

Reactions of $M(\text{CO})_5\text{X}$ ($M = \text{Mn}, \text{Re}; \text{X} = \text{Cl}, \text{Br}$) with $\{\text{Ph}_2\text{PCH}_2\}_3\text{CCH}_3$ (P_3) and $\{\text{Ph}_2\text{P}(\text{CH}_2)_2\}_3\text{P}$ ($\text{P}_3\text{P}'$): Synthetic, Spectroscopic, Electrochemical, and Electrospray Mass Spectrometric Studies

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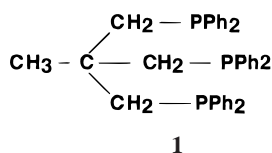
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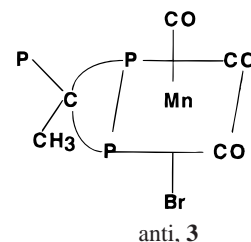
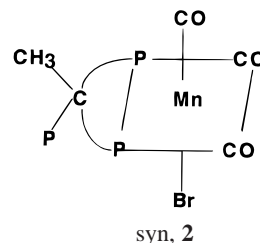
The reactions of $M(\text{CO})_5\text{X}$ ($M = \text{Mn}, \text{Re}; \text{X} = \text{Cl}, \text{Br}$) with $\{\text{Ph}_2\text{PCH}_2\}_3\text{CCH}_3$ (P_3) and $\{\text{Ph}_2\text{P}(\text{CH}_2)_2\}_3\text{P}$ ($\text{P}_3\text{P}'$) are investigated, and the products are characterized by IR, NMR (^{31}P and ^{13}C), and electrospray mass spectrometric (ESMS) techniques. With P_3 , the major products are *fac*- $M(\text{CO})_3(\eta^2\text{-P}_3)\text{X}$ (*syn* and *anti* isomers) and *cis, fac*- $M(\text{CO})_2(\eta^3\text{-P}_3)\text{X}$, and with $\text{P}_3\text{P}'$, the major product for each metal is *cis, mer*- $M(\text{CO})_2(\eta^3\text{-P}_3\text{P}')\text{X}$, but *cis*- $[M(\text{CO})_2(\eta^4\text{-P}_3\text{P}')\text{X}]$ and *fac*- $[\text{Re}(\text{CO})_3(\eta^3\text{-P}_3\text{P}')\text{X}]$ are also characterized. Addition of MeI to those complexes containing pendant phosphine groups produces the corresponding phosphonium cations without affecting the remainder of the molecule. On the voltammetric time scale, electrochemical oxidation of *cis, fac*- $\text{Mn}(\text{CO})_2(\eta^3\text{-P}_3)\text{X}$ yields the corresponding 17e cation *cis, fac*- $[\text{Mn}(\text{CO})_2(\eta^3\text{-P}_3)\text{X}]^+$, but on the longer time scale of exhaustive electrolysis or chemical oxidation, the product is *fac*- $[\text{Mn}(\text{CO})_3(\eta^3\text{-P}_3)]^+$. In contrast, the rhenium cation *cis, fac*- $[\text{Re}(\text{CO})_2(\eta^3\text{-P}_3)\text{X}]^+$ is stable on the synthetic time scale, but upon oxidation of *cis, fac*- $\text{Re}(\text{CO})_2(\eta^3\text{-P}_3)\text{X}$ with NOBF_4 , the final product is the 18e $[\text{Re}(\text{CO})(\text{NO})(\eta^3\text{-P}_3)\text{X}]^+$. *cis, mer*- $\text{Mn}(\text{CO})_2(\eta^3\text{-P}_3\text{P}')\text{X}$ is reversibly oxidized to *cis, mer*- $[\text{Mn}(\text{CO})_2(\eta^3\text{-P}_3\text{P}')\text{X}]^+$ on the voltammetric time scale, but on the longer synthetic time scale, the product isomerizes to *trans*- $[\text{Mn}(\text{CO})_2(\eta^3\text{-P}_3\text{P}')\text{X}]^+$, which can be reduced to *trans*- $\text{Mn}(\text{CO})_2(\eta^3\text{-P}_3\text{P}')\text{X}$. Upon voltammetric oxidation, the corresponding rhenium complexes show an initial irreversible response associated with the pendant phosphine group prior to the reversible oxidation of the metal on the synthetic time scale; spectroscopic data indicate formation of *cis, mer*- $\text{Re}(\text{CO})_2(\eta^3\text{-P}_3\text{P}'\text{O})\text{X}$. The complex *cis, mer*- $[\text{Re}(\text{CO})_2(\eta^3\text{-P}_3\text{P}'\text{Me})\text{X}]^+$ shows only the reversible metal oxidation response. ESMS data are obtained directly for the methylated cationic complexes, and neutral complexes are either oxidized or adducted with sodium ions to produce cationic species.

Introduction

Manganese carbonyl halide complexes containing the potentially tridentate ligand $\{\text{Ph}_2\text{PCH}_2\}_3\text{CCH}_3$ (P_3 ; structure **1**) have



been reported by Ellermann and co-workers.¹ Reaction between $\text{Mn}_2(\text{CO})_{10}$ and P_3 with subsequent addition of HX and irradiation of the solution with UV light gave *fac*- $\text{Mn}(\text{CO})_3(\eta^2\text{-P}_3)\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$). Liu and co-workers² showed that two stereoisomers of *fac*- $\text{Mn}(\text{CO})_3(\eta^2\text{-P}_3)\text{Br}$ exist. Separation of the *syn* isomer (structure **2**; uncoordinated phosphorus atom on the same side of the six-membered chelate ring as the bromide) was achieved, but the *anti* isomer (structure **3**) was not isolated in a pure form. It was found^{1,2} that when *fac*- $\text{Mn}(\text{CO})_3(\eta^2\text{-P}_3)\text{X}$ was refluxed in polar solvents, *cis*- $\text{Mn}(\text{CO})_2(\eta^3\text{-P}_3)\text{X}$ formed.



fac- $\text{Re}(\text{CO})_3(\eta^2\text{-P}_3)\text{Cl}$ was prepared from $\text{Re}_2(\text{CO})_{10}$ and P_3 in dichloromethane under photolytic conditions.³ *fac*- $\text{Re}(\text{CO})_3(\eta^2\text{-P}_3\text{O})\text{Cl}$, in which the pendant phosphorus atom is oxidized, was characterized as a minor product.⁴ *cis*- $\text{Re}(\text{CO})_2(\eta^3\text{-P}_3)\text{Cl}$ has been prepared by the reaction of $\text{Re}(\text{PPh}_3)(\text{N}_2\text{COPh})\text{Cl}_2$ with

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(1) Ellermann, J.; Lindner, H. A.; Moll, M. *Chem. Ber.* **1979**, *112*, 3441.

(2) Liu, S. T.; Wang, H. E.; Yiin, L. M.; Tsai, S. C.; Liu, K. J.; Wang, Y. M.; Cheng, M. C.; Peng, S. M. *Organometallics* **1993**, *12*, 2277.

(3) Lin, S. C.; Cheng, C. P.; Lee, T. Y.; Lee, T. J.; Peng, S. M. *Acta Crystallogr.* **1986**, *C42*, 1733.

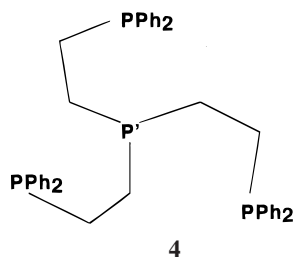
(4) Liu, L. K.; Lin, S. C.; Cheng, C. P. *Acta Crystallogr.* **1988**, *C44*, 1402.

