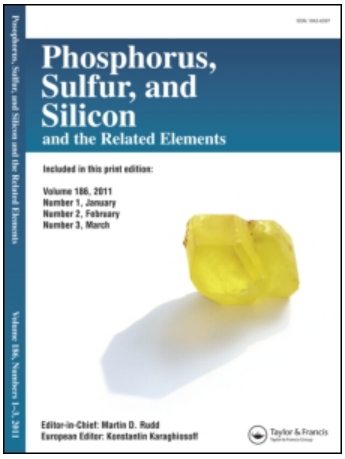

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SYNTHESES AND REACTIONS OF HALOPHOSPHINE COMPLEXES OF GROUP 7 TRANSITION METALS (Mn AND Re)

Do W. Lee[a]; Joseph G. Morse[ab]
[a] Department of Chemistry and Biochemistry, Utah State University, Logan, UT, USA [b] Department of Chemistry, Western Washington University, Bellingham, WA

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SYNTHESES AND REACTIONS OF HALOPHOSPHINE COMPLEXES OF GROUP 7 TRANSITION METALS (Mn AND Re)

DO W. LEE and JOSEPH G. MORSE*†

Contribution from the Department of Chemistry and Biochemistry, Utah State University, Logan, UT 84322-0300, USA

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The photochemical reactions of the "piano stool" complexes $CpMn(CO)_3$, $CpRe(CO)_3$, and $Cp^*Mn(CO)_3$ ($Cp^* = \eta^5$-C_5Me_5) with the bidentate halophosphine ligand 1,2-bis(dichlorophosphino)ethane, $Cl_2PCH_2CH_2PCl_2$ (dcpe), gave the chelate complexes CpMn(CO)dcpe (**1**), CpRe(CO)dcpe (**2**), and Cp^*Mn(CO)dcpe (**3**), respectively. Reactions of the dihalophosphine complexes **1**,**2** with excess F^{1-} and MeO^{1-} gave the substituted compounds $CpM(CO)(R_2PCH_2CH_2PR_2)$ (**4**, M = Mn, R = F; **5**, M = Mn, R = MeO; **6**, M = Re, R = F). The ligand-bridged bimetallic complexes $[CpM(CO)_2](\mu$-dcpe$)[(CO)_2M'Cp]$ (**9**, M,M' = Mn; **10**, M,M' = Re; **11**, M = Mn, M' = Re) were prepared by treatment of the dangling compounds $CpM(CO)_2$ dcpe (**7**, M = Mn; **8**, M = Re) with the solvento complex $CpM'(CO)_2$(THF) (M' = Mn or Re). The crystal structures of **1**, **2**, and **6** were determined by single crystal X-ray structure analyses. **1**: monoclinic, $P2_1/c$, a = 12.008(2) Å, b = 15.685(2) Å, c = 14.980(2) Å, β = 91.01(2)°, V = 2821.0(6) Å^3, Z = 8, R = 0.046; **2**: monoclinic, $P2_1/c$, a = 12.551(2) Å, b = 8.786(2) Å, c = 12.998(2) Å, β = 92.71(2)°, V = 1431.8(4) Å^3, Z = 4, R = 0.040; **6**: triclinic, P1, a = 6.604(2) Å, b = 8.790(2) Å, c = 11.007(2) Å, α = 87.81(2)°, β = 75.48(2)°, γ = 68.27(2)°, V = 573.54(6) Å^3, Z = 2, R = 0.038.

Key words: Halophosphines, complexes, reactivity, rhenium, manganese, chlorophosphine.

INTRODUCTION

Phosphine ligands are among the most useful of ligands in inorganic chemistry, binding to metals in a variety of oxidation states, especially in low oxidation states. Bidentate ligands offer the added advantage of stereochemical control. There is incentive, therefore to develop synthetic methods for preparation of bidentate phosphines with new electronic and structural characteristics as well as to develop methods for incorporation of such phosphines into metal complexes. PCl_3 has long served as the principal starting material for monodentate ligands. The synthesis of $Cl_2PCH_2CH_2PCl_2$ (dcpe) by Toy and Uhing[1] and its commercial availability thus provides not only a bidentate phosphine ligand with strong π-acidity but also a potential starting material for other bidentate phosphines. Previous studies with this compound have demonstrated this utility.[2,3] In particular, previous work in our laboratory demonstrated that it can serve as a precursor to the very strong π-acid ligand $F_2PCH_2CH_2PF_2$ (dfpe),[4] which had been previously prepared in low yield by the photochemical reaction of P_2F_4 with ethene.[5] Like PCl_3, however, its

†Current address: Department of Chemistry, Western Washington University, Bellingham, WA 98225.

routine use is limited to uniformly substituted derivatives because of the high reactivity of the P—Cl bond to nucleophilic substitution.

