-atom method. After refinement of the heavy atoms, a difference-Fourier map revealed maxima of residual electronic density close to the positions expected for hydrogen atoms; they were introduced in structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors of 1 Å$^2$ more than the bonded C atom, but not refined. Full least-squares refinement converged to $R(F) = 0.035$ and $R_\omega(F) = 0.048$ ($\omega = 1/(\sigma^2(\text{count}) + (pI)^2)$). The unit-weight observation was 1.04 for $p = 0.08$. A final difference map revealed no significant maxima.

**Registry No.** **4**, 86272-21-1; **5**, 30540-36-4; **6**, 67918-40-5; **7** (charged form), 86272-22-2; **7** (uncharged form), 86272-23-3; **8**, 37737-13-6; **9**, 86272-18-6; **10**, 86272-19-7; **11**, 86272-20-0; **12**, 86288-20-2; $Fe_2(CO)_9$, 15321-51-4; $Co_2(CO)_8$, 10210-68-1.

**Supplementary Material Available:** Tables of atomic coordinates and thermal parameters (Tables I and V) and a listing of observed and calculated structure factors (×10) (Table IV) (8 pages). Ordering information is given on any current masthead page.

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[19] M. S. Lehmann and F. K. Larsen, *Acta Crystallogr., Sect A*, **A30**, 580 (1974).

[20] "International tables for X-ray crystallography", Vol. II, Kynoch Press, Birmingham, England, 1959, p 302.

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# Organometallic Nitrosyl Chemistry. 19.[1] Protonation vs. Oxidative Cleavage of the Isoelectronic Complexes $[(\eta^5\text{-}C_5H_4R)M(LO)_2]_2$ (M = Cr, Mn, or Fe; L = C or N; R = H or Me) by $HBF_4$

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Treatment of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ with an equimolar amount of $HBF_4{\cdot}OMe_2$ in $CH_2Cl_2$ results in the clean formation of $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4H]BF_4$ which may be isolated in good yield. In contrast, 2 equiv of the acid are required to consume completely $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$, the principal organometallic product being $(\eta^5\text{-}C_5H_5)Cr(NO)_2BF_4$. This latter complex is not isolable, but it can be identified spectroscopically and by its derivative chemistry. Some of the workup procedures employed also afford new organometallic nitrosyl complexes of chromium such as $[\{(\eta^5\text{-}C_5H_5)Cr(NO)_2\}_2OH]BF_4$ and $(\eta^5\text{-}C_5H_5)Cr(NO)_2(OHBPh_3)$ which have been characterized by conventional methods. Two equivalents of $HBF_4{\cdot}OMe_2$ also consume $[(\eta^5\text{-}C_5H_4R)Mn(CO)(NO)]_2$ (R = H or Me), but a complex mixture of products results. Two well-known (i.e., $[(\eta^5\text{-}C_5H_4R)Mn(CO)_2(NO)]^+$ and $(\eta^5\text{-}C_5H_4R)_2Mn_2(NO)_3(NO_2)$) and two novel (i.e., $[(\eta^5\text{-}C_5H_4R)_3Mn_3(NO)_3NH]^+$ and $[(\eta^5\text{-}C_5H_4R)_2Mn_2(NO)_2(CO)(NH_2)]^+$) types of manganese nitrosyl complexes are produced in each case, the novel cations being ultimately isolable in low yields as the $BF_4^-$ and $BPh_4^-$ salts, respectively. Cyclic voltammograms of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ recorded under identical experimental conditions reveal that the chromium dimer undergoes oxidation at a slightly more positive potential. The propensities of the $[(\eta^5\text{-}C_5H_4R)M(LO)_2]_2$ (M = Cr, Mn, or Fe; L = C or N; R = H or Me) dimers to undergo protonation or oxidative cleavage when treated with $H^+$ are thus rationalized in terms of the stabilities of the initially formed $[(\eta^5\text{-}C_5H_4R)M(LO)_2]_2H^+$ adducts. Interestingly, treatment of $[(\eta^5\text{-}C_5H_5)Co(NO)]_2$ with $HBF_4{\cdot}OMe_2$ in $CH_2Cl_2$ results in simple oxidation, the known $[(\eta^5\text{-}C_5H_5)Co(NO)]_2BF_4$ complex being obtainable in good yield.

## Introduction

We recently reported the preparation and characterization of the bimetallic cations $[(\eta^5\text{-}C_5H_5)_2M_2(NO)_4H]^+$ (M = Mo or W).[2] Salts containing these cations were synthesized in good yields by treatment of the monomeric hydrides $(\eta^5\text{-}C_5H_5)M(NO)_2H$ (M = Mo or W) with hydride-abstracting carbocations in nondonor solvents, e.g.

$$2(\eta^5\text{-}C_5H_5)W(NO)_2H + Ph_3CBF_4 \xrightarrow{CH_2Cl_2} [(\eta^5\text{-}C_5H_5)_2W_2(NO)_4H]BF_4 + Ph_3CH$$

Unlike related carbonyl complexes, the bimetallic cations are not deprotonated by a variety of bases to afford the as yet unknown $[(\eta^5\text{-}C_5H_5)M(NO)_2]_2$ (M = Mo or W) dimers. Instead, they are cleaved to the monomeric products $(\eta^5\text{-}C_5H_5)M(NO)_2H$ and $[(\eta^5\text{-}C_5H_5)M(NO)_2(B)]^+$ (B = base) by these reagents. In the light of these observations, two questions came 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 indicated that both questions could be answered in the negative.[2] We have now completed a more detailed investigation of the reaction of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ with $HBF_4$, and in this paper we present results that permit us to answer the above questions more fully.

Of continuing interest during our work with organometallic nitrosyl compounds is how the physical and chemical properties of the nitrosyl complexes differ from

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[1] Part 18: Legzdins, P.; Nurse, C. R.; Rettig, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 3727.

[2] Hames, B. W.; Legzdins, P. *Organometallics* **1982**, *1*, 116.

0276-7333/83/2302-1238$01.50/0

those exhibited by their isoelectronic and isostructural carbonyl analogues.[3] Consequently, we have extended our study of the protonation of the chromium dimer to encompass the analogous reactions of $H^+$ with $[(\eta^5\text{-}C_5H_4R)Mn(CO)(NO)]_2$ (R = H or Me) and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$. The combined results of these investigations permit us to assess qualitatively the propensities of the three dimeric complexes to undergo protonation vs. oxidative cleavage under these experimental conditions.

## Experimental Section

General procedures routinely employed in these laboratories have been described previously.[2]

**Electrochemical Measurements.** All operations were performed under an atmosphere of prepurified nitrogen. The $CH_2Cl_2$ solvent (Fisher Spectranalyzed) was first deaerated and then distilled from $CaH_2$. The $n\text{-}Bu_4NPF_6$ supporting electrolyte was prepared by metathesis of $n\text{-}Bu_4NI$ with $NH_4PF_6$ in refluxing acetone[4] and was recrystallized thrice from ethanol (86% yield). The solutions employed during cyclic voltammetry studies were typically $5 \times 10^{-4}$ M in the organometallic complex and 0.1 M in $n\text{-}Bu_4NPF_6$.