Table 1. IR Data (20 °C) for Dichloromethane Solutions of the P₃ Complexes and Their Derivatives

complex	ν_{CO} (cm ⁻¹)					
	<i>syn</i>			<i>anti</i>		
<i>fac</i> -Mn(CO) ₃ (η^2 -P ₃)Cl	2029	1962	1904	2029	1962	1909
<i>fac</i> -Mn(CO) ₃ (η^2 -P ₃)Br	2028	1963	1903	2028	1962	1909
<i>fac</i> -[Mn(CO) ₃ (η^2 -P ₃ Me)Cl]I	2029	1962	1904	2029	1962	1909
<i>fac</i> -[Mn(CO) ₃ (η^2 -P ₃ Me)Br]I	2028	1963	1903	2028	1963	1908
<i>fac</i> -Re(CO) ₃ (η^2 -P ₃)Cl	2036	1958	1893	2035	1957	1899
<i>fac</i> -Re(CO) ₃ (η^2 -P ₃)Br	2036	1961	1894	2035	1959	1899
<i>fac</i> -[Re(CO) ₃ (η^2 -P ₃ Me)Cl]I	2036	1958	1894	2036	1958	1899
<i>fac</i> -[Re(CO) ₃ (η^2 -P ₃ Me)Br]I	2036	1960	1894	2036	1959	1898

complex	ν_{CO} (cm ⁻¹)					
	complex			ν_{CO} (cm ⁻¹)		
<i>cis</i> -Mn(CO) ₂ (η^3 -P ₃)Cl	1953	1894	<i>cis</i> -Re(CO) ₂ (η^3 -P ₃)Br	1952	1893	
<i>cis</i> -Mn(CO) ₂ (η^3 -P ₃)Br	1953	1893	<i>cis</i> -[Re(CO) ₂ (η^3 -P ₃)Br]BF ₄	2036	1930	
<i>cis</i> -Re(CO) ₂ (η^3 -P ₃)Cl	1958	1895	<i>cis</i> -[Re(CO)(NO)(η^3 -P ₃)Cl]BF ₄	2044		1778 (ν_{NO})
<i>cis</i> -[Re(CO) ₂ (η^3 -P ₃)Cl]BF ₄	2037	1931	<i>cis</i> -[Re(CO)(NO)(η^3 -P ₃)Br]BF ₄	2044		1778 (ν_{NO})

P₃ in refluxing benzene under carbon monoxide.⁵ With the potentially quadridentate ligand {Ph₂P(CH₂)₂}₃P (P₃P'; structure **4**) only the reaction with Mn(CO)₅Br in refluxing benzene to give *cis*-Mn(CO)₂(η^3 -P₃P')Br has been reported.⁶



In this study, *fac*-M(CO)₃(η^2 -P₃)X, *cis*-M(CO)₂(η^3 -P₃)X, and M(CO)₂(η^3 -P₃P')X (M = Mn, Re; X = Cl, Br) and related compounds have been prepared from the direct reactions of M(CO)₅X with P₃ and P₃P'. Reactions with methyl iodide have been investigated for species with a pendant phosphorus atom, and the products of all reactions have been characterized by spectroscopic and electro spray mass spectrometric (ESMS) techniques. Electrochemical and chemical oxidation reactions have been explored for many of the compounds. These studies have led to the characterization of a new and extensive series of 17e species whose reactivities can be compared with those of their 18e unoxidized counterparts.

Experimental Section

Materials. All solvents were of analytical reagent grade. Manganese and rhenium carbonyls, P₃, P₃P', NOBF₄, and "magic blue", (BrC₆H₄)₃-NSbCl₆ (Strem), were used as supplied. The pentacarbonyl halides were prepared by the interactions of the carbonyls with halogens.⁷ All preparations were performed under a nitrogen atmosphere.

Syntheses. A. Complexes Containing P₃. Spectroscopic data for complexes containing P₃ are given in Tables 1 and 2. ESMS was used to determine molecular formulas, and data for the intact ions are summarized in Table 3.

(i) *fac*-Mn(CO)₃(η^2 -P₃)X. A 0.5–0.7 g sample of Mn(CO)₅Br and P₃ (1:1 mole ratio) were reacted in refluxing chloroform for 3 h. The IR spectrum showed three strong carbonyl bands, and the ³¹P NMR spectrum showed two resonances near the signal of the free P₃ ligand and another two overlapping signals at higher frequency. These spectra

Table 2. ³¹P NMR Data (22 °C) for Dichloromethane Solutions of the P₃ Complexes and Their Derivatives^a

complex	³¹ P δ (ppm)			
	<i>syn</i>		<i>anti</i>	
<i>fac</i> -Mn(CO) ₃ (η^2 -P ₃)Cl	30.4 (2)	-28.2 (1)	30.4 (2)	-29.0 (1)
<i>fac</i> -Mn(CO) ₃ (η^2 -P ₃)Br	28.0 (2)	-28.4 (1)	28.0 (2)	-29.2 (1)
<i>fac</i> -[Mn(CO) ₃ (η^2 -P ₃ Me)Cl]I	32.6 (2)	17.1 (1)	29.9 (2)	17.1 (1)
<i>fac</i> -[Mn(CO) ₃ (η^2 -P ₃ Me)Br]I	29.3 (2)	17.0 (1)	27.3 (2)	17.0 (1)
<i>fac</i> -Re(CO) ₃ (η^2 -P ₃)Cl	-12.4 (2)	-29.3 (1)	-12.3 (2)	-30.4 (1)
<i>fac</i> -Re(CO) ₃ (η^2 -P ₃)Br	-15.8 (2)	-28.6 (1)	-15.4 (2)	-29.7 (1)
<i>fac</i> -[Re(CO) ₃ (η^2 -P ₃)Cl]I	-9.7 (2)	17.3 (1)	-13.1 (2)	16.8 (1)
<i>fac</i> -[Re(CO) ₃ (η^2 -P ₃)Br]I	-13.5 (2)	16.9 (1)	-16.3 (2)	16.4 (1)

complex	³¹ P δ (ppm)		
	<i>cis</i> -Mn(CO) ₂ (η^3 -P ₃)Cl	67.1 (1)	22.0 (2)
<i>cis</i> -Mn(CO) ₂ (η^3 -P ₃)Br	69.0 (1)	21.2 (2)	
<i>cis</i> -Re(CO) ₂ (η^3 -P ₃)Cl	1.6 (1)	-19.1 (2)	
<i>cis</i> -Re(CO) ₂ (η^3 -P ₃)Br	0.7 (1)	-21.6 (2)	
<i>cis</i> -[Re(CO)(NO)(η^3 -P ₃)Cl]BF ₄	-11.3 (1)	-24.4 (1)	-27.3 (1)
<i>cis</i> -[Re(CO)(NO)(η^3 -P ₃)Br]BF ₄	-14.3 (1)	-27.7 (1)	-30.5 (1)

^a Numbers in parentheses are relative intensities of the resonances.

are similar to those in the literature⁷ and are due to the presence of the *syn* and *anti* isomers of *fac*-Mn(CO)₃(η^2 -P₃)Br. The solid products were obtained by removing the solvent under vacuum. Fractional recrystallization from either dichloromethane/hexane or chloroform/hexane solutions yielded the *syn* isomer as the first product, while the more soluble *anti* isomer was isolated from the filtrate and recrystallized several times by dissolution in dichloromethane and fractional precipitation with hexane. Total yield: 90 ± 5%. The corresponding chloro derivatives were prepared similarly.

(ii) *fac*-[Mn(CO)₃(η^2 -P₃Me)X]I. These compounds were prepared by the addition of 1 equiv amounts of methyl iodide to 0.7 g of each isomer of *fac*-Mn(CO)₃(η^2 -P₃)X, and the products were isolated by evaporation of the solutions. Total yield: 95 ± 2%. Several recrystallizations from dichloromethane/hexane yielded analytically pure crystals. The IR spectra indicate that the carbonyl bands are virtually unaffected by the methylation, whereas the ³¹P NMR resonances of the originally pendant phosphorus atoms shift to the higher frequencies characteristic of phosphonium derivatives.⁸ ESMS gives the intact ion in each case (Table 3).

(iii) *cis*-Mn(CO)₂(η^3 -P₃)X. A 0.5–0.7 g sample of Mn(CO)₅Cl or Mn(CO)₅Br and P₃ (1:1 mole ratio) were reacted in refluxing chloroform for 30 h. Upon cooling, an orange solid precipitated and was collected by filtration. IR and ³¹P NMR data agree with the literature values.¹ Yield: 85 ± 5%.

(5) Chatt, J.; Dilworth, J. R.; Gunz, H. P.; Leigh, G. J. *J. Organomet. Chem.* **1974**, *64*, 245.

(6) King, R. B.; Kapoor, R. N.; Saran, M. S.; Kapoor, P. N. *Inorg. Chem.* **1971**, *10*, 1851.