During the course of our earlier work with dcpe and dfpe, we noted that the reactivity of dcpe was significantly altered upon coordination.[4] For example, dcpeCr$(CO)_4$ can be handled in the open air in the laboratory without difficulty while dcpe smokes and fumes upon exposure even to dry Utah air. Some difference is expected both because the ligand's electronic characteristics are altered on coordination and because an additional coordination site on phosphorus is occupied, factors which clearly alter a metal's chemistry. The substitution chemistry of trihalophosphine oxides also differs significantly from that of the phosphines.[6] A few reports of such differences for coordinated monodentate chlorophosphines have appeared.[7-11] These factors suggested that exploration of the reactivity of dcpe upon coordination to metals might prove fruitful.

In the present study, we examined the synthesis and reactivity of derivatives of $CpMn(CO)_3$, $CpRe(CO)_3$, and $Cp^*Mn(CO)_3$. These were selected because models suggest that the presence of the Cp ring might lead to significant steric differentiation between the P—Cl bonds on the two opposing sides of the chelate ring in addition to whatever reactivity difference may arise in consequence of electronic factors or effects due to closing the open coordination site upon coordination of the phosphorus. It was also anticipated that reactivity differentiation would likely arise when the phosphine bridged two different metal centers or when one phosphorus site remained uncoordinated. Because few reports of phosphine derivatives[12-18] and fewer bisphosphine derivatives of these compounds existed[19,20] [none, to our knowledge, of $CpRe(CO)_3$ or $Cp^*Mn(CO)_3$], we had first to develop preparative methods and to characterize the derivatives desired. We now report their preparation and the reactivity toward nucleophilic substitution of some of the derivatives.

EXPERIMENTAL

All reactions were carried out using standard Schlenk techniques under dry N_2 or Ar. Solvents were dried according to standard procedures and saturated with prepurified nitrogen or argon gas. Photochemistry was carried out in a quartz reaction vessel. A Rayonet Photochemical Reactor emitting ultraviolet light (Lamp Cat. # R.P.R. 3000) was used for small scale reactions (preparation of **1**, **2**, **3**, **7**, **8**). For larger scale reactions a quartz vessel equipped with a cooling jacket and a 100 W medium pressure mercury lamp was used (**7**, **8**, **9**, **10**, **11**). ^1H and ^{13}C nmr spectra were recorded on a Varian XL-300 spectrometer (at 300.19 and 75.44 MHz, respectively) with tetramethylsilane as internal reference in chloroform-*d* at 293 K. ^{31}P and ^{19}F NMR spectra were recorded on the same spectrometer (at 121.4 and 282.19 MHz, respectively) with 85% H_3PO_4 and CF_3COOH as external references in appropriate solvents at 293 K. Infrared spectra were recorded on a Mattson Polaris FT-IR. Single-crystal X-ray diffraction analysis was performed on a Siemens P4 autodiffractometer utilizing SHELXTL-PLUS software for structure solution and refinement. Elemental analyses were obtained from Atlantic Microlab Inc., Norcross, GA. (η^5-C_5H_5)$Mn(CO)_3$ [$CpMn(CO)_3$], (η^5-C_5H_5)$Re(CO)_3$ [$CpRe(CO)_3$], and $Mn_2(CO)_{10}$ were purchased from Strem Chemicals Inc. and were sublimed before use. $Cl_2PCH_2CH_2PCl_2$ (dcpe) and C_5Me_5H were purchased from Strem Chemicals Inc. and were used as received. (η^5-C_5Me_5)$Mn(CO)_3$ [$Cp^*Mn(CO)_3$] was prepared by the cited method.[21] Sodium methoxide was prepared from sodium metal and methanol. $KF \cdot 2H_2O$, $(n\text{-}Bu)_4NCl$, $CDCl_3$, and Florisil were purchased from Aldrich Chemicals Inc., and were used as received.

Synthesis of (η^5-C_5H_5)$Mn(CO)(Cl_2PCH_2CH_2PCl_2)$ (**1**): A mixture of 55 mg (0.27 mmol) of $CpMn(CO)_3$ and 76 mg (0.05 mL, 0.33 mmol) of dcpe in 100 mL of *n*-hexane was exposed to ultraviolet irradiation for 30 min at room temperature. After removing solvent the residue in CH_2Cl_2 was applied to a 1.0 ×

30.0 cm Florisil column. The orange band was eluted with CH_2Cl_2/Et_2O(1:1). Sublimation of eluant at ca. 60°C (10^{-2} Torr) gave an air-stable yellow-orange solid complex **1**: Yield: 46 mg, 44%; mp 200–202°C; ^1H NMR ($CDCl_3$) δ = 4.72 (C_5H_5, t, J_{HP} = 2.4 Hz, 5H), 2.96, 3.15 (CH_2CH_2, m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 85.38 (C_5H_5, s), 49.72 (CH_2CH_2, t, J_{CP} = 17 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = 223.9 (s); IR ν_{CO} 1924 (CH_2Cl_2), 1941 (*n*-hexane) cm^{-1}; Anal. Calcd. for $C_8H_9Cl_4MnOP_2$: C, 25.30; H, 2.39. Found: C, 25.43; H, 2.45.