Electrochemical measurements were effected with a Princeton Applied Research Model 173 potentiostat equipped with a Model 176 current-to-voltage converter and a Model 178 electrometer probe. The probe was mounted external to the potentiostat, the connection to the reference electrode being made by a minimum length of high impedance wire. Cyclic voltammograms were recorded on a Hewlett-Packard Model 7035B X-Y recorder. The electrochemical cell used was similar in design to that described by van Duyne and Reilley.[5]

**Reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ with $HBF_4\cdot OMe_2$.** To a stirred, dark red-violet solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (1.0 g, 2.8 mmol) in $CH_2Cl_2$ (30 mL) was added 13.6 M $HBF_4\cdot OMe_2$ (0.48 mL, 6.5 mmol) whereupon the solution lightened in color. The reaction mixture was stirred at ambient temperature for 30 min, and the final red solution was then filtered through a short (2 × 3 cm) column of Celite. The volume of the filtrate was reduced to ~15 mL in vacuo, and $Et_2O$ (40 mL) was then added. This resulted in the precipitation of 0.54 g (43% yield) of $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4H]BF_4$ as a red-violet, crystalline solid which was collected by filtration: IR ($CH_2Cl_2$) $\nu_{CO}$ 2068 (s), 2045 (s), 2008 (s) $cm^{-1}$; $^1H$ NMR ($CD_2Cl_2$) $\delta$ 5.32 (s, 10 H, $C_5H_5$), −26.61 (s, 1 H, $Fe_2H$).

Anal. Calcd for $C_{14}H_{11}Fe_2O_4BF_4$: C, 38.07; H, 2.51. Found: C, 37.77; H, 2.52.

**Reaction of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ with $HBF_4\cdot OMe_2$.** A stirred, red-violet solution of (0.21 g, 0.60 mmol) in $CH_2Cl_2$ (25 mL) was treated with 13.6 M $HBF_4\cdot OMe_2$ (0.09 mL, 1.2 mmol), whereupon the color of the solution changed to green-brown immediately and a small amount of a dark solid precipitated. An IR spectrum of the supernatant solution exhibited two strong, sharp absorptions at 1838 and 1728 $cm^{-1}$. The reaction mixture was then filtered through a column of Celite (2 × 3 cm), and the volume of the filtrate was reduced in vacuo to ~10 mL. The nature of the organometallic products isolated from this dark green filtrate depended upon the workup procedures employed in the manner described below.

**Procedure A.** The filtrate was treated dropwise with $Et_2O$ until the mixture became turbid, and it was then cooled at −10 °C for 48 h. Rapid filtration of the final, cooled mixture afforded variable amounts (typically 0.04–0.1 g, 15–36% yield) of analytically pure $[\{(\eta^5\text{-}C_5H_5)Cr(NO)_2\}_2OH]BF_4$ as a microcrystalline, dark green solid: IR (Nujol mull) $\nu_{NO}$ 1806 (s, br), 1677 (s, br) $cm^{-1}$, also 3505 (w, br), 3115 (w), 1088 (m, br), 1054 (m, br), 1014 (m), 846 (m) $cm^{-1}$; IR ($CH_2Cl_2$) $\nu_{NO}$ 1820 (s), 1807 (sh), 1719 (s, br), 1698 (sh) $cm^{-1}$; also 3484 (w, br), 3109 (w), 1076 (m, br), 845 (m) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 5.78 (s, 10 H, $C_5H_5$), 0.11 (s, 1 H, OH); mp (in air) 130 °C dec.

Anal. Calcd for $C_{10}H_{11}Cr_2N_4O_5BF_4$: C, 26.22; H, 2.42; N, 12.23. Found: C, 25.87; H, 2.51; N, 12.26.

The same ultimate product was isolated in comparable yields even when 0.01 mL of $H_2O$ was deliberately added to the initial reaction mixture.

**Procedure B.** The dark green filtrate was taken to dryness in vacuo, and the resulting residue was extracted with $H_2O$ (3 × 10 mL). A solution of $NaBPh_4$ (0.60 g, 1.7 mmol) in $H_2O$ (15 mL) was slowly added to the extracts to induce the formation of a finely divided yellow precipitate. The precipitate was collected by filtration, washed with $H_2O$ (3 × 10 mL), and dried in vacuo ($5 \times 10^{-3}$ mmHg). Recrystallization of this solid from $CH_2Cl_2$–hexanes produced 0.16 g (31% yield) of $(\eta^5\text{-}C_5H_5)Cr(NO)_2(OHBPh_3)$ as a fine green-brown powder: IR (Nujol mull) $\nu_{NO}$ 1813 (s), 1714 (s) $cm^{-1}$; IR ($CH_2Cl_2$) $\nu_{NO}$ 1823 (s), 1712 (s) $cm^{-1}$; $^1H$ NMR ($(CD_3)_2CO$) $\delta$ 7.51–7.04 (m, 15 H, $B(C_6H_5)_3$), 5.60 (s, 5 H, $C_5H_5$), 3.13 (s, 1 H, OH); mp (in air) 104 °C dec.

Anal. Calcd for $C_{23}H_{21}CrN_2O_3B$: C, 63.33; H, 4.85; N, 6.42. Found: C, 63.23; H, 4.77; N, 6.37.

**Procedure C.** The dark green filtrate was treated with solid [PPN]Br[7] (0.76 g, 1.2 mmol), and the resulting mixture was stirred for 15 min. Volatile components were then removed under reduced pressure, and the residue was extracted with $Et_2O$ (3 × 15 mL). The combined golden extracts were filtered through a short (2 × 3 cm) column of Florisil supported on a medium-porosity frit. The volume of the filtrate was doubled by addition of hexanes. Slow concentration of the resulting solution in vacuo induced the crystallization of 0.19 g (63% yield) of golden $(\eta^5\text{-}C_5H_5)Cr(NO)_2Br$ which was identified by comparison of its spectroscopic properties with those of an authentic sample:[8] IR ($CH_2Cl_2$) $\nu_{NO}$ 1819 (s), 1713 (s) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 5.75 (s, $C_5H_5$); low-resolution mass spectrum (probe 80 °C), *m/z* 256 ($P^+$), 226 ($(P - NO)^+$), 196 ($(P - 2NO)^+$), 131 ($(P - 2NO - C_5H_5)^+$), 117 ($(P - 2NO - Br)^+$).

**Alternate Preparation of $[\{(\eta^5\text{-}C_5H_5)Cr(NO)_2\}_2OH]BF_4$.** To a stirred, golden solution of $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$[6b] (0.47 g, 2.2 mmol) in $CH_2Cl_2$ (25 mL) was added solid $AgBF_4$ (0.43 g, 2.2 mmol). A white precipitate formed immediately, and the supernatant solution became dark green. After being stirred for 15 min to ensure completion of the reaction, the mixture was filtered to obtain a dark green filtrate whose IR spectrum displayed strong nitrosyl absorptions at 1838 and 1728 $cm^{-1}$ attributable to $(\eta^5\text{-}C_5H_5)Cr(NO)_2BF_4$.[9] Treatment of the filtrate with $H_2O$ (20 μL, 1.1 mmol) and stirring of the resulting mixture for an additional 18 h produced no change in these absorptions. The mixture was then treated with ~5.4 M aqueous KOH (200 μL, ~1.1 mmol), whereupon the mixture darkened in color and deposited a dark green oil. After 0.5 h, the final mixture was taken to dryness in vacuo, and the residue was extracted with $CH_2Cl_2$ (3 × 10 mL). The extracts were concentrated under reduced pressure to ~7 mL, and $Et_2O$ was then added dropwise to induce the formation of a dark green microcrystalline precipitate. Collection of this solid by filtration afforded 0.21g (41% yield based on Cr) of $[\{\eta^5\text{-}C_5H_5)Cr(NO)_2\}_2OH]BF_4$ which was identified by its characteristic spectroscopic properties (vide supra).

The use of a stoichiometric amount of neat $Et_3N$ in place of KOH in the above procedure resulted in the isolation of the identical product, but in only 12% yield.