(7) Colton, R.; McCormick, M. J. *Aust. J. Chem.* **1976**, *29*, 1657.

(8) Colton, R.; Harvey, J.; Traeger, J. C. *Org. Mass Spectrom.* **1992**, *27*, 1030.

Table 3. Electrospray Mass Spectrometric Data (Intact Ions Only)

complex	additive	ion	<i>m/z</i>
<i>fac</i> -[Mn(CO) ₃ (η ² -P ₃ Me)Cl]I		[Mn(CO) ₃ (P ₃ Me)Cl] ⁺	813
<i>fac</i> -[Mn(CO) ₃ (η ² -P ₃ Me)Br]I		[Mn(CO) ₃ (P ₃ Me)Br] ⁺	859
<i>fac</i> -[Re(CO) ₃ (η ² -P ₃ Me)Cl]I		[Re(CO) ₃ (P ₃ Me)Cl] ⁺	945
<i>fac</i> -[Re(CO) ₃ (η ² -P ₃ Me)Br]I		[Re(CO) ₃ (P ₃ Me)Br] ⁺	989
<i>cis</i> -Mn(CO) ₂ (η ³ -P ₃)Cl	NOBF ₄	[Mn(CO) ₂ (P ₃)Cl] ⁺	763
<i>cis</i> -Mn(CO) ₂ (η ³ -P ₃)Br	NOBF ₄	[Mn(CO) ₂ (P ₃)Br] ⁺	763
<i>cis</i> -Re(CO) ₂ (η ³ -P ₃)Cl	magic blue	[Re(CO) ₂ (P ₃)Cl] ⁺	902
<i>cis</i> -Re(CO) ₂ (η ³ -P ₃)Br	NOBF ₄	[Re(CO) ₂ (NO)(P ₃)Cl] ⁺	904
<i>cis</i> -Re(CO) ₂ (η ³ -P ₃)Br	NOBF ₄	[Re(CO) ₂ (NO)(P ₃)Br] ⁺	948
<i>cis</i> -[Mn(CO) ₂ (η ⁴ -P ₃ P')]Br		[Mn(CO) ₂ (P ₃ P')] ⁺	781
<i>cis,mer</i> -[Mn(CO) ₂ (η ³ -P ₃ P'Me)Cl]PF ₆		[Mn(CO) ₂ (P ₃ P'Me)Cl] ⁺	831
<i>cis,mer</i> -[Mn(CO) ₂ (η ³ -P ₃ P'Me)Br]PF ₆		[Mn(CO) ₂ (P ₃ P'Me)Br] ⁺	877
<i>fac</i> -[Re(CO) ₃ (η ³ -P ₃ P')]Br		[Re(CO) ₃ (P ₃ P')] ⁺	941
<i>cis</i> -[Re(CO) ₂ (η ⁴ -P ₃ P')]Br		[Re(CO) ₂ (P ₃ P')] ⁺	913
<i>cis,mer</i> -Re(CO) ₂ (η ³ -P ₃ P')Cl	NaOAc	[Na + Re(CO) ₂ (P ₃ P')Cl] ⁺	971
<i>cis,mer</i> -[Re(CO) ₂ (η ³ -P ₃ P'Me)Cl]I		[Re(CO) ₂ (P ₃ P'Me)Cl] ⁺	963
<i>cis,mer</i> -[Re(CO) ₂ (η ³ -P ₃ P'Me)Br]PF ₆		[Re(CO) ₂ (P ₃ P'Me)Br] ⁺	1007

Table 4. IR Data (20 °C) for Dichloromethane Solutions of the P₃P' Complexes and Their Derivatives

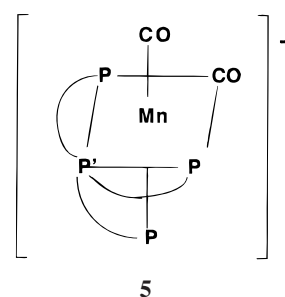
complex	<i>ν</i> _{CO} (cm ⁻¹)	
<i>cis</i> -[Mn(CO) ₂ (η ⁴ -P ₃ P')]Cl	1949	1891
<i>cis,mer</i> -Mn(CO) ₂ (η ³ -P ₃ P')Cl	1936	1858
<i>cis,mer</i> -[Mn(CO) ₂ (η ³ -P ₃ P')Cl] ⁺	2035	1967
<i>trans</i> -Mn(CO) ₂ (η ³ -P ₃ P')Cl	1893	
<i>trans</i> -[Mn(CO) ₂ (η ³ -P ₃ P')Cl] ⁺	1969	
<i>cis,mer</i> -[Mn(CO) ₂ (η ³ -P ₃ P'Me)Cl]PF ₆	1939	1849
<i>cis</i> -[Mn(CO) ₂ (η ⁴ -P ₃ P')]Br	1948	1891
<i>cis,mer</i> -Mn(CO) ₂ (η ³ -P ₃ P')Br	1937	1862
<i>cis,mer</i> -[Mn(CO) ₂ (η ³ -P ₃ P')Br] ⁺	2033	1965
<i>trans</i> -Mn(CO) ₂ (η ³ -P ₃ P')Br	1893	
<i>trans</i> -[Mn(CO) ₂ (η ³ -P ₃ P')Br] ⁺	1967	
<i>cis,mer</i> -[Mn(CO) ₂ (η ³ -P ₃ P'Me)Br]PF ₆	1940	1851
<i>cis</i> -[Re(CO) ₂ (η ⁴ -P ₃ P')]Cl	1964	1905
<i>fac</i> -[Re(CO) ₃ (η ³ -P ₃ P')]Cl	2036	1959
<i>cis,mer</i> -Re(CO) ₂ (η ³ -P ₃ P')Cl	1940	1857
<i>cis,mer</i> -Re(CO) ₂ (η ³ -P ₃ P'O)Cl	1942	1862
<i>cis,mer</i> -[Re(CO) ₂ (η ³ -P ₃ P'Me)Cl]I	1942	1867
<i>cis</i> -[Re(CO) ₂ (η ⁴ -P ₃ P')]Br	1963	1905
<i>fac</i> -[Re(CO) ₃ (η ³ -P ₃ P')]Br	2037	1958
<i>cis,mer</i> -Re(CO) ₂ (η ³ -P ₃ P')Br	1942	1860
<i>cis,mer</i> -Re(CO) ₂ (η ³ -P ₃ P'O)Br	1943	1864
<i>cis,mer</i> -[Re(CO) ₂ (η ³ -P ₃ P'Me)Br]I	1943	1869

(iv) **Rhenium Complexes.** Reactions between 0.5–0.7 g of Re(CO)₅X and P₃ (1:1 mole ratio) under conditions similar to those given for the manganese complexes, except that the dicarbonyl complexes required the use of the higher boiling solvent xylene, yielded products or mixtures of isomers analogous to those produced in the cases of the rhenium complexes. Isomers were separated by chromatography on silica using dichloromethane as the eluent, and all solids were recrystallized using dichloromethane/hexane. Total yield: 85 ± 5%. A crystal structure determination for one isomer of *fac*-Re(CO)₃(η²-P₃)Cl was reported in the literature;³ however, the ³¹P NMR resonances for this complex were given as δ -11.26 and -11.43 ppm and attributed to the two signals of a single isomer of *fac*-Re(CO)₃(η²-P₃)Cl. It seems that the *syn* and *anti* isomers were both present in the solution, but the resonances of the pendant phosphorus atoms were not reported. *fac*-[Re(CO)₃(η²-P₃Me)X]I compounds were prepared by procedures analogous to those described above for their manganese counterparts.

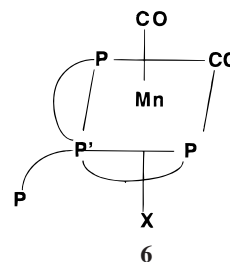
B. Complexes Containing P₃P'. Spectroscopic data for the P₃P' complexes are summarized in Tables 4 and 5, and ESMS data, in Table 3.