Synthesis of (η^5-C_5H_5)*Re(CO)*($Cl_2PCH_2CH_2PCl_2$) (**2**): A mixture of 59 mg (0.18 mmol) of $CpRe(CO)_3$ and 46 mg (0.03 mL, 0.20 mmol) of dcpe in 130 mL of Et_2O was irradiated for 3 h at room temperature then filtered through a fritted glass funnel. After removing solvent the residue was dissolved in CH_2Cl_2 and applied to 1.0 × 30.0 cm Florisil column. The light brown band was eluted with CH_2Cl_2/Et_2O (1:1). After removing solvent this residue was again dissolved in CH_2Cl_2 and applied to a 1.0 × 50.0 cm Florisil column on which four bands formed. The first band was eluted with Et_2O/hexane (1:9). Sublimation of the eluant at ca. 50°C (10^{-2} Torr) gave an air-stable pale yellow solid complex **2**. Yield: 16 mg, 18%; mp 191–192°C; ^1H NMR ($CDCl_3$) δ = 5.28 (C_5H_5, s, 5H), 2.80, 3.00 (CH_2CH_2, m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 85.79 (C_5H_5, s), 53.68 (CH_2CH_2, t, J_{CP} = 20.7 Hz), 197.94 (*CO*, br.s); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = 121.04 (s); IR (CH_2Cl_2) ν_{CO} 1932 cm^{-1}; Anal. Calcd. for $C_8H_9Cl_4OP_2Re$: C, 18.79; H, 1.77. Found: C, 18.79; H, 1.80. The second and third bands corresponded to $CpRe(CO)_3$ (trace) and complex **8** (trace). The fourth band was not identified.

Synthesis of (η^5-C_5Me_5)*Mn(CO)*($Cl_2PCH_2CH_2PCl_2$) (**3**): A mixture of 70 mg (0.25 mmol) of $Cp^*Mn(CO)_3$ and 70 mg (0.05 mL, 0.33 mmol) of dcpe in 130 mL of *n*-hexane was irradiated for 35 min at room temperature under argon gas (N_2 gas was not used in order to avoid an N_2 complex). After removing solvent the residue in CH_2Cl_2 was applied to a 1.0 × 30.0 cm Florisil column. The first yellow band was eluted with CH_2Cl_2/Et_2O (1:1). C_5Me_5H and its dimer and $Cp^*Mn(CO)_3$ were removed under high vacuum and the remaining residue was sublimed at ca. 60°C (10^{-2} Torr) to give a deep-yellow solid complex **3**. The solid was relatively air-stable but decomposed quickly in solution. Yield: 32 mg, 29%; mp 131°C (decomposed); ^1H NMR ($CDCl_3$) δ = 2.94, 3.24 (CH_2CH_2, m, 4H), 1.90 (C_5Me_5, s, 15H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 97.57 (C_5Me_5, s), 49.30 (CH_2CH_2, t, J_{CP} = 15 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = 207.52 (s); IR ν_{CO} 1912 ($CDCl_3$), 1919 (*n*-hexane) cm^{-1}. Anal. Calcd. for $C_{13}H_{19}Cl_4MnOP_2$: C, 34.68; H, 4.25. Found: C, 34.61; H, 4.18.

Reaction of **1** *with* $KF\cdot 2H_2O$: To a solution of $KF\cdot 2H_2O$ (80 mg, 0.83 mmol) and $(n\text{-}Bu)_4N^+Cl^-$ (230 mg, 0.83 mmol) in 20 mL of CH_3CN was added a solution of **1** (53 mg, 0.14 mmol) in 10 mL of CH_3CN dropwise over 1 h at room temperature. When the addition was complete, the reaction mixture was stirred for several hours. After removing solvent, the residue in CH_2Cl_2 was applied to a 1.0 × 30.0 cm Florisil column. The pale-yellow band was eluted with CH_2Cl_2/Et_2O (1:1). Sublimation of the eluant at 25°C (10^{-2} Torr) gave an air-stable pale-yellow solid, $CpMn(CO)(F_2PCH_2CH_2PF_2)$ (**4**): Yield: 41 mg, 95%; mp 71–72°C; ^1H NMR ($CDCl_3$) δ = 4.64 (C_5H_5, t, J_{HP} = 1.8 Hz, 5H), 2.25 (CH_2CH_2, m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 80.24 (C_5H_5, s), 36.0 (CH_2CH_2, br.s); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = 301.78 (t, J_{PF} = 1143 Hz); $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ = 49.06 (d, J_{PF} = 1152 Hz), 46.25 (d, J_{PF} = 1138 Hz); IR(CH_2Cl_2) ν_{CO} 1915 cm^{-1}. Anal. Calcd. for $C_8H_9F_4MnOP_2$: C, 30.59; H, 2.89. Found: C, 30.70; H, 2.88.

