

Manganese(I) and Chromium(0) Complexes of Phenyl Isocyanide

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The syntheses of $[\text{Mn}(\text{CO})_{6-n}(\text{CNC}_6\text{H}_5)_n]\text{PF}_6$ complexes ($n = 2-6$) are accomplished from reactions of $\text{Mn}(\text{CO})_{5-n}(\text{CNC}_6\text{H}_5)_n\text{Br}$, either CO or CNC_6H_5 , and a halide acceptor. Stereospecific replacement of Br^- by CO or CNC_6H_5 occurs in these syntheses; this specificity permits the syntheses of the isomers *fac*- and *mer*- $[\text{Mn}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3]\text{PF}_6$ and *cis*- and *trans*- $[\text{Mn}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4]\text{PF}_6$. Cyclic voltammetry defines $E_{1/2}$ values for one-electron oxidations of each member of this series. The values of $E_{1/2}$ decrease in a linear fashion with each additional CNC_6H_5 substitution. The syntheses of *cis*- $\text{Cr}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4$ and $\text{Cr}(\text{CO})(\text{CNC}_6\text{H}_5)_5$ from $\text{Cr}(\text{CO})_6$ and $\text{Cr}(\text{CNC}_6\text{H}_5)_6$ are described. Electrochemical data on these compounds are obtained, but this investigation is complicated by rapid ligand redistribution of the products derived on one-electron oxidation. From a reevaluation of the redox data for the series of compounds $\text{Cr}(\text{CO})_{6-n}(\text{CNC}_6\text{H}_5)_n$ ($n = 0-6$), we conclude that the previously suggested 1-oxidation state complexes $[\text{Cr}(\text{CNR})_6]^-$ are incorrectly formulated. The electrochemical data on this system seem best in accord with the three sequential one-electron oxidation processes $\text{Cr}(\text{CNR})_6 = [\text{Cr}(\text{CNR})_6]^+ = [\text{Cr}(\text{CNR})_6]^{2+} = [\text{Cr}(\text{CNR})_6]^{3+}$.

Introduction

The compounds $[\text{Mn}(\text{CO})_{6-n}(\text{CNCH}_3)_n]\text{PF}_6$ ($n = 1-6$), synthesized in our group, have been shown to undergo one-electron oxidations according to cyclic voltammetry.^{1,2} The potentials required for these oxidation processes decrease regularly with CNCH_3 substitution (increasing n in the formula). This result is attributable to a buildup of negative charge on the metal site, imposed by the presence of additional CNCH_3 ligands which are better electron donors than CO. A recent theoretical study³ showed that the experimental values of $E_{1/2}$ correlate directly with calculated HOMO energy values.

One might expect the electrochemistry of isoelectronic chromium(0) complexes of phenyl isocyanides, $\text{Cr}(\text{CO})_{6-n}(\text{CNC}_6\text{H}_5)_n$, to be quite similar, but the first data on these complexes suggested that perhaps this might not be the case. The value of $E_{1/2}$ assigned⁴ to the couple $\text{Cr}(\text{CNC}_6\text{H}_4\text{CH}_3)_6 = [\text{Cr}(\text{CNC}_6\text{H}_4\text{CH}_3)_6]^+ + e^-$, 0.15 V vs. SCE in CH_2Cl_2 , is distinctly higher than might have been anticipated from the $E_{1/2}$ data reported earlier by McCleverty and co-workers⁵ on the compounds $\text{Cr}(\text{CO})_{6-n}(\text{CNC}_6\text{H}_4\text{CH}_3)_n$ ($n = 0-3$) in the same solvent. However, at the time of the work we attributed no significance to this fact, assuming that an explanation existed, perhaps based on uncertainty of the extrapolation (since the chromium(0) compounds $\text{Cr}(\text{CO})_{6-n}(\text{CNC}_6\text{H}_5)_n$, $n = 2$, *trans* isomer, $n = 3$, *mer* isomer, and $n = 4, 5$, were unknown) or perhaps because of inaccuracy of the simple theory rationalizing these results. However, as the work described here shows, the message in the earlier work is real enough; it is pointing to an error in our original assignment of the $E_{1/2}$ value to this oxidation process.

The work described in this paper is on two different studies. One is the synthesis and electrochemistry of the complexes $[\text{Mn}(\text{CO})_{6-n}(\text{CNC}_6\text{H}_5)_n]\text{PF}_6$, isoelectronic with $\text{Cr}(\text{CO})_{6-n}(\text{CNC}_6\text{H}_5)_n$. This study was initiated for a second purpose as well, to provide further examples of the stereospecific replacement of a halide ion in the complexes $\text{Mn}(\text{CO})_{5-n}(\text{CNC}_6\text{H}_5)_n\text{Br}$ by an entering ligand (CO or CNC_6H_5).² The second study concerns the synthesis of two missing members of the chromium(0) series, $\text{Cr}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4$ and $\text{Cr}(\text{CO})(\text{CNC}_6\text{H}_5)_5$. The electrochemical data on these species turn out to be peculiar but nonetheless informative to the overall problem described here.

Experimental Section

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Melting points were taken with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on Beckman IR-10 and Perkin-Elmer 457 spectrophotometers. Proton NMR spectra were recorded on a Jeol MH-100

spectrometer. Infrared and NMR data are presented in Table I.

Electrochemical measurements were made at 25 °C by using a three electrode configuration, employing a stationary platinum bead working electrode, a platinum spiral counter electrode, and a saturated calomel (aqueous KCl) reference electrode. Voltage and current functions were controlled with a Princeton Applied Research electrochemistry system, Model 169, incorporating compensation for internal resistive potential drop. Tetrabutylammonium perchlorate (0.1 M) was employed as the base electrolyte. Dry CH_2Cl_2 was used as a solvent. Substrate concentrations were $\sim 5 \times 10^{-3}$ M. Sweep rates were varied from 50 to 500 mV/s in order to achieve optimum peak shapes. Data are given in Table II.