(i) *cis*-Mn(CO)₂(η⁴-P₃P) and *cis,mer*-Mn(CO)₃(η³-P₂P')X. A 0.5–0.7 g sample of Mn(CO)₅Br and P₃P' (1:1 mole ratio) were reacted in refluxing xylene until a pale yellow precipitate began to form (about 2 h). After cooling of the solution and collection of the solid by filtration (yield 10 ± 3%), the solid was dissolved in dichloromethane. The resultant solution exhibited two strong carbonyl stretches consistent with a *cis*-dicarbonyl geometry and a ³¹P NMR spectrum consistent

only with the formulation *cis*-[Mn(CO)₂(η⁴-P₃P')]Br (structure 5). The



ES mass spectrum gave a strong peak for the intact ion [Mn(CO)₂(P₃P')]⁺ (*m/z* 781). The filtrate from the reaction mixture was evaporated to a small volume and cooled, which resulted in the precipitation of orange crystals. The IR spectrum indicated a *cis*-dicarbonyl geometry, agreeing with the literature,⁶ and the ³¹P NMR spectrum was consistent only with η³ coordination of the P₃P' ligand. The ¹³C NMR spectrum of the bromo complex (two resonances) identified the compound as *cis,mer*-Mn(CO)₂(η³-P₃P')Br (structure 6). Yield: 75 ± 5%. Similar results were obtained for the corresponding chloro compounds.



(ii) *cis,mer*-[Mn(CO)₃(η³-P₂P'Me)X]PF₆. Addition of excess MeI to a solution containing 0.1 g of *cis,mer*-Mn(CO)₂(η³-P₃P')Cl in dichloromethane methylated the pendant phosphine. The iodide salt was isolated by evaporation of the solution. Yield: 90 ± 3%. IR and ³¹P NMR spectra indicated no other change in this reaction, and the ES mass spectrum of the product gave a strong peak at *m/z* 831, attributable to the intact anion [Mn(CO)₂(P₃P')Cl]⁺. An acetone solution of this compound was passed through an ion exchange column that had been pretreated with KPF₆ to replace the electrochemically active iodide ion with the PF₆⁻ ion.

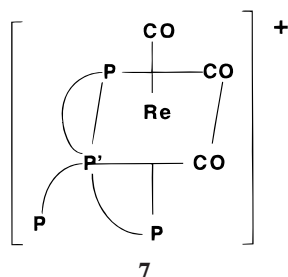
(iii) **Reaction between Re(CO)₅X and P₃P'.** A 0.5–0.7 g sample of Re(CO)₅X and P₃P' (1:1 mole ratio) were reacted in refluxing mesitylene for 3–5 h. The ³¹P NMR spectrum of the mesitylene solution then showed numerous peaks, indicating the presence of several species. Successive additions of hexane to the solution resulted in the formation of white precipitates which were recrystallized several times from dichloromethane/hexane to yield three compounds. The least soluble

Table 5. ³¹P and ¹³C NMR Data (22 °C) for Dichloromethane Solutions of the P₃P' Complexes and Their Derivatives (ppm)

complex	³¹ P δ (CH ₂ Cl ₂)			¹³ C δ (CDCl ₃) CO
	P'	P2	P1	
<i>cis,mer</i> -Mn(CO) ₂ (η ³ -P ₃ P')Cl	122.1	86.1	-14.2	224.7 ^a
<i>trans</i> -Mn(CO) ₂ (η ³ -P ₃ P')Cl	138.2	69.9	-13.9	
<i>cis,mer</i> -[Mn(CO) ₂ (η ³ -P ₃ P'Me)Cl]PF ₆	126.8	87.0	24.0	
<i>cis</i> -[Mn(CO) ₂ (η ⁴ -P ₃ P')]Br	155.2	82.4	79.3	
<i>cis,mer</i> -Mn(CO) ₂ (η ³ -P ₃ P')Br	121.7	84.9	-14.2	232.5, 231.3
<i>trans</i> -Mn(CO) ₂ (η ³ -P ₃ P')Br	141.3	70.6	-14.0	
<i>cis,mer</i> -[Mn(CO) ₂ (η ³ -P ₃ P'Me)Br]PF ₆	127.5	86.2	24.9	
<i>cis,mer</i> -Re(CO) ₂ (η ³ -P ₃ P')Cl	79.5	37.8	-14.1	195.6, 201.9 (d, J(C,P) = 58 Hz)
<i>cis,mer</i> -Re(CO) ₂ (η ³ -P ₃ P'O)Cl	79.5	37.9	34.3	
<i>cis,mer</i> -[Re(CO) ₂ (η ³ -P ₃ P'Me)Cl]I	85.8	39.5	23.7	
<i>cis</i> -[Re(CO) ₂ (η ⁴ -P ₃ P')]Br	114.1	26.3	31.0	
<i>fac</i> -[Re(CO) ₃ (η ³ -P ₃ P')]Br	67.7	27.9	-13.8	
<i>cis,mer</i> -Re(CO) ₂ (η ³ -P ₃ P')Br	77.5	35.2	-14.0	194.8, 201.2 (d, J(C,P) = 56 Hz)
<i>cis,mer</i> -Re(CO) ₂ (η ³ -P ₃ P'O)Br	77.5	35.1	31.4	
<i>cis,mer</i> -[Re(CO) ₂ (η ³ -P ₃ P'Me)Br]I	84.4	37.1	23.6	

^a May be two overlapping peaks.

compound in the mesitylene/hexane and dichloromethane/hexane mixtures showed IR and ³¹P NMR spectra similar to those observed for *cis*-[Mn(CO)₂(η⁴-P₃P')]Br (5), suggesting that the compound is *cis*-[Re(CO)₂(η⁴-P₃P')]Br. ESMS data confirmed the presence of the [Re(CO)₂(P₃P')]⁺ cation. The IR and ³¹P NMR spectra of a dichloromethane solution of the second compound (bromo) are very similar to those for *fac*-[Re(CO)₃(η³-P₃P')]Br¹¹ (except for an additional NMR resonance due to the pendant phosphine), suggesting the product is *fac*-[Re(CO)₃(η³-P₃P')]Br (structure 7). ESMS data confirm the presence of [Re-



(CO)₃(P₃P')]⁺ (*m/z* 941). The least soluble compound in the mixture is identified as *cis,mer*-Re(CO)₂(η³-P₃P')Br. Total yield: 80 ± 5%.

(iv) *cis,mer*-[Re(CO)₂(η³-P₃P'Me)X]I. Samples (0.1 g) of *cis,mer*-Re(CO)₂(η³-P₃P')X were reacted with excess MeI in dichloromethane solutions, and the products were isolated by evaporating the solutions. Yield: 90 ± 5%. The IR and ³¹P NMR data indicate that only the pendant phosphorus atoms were affected by the reactions. The iodide anion was exchanged with PF₆⁻ to obtain the bromo complex used in electrochemical studies. ES mass spectra confirmed the presence of [Re(CO)₂(P₃P'Me)X]⁺ ions (*m/z* 963 (Cl), 1007 (Br)).

Analysis of Solids. ³¹P NMR data for dichloromethane solutions of the compounds showed no evidence for phosphine ligand impurities or any other diamagnetic phosphine-containing impurities. Voltammetric analysis was used to confirm the presence or absence (<0.1%) of free halide. ¹³C and ¹H NMR data obtained for deuterated acetonitrile solutions revealed the presence of dichloromethane, chloroform, or MeI as appropriate in many of the solid samples. Crystal structures on related compounds also have revealed¹¹ the presence of solvent.

Representative elemental microanalyses for a range of new compounds prepared in this work were performed by Chemsearch, University of Otago, New Zealand, and provided the following data.

- (9) Bond, A. M.; Colton, R.; Gable, R. W.; Mackay, M. F.; Walter, J. N. *Inorg. Chem.* **1997**, *36*, 1181.
 (10) Bond, A. M.; Grabaric, B. S.; Grabaric, Z. *Inorg. Chem.* **1978**, *17*, 1013.
 (11) (a) Bond, A. M.; Colton, R.; Jackowski, J. J. *Inorg. Chem.* **1975**, *14*, 274. (b) Bond, A. M.; Colton, R.; McCormick, M. J. *Inorg. Chem.* **1977**, *16*, 155. (c) Bond, A. M.; Carr, S. W.; Colton, R. *Inorg. Chem.* **1984**, *23*, 2343.