Reaction of **1** *with NaOMe*: To a solution of NaOMe (4.6 M in MeOH, 0.27 mL, 1.25 mmol) in 30 mL of THF was added a solution of **1** (59 mg, 0.16 mmol) in 30 mL of THF dropwise over 2 h at room temperature. After the addition was complete, the reaction mixture was stirred for an additional 2 h. The reaction mixture was filtered and the solvent was removed. Sublimation of the yellow oil at ca. 60°C (10^{-2} Torr) gave an air-stable pale-yellow oily compound, $CpMn(CO)[(MeO)_2PCH_2CH_2P(OMe)_2]$ (**5**): Yield: 54 mg, 93%; ^1H NMR ($CDCl_3$) δ = 4.40(C_5H_5, t, J_{HP} = 1.5 Hz, 5H), 1.74, 1.96 (CH_2CH_2, m, 4H), 3.52 (O*Me*, d, J_{HP} = 9.9 Hz, 6H), 3.67 (O*Me*, d, J_{HP} = 12.6 Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 78.46 (C_5H_5, s), 30.62 (CH_2CH_2, t, J_{CP} = 26 Hz), 51.8 (O*Me*, two s); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = 264.6 (s); IR (CH_2Cl_2) ν_{CO} 1853 cm^{-1}. Anal. Calcd. for $C_{12}H_{21}MnO_5P_2$: C, 39.79; H, 5.85. Found: C, 39.95; H, 5.91.

Reaction of **2** *with* $KF\cdot 2H_2O$: To a solution of $KF\cdot 2H_2O$ (45 mg, 0.48 mmol) and $(n\text{-}Bu)_4N^+Cl^-$ (130 mg, 0.48 mmol) in 30 mL of CH_3CN was added a solution of **2** (30 mg, 0.060 mmol) in 20 mL of CH_3CN dropwise over 1 h at room temperature. After the addition was complete, the reaction mixture was stirred for several hours. After removing solvent, the residue in CH_2Cl_2 was applied to a 1.0 × 30.0 cm Florisil column. The first band (as identified on a TLC plate) was eluted with CH_2Cl_2/Et_2O (1:1). Sublimation of eluant at 25°C (10^{-2} Torr) gave an air-stable colorless solid, $CpRe(CO)(F_2PCH_2CH_2PF_2)$ (**6**): Yield: 23 mg, 85%; mp 104–105°C; ^1H NMR ($CDCl_3$) δ = 5.23

(C_5H_5, s, 5H), 2.07, 2.26 (CH_2CH_2, m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 81.96 (C_5H_5, s), 41.0 (CH_2CH_2, br.s); $^{31}P\{^1H\}$ NMR (Et_2O) δ = 227.80 (t, J_{PF} = 1081 Hz); $^{19}F\{^1H\}$ NMR (Et_2O) δ = 45.33 (d, J_{FP} = 1108 Hz), δ = 42.43 (d, J_{PF} = 1069 Hz); IR (CH_2Cl_2) ν_{CO} 1919 cm^{-1}. Anal. Calcd. for $C_8H_9F_4OP_2Re$: C, 21.57; H, 2.04. Found: C, 21.66; H, 2.04.

Reaction of **2** *with NaOMe*: To a solution of NaOMe (4.6 M in MeOH, 0.13 mL, 0.60 mmol) in 30 mL of THF was added a solution of **2** (38 mg, 0.075 mmol) in 30 mL of THF dropwise over 1 h at room temperature. When the addition was complete, the reaction mixture was refluxed overnight. After cooling to room temperature the reaction mixture was filtered and the solvent was removed. Sublimation of the residue at ca. 55°C (10^{-2} Torr) gave a colorless oily compound which was sufficiently unstable that we did not obtain acceptable elemental analysis. Spectral data are consistent, however, with the anticipated product $CpRe(CO)[(MeO)_2PCH_2CH_2P(OMe)_2]$: Yield: 26 mg, 70%; ^1H NMR ($CDCl_3$) δ = 5.06 (C_5H_5, s, 5H), 1.75, 2.02 (CH_2CH_2, m, 4H), 3.45 (O*Me*, d, J_{HP} = 11.1 Hz, 6H), 3.63 (O*Me*, d, J_{HP} = 13.2 Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ = 79.77 (C_5H_5, s), 35.21 (CH_2CH_2, t, J_{CP} = 32 Hz), 51.65, 53.24 (O*Me*, s); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = 197.28 (s); IR ($CDCl_3$) ν_{CO} 1857 cm^{-1}.

Synthesis of crude (η^5-C_5H_5)$Mn(CO)_2(Cl_2PCH_2CH_2PCl_2)$ (**7**): A solution of 200 mg (1.00 mmol) of $CpMn(CO)_3$ in 200 mL of THF was irradiated for 30 min at room temperature. Then 460 mg (0.30 mL, 2.00 mmol) of $Cl_2PCH_2CH_2PCl_2$ was added to the red-carmine solution of $CpMn(CO)_2(THF)$. The reaction mixture was stirred for 2 h at room temperature; solvent was removed; and the residue in *n*-hexane was filtered. Solvent was removed under vacuum and the residue was heated under reduced pressure to remove $Cl_2PCH_2CH_2PCl_2$ and $CpMn(CO)_3$. Remaining was an air-sensitive oily yellow compound **7** which still contained **9** and $Cl_2PCH_2CH_2PCl_2$ (characterized by ^1H and ^{31}P NMR spectroscopy) as impurities: Yield: 230 mg, 57% (corrected for impurities via nmr peak areas); ^1H NMR ($CDCl_3$) δ = 4.75 (C_5H_5, s, 5H), 2.88, 3.12 (CH_2CH_2, m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 84.54 (C_5H_5, s), 36.5, 45.0 (CH_2CH_2, m); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = 188.2 (s), 229.0 (s); IR ν_{CO} 1910, 1969 ($CDCl_3$), 1919, 1973 (*n*-hexane) cm^{-1}.