**Reaction of $[\{(\eta^5\text{-}C_5H_5)Cr(NO)_2\}_2OH]BF_4$ with $NaBPh_4$.** A solution of $NaBPh_4$ (0.31 g, 0.90 mmol) in $H_2O$ (70 mL) was added dropwise to a stirred suspension of $[\{(\eta^5\text{-}C_5H_5)Cr(NO)_2\}_2OH]BF_4$ (0.41 g, 0.90 mmol) in the same solvent (40 mL), whereupon a flocculent yellow-green precipitate formed. The final mixture was stirred for 0.5 h and was then filtered. The collected solid was dried in vacuo and recrystallized from $CH_2Cl_2$–$Et_2O$ to obtain 0.30 g (48% yield) of analytically pure $[\{(\eta^5\text{-}C_5H_5)Cr(NO)_2\}_2OH]BPh_4$ as a yellow-green solid: IR ($CH_2Cl_2$) $\nu_{NO}$ 1822 (s), 1812 (sh), 1721 (s), 1703 (sh) $cm^{-1}$, also 3505 (w, br), 836 (w); $^1H$ NMR ($(CD_3)_2CO$) $\delta$ 7.47–6.77 (m, 20 H, $B(C_6H_5)_4$), 5.92 (s, 10

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[3] Cf. Kolthammer, B. W. S.; Legzdins, P. *J. Chem. Soc., Dalton Trans.* **1978**, 31.

[4] Geiger, W. E., personal communication.

[5] Van Duyne, R. P.; Reilley, C. N. *Anal. Chem.* **1972**, *44*, 142.

[6] (a) Kolthammer, B. W. S.; Legzdins, P.; Malito, J. T. *Inorg. Synth.* **1979**, *19*, 208. (b) Hoyano, J. K.; Legzdins, P.; Malito, J. T. *Ibid.* **1978**, *18*, 126.

[7] Chemical Abstracts recommended name for $[PPN]^+$ is bis(triphenylphosphoranediyl)nitrogen(1+).

[8] Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *2*, 38.

[9] Cf. $(\eta^5\text{-}C_5H_5)Cr(NO)_2PF_6$ described by Regina and Wojcicki.[21]

H, $C_5H_5$), 0.83 (s, 1 H, OH); mp (in air) 145 °C dec.

Anal. Calcd for $C_{34}H_{31}Cr_2N_4O_5B$: C, 59.15; H, 4.53; N, 8.12. Found: C, 59.13; H, 4.64; N, 8.02.

**Reaction of $[(\eta^5\text{-}C_5H_5)Mn(CO)(NO)]_2$ with $HBF_4\cdot OMe_2$.** Typically, 13.6 M $HBF_4\cdot OMe_2$ (0.29 mL, 4.0 mmol) was added to a stirred, red-violet solution of $[(\eta^5\text{-}C_5H_5)Mn(CO)(NO)]_2$[10] (0.71 g, 2.0 mmol) in $CH_2Cl_2$ (30 mL). The solution became brown in color immediately, and a brown solid precipitated. After being stirred for 2 h to ensure completion of the reaction, $H_2O$ (60 mL) was added, and the mixture was concentrated in vacuo to remove the $CH_2Cl_2$. At this stage, the reaction mixture, which consisted of a black solid and a red-brown aqueous solution, was filtered through Celite (2 × 3 cm), and the collected solid was washed with $H_2O$ (4 × 20 mL). The black solid and the combined red-brown filtrates were then worked up separately in the manner described below (see Scheme II).

**Workup of the Black Solid.** The collected solid was first dried for 2 h at room temperature and $5 \times 10^{-3}$ mm pressure. It was then removed from the Celite column with $CH_2Cl_2$ (3 × 15 mL), a process that afforded a dark green solution which in turn was taken to dryness under reduced pressure. Extraction of this residue with toluene (3 × 2 mL) produced a brown solution which upon slow concentration in vacuo deposited a small amount of a brown solid. This solid was tentatively identified as $(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_3(NO_2)$ by IR spectroscopy [$(CH_2Cl_2)$ $\nu_{NO}$ 1754 (s), 1532 (s) $cm^{-1}$].[11]

Further extraction of the residue with $CH_2Cl_2$ (3 × 10 mL) afforded a dark green solution. Addition of toluene (10 mL) to this solution and careful concentration of the resulting solution under reduced pressure caused the crystallization of ~80 mg (~10% yield) of black $[(\eta^5\text{-}C_5H_5)_3Mn_3(NO)_3(NH)]BF_4$ which was collected by filtration. This trimetallic complex was identified spectroscopically [IR $(CH_2Cl_2)$ $\nu_{NO}$ 1586 (s), 1532 (s) $cm^{-1}$; $^1H$ NMR $((CD_3)_2CO)$ $\delta$ 22.52 (t, 1 H, $J_{^1H-^{14}N} = 62.5$ Hz, NH), 5.59 (s, 15 H, $C_5H_5$)].[12]

**Workup of the Red-Brown Aqueous Solution.** The original combined filtrates were treated with a saturated aqueous solution of $NaBPh_4$ (1.03 g, 3.00 mmol) whereupon a brown solid precipitated, leaving an essentially colorless supernatant solution. The brown solid was collected by filtration, washed with $H_2O$ (3 × 20 mL), and dried for 2 h at room temperature under high vacuum. Extraction of the dried solid with $CH_2Cl_2$ (3 × 20 mL) produced a brown solution which was concentrated to ~10 mL under reduced pressure. Dropwise addition of $Et_2O$ (40 mL) to this solution caused the precipitation of a brown, microcrystalline solid in ~15% yield with respect to Mn. This solid was identified as $[(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_2(CO)(NH_2)]BPh_4\cdot 0.5CH_2Cl_2$: IR $(CH_2Cl_2)$ $\nu_{NH}$ 3330 (w), 3259 (w) $cm^{-1}$, $\nu_{CO}$ 1855 (m) $cm^{-1}$, $\nu_{NO}$ 1764 (s) $cm^{-1}$; IR $(CH_3CN)$ $\nu_{CO}$ 1864 (m) $cm^{-1}$, $\nu_{NO}$ 1785 (m), 1759 (s) $cm^{-1}$; $^1H$ NMR $((CD_3)_2CO)$ $\delta$ 7.35–6.75 (m, 20 H, $C_6H_5$), 5.81 (s, 9 H, $C_5H_5$), 5.58 (s, 1 H, $C_5H_5$), 5.62 (s, 1 H, $CH_2Cl_2$).

Anal. Calcd for $C_{35.5}H_{33}Mn_2N_3O_3BCl$: C, 60.41; H, 4.71; N, 5.96. Found: C, 60.69; H, 4.85; N, 6.25.

When $[(\eta^5\text{-}C_5H_4Me)Mn(CO)(NO)]_2$ was subjected to the identical experimental procedure, methylcyclopentadienyl analogues of the products described above were obtained in comparable yields. The spectroscopic properties of the $C_5H_4Me$-containing complexes are presented below.

**$(\eta^5\text{-}C_5H_4Me)_2Mn_2(NO)_3(NO_2)$:** IR $(CH_2Cl_2)$ $\nu_{NO}$ 1744 (s), 1536 (s) $cm^{-1}$.[11]

**$[(\eta^5\text{-}C_5H_4Me)_3Mn_3(NO)_3(NH)]BF_4$:** IR $(CH_2Cl_2)$ $\nu_{NH}$ 3275 (w) $cm^{-1}$, $\nu_{NO}$ 1574 (s), 1526 (s) $cm^{-1}$; $\nu_{BF}$ 1068 (s) $cm^{-1}$; $^1H$ NMR $(CD_2Cl_2)$ $\delta$ 21.95 (t, 1 H, $J_{^1H-^{14}N} = 61$ Hz, NH), 5.26 (s, 6 H, $C_5\mathit{H}_4Me$), 5.18 (s, 6 H, $C_5\mathit{H}_4Me$), 1.80 (s, 9 H, $C_5H_4\mathit{Me}$).