The compounds $\text{Mn}(\text{CO})(\text{CNC}_6\text{H}_5)_4\text{Br}$, $[\text{Mn}(\text{CNC}_6\text{H}_5)_6]\text{PF}_6$, and $[\text{Mn}(\text{CO})(\text{CNC}_6\text{H}_5)_5]\text{PF}_6$ were prepared by published procedures.¹ Purity was verified by infrared data and by melting point. The known compounds $\text{Cr}(\text{CO})_{6-n}(\text{CNC}_6\text{H}_5)_n$ were prepared by the cited methods: $\text{Cr}(\text{CO})_5(\text{CNC}_6\text{H}_5)$, from $[\text{Cr}(\text{CO})_5\text{Cl}]^- + \text{CNC}_6\text{H}_5$;⁶ *cis*- $\text{Cr}(\text{CO})_4(\text{CNC}_6\text{H}_5)_2$, from $\text{Cr}(\text{CO})_4(\text{bicycloheptadiene}) + \text{CNC}_6\text{H}_5$;⁵ *fac*- $\text{Cr}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3$, from $\text{Cr}(\text{CO})_3(\text{cycloheptatriene}) + \text{CNC}_6\text{H}_5$.⁷ Each product was purified by repeated crystallizations and characterized by infrared data ($\nu(\text{CO})$ and $\nu(\text{CN})$) and melting point.⁶

The compounds *fac*- $\text{Mn}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3\text{Br}$ and *mer-cis*- $\text{Mn}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4\text{Br}$ are known,⁸ but reported synthetic procedures were difficult to reproduce, so these syntheses are described below.

Preparation of *fac*- $\text{Mn}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3\text{Br}$. A sample of $\text{Mn}(\text{CO})_5\text{Br}$ (2.75 g, 1.0 mmol) was dissolved in 50 mL of THF and 2.06 g (2.0 mmol) of CNC_6H_5 added. The solution was stirred for 30 h at room temperature, the solvent evaporated, and the residue recrystallized from dichloromethane/heptane giving 3.7 g (86% yield) of yellow crystals (mp 84–86 °C; $\nu(\text{CN})$ 2198 (m), 2174 (s); $\nu(\text{CO})$ 2053 (s), 2004 (s), 1954 (s) cm^{-1}).⁸

Preparation of *mer-cis*- $\text{Mn}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4\text{Br}$. Solid $\text{Mn}(\text{CO})_5\text{Br}$ (2.06 g, 0.75 mmol) is dissolved in 75 mL of THF, and 2.31 g (22.4 mmol) of freshly distilled phenyl isocyanide was added. The reaction was brought to reflux for 2 h, and the solvent was evaporated. Chromatography of a portion of the residue was carried out on a 15-in. column of alumina packed on chloroform. Two yellow bands develop with the use of CHCl_3 ; the first was mostly $\text{Mn}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3\text{Br}$; the second, a broad band (mostly $\text{Mn}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4\text{Br}$), was eluted in fractions, the $\nu(\text{CN})$ stretching frequencies being examined until $\text{Mn}(\text{CO})(\text{CNC}_6\text{H}_5)_4\text{Br}$ was detected. This chromatographic fraction was evaporated and the residue crystallized from $\text{CH}_2\text{Cl}_2/\text{C}_7\text{H}_{16}$ giving 1.5 g (40% yield) of $\text{Mn}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4\text{Br}$ yellow crystals (mp 129–130 °C; $\nu(\text{CN})$ 2173 (w), 2133 (m), 2109 (s); $\nu(\text{CO})$ 2020 (s), 1942 (s) cm^{-1}).⁸ Also obtained from this reaction was ~ 0.6 g (20% yield) of $\text{Mn}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3\text{Br}$ and ~ 1.1 g (25% yield) of $\text{Mn}(\text{CO})(\text{CNC}_6\text{H}_5)_4\text{Br}$. It is noted the relative yields of the di-, tri-, and tetrasubstituted compounds can vary substantially.

Preparation of *cis*- $[\text{Mn}(\text{CO})_4(\text{CNC}_6\text{H}_5)_2]\text{PF}_6$. A sample of AlCl_3 (1.2 g, 9 mmol) was suspended in 40 mL of benzene, and carbon monoxide was bubbled slowly through for 1 min. A solution of 1.3 g (3.0 mmol) of $\text{Mn}(\text{CO})_3(\text{CNC}_6\text{H}_5)_2\text{Br}$ dissolved in 15 mL of benzene was then added and CO bubbling continued for 30 min. Benzene was decanted, and the red oil that remained was taken up in ice water

Table I. Infrared and NMR Data

	$\nu(\text{CN})^a, \text{cm}^{-1}$	$\nu(\text{CO})^a, \text{cm}^{-1}$	NMR, δ^b
<i>cis</i> -[Mn(CO) ₄ (CNC ₆ H ₅) ₂]PF ₆	2208 m, 2182 m	2117 s, 2064 vs, sh, 2052 vs	7.60 m
<i>mer</i> -[Mn(CO) ₃ (CNC ₆ H ₅) ₃]PF ₆	2204 w, 2167 s, sh, 2151 vs	2094 m, 2032 vs	7.66 m
<i>fac</i> -[Mn(CO) ₃ (CNC ₆ H ₅) ₃]PF ₆	2208 w, 2171 s, 2136 w	2068 s, 2024 s, br	7.58 m
<i>cis</i> -[Mn(CO) ₂ (CNC ₆ H ₅) ₄]PF ₆	2200 w, 2152 s, 2133 vs	2027 s, 1998 m	7.54 m
<i>trans</i> -[Mn(CO) ₂ (CNC ₆ H ₅) ₄]PF ₆	2126 vs	2000 s	7.54 s ^c
[Mn(CO)(CNC ₆ H ₅) ₅]PF ₆ ^d	2192 w, 2136 sh, 2111 vs	1991 s	
[Mn(CNC ₆ H ₅) ₆]PF ₆ ^d	2088 vs		
<i>cis</i> -Cr(CO) ₂ (CNC ₆ H ₅) ₄	2125 w, 2015 s, 2005 s, 1985 s	1945 s, 1900 vs, b	
Cr(CO)(CNC ₆ H ₅) ₅	2100 w, 1995 m, 1975 s, br	1885 s, b	

^a CH₂Cl₂ solutions; $\nu(\text{CO})$, $\nu(\text{CN})$ data on a PE 457 ± 1 cm⁻¹. ^b CDCl₃ solutions, except noted, vs. Me₄Si. ^c CD₃CN solution. ^d Literature values.¹