Anal. Found (calcd) for [Mn(CO)₂(η³-P₃Me)Cl]I: C, 57.7 (57.9); H, 4.7 (4.6). Found (calcd) for Re(CO)₃(η²-P₃Br): C, 54.1 (54.2); H, 3.9 (4.0); P, 9.3 (9.5). Found (calcd) for Mn(CO)₃(η²-P₃Cl)·0.67CH₂Cl₂: C, 63.0 (62.7); H, 4.5 (4.8), Cl, 9.7 (9.7). Found (calcd) for [Re(CO)₃(η²-P₃Me)Br]I·CH₃I: C, 43.6 (43.9); H, 3.1 (3.6); P, 7.9 (7.4). Found (calcd) for [Mn(CO)₂(η⁴-P₃P')]Cl·CHCl₃: C, 58.0 (57.6), H, 4.8 (4.8). Found (calcd) for [Re(CO)₂(η⁴-P₃P')]Br: C, 53.9 (53.2); H, 4.7 (4.3); Br, 8.1 (8.1).

Electrochemical Methods. Conventional voltammetric measurements were typically obtained with 1.0 mM solutions of the compound in dichloromethane (0.1 M Bu₄NPF₆) using a Cypress Systems (Lawrence, KS) Model CYSY-1 computer-controlled electrochemical system or a BAS (Bioanalytical Systems, West Lafayette, IN) 100A electrochemical analyzer. The working electrode was a glassy carbon disk (radius 0.5 mm), the auxiliary electrode was a platinum wire, and the reference electrode was Ag/AgCl (saturated LiCl in dichloromethane (0.1 M Bu₄NPF₆)) separated from the test solution by a salt bridge. The reversible voltammetry of an approximately 1.0 mM ferrocene (Fc) solution in the same solvent was used as a reference redox couple, and all potentials are quoted relative to Fc⁺/Fc. Near-steady-state voltammograms were recorded using a 12.5 μm radius platinum microdisk electrode. Solutions were purged with solvent-saturated nitrogen before voltammetric measurements and then maintained under an atmosphere of nitrogen during measurements.

Bulk electrolysis experiments were undertaken with the BAS 100A electrochemical analyzer using a large platinum basket working electrode, a platinum gauze auxiliary electrode separated from the test solution by a salt bridge, and the same reference electrode as used in the voltammetric studies. Coulometric determinations gave *n* values of 1 ± 0.1 per molecule for all oxidations.

Spectroscopic Methods. NMR spectra were recorded on a Bruker AM 300 spectrometer, ³¹P at 121.496 MHz in dichloromethane and ¹³C at 75.469 MHz in CDCl₃ solution. The high-frequency positive convention is used for ³¹P and ¹³C chemical shifts with external 85% H₃PO₄ and internal TMS references, respectively. Infrared spectra were recorded on a Perkin-Elmer FT-IR 1720X or a Perkin-Elmer 1430 IR spectrometer.

Electrospray Mass Spectrometry. Electrospray mass spectra of cationic complexes were obtained with a VG Bio-Q triple-quadrupole mass spectrometer using a water/methanol/acetic acid (50:50:1) mobile phase. Solutions of the compounds (2.0 mM in dichloromethane) were mixed, if necessary, with oxidant or sodium acetate as described under Results and Discussion. A mixed solution, diluted 1:10 with methanol, was immediately injected directly into the spectrometer via a Rheodyne injector fitted with a 10 μL loop. A Phoenix 20 micro LC syringe pump delivered the solution to the vaporization nozzle of the electrospray source at a flow rate of 5 μL min⁻¹. Nitrogen was used as the drying gas and for nebulization with flow rates of approximately 3 L min⁻¹ and 100 mL min⁻¹, respectively. The potential on the first skimmer (B1) was usually 40 V. Peaks were identified by the most abundant

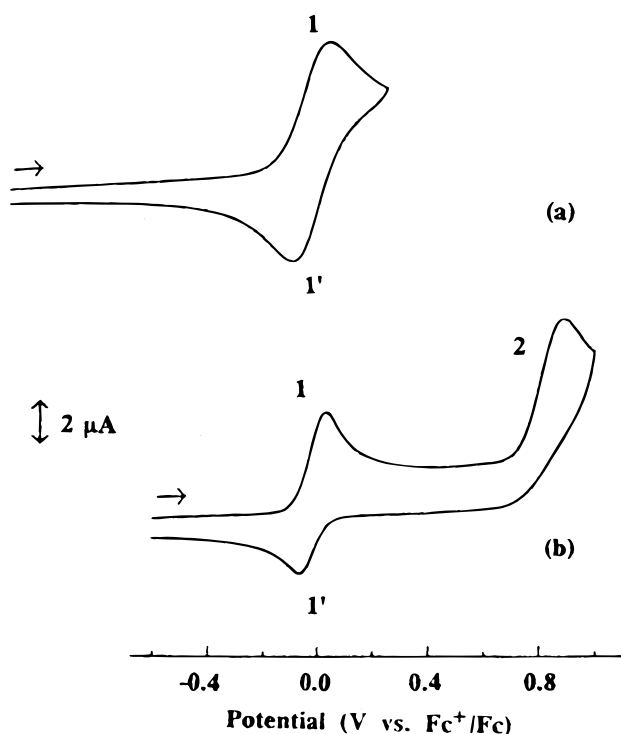
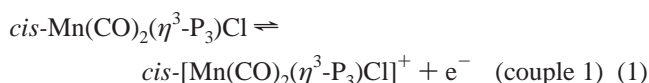


Figure 1. (a) Oxidative cyclic voltammogram recorded at a glassy carbon macrodisk electrode (scan rate 200 mV s^{-1}) at 20°C for a 1.0 mM solution of $\text{cis-Mn}(\text{CO})_2(\eta^3\text{-P}_3)\text{Cl}$ in dichloromethane (0.1 M NBu_4NPF_6). (b) Voltammogram for similar conditions over an extended potential range.

mass in the isotopic mass distribution. In all cases, the agreement between experimental and theoretical isotopic mass patterns was excellent.

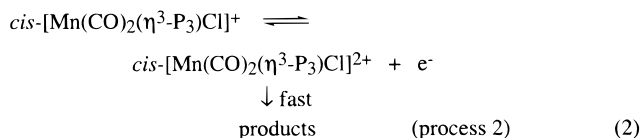
Results and Discussion

Electrochemical Studies of P_3 Complexes. A. Manganese Dicarbonyl Complexes. (i) Cyclic Voltammetry. Figure 1a shows an oxidative cyclic voltammogram recorded at a glassy carbon electrode (scan rate 200 mV s^{-1}) for a 1.0 mM solution of $\text{cis-Mn}(\text{CO})_2(\eta^3\text{-P}_3)\text{Cl}$ in dichloromethane (0.1 M NBu_4PF_6) at 20°C . A reversible couple is observed at $E_{1/2}^r = -0.020 \text{ V}$ (couple 1) ($E_{1/2}^r =$ reversible half-wave potential), and second and subsequent cycles are similar. The separation, ΔE_p , between the oxidation peak potential (E_p^{ox}) and the reduction peak potential (E_p^{red}) is 85 mV . A similar value is observed under these conditions for the known one-electron reversible couple Fc^+/Fc . At more positive potentials, an irreversible response at 0.885 V (process 2) is apparent (Figure 1b). This response remains irreversible for the temperature range -60 to $+20^\circ \text{C}$ and for scan rates of $100\text{--}50\,000 \text{ mV s}^{-1}$. A near-steady-state voltammogram recorded at a platinum microdisk electrode for the first oxidation process indicates that it involves one electron by comparison of its limiting current with that for the first oxidation of an equimolar solution of $\text{fac-Mn}(\text{CO})_3(\eta^2\text{-dpe})\text{Br}$ ($\text{dpe} = \text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$), which is known to be a one-electron process.¹⁰ Thus, redox couple 1 is assigned to the reaction



The usual isomerization to trans^+ , after oxidation to a 17e species,¹¹ is not observed because P_3 can only coordinate in a

facial geometry. Process 2 involves further oxidation to an unstable 16e $\text{Mn}(\text{III})$ species



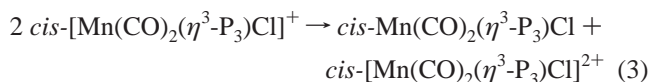
Voltammetric data for these and all other complexes studied are listed in Table 6. For all compounds in this paper, couple 1 will refer to the reversible one-electron oxidation of the metal ($18\text{e} \rightleftharpoons 17\text{e}$) and process 2 will refer to further irreversible oxidation of the metal complex.