**$(\eta^5\text{-}C_5H_4Me)_2Mn_2(NO)_2(CO)(NH_2)]BPh_4$:** IR $(CH_2Cl_2)$ $\nu_{NH}$ 3336 (w), 3272 (w) $cm^{-1}$, $\nu_{CO}$ 1856 (m) $cm^{-1}$, $\nu_{NO}$ 1754 (s) $cm^{-1}$; IR $(CH_3CN)$ $\nu_{CO}$ 1864 (m) $cm^{-1}$, $\nu_{NO}$ 1785 (m), 1754 (s) $cm^{-1}$; $^1H$ NMR $((CD_3)_2CO)$ $\delta$ 7.35–6.76 (m, 20 H, $C_6H_5$), 5.96 (s, 2 H, $C_5\mathit{H}_4Me$), 5.72 (s, 1 H, $C_5\mathit{H}_4Me$), 5.59 (s, 1 H, $C_5\mathit{H}_4Me$), 5.34 (s, 1 H, $C_5\mathit{H}_4Me$), 5.19 (s, 2 H, $C_5\mathit{H}_4Me$), 4.99 (s, 1 H, $C_5\mathit{H}_4Me$), 2.38 (s, 3 H, $C_5H_4\mathit{Me}$), 2.26 (s, 3 H, $C_5H_4\mathit{Me}$).

**Reaction of $[(\eta^5\text{-}C_5H_5)Co(NO)]_2$ with $HBF_4\cdot OMe_2$.** A rapidly stirred brown solution of $[(\eta^5\text{-}C_5H_5)Co(NO)]_2$[13] (0.55 g, 1.8 mmol) in $CH_2Cl_2$ (30 mL) was treated with 13.6 M $HBF_4\cdot OMe_2$ (0.26 mL, 3.5 mmol). The solution immediately became red-violet, and a small amount of a dark solid precipitated. After being stirred for 30 min, the reaction mixture was filtered through a Celite column (2 × 3 cm) supported on a medium-porosity frit. The column was then washed with $CH_2Cl_2$ (3 × 15 mL), and the combined filtrates were concentrated under reduced pressure to a volume of ~15 mL. Dropwise addition of $Et_2O$ (50 mL) to this solution induced the precipitation of 0.51 g (73% yield) of purple, microcrystalline $[(\eta^5\text{-}C_5H_5)Co(NO)]_2BF_4$ which was collected by filtration: IR $(CH_2Cl_2)$: $\nu_{NO}$ 1622 (m) $cm^{-1}$; $\nu_{BF}$ 1057 (m), 1034 (m) $cm^{-1}$.

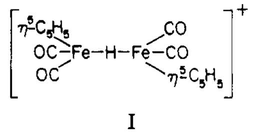
Anal. Calcd for $C_{10}H_{10}Co_2N_2O_2BF_4$: C, 30.42; H, 2.55; N, 7.10. Found: C, 30.59; H, 2.75; N, 6.95.

## Results and Discussion

The reactions of the isoelectronic $[(\eta^5\text{-}C_5H_4R)M(LO)_2]_2$ (M = Cr, Mn, or Fe; L = C or N; R = H or Me) complexes with $HBF_4$ are best systematized in terms of the individual organometallic reactants.

**(A) $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$.** In accordance with the published observations of other investigators concerning the behavior of the iron dimer in strongly protic media,[14-16] we find that treatment of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ with $HBF_4\cdot OMe_2$ in $CH_2Cl_2$ results in the clean formation of $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4H]BF_4$ which can be isolated in good yields, i.e., eq 1. The spectroscopic properties of this red-violet, air-sensitive complex [IR $(CH_2Cl_2)$ $\nu_{CO}$ 2068 (s), 2045 (s), 2008 (s) $cm^{-1}$; $^1H$ NMR $(CD_2Cl_2)$ $\delta$ 5.32 (s, 10 H, $C_5H_5$, −26.61 (s, 1 H, $Fe_2H$)] are consistent with the bimetallic cation possessing, on average, the molecular structure I. Its $^1H$ NMR spectrum does not exclude the possibility that the closed three-center–two-electron Fe–H–Fe linkage may well be bent in instantaneous structures.[17] However, its IR spectrum does reveal that in solutions the complex exists as a mixture of rotamers.[16]

$$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2 + HBF_4\cdot OMe_2 \xrightarrow{CH_2Cl_2} [(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4H]BF_4 + OMe_2 \quad (1)$$



I

Reaction 1 is reversible, the $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4H]^+$ cation being converted to the parent neutral dimer by a variety of Lewis bases such as aqueous acetone[14] or $Et_3N$. This fact explains a previous report[18] that acetone solutions of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ are virtually unchanged by the addition of aqueous $HBF_4$. Furthermore, in the light of reaction 1, it is clear why oxidations of the iron dimer in aqueous acetone to $[(\eta^5\text{-}C_5H_5)Fe(CO)_2L]^+$ (L = $H_2O$[18] or $\eta^2$-alkene[19]) species require molecular oxygen in addition to $HBF_4$ in order to be effected successfully.

**(B) $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$.** The addition of $HBF_4\cdot OMe_2$ to a red-violet $CH_2Cl_2$ solution of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ results in an immediate reaction, as evidenced by the so-

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(10) King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1964**, *3*, 791.

(11) Hames, B. W.; Kolthammer, B. W. S.; Legzdins, P. *Inorg. Chem.* **1981**, *20*, 650.

(12) By comparison with the spectroscopic properties of its methylcyclopentadienyl analogue, a complex that we have characterized completely.[1]

(13) Brunner, H. *J. Organomet. Chem.* **1968**, *12*, 517.

(14) Davison, A.; McFarlane, W.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 3653.

(15) Symon, D. A.; Waddington, T. C. *J. Chem. Soc. A* **1971**, 953.

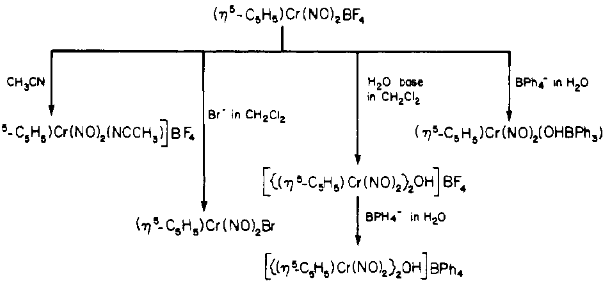
(16) Harris, D. C.; Gray, H. B. *Inorg. Chem.* **1975**, *14*, 1215.

(17) Petersen, J. L.; Brown, R. K.; Williams, J. M.; McMullan, R. K. *Inorg. Chem.* **1979**, *18*, 3493 and references cited therein.

(18) Dombek, B. D.; Angelici, R. J. *Inorg. Chim. Acta* **1973**, *7*, 345.

(19) Boyle, P. F.; Nicholas, K. M. *J. Organomet. Chem.* **1976**, *114*, 307.

Scheme I



lution becoming green-brown. Monitoring of the progress of the conversion by IR spectroscopy reveals that the strong nitrosyl absorptions due to the reactant at 1667 and 1512 $cm^{-1}$ gradually diminish in intensity. Concomitantly, new absorptions attributable to terminal nitrosyl ligands appear and grow at 1838 and 1728 $cm^{-1}$. After 1 equiv of acid has been added, the reaction mixture appears to contain approximately equal amounts of the reactant and the new nitrosyl-containing species. Addition of a further equivalent of acid consumes completely the remaining $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ and doubles the concentration of the new species. Similar observations are made when the course of the reaction in $CD_3NO_2$ is monitored by $^1H$ NMR spectroscopy. Again, complete consumption of the nitrosyl dimer requires 2 equiv of acid, and the final reaction mixture contains predominantly one organometallic product. The spectrum of this mixture displays a strong, singlet resonance in the region characteristic of $\eta^5\text{-}C_5H_5$ protons. However, the position of this resonance ($\delta$ 6.03) is shifted down field considerably from that exhibited by $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ ($\delta$ 4.89). This indicates that there is less electron density on the cyclopentadienyl ligand in the former species.