Table II. Electrochemical Data^a

compd	$1/2[E_{p,c} + E_{p,a}], \text{V}$	$ E_{p,c} - E_{p,a} , \text{V}$	comments
<i>cis</i> -[Mn(CO) ₄ (CNC ₆ H ₅) ₂]PF ₆	2.28	0.125	
<i>mer</i> -[Mn(CO) ₃ (CNC ₆ H ₅) ₃]PF ₆	1.98	0.226	
<i>fac</i> -[Mn(CO) ₃ (CNC ₆ H ₅) ₃]PF ₆	2.12	0.210	
<i>cis</i> -[Mn(CO) ₂ (CNC ₆ H ₅) ₄]PF ₆	1.70	0.176	
<i>trans</i> -[Mn(CO) ₂ (CNC ₆ H ₅) ₄]PF ₆	1.54	0.216	
[Mn(CO)(CNC ₆ H ₅) ₅]PF ₆ ^b	1.28, 2.21	0.248, 0.234	
[Mn(CNC ₆ H ₅) ₆]PF ₆ ^b	1.00, 1.90	0.193, 0.200	
Cr(CO) ₆	1.43	0.105	
Cr(CO) ₅ (CNC ₆ H ₅)	1.09		
<i>cis</i> -Cr(CO) ₄ (CNC ₆ H ₅) ₂	0.74, 1.67	0.125 ^d	
<i>fac</i> -Cr(CO) ₃ (CNC ₆ H ₅) ₃	0.56, 1.29	0.120, 0.320	
<i>cis</i> -Cr(CO) ₂ (CNC ₆ H ₅) ₄	-0.71	0.200	
	0.14	0.130	Cr(CO)L ₄ ⇌ [Cr(CO) ₂ L ₄] ⁺ + e ⁻
	0.48	0.090	Cr(CO) ₃ L ₃ →
	0.81	0.230	[Cr(CO) ₂ L ₄] ⁺ ⇌ [Cr(CO) ₂ L ₄] ²⁺ + e ⁻ and Cr(CO) ₄ L ₂ →
	1.26	<i>d</i>	Cr(CO) ₃ L ₃ →
	1.60	<i>d</i>	[Cr(CO) ₄ L ₂] ⁺ →
Cr(CO)(CNC ₆ H ₅) ₅	-0.55	0.040	
	-0.15	0.060	Cr(CO)L ₅ ⇌ [Cr(CO)L ₅] ⁺ + e ⁻
	0.13	0.080	Cr(CO) ₂ L ₄ →
	0.51	0.130	[Cr(CO)L ₅] ⁺ ⇌ [Cr(CO)L ₅] ²⁺ + e ⁻ and Cr(CO) ₃ L ₃ →
	0.80	0.110	[Cr(CO) ₂ L ₄] → and Cr(CO) ₄ L ₂ →
	1.23	0.190	[Cr(CO) ₃ L ₃] →
	1.60	<i>d</i>	[Cr(CO) ₄ L ₂] ⁺ →
Cr(CNC ₆ H ₅) ₆ ^c	-0.32	0.090	CrL ₆ ⇌ [CrL ₆] ⁺ + e ⁻
	0.15	0.080	[CrL ₆] ⁺ ⇌ [CrL ₆] ²⁺ + e ⁻
	0.90	0.095	[CrL ₆] ²⁺ ⇌ [CrL ₆] ³⁺ + e ⁻

^a Concentration of compound approximately 5 × 10⁻³ M; tetrabutylammonium perchlorate (0.1 M) used as supporting electrolyte; peak potentials reported in V vs. SCE (aqueous KCl). ^b Reference 1. ^c Reference 4. ^d Anodic peak observed only. ^e See text.

and excess NH₄PF₆ added, and the white precipitate that formed was filtered. The precipitate was dissolved in THF and filtered through anhydrous MgSO₄, followed by filtration through a 1-in. column of alumina packed with THF. Solvent was evaporated, and the white solid product remaining was recrystallized from acetone/ether. The compound melted at 175 °C and decomposed at 179 °C (85% yield). Anal. Calcd for C₁₈H₁₀F₆O₄N₂PmN: C, 41.70; N, 5.41; H, 1.93. Found: C, 41.68; N, 5.80; H, 1.95.

Preparation of *mer*-[Mn(CO)₃(CNC₆H₅)₃]PF₆. This compound was prepared as above from *mer-cis*-Mn(CO)₂(CNC₆H₅)₃Br, AlCl₃, and CO, followed by metathesis with NH₄PF₆. It was isolated as yellow-white crystals, mp 189–91 °C (87% yield). Anal. Calcd for C₂₄H₁₅F₆N₃O₃Mn: C, 48.59; N, 7.08; H, 2.55. Found: C, 48.78; N, 6.86; H, 2.50.

Preparation of *trans*-[Mn(CO)₂(CNC₆H₅)₄]PF₆. Aluminum chloride (0.35 g, 2.6 mmol) was suspended in 40 mL of benzene, and carbon monoxide was slowly bubbled through the mixture for 1 min. A solution of 1.0 g (1.7 mmol) of Mn(CO)(CNC₆H₅)₃Br in 20 mL of benzene was then added, and CO bubbling was continued for 30 min. To the resulting red-black solution was added aqueous NH₄PF₆. The brown precipitate that formed was filtered and washed with a 1/1 benzene/tetrahydrofuran mixture to give a white product, which was dissolved in THF. This solution was passed through a 1-in. column of alumina packed with THF. The solvent was evaporated, giving a white product which was recrystallized from acetone/ether. The compound darkened at 212 °C and decomposed at 214–217 °C (24% yield). Anal. Calcd for C₃₀H₂₀F₆N₄O₂Mn: C, 53.93; N, 8.39; H,

3.02. Found: C, 53.74; N, 8.26; H, 3.06.

Preparation of *fac*-[Mn(CO)₃(CNC₆H₅)₃]PF₆. A solution of 1.35 g (5.5 mmol) of AgPF₆ and 0.42 g (4.0 mmol) of phenyl isocyanide in 25 mL of THF was prepared. A solution of 1.3 g (3.0 mmol) of Mn(CO)₃(CNC₆H₅)₂Br in 25 mL of THF was added, and the reaction was stirred for 2.0 h. Solvent was evaporated, and the residue was dissolved in CH₂Cl₂ and filtered. This solvent was evaporated, and the material remaining was dissolved in THF and filtered through a 1-in. column of alumina packed on THF. After evaporation of THF, the white solid was recrystallized from acetone/ether; mp 160–161 °C (64% yield). Anal. Calcd for C₂₄H₁₅F₆N₃O₃Mn: C, 48.59; N, 7.08; H, 2.55. Found: C, 48.94; N, 6.94; H, 2.87.