Synthesis of crude (η^5-C_5H_5)$Re(CO)_2(Cl_2PCH_2CH_2PCl_2)$ (**8**): A solution of 15 mg (0.44 mmol) of $CpRe(CO)_3$ in 250 mL of THF was irradiated for 10 min at room temperature. Then 230 mg (0.15 mL, 1.00 mmol) of $Cl_2PCH_2CH_2PCl_2$ was added to the lemon-yellow solution of $CpRe(CO)_2(THF)$ and the reaction mixture was stirred for 2–3 h at room temperature. After removing solvent the residue dissolved in CH_2Cl_2 was filtered. CH_2Cl_2 was removed under vacuum and the residue was heated under reduced pressure to eliminate remaining $Cl_2PCH_2CH_2PCl_2$ and $CpRe(CO)_3$. Remaining was an air-sensitive oily colorless compound **8** which still contained **10** and $Cl_2PCH_2CH_2PCl_2$ (characterized by ^1H and ^{31}P NMR spectroscopy) as impurities: Yield: 58 mg, 25% (corrected for impurities); ^1H NMR ($CDCl_3$) δ = 5.35 (C_5H_5, s, 5H), 2.68, 3.28 (CH_2CH_2, m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 85.62 (C_5H_5, s), 36.80 (CH_2, dd, $^1J_{CP}$ = 50 Hz, $^2J_{CP}$ = 6 Hz), 47.84 (CH_2, dd, $^1J_{CP}$ = 27 Hz, $^2J_{CP}$ = 9 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = 109.09 (d, $^3J_{PCCP}$ = 9.2 Hz), 189.13 (d, $^3J_{PCCP}$ = 13.3 Hz); IR ($CDCl_3$) ν_{CO} 1906, 1967 cm^{-1}.

Synthesis of $[(\eta^5$-$C_5H_5)Mn(CO)_2]_2(\mu$-$Cl_2PCH_2CH_2PCl_2)$ (**9**): A solution of 50 mg (0.25 mmol) of $CpMn(CO)_3$ in 100 mL of THF was irradiated for 30 min at room temperature. Compound **7** (120 mg, 0.29 mmol) was added to the red-carmine solution of $CpMn(CO)_2(THF)$ and the reaction mixture stirred for 2 h at room temperature. After removing solvent the residue in CH_2Cl_2 was chromatographed on a 1.0 × 30.0 cm Florisil column. The first band was eluted with CH_2Cl_2/Et_2O (1:1). After removing solvent under vacuum, recrystallization with CH_2Cl_2/*n*-hexane (1:1) gave a relatively air-stable yellow solid **9**: Yield: 64 mg, 44%; mp 150–151°C; ^1H NMR ($CDCl_3$) δ = 4.75 (C_5H_5, s, 10H), 3.23 (CH_2CH_2, s, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 84.43 (C_5H_5, s), 47.21 (CH_2CH_2, d, J_{CP} = 11 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = 227.62 (s); IR ($CDCl_3$) ν_{CO} 1912, 1971 cm^{-1}. Anal. Calcd. for $C_{16}H_{14}Cl_4Mn_2O_4P_2$: C, 32.90; H, 2.42. Found: C, 32.98; H, 2.46.

Synthesis of $[(\eta^5$-$Re(CO)_2]_2(\mu$-$Cl_2PCH_2CH_2PCl_2)$ (**10**): A solution of 100 mg (0.30 mmol) of $CpRe(CO)_3$ in 250 mL of THF was irradiated for 10 min at room temperature. Compound **8** (200 mg, 0.38 mmol) was added to the lemon-yellow solution of $CpRe(CO)_2(THF)$. The reaction mixture was stirred for 5 h at room temperature; solvent was removed; and the residue in CH_2Cl_2 applied to a Florisil column. The second band (identified by TLC) was eluted with Et_2O/*n*-hexane (1:1); solvent was removed, and the residue recrystallized from CH_2Cl_2 to give a reasonably air-stable white solid **10**: Yield: 44 mg, 18%; mp 149–151°C; ^1H NMR ($CDCl_3$) δ = 5.35(C_5H_5, s, 10H), 3.32 (CH_2CH_2, t, J_{HP} = 3.23 Hz, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 85.55 (C_5H_5, s), 50.25 (CH_2CH_2, t, J_{CP} = 23.2 Hz); $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ = 105.9 (s); IR (CH_2Cl_2) ν_{CO} 1904, 1969 cm^{-1}. Anal. Calcd. for $C_{16}H_{14}Cl_4O_4P_2Re_2$: C, 22.70; H, 1.60. Found: C, 22.65; H, 1.65. The first band was a starting material, $CpRe(CO)_3$.