The observed stoichiometry of the reactants and the spectroscopic properties of the organometallic product are consistent with the occurrence of a simple oxidative cleavage process, i.e., eq 2. Unfortunately, we have been unable to isolate the $(\eta^5\text{-}C_5H_5)Cr(NO)_2BF_4$ product as such (vide infra).[20] In this sense, as well as in its spectroscopic properties, this complex thus resembles the recently reported $(\eta^5\text{-}C_5H_5)Cr(NO)_2PF_6$ which may be generated by the protonation of $(\eta^5\text{-}C_5H_5)Cr(NO)_2CH_3$ in $CH_3NO_2$.[21] Completely analogously, we have verified spectroscopically that treatment of the methyl precursor with $HBF_4\cdot OMe_2$ in $CH_2Cl_2$ or $CD_3NO_2$ affords solutions containing $(\eta^5\text{-}C_5H_5)Cr(NO)_2BF_4$.

$$[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2 + 2HBF_4\cdot OMe_2 \xrightarrow{CH_2Cl_2} 2(\eta^5\text{-}C_5H_5)Cr(NO)_2BF_4 + H_2 + 2OMe_2 \quad (2)$$

Our formulation of the organometallic product in reaction 2 is also supported by chemical evidence (summarized in Scheme I) which indicates that the $BF_4$ group is weakly ligated. For instance, solvent removal from $CH_2Cl_2$ or $CH_3NO_2$ solutions of $(\eta^5\text{-}C_5H_5)Cr(NO)_2BF_4$ produces a viscous, green oil. Dissolution of this oil in $CH_3CN$ results in the clean formation of the previously prepared $[(\eta^5\text{-}C_5H_5)Cr(NO)_2(NCCH_3)]BF_4$,[22] i.e., eq 3. Furthermore, the addition of solid [PPN]Br to $CH_2Cl_2$ solutions of $(\eta^5\text{-}C_5H_5)Cr(NO)_2BF_4$ initiates the metathesis reaction (4) from which the well-known[8] $(\eta^5\text{-}C_5H_5)Cr(NO)_2Br$ complex may be conveniently isolated in 63% yield.

$$(\eta^5\text{-}C_5H_5)Cr(NO)_2BF_4 + CH_3CN \xrightarrow{CH_3CN} [(\eta^5\text{-}C_5H_5)Cr(NO)_2(NCCH_3)]BF_4 \quad (3)$$

$$(\eta^5\text{-}C_5H_5)Cr(NO)_2BF_4 + [PPN]Br \xrightarrow{CH_2Cl_2} (\eta^5\text{-}C_5H_5)Cr(NO)_2Br + [PPN]BF_4 \quad (4)$$

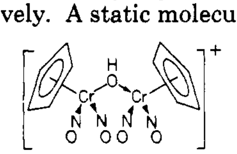
Our attempts to isolate $(\eta^5\text{-}C_5H_5)Cr(NO)_2BF_4$ from reaction 2 have afforded other new organometallic nitrosyl complexes of chromium. Thus, addition of $Et_2O$ to the final reaction mixture does not result in the precipitation of $(\eta^5\text{-}C_5H_5)Cr(NO)_2BF_4$ or even $[(\eta^5\text{-}C_5H_5)Cr(NO)_2(OEt_2)]BF_4$ but rather results in the deposition in low yields of $[\{(\eta^5\text{-}C_5H_5)Cr(NO)_2\}_2OH]BF_4$ as a dark green, microcrystalline solid. This hydroxo complex is a byproduct of reaction 2 which, we believe, arises from further reactions of the initially formed $(\eta^5\text{-}C_5H_5)Cr(NO)_2BF_4$. Consistent with this view is the fact that $[\{(\eta^5\text{-}C_5H_5)Cr(NO)_2\}_2OH]BF_4$ can also be synthesized directly by the sequential conversions (5) and (6) where base = $OH^-$ or $Et_3N$.

$$(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl + AgBF_4 \xrightarrow{CH_2Cl_2} (\eta^5\text{-}C_5H_5)Cr(NO)_2BF_4 + AgCl \quad (5)$$

$$2(\eta^5\text{-}C_5H_5)Cr(NO)_2BF_4 + H_2O + \text{base} \xrightarrow{CH_2Cl_2} [\{\eta^5\text{-}C_5H_5)Cr(NO)_2\}_2OH]BF_4 + \text{baseH}^+ + BF_4^- \quad (6)$$

Significantly, a stoichiometric amount of base is essential for the progress of reaction 6, the dimetallic hydroxo complex not being formed in the presence of water alone. Nevertheless, the conditions extant during the progress and workup of reaction 2 are such that the occurrence of subsequent reaction 6 can account for the amounts of $[\{(\eta^5\text{-}C_5H_5)Cr(NO)_2\}_2OH]BF_4$ eventually isolated.

The novel dichromium hydroxo complex is a dark olive-green, diamagnetic solid which can be handled in air for several hours without noticeable decomposition. It is soluble in $CH_2Cl_2$, $CH_3NO_2$, and acetone, sparingly soluble in $H_2O$, and virtually insoluble in $Et_2O$. Its IR spectrum as a Nujol mull displays two strong, broad absorptions at 1806 and 1677 $cm^{-1}$ characteristic of terminal nitrosyl ligands,[23] and its $^1H$ NMR spectrum (in $CDCl_3$) exhibits two sharp resonances at $\delta$ 5.78 and 0.11 of relative intensity 10:1 attributable to the cyclopentadienyl and hydroxo protons, respectively. A static molecular structure (II) of the cation which is consistent with these data is shown.



II

The bimetallic cation can thus be viewed as resulting from adduct formation between the hard Lewis acid[9] $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]^+$ and the hard donor site of the Lewis base $(\eta^5\text{-}C_5H_5)Cr(NO)_2OH$. The hydroxo cation thus resembles the recently reported $[\{(\eta^5\text{-}C_5H_5)Cr(NO)_2\}_2Cl]^+$ cation.[24] That the hydroxo cation possesses lower symmetry in solution or exists as a mixture of rapidly equilibrating rotamers is suggested by its IR spectrum in $CH_2Cl_2$ which displays four nitrosyl absorptions at 1820, 1807, 1719, and 1698 $cm^{-1}$.

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[20] A complex formulated as $(\eta^5\text{-}C_5H_5)Cr(NO)_2BF_4$ has been isolated from the mixtures resulting after the sequential treatment of aqueous solutions of $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ with $AgNO_3$ and $NaBF_4$.[8] This compound is probably better formulated as $[(\eta^5\text{-}C_5H_5)Cr(NO)_2(OH_2)]BF_4$.

[21] Regina, F. J.; Wojcicki, A. *Inorg. Chem.* **1980**, *19*, 3803.

[22] Malito, J. T. Ph.D. Dissertation, University of British Columbia, 1976. The characteristic spectral properties of this complex are as follows: IR ($CH_3NO_2$) $\nu_{NO}$ 1846 (s), 1742 (s) $cm^{-1}$; $^1H$ NMR ($(CD_3)_2CO$) $\delta$ 6.18 (s, 5 H, $C_5H_5$), 2.57 (s, 3 H, $NCCH_3$).

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

[24] Hartmann, G.; Froböse, R.; Mews, R.; Sheldrick, G. M. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 1234.