Preparation of *cis*-[Mn(CO)₂(CNC₆H₅)₄]PF₆. This compound was prepared as above from Mn(CO)₂(CNC₆H₅)₃Br, phenyl isocyanide, and AgPF₆. The white compound melted at 201–203 °C (70% yield). Anal. Calcd for C₃₀H₂₀F₆N₄O₂Mn: C, 53.93; N, 8.39; H, 3.02. Found: C, 54.03; N, 8.21; H, 3.07.

Repeated attempts were made to synthesize [Mn(CO)₅(CNC₆H₅)₂]PF₆ by various routes. A white powdery material, isolated in low yield from the reaction of Mn(CO)₄(CNC₆H₅)Br with AlCl₃ and CO, had a Nujol mull IR spectrum consistent with this compound ($\nu(\text{CN})$ 2209 (m) cm⁻¹; $\nu(\text{CO})$ 2155 (m), 2076 (vs, br) cm⁻¹), but this material could not be recrystallized without decomposition.

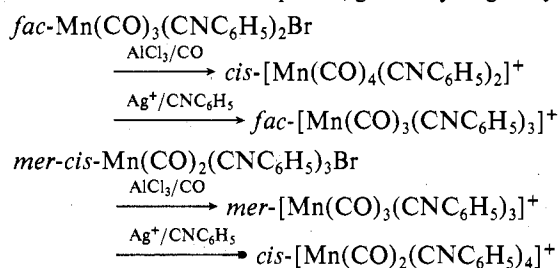
Preparation of *cis*-Cr(CO)₂(CNC₆H₅)₄. Hexakis(phenyl isocyanide)chromium(0) (1.0 g, 1.5 mmol), chromium hexacarbonyl (0.16 g, 0.75 mmol), and 10 mL of toluene were sealed in an evacuated Carius tube. The vessel was placed in an oven at 140 °C for 4 days.

At the end of this time, the tube was cooled to room temperature and then to -78°C and opened. The contents of the vessel were rinsed out with dichloromethane. The volume of this mixture was decreased to 10 mL, and this solution was placed on an acid-washed alumina chromatography column. Benzene was used to elute a large yellow band which was collected. The volume of the solution was reduced slightly, and then a (1/1) hexane and diethyl ether mixture was added. Cooling of this solution resulted in the formation of 0.5 g of a bright yellow precipitate, which was filtered, washed with hexane, and vacuum dried. It was recrystallized with difficulty from dichloromethane/hexane; mp $108\text{--}111^{\circ}\text{C}$ (64% yield). Anal. Calcd for $\text{C}_{30}\text{H}_{20}\text{O}_2\text{N}_4\text{Cr}$: C, 69.22; H, 3.87; N, 10.77. Found: C, 69.60; H, 4.06; N, 10.31.

Preparation of $\text{Cr}(\text{CO})(\text{CNC}_6\text{H}_5)_5$. A sealed-tube reaction between hexakis(phenyl isocyanide)chromium(0) (1.0 g, 1.5 mmol) and chromium hexacarbonyl (0.66 g, 0.3 mmol) was carried out in a manner analogous to the method employed for the preparation of $\text{Cr}(\text{CO})_2(\text{C}_6\text{H}_5\text{NC})_4$. Crystallization of the chromatographed fraction from dichloromethane/hexane yielded 0.40 g of bright orange crystals which were filtered from solution, washed with cold hexane, and vacuum dried; mp $115\text{--}117^{\circ}\text{C}$ (38% yield). Anal. Calcd for $\text{C}_{36}\text{H}_{25}\text{ON}_3\text{Cr}$: C, 72.59; H, 4.23; N, 11.76. Found: C, 71.43; H, 4.30; N, 11.54.

Discussion

The synthesis of the manganese(I) complexes, $[\text{Mn}(\text{CO})_{6-n}(\text{CNC}_6\text{H}_5)_n]\text{PF}_6$, is quite straightforward. The precursors to these complexes, $\text{Mn}(\text{CO})_{5-n}(\text{CNC}_6\text{H}_5)_n\text{Br}$ ($n = 2\text{--}4$), can be prepared from $\text{Mn}(\text{CO})_5\text{Br}$ by carbonyl substitution reactions, the extent of substitution being controlled by the reaction stoichiometry and by the temperature.¹ Treating these compounds with additional ligand (CO or CNC_6H_5) in the presence of a halide acceptor (AlCl_3 or Ag^+) gives the desired cationic complexes, generally in good yield:



These complexes either were formed as PF_6^- salts when AgPF_6 was used as a halide acceptor or were converted to PF_6^- salts in metathesis reactions with NH_4PF_6 . The hexafluorophosphate salts are white to pale yellow, crystalline, and air stable. In addition to characterization by microanalytical data, the infrared spectra in the 2000-cm^{-1} region ($\nu(\text{CN})$ and $\nu(\text{CO})$; see Table I) confirmed the defined geometry.

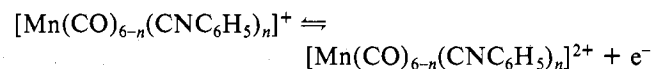
Evident is the stereospecificity of these reactions in which the entering ligand (either CO or CNC_6H_5) is attached to the metal at the site previously occupied by the halide ion. This result concurs with the results obtained in earlier syntheses of members of the $[\text{Mn}(\text{CO})_{6-n}(\text{CNCH}_3)_n]\text{PF}_6$ series.²

The synthesis of the two $\text{Cr}(\text{CO})_{6-n}(\text{CNC}_6\text{H}_5)_n$ compounds ($n = 4, 5$) presented more uncertainty. It seemed unlikely that direct replacement of more than three carbonyls in $\text{Cr}(\text{CO})_6$ by CNC_6H_5 was likely to occur; this reaction had been studied before, and, it appears, the final product is $\text{Cr}(\text{CO})_5(\text{CNC}_6\text{H}_5)$.⁶ To obtain $\text{Cr}(\text{CO})_4(\text{CNC}_6\text{H}_5)_2$ or $\text{Cr}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3$ it had been necessary to start with a chromium complex having ligands more easily replaced than CO, such as CH_3CN , NH_3 , Cl^- , or the hydrocarbons bicycloheptadiene or cycloheptatriene. Such reactions are not easily extendable to the synthesis of tetrasubstituted or pentasubstituted compounds since appropriate chromium precursors do not exist. It is noted, though, that such a route to the molybdenum and tungsten complexes, $\text{M}(\text{CO})_2(\text{CNC}(\text{CH}_3)_3)_4$, has been reported.⁹