(ii) Bulk Electrolysis and Electro spray Mass Spectrometry. Bulk electrolysis of a dichloromethane solution (0.4 M NBu_4ClO_4) of $\text{cis-Mn}(\text{CO})_2(\eta^3\text{-P}_3)\text{Cl}$ was undertaken at 0.100 V (i.e., slightly more positive than E_p^{ox} of couple 1) at a platinum gauze electrode. The amount of charge passed indicated a one-electron process, as expected. Surprisingly, a near-steady-state voltammogram of the oxidized solution obtained at a platinum microdisk electrode did not indicate the presence of the oxidized component of couple 1, demonstrating that $\text{cis-}[\text{Mn}(\text{CO})_2(\eta^3\text{-P}_3)\text{Cl}]^+$ is not stable on the longer synthetic time scale. The IR spectrum of the oxidized solution shows two carbonyl absorptions at 2031 and 1961 cm^{-1} .

A 2 mM solution of $\text{cis-Mn}(\text{CO})_2(\eta^3\text{-P}_3)\text{Cl}$ in acetone (2 mM NBu_4PF_6) was electrolyzed at room temperature exhaustively. (These nonstandard conditions were selected to minimize the amount of supporting electrolyte required, since excessive amounts of ionic species depress the intensities of peaks in electro spray mass spectra.) The ES mass spectrum of the resultant solution shows the intact ion $[\text{Mn}(\text{CO})_3(\text{P}_3)]^+$ at m/z 763 , confirming that this cation is produced upon oxidation of $\text{cis-Mn}(\text{CO})_2(\eta^3\text{-P}_3)\text{Cl}$.

Chemical oxidations of $\text{cis-Mn}(\text{CO})_2(\eta^3\text{-P}_3)\text{Cl}$ and $\text{cis-Mn}(\text{CO})_2(\eta^3\text{-P}_3)\text{Br}$ with NOBF_4 also led to the observation of $[\text{Mn}(\text{CO})_3(\text{P}_3)]^+$ in the ES mass spectra. The IR data for the oxidized solutions also are consistent with the formation of the cation $[\text{Mn}(\text{CO})_3(\eta^3\text{-P}_3)]^+$, and the IR spectral patterns indicate that the carbonyl ligands have a facial geometry. Thus, $\text{fac-}[\text{Mn}(\text{CO})_3(\eta^3\text{-P}_3)]^+$ is generated by either electrochemical or chemical oxidation of $\text{cis-Mn}(\text{CO})_2(\eta^3\text{-P}_3)\text{X}$.

A possible mechanism leading to $[\text{Mn}(\text{CO})_3(\eta^3\text{-P}_3)]^+$ involves the initial formation of $\text{cis-}[\text{Mn}(\text{CO})_2(\eta^3\text{-P}_3)\text{Cl}]^+$ as in eq 1. It is well-known¹² that where isomerization cannot occur for the 17e species, as in this case, reactions involving disproportionation usually occur:



The voltammetric studies have shown 16e $\text{cis-}[\text{Mn}(\text{CO})_2(\eta^3\text{-P}_3)\text{Cl}]^{2+}$ to be unstable, and it presumably decomposes with evolution of carbon monoxide, which probably reacts with further 17e $\text{cis-}[\text{Mn}(\text{CO})_2(\eta^3\text{-P}_3)\text{Cl}]^+$ to give $\text{fac-}[\text{Mn}(\text{CO})_3(\eta^3\text{-P}_3)]^+$.

B. Rhenium Dicarboxyl Complexes. (i) Cyclic Voltammetry. An oxidative cyclic voltammogram (scan rate 200 mV s^{-1}) of a 1.0 mM solution of $\text{cis-Re}(\text{CO})_2(\eta^3\text{-P}_3)\text{Cl}$ in dichloromethane (0.1 M NBu_4PF_6) at 20°C (Figure 2a) shows a

(12) (a) Bond, A. M.; Bowden, J. A.; Colton, R. *Inorg. Chem.* **1974**, *13*, 602. (b) Bond, A. M.; Colton, R.; Kevekorides, J. E.; Panagiotidou, P. *Inorg. Chem.* **1987**, *26*, 1430.

Table 6. Voltammetric Data Recorded at a Glassy Carbon Macrodisk Electrode (Scan Rate 200 mV s⁻¹) for 1.0 mM Solutions in Dichloromethane (0.1 M Bu₄NPF₆) at 20 °C^a

complex	couple	potentials (V vs Fc ⁺⁰)			ΔE _p (mV)
		E _p ^{ox}	E _p ^{red}	E _{1/2} ^r	
<i>cis</i> -Mn(CO) ₂ (η ³ -P ₃)Cl	1	0.025	-0.060	-0.020	85
	irrev 2	0.890			
<i>cis</i> -Mn(CO) ₂ (η ³ -P ₃)Br	1	0.065	-0.025	0.020	90
	irrev 2	0.920			
<i>cis</i> -Re(CO) ₂ (η ³ -P ₃)Cl	1	0.375	0.290	0.330	85
	irrev 2	1.040			
<i>cis</i> -Re(CO) ₂ (η ³ -P ₃)Br	1	0.385	0.295	0.340	90
	irrev 2	1.030			
<i>cis,mer</i> -Mn(CO) ₂ (η ³ -P ₃ P')Cl	1	0.195	0.105	0.150	90
	3	-0.390	-0.470	-0.430	
<i>cis,mer</i> -[Mn(CO) ₂ (η ³ -P ₃ P'Me)Cl]PF ₆	1	0.265	0.175	0.220	90
	1	0.225	0.135	0.180	
<i>cis,mer</i> -Mn(CO) ₂ (η ³ -P ₃ P')Br	1	0.225	0.135	0.180	90
	3	-0.350	-0.435	-0.395	
<i>cis,mer</i> -[Mn(CO) ₂ (η ³ -P ₃ P'Me)Br]PF ₆	1	0.295	0.205	0.250	90
	irrev	0.560			
<i>cis,mer</i> -Re(CO) ₂ (η ³ -P ₃ P')Cl	1	0.610	0.520	0.565	90
	4	0.485	0.410	0.450	
	irrev	0.560			75
	1	0.615	0.525	0.570	
<i>cis,mer</i> -Re(CO) ₂ (η ³ -P ₃ P')Br	1	0.615	0.525	0.570	90
	4	0.485	0.410	0.450	
	irrev	0.560			75
	1	0.635	0.540	0.590	
<i>cis,mer</i> -[Re(CO) ₂ (η ³ -P ₃ P'Me)Br]PF ₆	1	0.635	0.540	0.590	95
	4	0.500	0.430	0.465	

^a E_p^{ox} = oxidation peak potential; E_p^{red} = reduction peak potential; ΔE_p = separation in reduction and oxidation peak potentials; E_{1/2}^r = reversible half-wave potential, which is approximately equal to the reversible formal potential and is calculated as (E_p^{ox} + E_p^{red})/2.