Attempts to isolate the principal organometallic product of reaction 2 as its $BPh_4^-$ salt by metathesis in aqueous solutions result instead in the formation of $(\eta^5\text{-}C_5H_5)Cr(NO)_2(OHBPh_3)$, i.e., eq 7, the final organometallic com-

$$(\eta^5\text{-}C_5H_5)Cr(NO)_2BF_4 + H_2O + BPh_4^- \xrightarrow{H_2O} (\eta^5\text{-}C_5H_5)Cr(NO)_2(OHBPh_3) + PhH + BF_4^- \quad (7)$$

plex being isolable in moderate yields. The same product results when $(\eta^5\text{-}C_5H_5)Cr(NO)_2BF_4$ generated by reaction 5 is treated with $NaBPh_4$ in $H_2O$. Conversion 7 probably proceeds via deprotonation of the coordinated aquo ligand in $[(\eta^5\text{-}C_5H_5)Cr(NO)_2(OH_2)]^+$ by $BPh_4^-$ as one of its steps. It certainly does *not* involve unsymmetrical cleavage of preformed $[\{(\eta^5\text{-}C_5H_5)Cr(NO)_2\}_2OH]^+$ by $BPh_4^-$, i.e., eq 8,

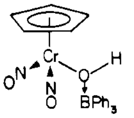
$$[\{(\eta^5\text{-}C_5H_5)Cr(NO)_2\}_2OH]^+ + BPh_4^- \overset{H_2O}{\not\longrightarrow} (\eta^5\text{-}C_5H_5)Cr(NO)_2(OHBPh_3) + (\eta^5\text{-}C_5H_5)Cr(NO)_2Ph \quad (8)$$

since we have established independently that these two reactants engage only in simple metathesis under these experimental conditions, i.e., eq 9. The organometallic

$$[\{(\eta^5\text{-}C_5H_5)Cr(NO)_2\}_2OH]BF_4 + NaBPh_4 \xrightarrow{H_2O} [\{(\eta^5\text{-}C_5H_5)Cr(NO)_2\}_2OH]BPh_4 + NaBF_4 \quad (9)$$

product of reaction 9 is an olive green, air-stable solid which is soluble in acetone and $CH_2Cl_2$ but is insoluble in $H_2O$. Its spectroscopic properties are similar to those exhibited by its $BF_4$ analogue (vide supra).

The new complex $(\eta^5\text{-}C_5H_5)Cr(NO)_2(OHBPh_3)$ resembles other $(\eta^5\text{-}C_5H_5)Cr(NO)_2X$ species which have been shown to have monomeric, three-legged piano-stool molecular structures.[25] It is a green-brown, air-stable solid whose IR spectra both in solution and in the solid state display two strong absorptions at ~1818 and ~1713 $cm^{-1}$ due to terminal nitrosyl ligands. Furthermore, its $^1H$ NMR spectrum (in $(CD_3)_2CO$) consists of signals readily attributable to Ph (δ 7.51–7.04), $C_5H_5$ (δ 5.60), and OH (δ 3.13) protons, as expected for III, which again involves a relatively hard-hard Lewis acid-base interaction. However, this adduct linkage is not particularly strong as evidenced by the fact that the 70-eV mass spectrum of the complex only displays signals due to ions resulting from the fragmentation of the individual acid and base entities, the parent ion not being detectable.

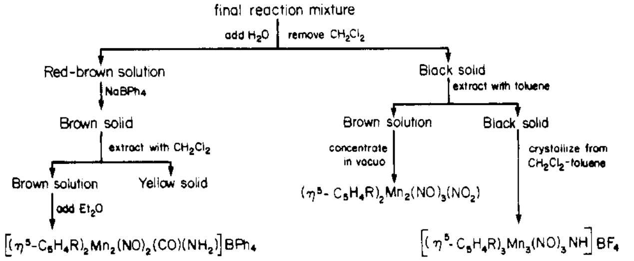


III

These results verify that the two questions posed in the Introduction concerning the protonation of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ can indeed be answered in the nagative. In addition, this work indicates that the unidentified solid which we isolated previously[2] from $CH_2Cl_2$ solutions of the dimer which had been treated with aqueous solutions of $HPF_6$ or $HBF_4\cdot OMe_2$ does mot correspond to any of the organometallic nitrosyl complexes of chromium described in this paper. Apparently, the former species requires an excess of the protic acid to be formed in significant amounts.

**(C) $[(\eta^5\text{-}C_5H_4R)Mn(CO)(NO)]_2$ (R = H or Me).** Just as for the related iron and chromium dimers, treatment of red-violet $[(\eta^5\text{-}C_5H_4R)Mn(CO)(NO)]_2$ (R = H or Me) with $HBF_4\cdot OMe_2$ in $CH_2Cl_2$ results in an immediate reaction, the mixture becoming brown in color. Again, 2 equiv of acid are required to consume completely the dimeric reactants. However, unlike the other two systems considered above, these reactions involving the manganese dimers afford a complex mixture of products. Fortunately, most of the organometallic products may be separated by virtue of their differing solubility properties in the manner summarized in Scheme II. Careful IR monitoring of the progress of the original reactions verifies that the nitrosyl-containing complexes indicated in Scheme II, as well as $[(\eta^5\text{-}C_5H_4R)Mn(CO)_2(NO)]^+$ (R = H or Me) which probably ends up as a component of the yellow solid, are formed initially and not during the subsequent workup procedures.

Scheme II



The protonation of $[(\eta^5\text{-}C_5H_4R)Mn(CO)(NO)]_2$ (R = H or Me) thus produces ultimately two well-known and two novel organometallic nitrosyl complexes of manganese in each case. The familiar $[(\eta^5\text{-}C_5H_4R)Mn(CO)_2(NO)]^+$ cations[10,26] (IR ($CH_2Cl_2$) R = H, $\nu_{CO}$ 2125, 2075 $cm^{-1}$, $\nu_{NO}$ 1840 $cm^{-1}$, R = Me, $\nu_{CO}$ 2116, 2075 $cm^{-1}$, $\nu_{NO}$ 1846 $cm^{-1}$) have been synthesized by the high-yield reactions (10), and we

$$(\eta^5\text{-}C_5H_4R)Mn(CO)_3 + NO^+ \xrightarrow{CH_3CN} [(\eta^5\text{-}C_5H_4R)Mn(CO)_2(NO)]^+ + CO \quad (10)$$

have previously reported[11] the subsequent conversion of these cations to $(\eta^5\text{-}C_5H_4R)_2Mn_2(NO)_3(NO_2)$ (IR ($CH_2Cl_2$) R = H, $\nu_{NO}$ 1754, 1532 $cm^{-1}$, R = Me, $\nu_{NO}$ 1744, 1536 $cm^{-1}$) in moderate yields, i.e., eq 11. Very recently we discov-

$$[(\eta^5\text{-}C_5H_4R)Mn(CO)_2(NO)]^+ + NO_2^- \xrightarrow{\text{acetone}} (\eta^5\text{-}C_5H_4R)_2Mn_2(NO)_3(NO_2) \quad (11)$$

ered[1] that the novel trimetallic products $[(\eta^5\text{-}C_5H_4R)_3Mn_3(NO)_3NH]BF_4$ (IR ($CH_2Cl_2$) R = H, $\nu_{NO}$ 1586, 1532 $cm^{-1}$, R = Me, $\nu_{NO}$ 1574, 1526 $cm^{-1}$), which are isolable from this reaction in ~10% yields can also be prepared in comparable yields by the stoichiometric transformations

$$(\eta^5\text{-}C_5H_4R)_3Mn_3(NO)_4 + 3HBF_4 + 2e^- \xrightarrow{CH_2Cl_2} [(\eta^2\text{-}C_5H_4R)_3Mn_3(NO)_3NH]BF_4 + \{H_2O\} \quad (12)$$

the requisite electrons probably being provided intermolecularly by the manganese atoms of the cluster. The triply bridging nature of the unique imido ligand in the trimetallic cations has been revealed spectroscopically and by a single-crystal X-ray crystallographic analysis of the $PF_6^-$ salt of the methylcyclopentadienyl cation.[1]