Synthesis of $[(\eta^5\text{-}C_5H_5)Mn(CO)_2](\mu\text{-}Cl_2PCH_2CH_2PCl_2)[(OC)_2Re(\eta^5\text{-}C_5H_5)]$ (**11**): A solution of 50 mg (0.15 mmol) of $CpRe(CO)_3$ in 250 mL of THF was irradiated for 10 min at room temperature. Compound **7** (80 mg, 0.20 mmol) was added to the lemon-yellow solution and the reaction mixture stirred for 5 h at room temperature. After removing solvent the residue in CH_2Cl_2 was chromatographed on Florisil (1.0 × 30 cm column). The first pale yellow band was eluted with CH_2Cl_2/Et_2O (1:1). After removing solvent, the residue was heated at reduced pressure to remove remaining $CpMn(CO)_3$ and $CpRe(CO)_3$. The residue was dissolved in CH_2Cl_2 and chromatographed again (1.0 × 60 cm Florisil column). The first band eluted was **9**. The second pale-yellow band was eluted with Et_2O/*n*-hexane (1:9). Recrystallization of the eluant from CH_2Cl_2/*n*-hexane (1:1) gave a reasonably air-stable pale-yellow solid **11**: Yield: 16 mg, 15%; mp 156–158°C; ^1H NMR ($CDCl_3$) δ = 4.75 (C_5H_5, s, 5H), 5.34 (C_5H_5, s, 5H), 3.15 (CH_2, d, J_{HP} = 2.4 Hz, 2H), 3.39 (CH_2, d, J_{HP} = 1.2 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 84.41, 85.55 (C_5H_5, s), 49.81 (CH_2, d, J_{CP} = 27.0 Hz), 47.59 (CH_2, d, J_{CP} = 14.9 Hz); $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ = 107.10 (d, $^3J_{PCCP}$ = 51.2 Hz), 227.03 (br.s); IR (CH_2Cl_2) ν_{CO} 1904, 1912, 1966, 1971 cm^{-1}. Anal. Calcd. for $C_{16}H_{14}Cl_4MnO_4P_2Re$: C, 26.86; H, 1.97. Found: C, 26.94; H, 1.98.

X-ray Single-Crystal Structure Determinations of **1**, **2**, *and* **6**: Single crystals were grown from *n*-pentane/*n*-hexane (1:1) at room temperature. The colors and habits of **1**, **2**, and **6** are yellow-orange prism, pale-yellow plate, and colorless needle, respectively. A suitable crystal of each was mounted in a 0.5 mm glass X-ray capillary and centered automatically on a Siemens P4 autodiffractometer using

TABLE I

Crystallographic data of "piano stool" halophosphine complexes

	1	**2**	**6**
empirical formula	$C_8H_9Cl_4MnOP_2$	$C_8H_9Cl_4OP_2Re$	$C_8H_4F_4OP_2Re$
formula weight	379.8	511.1	440.3
crystal size, mm	0.3×0.4×0.4	0.2×0.4×0.5	0.2×0.2×0.65
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a, Å	12.008(2)	12.551(2)	6.604(2)
b, Å	15.685(2)	8.786(2)	8.790(2)
c, Å	14.980(2)	12.998(2)	11.007(2)
α, deg	-	-	87.81(2)
β, deg	91.01(2)	92.71(2)	75.48(2)
γ, deg	-	-	68.27(2)
V, $Å^3$	2821.0(6)	1431.8(4)	573.54(16)
Z	8	4	2
λ, Å	0.71073	0.71073	0.71073
ρ_{calc}, g/cm^3	1.789	2.371	2.549
abs coeff, mm^{-1}	1.895	9.432	10.898
F(000)	1504	952	402
temp, K	294	294	294
2θ(max), deg	50.0	50.0	50.0
no. of data collcd	5437	2840	2224
no. of data with F > 8σ(F)	3038	1990	2046
no. of variables	249	145	141
R/R_w, %	4.60/6.28	4.03/5.91	3.84/5.60

25 randomly selected reflections with $15° < 2\theta < 30°$. The structure was solved by direct methods and all non-hydrogen atoms were located by iterative difference maps and Fourier syntheses. Hydrogen atoms were generated in idealized locations with fixed isotropic thermal parameters and were not refined. Least squares refinement was carried out to anisotropic convergence for all non-hydrogen atoms. The data were corrected by an empirical absorption correction based on psi scan data. For compound **2**, no attempt was made to model the slight disorder in the cyclopentadienyl ring since the atoms were well behaved anisotropically. For compound **6**, the cyclopentadienyl ring was disordered; an isotropic refinement model involving two staggered rings in a 65:35 occupancy ratio was found to be optimal. Details relating to the crystal data, the data collection, and solution and refinement are summarized in Table I. Atomic coordinates and equivalent isotropic displacement coefficients are shown in Tables II, IV, and VI. Some selected bond distances and angles are listed in Tables III, V, and VII.