We chose to investigate two alternatives for syntheses of $\text{Cr}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4$ and $\text{Cr}(\text{CO})(\text{CNC}_6\text{H}_5)_5$. The first was carbonylation of $\text{Cr}(\text{CNC}_6\text{H}_5)_6$, utilizing moderate temperature and pressure. Although infrared data on these reaction products seemed to indicate the formation of new products, this route was eventually discarded. Yields were clearly low, and mixtures seemed to be present; moreover, there was a tendency for the reaction to proceed past the desired species to complexes having three or more carbonyls. Ultimately we chose a sealed-tube reaction of $\text{Cr}(\text{CO})_6$ and $\text{Cr}(\text{CNC}_6\text{H}_5)_6$ as a route to these compounds. Here the stoichiometry could be precisely controlled to give the desired products.

These compounds are crystalline solids, orange in the case of $\text{Cr}(\text{CO})(\text{CNC}_6\text{H}_5)_5$ and yellow for the second compound, $\text{Cr}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4$. The progression of color, from the dark red of $\text{Cr}(\text{CNC}_6\text{H}_5)_6$ through orange and bright yellow to the pale yellow of $\text{Cr}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3$, is striking. The infrared spectrum of $\text{Cr}(\text{CO})(\text{CNC}_6\text{H}_5)_5$ shows a single $\nu(\text{CO})$ at 1885 cm^{-1} and the expected three $\nu(\text{CN})$ bands for C_{4v} symmetry at 2100 (w), 1995 (m), and 1975 (s) cm^{-1} . In comparison the values of $\nu(\text{CO})$ at 1991 cm^{-1} and $\nu(\text{CN})$ at 2192 (w), 2136 (sh), and 2111 (s) cm^{-1} for the isoelectronic complex $[\text{Mn}(\text{CO})(\text{CNC}_6\text{H}_5)_5]^+$, as the PF_6^- salt, are noted.¹ Two $\nu(\text{CO})$ peaks at 1945 (s) and 1900 (vs) and four $\nu(\text{CN})$ peaks at 2125 (w), 2015 (s), 2005 (s), and 1985 (s) cm^{-1} are recorded for $\text{Cr}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4$. These data identify the species as the cis isomer, although it is not possible to be sure of the complete absence of small amounts of the trans compound. The infrared pattern is the same pattern as was seen for *cis*- $[\text{Mn}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4]^+$ but is shifted to lower frequency, as expected, due to the lower net charge on the complex.

Each member of the series $[\text{Mn}(\text{CO})_{6-n}(\text{CNC}_6\text{H}_5)_n]\text{PF}_6$ was shown by cyclic voltammetry to undergo a one-electron oxidation, viz.



Anodic and cathodic currents are equal, indicating chemical reversibility in these systems. In addition, the compounds with $n = 5$ and $n = 6$ show a second one-electron oxidation, corresponding to formation of a manganese(III) species. The separations of peaks for the anodic and cathodic processes are always greater than 0.060 V, and these values vary with scan rate, indicative of quasi-reversible processes. In all respects this is the same behavior as had been observed with $[\text{Mn}(\text{CO})_{6-n}(\text{CNCH}_3)_n]^+$ complexes.¹ The voltages measured in the two series are different, of course, the higher $E_{1/2}$ values in the phenyl isocyanide complexes reflecting the fact that this ligand is a better acceptor than CNCH_3 .¹⁰

It is noted, in passing, that there has been considerable study of the chemical oxidations of $[\text{Mn}(\text{CNR})_6]^+$ complexes to the isolable $[\text{Mn}(\text{CNR})_6]^{2+}$ complexes. It is on the basis of this chemistry that these oxidation processes are assigned.

Substitution of CNC_6H_5 for CO in this series lowers the value of $E_{1/2}$ by about 0.30 V, a consequence of increasing electron density at the metal site because of the relative donor ability of CNC_6H_5 vs. CO. *cis*- and *trans*- $[\text{Mn}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4]\text{PF}_6$ and *fac*- and *mer*- $[\text{Mn}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3]\text{PF}_6$ have somewhat different $E_{1/2}$ values, the *trans* and *mer* isomers oxidizing at lower potentials than the *cis* and *fac* isomers, respectively. This is the same result as that obtained for the $[\text{Mn}(\text{CO})_{6-n}(\text{CNCH}_3)_n]\text{PF}_6$ ($n = 3, 4$) compounds, and the rationale offered in the earlier work² based on preferential stabilization of d_{xy} , d_{xz} , or d_{yz} orbitals applies here also.

Specific attention is directed to Figure 1, representing $E_{1/2}$ vs. n in $[\text{Mn}(\text{CO})_{6-n}(\text{CNR})_n]\text{PF}_6$ ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$). The regular decrease of $E_{1/2}$ with increasing CNR substitution is clearly identified for both series. The values of $E_{1/2}$ decrease

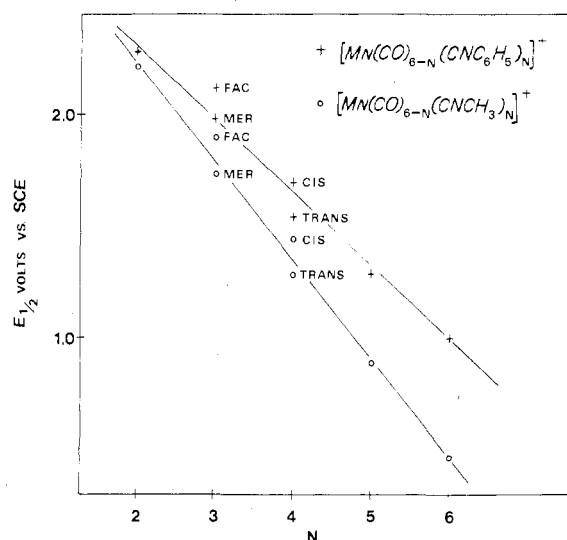
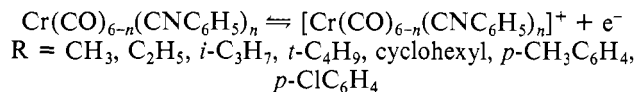


Figure 1. $E_{1/2}$ vs. n , the number of isocyanide ligands, for the processes $[\text{Mn}(\text{CO})_{6-n}(\text{CNR})_n]^+ \rightleftharpoons [\text{Mn}(\text{CO})_{6-n}(\text{CNR})_n]^{2+} + e^-$ ($\text{R} = \text{CH}_3$, C_6H_5) in CH_2Cl_2 .

more rapidly within the series of methyl isocyanide complexes. This indicates that CNCH_3 effects a greater negative charge buildup than the better π acceptor CNC_6H_5 .