The previously unreported bimetallic amido complexes $[(\eta^5\text{-}C_5H_4R)_2Mn_2(NO)_2(CO)(NH_2)]BPh_4$ are obtainable in ~15% yield from the original protonation reaction, the cyclopentadienyl complex crystallizing from $CH_2Cl_2\text{–}Et_2O$ as the 0.5 M $CH_2Cl_2$ solvate. The compounds are brown, microcrystalline solids which dissolve in polar organic solvents to produce air-sensitive solutions. Their spec-

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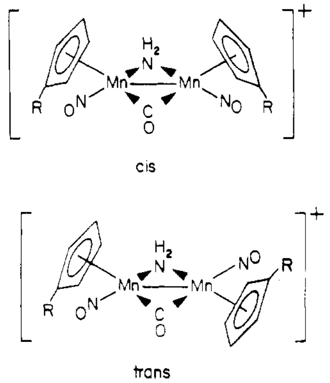
(25) Greenhough, T. J.; Kolthammer, B. W. S.; Legzdins, P.; Trotter, J. *Acta Crystallogr., Sect. B* **1980**, *B36*, 795.

(26) Connelly, N. G. *Inorg. Synth.* **1974**, *15*, 91.

troscopic properties are consistent with the cations existing in solutions as a mixture of the diastereomers IV, the trans



IV

form being predominant in less polar solvents and the cis isomer (an enantiomeric pair) becoming relatively more abundant in more polar solvents.[27] Thus, their $CH_2Cl_2$ solutions display IR absorptions attributable to bridging $NH_2$ groups (R = H, $\nu_{NH}$ 3330, 3259 $cm^{-1}$, R = Me, $\nu_{NH}$ 3336, 3272 $cm^{-1}$), bridging carbonyl (R = H, $\nu_{CO}$ 1855 $cm^{-1}$, R = Me, $\nu_{CO}$ 1856 $cm^{-1}$), and terminal nitrosyl ligands (R = H, $\nu_{NO}$ 1764 $cm^{-1}$, R = Me, $\nu_{NO}$ 1754 $cm^{-1}$). However, when dissolved in the more polar $CH_3CN$, the complexes exhibit two IR absorptions due to the NO groups (R = H, $\nu_{NO}$ 1785 (m), 1759 (s) $cm^{-1}$, R = Me, $\nu_{NO}$ 1785 (m), 1754 (s) $cm^{-1}$), the higher energy bands being assignable to the cis isomer. The $^1H$ NMR spectrum of the cyclopentadienyl compound in $(CD_3)_2CO$ (a solvent of intermediate polarity) reveals the presence of the $CH_2Cl_2$ of solvation and the tetraphenylborate anion but does not contain detectable signals due to the $NH_2$ group. Furthermore, it displays two sharp resonances in the cyclopentadienyl region at $\delta$ 5.81 and 5.58 of relative intensity 9:1 which we assign to the trans and cis isomers, respectively. The analogous spectrum of the methylcyclopentadienyl compound is more complex, exhibiting six distinct signals for the ring protons and two separate signals for the methyl protons in addition to the complex multiplet due to the $BPh_4^-$ anion. While the exact assignment of these resonances due to the $\eta^5$-$C_5H_5Me$ ligands is not possible at the present time, this complexity is nevertheless indicative of each methylcyclopentadienyl ligand being bound to an asymmetric manganese center.[11]

**Protonation vs. Oxidative Cleavage.** It is clear from the preceding results that treatment of the $[(\eta^5\text{-}C_5H_4R)M(LO)_2]_2$ (M = Cr, Mn, or Fe; L = C or N; R = H or Me) dimers with $HBF_4{\cdot}OMe_2$ in $CH_2Cl_2$ results in markedly different types of products. A possible explanation for these varied experimental observations is that entirely different reaction pathways are being followed during the various conversions. For instance, one pathway might involve initial proton transfer (protonation), i.e. eq 13,

$$[(\eta^5\text{-}C_5H_4R)M(LO)_2]_2 + H^+ \xrightarrow{CH_2Cl_2} [(\eta^5\text{-}C_5H_4R)M(LO)_2]_2H^+ \quad (13)$$

whereas another might have electron transfer (oxidative cleavage) as the first step, i.e., eq 14. In other words, it

$$[(\eta^5\text{-}C_5H_4R)M(LO)_2]_2 + 2H^+ \xrightarrow{CH_2Cl_2} 2[(\eta^5\text{-}C_5H_4R)M(LO)_2]^+ + H_2 \quad (14)$$

is possible that the differing chemical behavior of the organometallic dimers toward $H^+$ may simply be a manifestation of their intrinsically differing tendencies to undergo oxidation. This view seems to be supported at first glance by previously documented chemistry of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ which indicates that the Cr–Cr bond in the chromium dimer is more readily cleaved by electrophiles. Thus, while reaction

$$[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2 + PbCl_2 \xrightarrow[\text{reflux}]{THF} 2(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl + Pb \quad (15)$$

proceeds cleanly, the iron dimer apparently does not react with $PbCl_2$.[3] In similar fashion, the chromium complex dehalogenates vicinal or benzylic organic halides whereas the iron complex does not.[28] Furthermore, $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ is oxidized rapidly (~10 min) by 2 equiv of $Ph_3CBF_4$, i.e., eq 16, whereas when $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ in

$$[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2 \xrightarrow[CH_2Cl_2]{2Ph_3CBF_4} 2(\eta^5\text{-}C_5H_5)Cr(NO)_2BF_4 \quad (16)$$

$CH_2Cl$ is treated with approximately 3 equiv of $Ph_3CF_4$,[19] the dimer is only slowly consumed in ~45 h.[29]

To gain some quantitative information about the redox properties of the reactant dimers, we have initiated electrochemical investigations. Although these studies are presently at a relatively early stage, some interesting and pertinent results have begun to emerge. Thus, employing a platinum bead electrode with $n$-$Bu_4NPF_6$ as the supporting electrolyte, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ in $CH_2Cl_2$ exhibits a cyclic voltammogram having a high degree of reversibility with $E_{1/2}$ = +0.68 V (vs. SCE) and a peak separation ($\Delta E_p$) of 100 mV at a scan rate of 0.067 V $s^{-1}$.[31] In contrast, the isoelectronic $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ is oxidized irreversibly under the same experimental conditions, $E_{pa}$ being +0.85 V at a scan rate of 0.077 V $s^{-1}$. Although a direct comparison of $E_{1/2}$ values cannot be made, it is clear that the chromium complex undergoes oxidation at a more positive potential. In the context of the reactions being considered in this paper, this observation indicates that if $H^+$ is a sufficiently strong oxidant to oxidize $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ in $CH_2Cl_2$ according to eq 14, then it should certainly be sufficiently potent to effect the same oxidative cleavage of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$. The fact that the iron dimer is simply protonated instead (eq 13) suggests that viewing the reaction of the $[(\eta^5\text{-}C_5H_4R)M(LO)_2]_2$ dimers with $HBF_4{\cdot}OMe_2$ in $CH_2Cl_2$ as involving simple electron transfer is too simplistic.