TABLE II

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) of **1**

Atom	x	y	z	U(eq)[a]
Mn(1)	3080(1)	4085(1)	873(1)	45(1)
C(1)	3580(8)	4002(9)	2240(6)	90(4)
C(2)	4026(10)	3342(8)	1765(8)	99(5)
C(3)	4711(8)	3679(10)	1127(8)	106(6)
C(4)	4669(9)	4557(9)	1202(8)	99(5)
C(5)	3968(10)	4746(8)	1885(8)	94(5)
C(6)	1291(7)	6168(8)	-525(8)	125(5)
C(7)	585(7)	3452(8)	174(6)	104(5)
C(8)	2679(6)	4995(5)	242(5)	50(2)
O(1)	2461(5)	5592(3)	-191(4)	74(2)
P(1)	1372(1)	3836(1)	1130(1)	47(1)
P(2)	2753(2)	3301(1)	-252(1)	48(1)
Cl(1)	337(2)	4790(2)	1580(2)	101(1)
Cl(2)	958(2)	2947(1)	2074(2)	79(1)
Cl(3)	3260(2)	2055(1)	-234(2)	93(1)
Cl(4)	3378(2)	3600(1)	-1490(1)	79(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE III

Selected bond distances (Å) and angles (deg) of **1**

Mn(1)-C(1)	2.134(9)	Mn(1)-C(8)	1.768(7)
Mn(1)-C(2)	2.105(12)	Mn(1)-P(1)	2.106(2)
Mn(1)-C(3)	2.111(11)	Mn(1)-P(2)	2.113(2)
Mn(1)-C(4)	2.119(11)	P(1)-C(7)	1.807(9)
Mn(1)-C(5)	2.122(11)	P(2)-C(6)	1.808(9)
C(1)-C(2)	1.370(18)	C(6)-C(7)	1.430(14)
C(2)-C(3)	1.378(17)	P(1)-Cl(1)	2.066(3)
C(3)-C(4)	1.382(21)	P(1)-Cl(2)	2.052(3)

TABLE III (*Continued*)

C(4)-C(5)	1.369(16)	P(2)-Cl(3)	2.047(3)
C(5)-C(1)	1.367(18)	P(2)-Cl(4)	2.067(3)
C(8)-O(1)	1.166(9)		
C(2)-C(1)-C(5)	107.7(9)	Mn(1)-P(2)-C(6)	113.7(4)
C(1)-C(2)-C(3)	108.3(12)	P(1)-C(7)-C(6)	112.1(6)
C(2)-C(3)-C(4)	107.5(11)	P(2)-C(6)-C(7)	112.6(8)
C(3)-C(4)-C(5)	107.5(11)	Mn(1)-P(1)-Cl(1)	120.8(1)
C(4)-C(5)-C(1)	108.9(11)	Mn(1)-P(1)-Cl(2)	119.9(1)
C(1)-Mn(1)-C(2)	37.7(5)	Mn(1)-P(2)-Cl(3)	119.8(1)
C(2)-Mn(1)-C(3)	38.2(5)	Mn(1)-P(2)-Cl(4)	121.5(1)
C(3)-Mn(1)-C(4)	38.1(6)	C(7)-P(1)-Cl(1)	101.0(4)
C(4)-Mn(1)-C(5)	37.6(4)	C(7)-P(1)-Cl(2)	101.0(4)
C(5)-Mn(1)-C(1)	37.5(5)	C(6)-P(2)-Cl(3)	100.4(4)
C(8)-Mn(1)-P(1)	90.4(2)	C(6)-P(2)-Cl(4)	101.0(4)
C(8)-Mn(1)-P(2)	90.2(2)	Cl(1)-P(1)-Cl(2)	96.5(1)
P(1)-Mn(1)-P(2)	83.3(1)	Cl(3)-P(2)-Cl(4)	96.7(1)
Mn(1)-P(1)-C(7)	114.1(3)	Mn(1)-C(8)-O(1)	177.7(6)

TABLE IV

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) of **2**

Atom	x	y	z	U(eq)[a]
Re	2697(1)	1080(1)	1563(1)	32(1)
C(1)	3224(20)	3543(14)	1794(13)	89(8)
C(2)	2134(18)	3530(16)	1700(19)	96(9)
C(3)	1843(17)	3034(18)	733(19)	98(8)
C(4)	2753(23)	2751(16)	254(11)	92(8)
C(5)	3611(12)	3041(15)	863(16)	75(6)
C(6)	2006(11)	-2500(13)	723(9)	53(4)
C(7)	1477(12)	-2369(12)	1732(10)	56(4)
C(8)	3462(10)	314(13)	2767(9)	49(4)
O	3958(9)	-108(11)	3484(7)	72(4)
P(1)	3072(3)	-1069(3)	738(2)	41(1)
P(2)	1338(2)	-344(3)	2017(2)	33(1)
Cl(1)	4339(3)	-2422(4)	1222(3)	77(1)
Cl(2)	3356(5)	-1017(4)	-805(3)	83(2)
Cl(3)	889(3)	-442(4)	3537(2)	59(1)
Cl(4)	-165(2)	86(4)	1361(2)	56(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE V