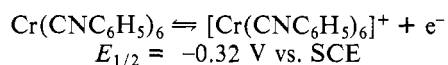
Electrochemistry on the chromium complexes proved to be not so straightforward however. Preceding the work described here, it was shown⁶ that the earlier members of the series $\text{Cr}(\text{CO})_{6-n}(\text{CNR})_n$ ($n = 1-3$) undergo single reversible one-electron oxidations, corresponding to the half reactions



In addition, three sequential one-electron oxidations were identified for $\text{Cr}(\text{CNC}_6\text{H}_5)_6$ and for other $\text{Cr}(\text{CNR})_6$ complexes.^{4,11} These were initially assigned to one-electron oxidation processes involving the complexes $[\text{Cr}(\text{CNR})_6]^-$, $\text{Cr}(\text{CNR})_6$, $[\text{Cr}(\text{CNR})_6]^+$, and $[\text{Cr}(\text{CNR})_6]^{2+}$. Examples of the last three types of complexes were isolated and characterized in our earlier work.⁴ However, attempts to reduce $\text{Cr}(\text{CNR})_6$ compounds to give $[\text{Cr}(\text{CNR})_6]^-$ species have not been successful, a result about which we have held some concern.

We were also concerned, though not excessively, by the formulation of complexes $[\text{Cr}(\text{CNR})_6]^-$ which are one electron in excess of an EAN configuration. No similar species are suggested by electrochemical data on the isoelectronic manganese compounds $[\text{Mn}(\text{CNR})_6]^+$ or, for that matter, by electrochemical data on any mononuclear 18-electron isocyanide complex, $\text{M}(\text{CNR})_x^{n+}$.

The concern over the existence of a presumed $[\text{Cr}(\text{CNR})_6]^-$ complex was heightened, however, when we realized that extrapolation from $E_{1/2}$ values for the early members of the series $\text{Cr}(\text{CO})_{6-n}(\text{CNC}_6\text{H}_5)_n$ ($n = 1-3$) predicted an $E_{1/2}$ for $\text{Cr}(\text{CNC}_6\text{H}_5)_6$ of about -0.3 V (see Figure 2). The same extrapolation applies excellently in the series of isoelectronic manganese complexes. The value of -0.3 V is approximately the value that we had previously assigned to the $[\text{Cr}(\text{CNC}_6\text{H}_5)_6]^- \rightleftharpoons \text{Cr}(\text{CNC}_6\text{H}_5)_6 + e^-$ couple. Taken with the other data enumerated above, it makes more sense to assign the first oxidation of this species to the half-reaction



and subsequent oxidations to processes involving conversions

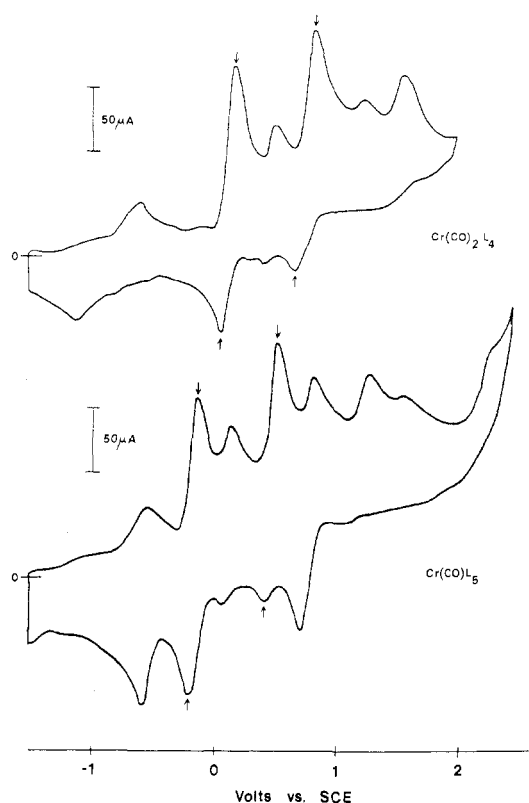
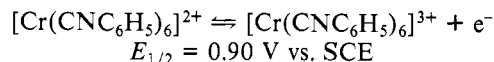
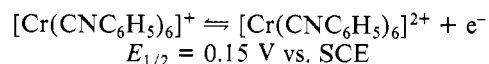


Figure 2. Cyclic voltammograms for $\text{Cr}(\text{CO})_{6-n}(\text{CNC}_6\text{H}_5)_n \rightleftharpoons [\text{Cr}(\text{CO})_{6-n}(\text{CNC}_6\text{H}_5)_n]^+ + e^-$ ($n = 4, 5$) in CH_2Cl_2 . Peaks for the designated compounds are denoted with arrows.

to the di- and trivalent states $[\text{Cr}(\text{CNC}_6\text{H}_5)_6]^{2+}$ and $[\text{Cr}(\text{CNC}_6\text{H}_5)_6]^{3+}$, respectively.



The formulation of $[\text{Cr}(\text{CNC}_6\text{H}_5)_6]^{3+}$ in the last step of this oxidation seems most reasonable, since chromium(III) complexes, having a d^3 configuration, are very common. These complexes were not isolated in earlier work⁴ on the oxidations of CrL_6 compounds. Low stability to ligand loss was found for $[\text{Cr}(\text{CNR})_6]^{2+}$ complexes, and the trivalent complexes are probably unstable, also decomposing by this route.