On the basis of the currently available data, we believe that a more unified rationale of the reactions of the dimers with $H^+$ is as follows. The first step consists of adduct formation to produce the cationic $[(\eta^5\text{-}C_5H_4R)M(LO)_2]_2H^+$ species as summarized in eq 13. This adduct may prove to be sufficiently stable to be isolable (as in the case of M = Fe). Alternatively, the adduct may undergo unsymmetrical dissociation. For instance, in the case of M = Cr, such dissociation, i.e., eq 17, would afford the ultimate

$$[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2H^+ \xrightarrow{CH_2Cl_2} (\eta^5\text{-}C_5H_5)Cr(NO)_2^+ + (\eta^5\text{-}C_5H_5)Cr(NO)_2H \quad (17)$$

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[27] We have previously established[11] that the cis:trans isomer ratio of the related $(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_3X$ complexes increases in more polar solvents.

[28] Kolthammer, B. W. S.; Legzdins, P.; Martin, D. T. *Tetrahedron Lett.* **1978**, 323.

[29] It is tempting to formulate the organometallic product formed in this reaction as $(\eta^5\text{-}C_5H_5)Fe(CO)_2BF_4$. However, the IR data reported[19] for this species (($CH_2Cl_2$) $\nu_{CO}$ 2050, 2010 $cm^{-1}$) do not agree with those displayed by authentic $(\eta^5\text{-}C_5H_5)Fe(CO)_2BF_4$ (($CH_2Cl_2$) $\nu_{CO}$ 2078, 2032 $cm^{-1}$) recently isolated by Mattson and Graham.[30]

[30] Mattson, B. M.; Graham, W. A. G. *Inorg. Chem.* **1981**, *20*, 3186.

[31] For ferrocene under the same conditions, $E_{1/2}$ = +0.47 V and $\Delta E_p$ = 80 mV.

$(\eta^5\text{-}C_5H_5)Cr(NO)_2^+$ product and the neutral hydrido complex $(\eta^5\text{-}C_5H_5)Cr(NO)_2H$. However, this latter compound is thermally unstable[32] and reverts to the original dimeric reactant via eq 18. Sequential recycling of conversions

$$2(\eta^5\text{-}C_5H_5)Cr(NO)_2H \xrightarrow{CH_2Cl_2} [(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2 + H_2 \tag{18}$$

13, 17, and 18 finally results in the net transformation (2) which is observed experimentally. In a similar manner when M = Mn, the initial $[(\eta^5\text{-}C_5H_4R)Mn(CO)(NO)]_2H^+$ adduct could cleave in a number of ways. One such unsymmetrical cleavage would produce the observed $[(\eta^5\text{-}C_5H_4R)Mn(CO)_2(NO)]^+$ cations and $(\eta^5\text{-}C_5H_4R)Mn(NO)H$, the latter complexes being logical precursors for the trimetallic reactants of reaction 12. Nevertheless, the origins of the bimetallic nitrosyl products presented in Scheme II remain to be ascertained, reactions 10 and 11 being unlikely in this system.

One final point merits mention. In principle, the initial cationic adducts formed via reaction 13 could also undergo inner-sphere electron-transfer processes, i.e., eq 19, the net

$$[(\eta^5\text{-}C_5H_4R)M(LO)_2]_2H^+ \xrightarrow{CH_2Cl_2} [(\eta^5\text{-}C_5H_4R)M(LO)_2]_2^+ + {}^1/_2H_2 \tag{19}$$

result being formation of the bimetallic monocations. We have not found any direct physical evidence for the existence of such bimetallic species in the iron, chromium, or manganese systems. Interestingly, however, we have observed this to be the principal mode of reaction when $[(\eta^5\text{-}C_5H_5)Co(NO)]_2$ is treated with a slight excess of $HBF_4{\cdot}OMe_2$ in $CH_2Cl_2$, i.e., eq 20. The previously reported,[33] paramagnetic $[(\eta^5\text{-}C_5H_5)Co(NO)]_2BF_4$ may be easily isolated as a purple microcrystalline solid in 73% yield from the final reaction mixture.

$$[(\eta^5\text{-}C_5H_5)Co(NO)]_2 + HBF_4{\cdot}OMe_2 \xrightarrow{CH_2Cl_2} [(\eta^5\text{-}C_5H_5)Co(NO)]_2BF_4 + {}^1/_2H_2 + OMe_2 \tag{20}$$

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**Registry No.** $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4H]BF_4$, 86365-53-9; $[\{(\eta^5\text{-}C_5H_5)Cr(NO)_2\}_2OH]BF_4$, 86365-55-1; $(\eta^5\text{-}C_5H_5)Cr(NO)_2(OHBPh_3)$, 86365-56-2; $(\eta^5\text{-}C_5H_5)Cr(NO)_2Br$, 77662-15-8; $[\{(\eta^5\text{-}C_5H_5)Cr(NO)_2\}_2OH]BPh_4$, 86365-57-3; $(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_3(NO_2)$, 36534-34-6; $[(\eta^5\text{-}C_5H_5)_3Mn_3(NO)_3(NH)]BF_4$, 86365-59-5; $[(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_2(CO)(NH_2)]BPh_4$ (cis isomer), 86365-61-9; $(\eta^5\text{-}C_5H_4Me)_2Mn_2(NO)_3(NO_2)$, 75847-53-9; $[(\eta^5\text{-}C_5H_4Me)_3Mn_3(NO)_3(NH)]BF_4$, 85649-58-7; $[(\eta^5\text{-}C_5H_4Me)_2Mn_2(NO)_2(CO)(NH_2)]BPh_4$ (cis isomer), 86365-63-1; $[(\eta^5\text{-}C_5H_5)Co(NO)]_2BF_4$, 84577-24-2; $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, 12154-95-9; $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$, 36607-01-9; $[(\eta^5\text{-}C_5H_5)Mn(CO)(NO)]_2$, 69120-59-8; $[(\eta^5\text{-}C_5H_5)Co(NO)]_2$, 51862-20-5; $[(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_2(CO)(NH_2)]BPh_4$ (trans isomer), 86391-48-2; $(\eta^5\text{-}C_5H_4Me)_2Mn_2(NO)_2(CO)(NH_2)]BPh_4$ (trans isomer), 86391-50-6.

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# Communications

## Catalytic Effect of Bases on the Formation of $HCo(CO)_4$ from $Co_2(CO)_8$ and $H_2$

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*Summary:* The hydrogenation of $Co_2(CO)_8$ to $HCo(CO)_4$ is catalyzed by tertiary amines, nitrogen heterocycles, tertiary phosphorus bases (with $pK_a \geq 5$), and halide ions. For example, with 28 mol % of pyridine based on $Co_2(CO)_8$, the rate of $HCo(CO)_4$ formation may be increased about 300-fold at 40 °C.

The stoichiometric reaction of $HCo(CO)_4$ with olefins to yield aldehydes proceeds smoothly at room temperature and atmospheric pressure.[1,2] However, cobalt-catalyzed hydroformylation is generally carried out at high pressures and temperatures.[3] Obviously, only the formation of $HCo(CO)_4$ from $Co_2(CO)_8$ by $H_2$ needs drastic conditions. Consequently the catalytic hydroformylation should be possible under much milder conditions if the very slow hydrogenation of $Co_2(CO)_8$ to $HCo(CO)_4$ could be accelerated.[4]

The effect of bases on hydroformylation was already the subject of numerous studies. Experiments were carried out under "hydroformylation conditions", and in most cases an inhibition or only a moderate activation was found.[3,5] The most detailed study was carried out by Iwanaga,[6] who observed that the effect of nitrogen bases depends on their basicity, pyridine and its derivatives giving the best results. In all these works, however, relatively large amounts of additives were used (above 1 mol/mol Co) which inevitably leads to $[Co(CO)_4]^-$ formation due to the disproportionation of $Co_2(CO)_8$.[7] Since

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