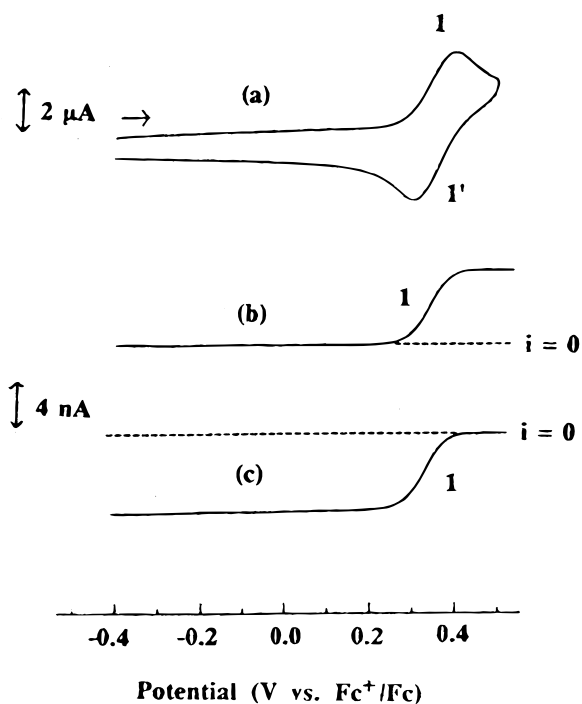


Figure 2. (a) Oxidative cyclic voltammogram recorded at a glassy carbon macrodisk electrode (scan rate 200 mV s⁻¹) at 20 °C for a 1.0 mM solution of *cis*-Re(CO)₂(η³-P₃)Cl in dichloromethane (0.1 M Bu₄NPF₆). (b) Near-steady-state voltammogram (scan rate 10 mV s⁻¹) recorded at a platinum microdisk electrode (radius 12.5 μm) at 20 °C for a 1.0 mM solution of *cis*-Re(CO)₂(η³-P₃)Cl in dichloromethane (0.4 M Bu₄NPF₆) before electrolysis. (c) Near-steady-state voltammogram of the same solution after subsequent exhaustive oxidative electrolysis.

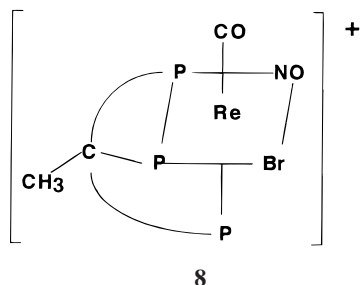
reversible couple at E_{1/2}^r = 0.335 V (couple 1). Upon a scan to more positive potentials, an irreversible oxidation response at 1.040 V (process 2, not shown) also is detected. The current obtained for a near-steady-state voltammogram of this solution indicates that process 1 is a one-electron process. Thus, the voltammetry is similar to that of the analogous manganese

compound. Similar voltammograms were obtained for *cis*-Re(CO)₂(η³-P₃)Br, and the voltammetric data are summarized in Table 6.

(ii) Bulk Electrolysis. Bulk oxidation of a solution of *cis*-Re(CO)₂(η³-P₃)Cl in dichloromethane (0.4 M NBu₄PF₆) at 20 °C was undertaken at 0.450 V at a platinum gauze electrode. A near-steady-state voltammogram of the colorless solution before the oxidation is shown in Figure 2b. After electrolysis, the amount of charge passed indicated a one-electron process and the solution was observed to be a red color. A near-steady-state voltammogram (Figure 2c) of the red solution shows a response with an E_{1/2}^r value and a limiting current identical to those for process 1 of the colorless solution before electrolysis. However, the sign of the current indicates that the oxidized species of redox couple 1 is present in solution. A cyclic voltammogram of this solution shows that both processes 1 and 2 remain after bulk oxidation. The IR spectrum of the oxidized solution displays two carbonyl bands which occur at higher frequencies than those of the neutral precursors and are consistent with the formation of *cis*-[Re(CO)₂(η³-P₃)Cl]⁺. Similar results were obtained for the bromo complex, except that a purple solution was produced by the electrolysis. Thus, *cis*-[Re(CO)₂(η³-P₃)X]⁺ appears stable on the synthetic time scale, unlike *cis*-[Mn(CO)₂(η³-P₃)X]⁺.

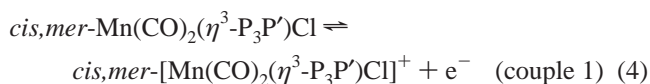
(iii) Chemical Oxidation. NOBF₄ was added to a dichloromethane solution of *cis*-Re(CO)₂(η³-P₃)Br. The colorless solution immediately became purple, and the IR spectrum confirmed the presence of *cis*-[Re(CO)₂(η³-P₃)Br]⁺. The addition of hexane to the dichloromethane solution led to isolation of the purple solid. A similar reaction for the chloro complex produced a red solid. When a dichloromethane solution of *cis*-Re(CO)₂(η³-P₃)X was stirred with NOBF₄ for 1–2 h, the purple or red solution was replaced by a brownish solution. A solid product obtained by adding hexane to the solution was purified by recrystallization from dichloromethane/hexane several times. The IR spectrum of the brown dichloromethane solution of the bromo complex shows a carbonyl band at 2044 cm⁻¹, while an absorption observed at 1778 cm⁻¹ is attributed to a nitrosyl stretch. The

^{31}P NMR spectrum shows three resonances of similar intensities. The formulation $[\text{Re}(\text{CO})(\text{NO})(\text{P}_3)\text{Br}]^+$ is confirmed by electrospray mass spectrometry. The nitrosyl and carbonyl ligands have a *cis* relationship by necessity, since the P_3 ligand requires a facial geometry. There is only one isomer of $[\text{Re}(\text{CO})(\text{NO})(\eta^3\text{-P}_3)\text{Br}]^+$ that conforms to these conditions, and this is shown in structure 8. Spectroscopic data are similar for the chloro



complex, and these species are characterized as *cis*- $[\text{Re}(\text{CO})(\text{NO})(\eta^3\text{-P}_3)\text{X}]\text{BF}_4$.

Electrochemical Studies of $\text{P}_3\text{P}'$ Complexes. A. Manganese Complexes. (i) Cyclic Voltammetry. An oxidative cyclic voltammogram of a 1.0 mM solution of *cis,mer*- $\text{Mn}(\text{CO})_2(\eta^3\text{-P}_3\text{P}')\text{Cl}$ in dichloromethane (0.1 M NBu_4PF_6) at 20 °C shows a reversible redox couple at $E_{1/2} = 0.150$ V (couple 1). Analysis of a near-steady-state voltammogram recorded at a platinum microdisk electrode also indicates that process 1 involves one electron per molecule. Redox couple 1 is therefore assigned to the reaction



A similar response was observed for *cis,mer*- $\text{Mn}(\text{CO})_2(\eta^3\text{-P}_3\text{P}')\text{Br}$ in dichloromethane, and the data are summarized in Table 6.

Cyclic voltammograms of 1.0 mM solutions of *cis,mer*- $[\text{Mn}(\text{CO})_2(\eta^3\text{-P}_3\text{P}'\text{Me})\text{X}]\text{PF}_6$ in dichloromethane or acetone (0.1 M NBu_4PF_6) at 20 °C show a single reversible oxidative response, in each case again assigned to couple 1.

(ii) Bulk Electrolysis. Exhaustive bulk oxidative electrolysis of a solution of *cis,mer*- $\text{Mn}(\text{CO})_2(\eta^3\text{-P}_3\text{P}')\text{Cl}$ in dichloromethane (0.4 M NBu_4ClO_4) at 20 °C was undertaken at 0.300 V (slightly more positive than the potential for process 1) at a platinum gauze working electrode. Upon completion of the electrolysis, the charge passed indicated a one-electron process and the solution which initially was yellow had changed to orange. A reductive cyclic voltammogram of the resultant solution indicates that process 1 now is absent; however a reversible response is observed at $E_{1/2} = -0.430$ V (couple 3). Parts a and b of Figure 3 show voltammograms obtained at a microdisk platinum electrode under near-steady-state conditions before and after oxidation. The sign of the current indicates that, after electrolysis, the compound giving rise to process 3 is in its oxidized form. The IR spectrum of this solution shows a single carbonyl band at 1969 cm^{-1} which is identical to the position of the single carbonyl stretch of the known⁹ compound *trans*- $[\text{Mn}(\text{CO})_2(\eta^3\text{-P}_2\text{P}')\text{Cl}]^+$ ($\text{P}_2\text{P}' = (\text{PPh}_2\text{CH}_2\text{CH}_2)_2\text{PPh}$). Thus, it seems likely that *trans*- $[\text{Mn}(\text{CO})_2(\eta^3\text{-P}_3\text{P}')\text{Cl}]^+$ is present in the oxidized solution.