The electrochemical data on $\text{Cr}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4$ and $\text{Cr}(\text{CO})(\text{CNC}_6\text{H}_5)_5$ were unexpectedly complicated but appear to support this extrapolation. Cyclic voltammograms on each of these complexes in CH_2Cl_2 at 25°C were run, showing a complicated pattern of oxidations and reductions (Figure 2). However, most of the $E_{1/2}$ values could be assigned. For the former compound, values of 0.14 and 0.81 V appear to correspond with the two processes $\text{Cr}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4 \rightleftharpoons [\text{Cr}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4]^+ + e^-$ and $[\text{Cr}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4]^+ \rightleftharpoons [\text{Cr}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4]^{2+} + e^-$, respectively. For the latter species, the oxidations at $E_{1/2} = -0.15$ V and $E_{1/2} = -0.51$ V were assigned to similar processes, $\text{Cr}(\text{CO})(\text{CNC}_6\text{H}_5)_5 \rightleftharpoons [\text{Cr}(\text{CO})(\text{CNC}_6\text{H}_5)_5]^+ + e^-$ and $[\text{Cr}(\text{CO})(\text{CNC}_6\text{H}_5)_5]^+ \rightleftharpoons [\text{Cr}(\text{CO})(\text{CNC}_6\text{H}_5)_5]^{2+} + e^-$. These results correspond to the predicted values well (see Figure 3).

In the CV experiment on $\text{Cr}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4$ the peaks at 0.48 and 1.26 V are very close to $E_{1/2}$ values for *fac*- $\text{Cr}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3$, and the value of 1.60 V is similar to the $E_{1/2}$ of the second oxidation of *cis*- $\text{Cr}(\text{CO})_4(\text{CNC}_6\text{H}_5)_2$. (The first oxidation of the latter species at 0.74 V would be masked by the oxidation of $[\text{Cr}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4]^+$.) For $\text{Cr}(\text{C}$

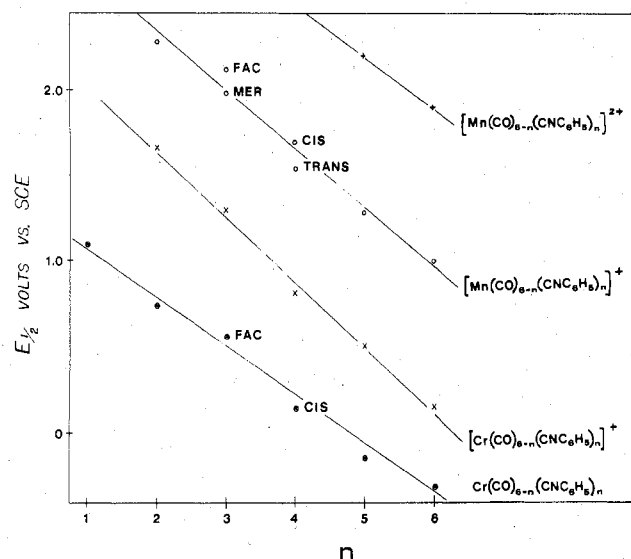


Figure 3. $E_{1/2}$ vs. n , the number of isocyanide ligands, for the processes $[\text{Mn}(\text{CO})_{6-n}(\text{CNC}_6\text{H}_5)_n]^{n+} \rightleftharpoons [\text{Mn}(\text{CO})_{6-n}(\text{CNC}_6\text{H}_5)_n]^{(n+1)+} + e^-$ ($M = \text{Mn}$ for processes $\text{Mn}^+ \rightarrow \text{Mn}^{2+}$, $\text{Mn}^{2+} \rightarrow \text{Mn}^{3+}$; $M = \text{Cr}$ for processes $\text{Cr}^0 \rightarrow \text{Cr}^+$, $\text{Cr}^+ \rightarrow \text{Cr}^{2+}$) in CH_2Cl_2 .

$\text{O}(\text{CNC}_6\text{H}_5)_5$, $E_{1/2}$ values at 0.13 and 0.80 V correspond to oxidation processes for $\text{Cr}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4$, and the $E_{1/2}$ values of 1.23 and 1.60 V are similar to the second oxidations of *fac*- $\text{Cr}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3$ and *cis*- $\text{Cr}(\text{CO})_4(\text{CNC}_6\text{H}_5)_2$. We are quite confident of the purity of the starting materials in these systems; they are crystalline products having clean melting points and no spurious $\nu(\text{CO})$ or $\nu(\text{CN})$ infrared absorptions. Thus we are led to the conclusion that upon oxidation these compounds must undergo a rapid exchange of ligands to generate the products observed by the CV ex-

periment in solution. We are currently trying to test out this hypothesis.

Registry No. *cis*- $[\text{Mn}(\text{CO})_4(\text{CNC}_6\text{H}_5)_2]\text{PF}_6$, 70800-83-8; *mer*- $[\text{Mn}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3]\text{PF}_6$, 70877-81-5; *fac*- $[\text{Mn}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3]\text{PF}_6$, 70800-85-0; *cis*- $[\text{Mn}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4]\text{PF}_6$, 70800-87-2; *trans*- $[\text{Mn}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4]\text{PF}_6$, 70831-77-5; *cis*- $\text{Cr}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4$, 70800-88-3; $\text{Cr}(\text{CO})(\text{CNC}_6\text{H}_5)_5$, 70800-89-4; *cis*- $[\text{Mn}(\text{CO})_4(\text{CNC}_6\text{H}_5)_2]^{2+}$, 70800-90-7; *mer*- $[\text{Mn}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3]^{2+}$, 70800-91-8; *fac*- $[\text{Mn}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3]^{2+}$, 70831-78-6; *cis*- $[\text{Mn}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4]^{2+}$, 70897-65-3; *trans*- $[\text{Mn}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4]^{2+}$, 70800-92-9; $[\text{Mn}(\text{CO})(\text{CNC}_6\text{H}_5)_5]\text{PF}_6$, 38889-71-3; $[\text{Mn}(\text{CO})(\text{CNC}_6\text{H}_5)_5]^{2+}$, 70800-93-0; $[\text{Mn}(\text{CNC}_6\text{H}_5)_6]\text{PF}_6$, 36786-48-8; $[\text{Mn}(\text{CNC}_6\text{H}_5)_6]^{2+}$, 47873-90-5; $\text{Cr}(\text{CO})_6^+$, 54404-20-5; $\text{Cr}(\text{CO})_5(\text{CNC}_6\text{H}_5)^+$, 70800-94-1; *cis*- $\text{Cr}(\text{CO})_4(\text{CNC}_6\text{H}_5)_2$, 70831-79-7; *cis*- $\text{Cr}(\text{CO})_4(\text{CNC}_6\text{H}_5)_2^+$, 70800-95-2; *fac*- $\text{Cr}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3$, 70831-80-0; *fac*- $\text{Cr}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3^+$, 70800-96-3; *cis*- $\text{Cr}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4^+$, 70800-97-4; *cis*- $\text{Cr}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4^{2+}$, 70800-98-5; $\text{Cr}(\text{CO})(\text{CNC}_6\text{H}_5)_5^+$, 70800-99-6; $\text{Cr}(\text{CO})(\text{CNC}_6\text{H}_5)_5^{2+}$, 70801-00-2; $\text{Cr}(\text{CNC}_6\text{H}_5)_6^+$, 57016-32-7; $\text{Cr}(\text{CNC}_6\text{H}_5)_6^{2+}$, 57016-35-0; $\text{Cr}(\text{CNC}_6\text{H}_5)_6^{3+}$, 70801-01-3; *fac*- $\text{Mn}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3\text{Br}$, 52730-08-2; *mer-cis*- $\text{Mn}(\text{CO})_2(\text{CNC}_6\text{H}_5)_3\text{Br}$, 70831-81-1; $\text{Mn}(\text{C}-\text{O})_5\text{Br}$, 14516-54-2; $\text{Mn}(\text{CO})(\text{CNC}_6\text{H}_5)_5\text{Br}$, 31392-78-6; $\text{Cr}(\text{CNC}_6\text{H}_5)_6$, 17375-15-4; $\text{Cr}(\text{CO})_6$, 13007-92-6; $\text{Cr}(\text{CO})_5(\text{CNC}_6\text{H}_5)$, 14782-94-6; $\text{Cr}(\text{CNC}_6\text{H}_5)_6^-$, 61506-06-7.

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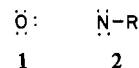
Complexes of (Arylimido)molybdenum(VI)

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The reaction of an aryl azide with either $\text{Mo}(\text{CO})_2(\text{Et}_2\text{dtc})_2$ or $\text{MoO}(\text{Et}_2\text{dtc})_2$ yields $\text{Mo}(\text{NR})_2(\text{Et}_2\text{dtc})_2$ and $\text{MoO}(\text{NR})(\text{Et}_2\text{dtc})_2$, respectively. The reaction of $\text{Mo}(\text{NR})_2(\text{Et}_2\text{dtc})_2$ with HCl gives $\text{Mo}(\text{NR})\text{Cl}_2(\text{Et}_2\text{dtc})_2$, and the reaction with CH_3Br results in $\text{Mo}(\text{NR})\text{Br}_2(\text{Et}_2\text{dtc})_2$. While the reaction of $\text{MoO}(\text{NPh})(\text{Et}_2\text{dtc})_2$ with HCl gives $\text{Mo}(\text{NPh})\text{Cl}_2(\text{Et}_2\text{dtc})_2$, the corresponding reaction with $\text{MoO}(\text{NPhNO}_2)(\text{Et}_2\text{dtc})_2$ ($\text{PhNO}_2 = p\text{-C}_6\text{H}_4\text{NO}_2$) leads to $\text{MoOCl}_2(\text{Et}_2\text{dtc})_2$. The metathesis of $\text{Mo}(\text{NR})\text{Cl}_2(\text{Et}_2\text{dtc})_2$ and Et_2dtc^- gives $\text{Mo}(\text{NR})(\text{Et}_2\text{dtc})_3^+$. The oxo analogue of this complex was prepared from the reaction of $\text{MoO}_2(\text{Et}_2\text{dtc})_2$ with HBF_4 . A plausible mechanism for protonation of complexes containing the MoO_2 , $\text{MoO}(\text{NR})$, and $\text{Mo}(\text{NR})_2$ fragments is suggested.

Complexes of molybdenum containing imido (nitrene) ligands constitute a small but growing area of investigation. Like the oxo ligand, a species which pervades the complexes of molybdenum when that metal is in one of its higher oxidation states, imido ligands have been found in either bridging or terminal positions. Occupancy of a bridging site occurs in $\text{Mo}_2\text{O}_3(\text{NH})(\text{Et}_2\text{dtp})_2$,^{1,2} while terminal sites are occupied in $\text{Mo}(\text{NH})\text{X}(\text{dppe})_2^+$ ($\text{X} = \text{halogen}$),^{1,3} $\text{Mo}(\text{NMe})(\text{Et}_2\text{dtc})_3^+$,^{1,4} $\text{Mo}(\text{NPh})_2(\text{Et}_2\text{dtc})_2$,^{1,5} $\text{Mo}(\text{NR})(\text{Et}_2\text{dtp})_3$, and $\text{Mo}(\text{NR})\text{Cl}(\text{Et}_2\text{dtp})_2$ ($\text{R} = \text{aryl}$).⁶ We have also postulated⁷ the transient existence of $\text{MoO}(\text{NH})(\text{Et}_2\text{dtc})_2$ during the oxidation of $\text{MoO}(\text{Et}_2\text{dtc})_2$ with HN_3 . Although we have previously recognized^{2,7} that the oxo and NH ligands are isoelectronic, a more useful view results from the recognition⁵ that both the oxygen atom (1) and a nitrene (2) can serve as either two- or



four-electron donors in the sense of the EAN rule. The amphoteric character of these ligands allows each of these complexes to conform to that rule. Moreover, a homologous series of complexes might be expected and can be found in certain instances. The oxo analogues of the mononuclear complexes listed above are $\text{MoOX}(\text{dppe})_2^+$,⁸ $\text{MoO}(\text{Et}_2\text{dtc})_3^+$,⁹ well-known $\text{MoO}_2(\text{Et}_2\text{dtc})_2$, $\text{MoO}(\text{Et}_2\text{dtp})_3$,¹⁰ and $\text{MoOCl}(\text{Et}_2\text{dtp})_2$,¹⁰ respectively. While the direct analogue of $\text{Mo}_2\text{O}_3(\text{NH})(\text{Et}_2\text{dtp})_2$ is unknown, a closely related series of compounds is found in $\text{Mo}_2\text{O}_4(\text{R}_2\text{dtc})_2$. Similar analogies can be found with complexes of rhenium¹¹ and osmium.¹²

The purpose of this paper is to demonstrate the existence