Bulk reduction of the orange solution was carried out at -0.570 V (slightly more negative than the potential of process 3). A one-electron process was determined from the charge

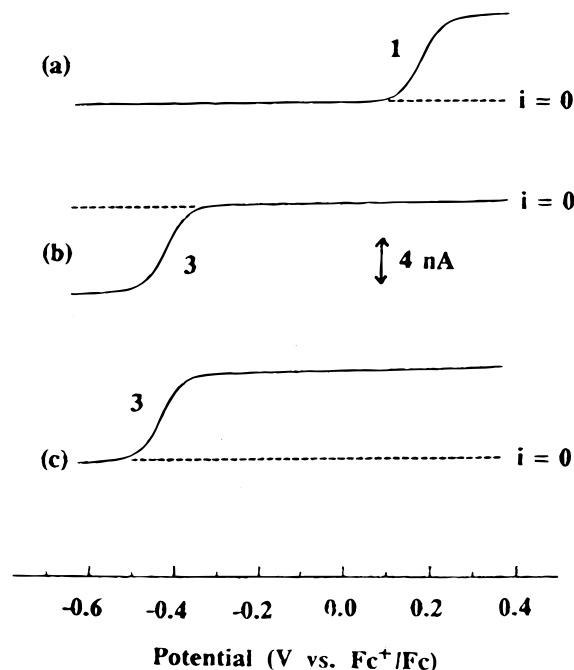
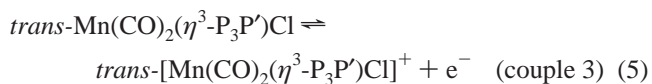
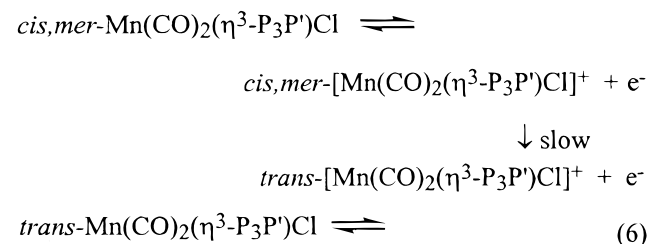


Figure 3. Near-steady-state voltammograms (scan rate 10 mV s^{-1}) recorded at a platinum microdisk electrode (radius $12.5\text{ }\mu\text{m}$) at 20 °C for a 1.0 mM solution of *cis,mer*- $\text{Mn}(\text{CO})_2(\eta^3\text{-P}_3\text{P}')\text{Cl}$ in dichloromethane (0.4 M NBu_4ClO_4): (a) before electrolysis; (b) after exhaustive oxidative electrolysis at a platinum gauze electrode; (c) after subsequent exhaustive reductive electrolysis.

passed during the reductive electrolysis, and the solution became red. A near-steady-state voltammogram indicates that the compound giving rise to process 3 now is in its reduced form (Figure 3c). The IR spectrum of the reduced solution shows a carbonyl band at 1893 cm^{-1} , and the compound present is assigned as *trans*- $\text{Mn}(\text{CO})_2(\eta^3\text{-P}_3\text{P}')\text{Cl}$. The ^{31}P NMR spectrum of the dichloromethane solution shows three peaks (intensity 1:2:1) at δ 138.2, 69.9, and -13.9 ppm; the signal at $\delta -13.9$ ppm is attributed to the pendant phosphorus atom. The resonances of the coordinated phosphorus atoms occur at positions similar to those for the signals of *trans*- $\text{Mn}(\text{CO})_2(\eta^3\text{-P}_2\text{P}')\text{Cl}$.¹² Redox couple 3 therefore is assigned as

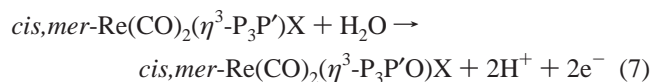


Thus, on the longer time scale, the usual partial square scheme involving isomerization of *cis,mer*⁺ to the electronically more favorable¹³ *trans*⁺ is observed:

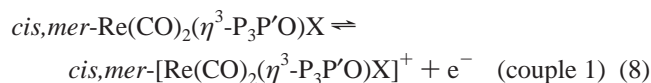


There is no indication of isomerization of *trans*⁰ to *cis,mer*⁰. Bulk electrolysis of a solution of *cis,mer*- $\text{Mn}(\text{CO})_2(\eta^3\text{-P}_3\text{P}')\text{Br}$ produced analogous results.

B. Rhenium Complexes. (i) Cyclic Voltammetry. Electrochemical studies were undertaken only for the complexes *cis,mer*-Re(CO)₂(η³-P₃P')X and *cis,mer*-[Re(CO)₂(η³-P₃P'Me)Br]-PF₆. A cyclic voltammogram of a 1.0 mM solution of *cis,mer*-Re(CO)₂(η³-P₃P')Br in dichloromethane (0.1 M NBu₄PF₆) at 20 °C (scan rate 200 mV s⁻¹) shows an oxidative response at 0.560 V which is shown to be irreversible when the scan direction is reversed immediately after this process. This process is designated as "irrev" in Table 6. Scanning to more positive potentials reveals that this irreversible process appears as a shoulder on a voltammogram for a reversible couple at E_{1/2}^r = 0.570 V (couple 1). The reverse scan and subsequent cycles show an additional weak reversible couple at 0.450 V (couple 4). Cyclic voltammograms of the chloro complex show similar features. The potential of the first irreversible oxidation indicates that it could be either ligand or metal based, since the oxidation of the free P₃P' ligand occurs at a similar potential. As evidenced later, the irreversible process involves oxidation of the pendant phosphorus atom from P(III) to P(V), as observed for the complexes *cis,mer*-Re(CO)₂(η¹-dpm)(η²-dpm)X (dpm = Ph₂-PCH₂PPh₂).¹⁴ The overall process involves reaction with traces of water:

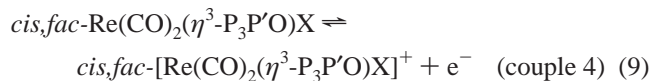


The reversible couple at 0.570 V (couple 1) is attributed to the usual one-electron oxidation of the metal center:



Couple 4 is only a weak feature and has not been fully characterized, but by analogy with the similar behavior of *cis,mer*-Re(CO)₂(η³-P₂P')X, it is probably associated with some initial isomerization of the oxidized *cis,mer*⁺ cation to the isomeric *cis,fac*⁺ cation, which then enables the following

reversible one-electron couple to be detected on second and subsequent cycles:



Voltammetric data are summarized in Table 6.

(ii) Bulk Electrolysis. Exhaustive oxidative bulk electrolysis of a solution of *cis,mer*-Re(CO)₂(η³-P₃P')Br in dichloromethane (0.4 M NBu₄ClO₄) at 20 °C was conducted at 0.500 V (platinum gauze working electrode). The solution remained colorless throughout the electrolysis, and the amount of charge passed corresponded to a two-electron process, as expected for a reaction involving oxidation of the pendant phosphorus atom. A cyclic voltammogram of the oxidized solution reveals only process 1 on the forward scan, while couples 1 and 4 are present in second and subsequent cycles. The IR spectrum of the oxidized solution shows two carbonyl IR bands, similar to those of the complex before electrolysis, while the ³¹P NMR spectrum shows three resonances (ratio 1:2:1), two of which occur at positions similar to those of *cis,mer*-Re(CO)₂(η³-P₃P')Br. However, the third signal, due to the pendant phosphorus atom, has shifted to higher frequency. Similar spectra are obtained for a solution of *cis,mer*-Re(CO)₂(η³-P₃P')Cl after electrolysis, and the data strongly suggest that the complexes *cis,mer*-Re(CO)₂(η³-P₃P'O)X are formed in the bulk electrolysis experiments.

An oxidative cyclic voltammogram of a 1.0 mM solution of *cis,mer*-[Re(CO)₂(η³-P₃P'Me)Br]PF₆ in dichloromethane (0.1 M NBu₄PF₆) at 20 °C shows a reversible couple at E_{1/2}^r = 0.590 V (couple 1), and the reverse scan displays a reduction response (process 4') which is shown to be reversible in a second cycle. A cyclic voltammogram obtained in acetone solution is similar to that obtained in dichloromethane, but process 4' is enhanced in acetone. These voltammograms appear similar to those obtained for *cis,mer*-Re(CO)₂(η³-P₂P')Br,¹² since the pendant phosphorus is methylated and thus cannot be oxidized, unlike the situation for *cis,mer*-Re(CO)₂(η³-P₃P')Br.

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(14) Walter, J. N. Ph.D. Thesis, La Trobe University, 1998.