Selected bond distances (Å) and angles (deg) of **2**

Re-C(1)	2.279(14)	Re-C(8)	1.918(12)
Re-C(2)	2.275(15)	Re-P(1)	2.233(3)
Re-C(3)	2.270(19)	Re-P(2)	2.218(3)
Re-C(4)	2.251(14)	P(1)-C(6)	1.835(13)
Re-C(5)	2.282(15)	P(2)-C(7)	1.828(11)
C(1)-C(2)	1.367(33)	C(6)-C(7)	1.502(18)
C(2)-C(3)	1.364(33)	P(1)-Cl(1)	2.059(5)
C(3)-C(4)	1.349(34)	P(1)-Cl(2)	2.054(4)
C(4)-C(5)	1.331(29)	P(2)-Cl(3)	2.082(4)
C(5)-C(1)	1.396(27)	P(2)-Cl(4)	2.068(4)
C(8)-O	1.157(15)		

C(2)-C(1)-C(5)	107.9(17)	Re-P(2)-C(7)	114.4(5)
C(1)-C(2)-C(3)	108.0(19)	P(1)-C(6)-C(7)	106.9(8)
C(2)-C(3)-C(4)	106.7(19)	P(2)-C(7)-C(6)	107.5(8)
C(3)-C(4)-C(5)	111.7(16)	Re-P(1)-Cl(1)	121.2(2)
C(4)-C(5)-C(1)	105.7(17)	Re-P(1)-Cl(2)	120.0(2)
C(1)-Re-C(2)	34.9(8)	Re-P(2)-Cl(3)	121.5(2)
C(2)-Re-C(3)	34.9(8)	Re-P(2)-Cl(4)	119.0(1)
C(3)-Re-C(4)	34.7(9)	C(6)-P(1)-Cl(1)	99.2(4)
C(4)-Re-C(5)	34.1(8)	C(6)-P(1)-Cl(2)	99.5(4)
C(5)-Re-C(1)	35.6(7)	C(7)-P(2)-Cl(3)	100.6(4)
C(8)-Re-P(1)	89.2(4)	C(7)-P(2)-Cl(4)	100.8(5)
C(8)-Re-P(2)	86.9(4)	Cl(1)-P(1)-Cl(2)	98.3(2)
P(1)-Re-P(2)	80.4(1)	Cl(3)-P(2)-Cl(4)	96.7(2)
Re-P(1)-C(6)	114.5(4)	Re-C(8)-O	177.1(11)

TABLE VI

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) of **6**

Atom	x	y	z	U(eq)[a]
Re	3343(1)	8338(1)	7657(1)	29(1)
C(1)	1207(31)	11086(17)	8177(16)	40(4)
C(2)	2533(22)	10912(17)	6901(16)	37(4)
C(3)	1764(27)	10047(18)	6188(14)	39(4)
C(4)	-66(34)	9628(20)	7091(23)	41(4)
C(5)	-321(27)	10239(20)	8249(16)	41(4)
C(6)	5097(15)	8153(10)	8814(8)	40(3)
C(7)	5344(17)	4152(10)	7760(10)	52(4)
C(8)	7242(17)	4461(10)	6907(10)	54(4)
O	6109(13)	8086(9)	9533(8)	63(3)
P(1)	2955(4)	6022(2)	8334(2)	36(1)

TABLE VI (*Continued*)

Atom	x	y	z	U(eq)[a]
P(2)	6338(4)	6525(2)	6364(2)	35(1)
F(1)	1038(12)	5540(9)	8036(9)	82(4)
F(2)	2337(12)	5778(7)	9780(5)	75(3)
F(3)	6172(11)	6261(7)	4985(5)	61(3)
F(4)	8659(9)	6766(7)	5907(6)	59(2)
C(1A)	2050(65)	11097(37)	7723(40)	52(8)
C(2A)	2349(48)	10412(36)	6398(31)	41(7)
C(3A)	818(68)	9653(38)	6609(36)	51(9)
C(4A)	-324(61)	9827(43)	7580(48)	56(10)
C(5A)	195(44)	10617(30)	8309(21)	27(6)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE VII

Selected bond distances (Å) and angles (deg) of **6**

Re-C(1)	2.308(13)	C(4A)-C(5A)	1.265(61)
Re-C(2)	2.299(15)	C(5A)-C(1A)	1.435(51)
Re-C(3)	2.336(15)	C(1)-C(1A)	0.651(42)
Re-C(4)	2.346(23)	C(2)-C(2A)	0.779(42)
Re-C(5)	2.318(14)	C(3)-C(3A)	0.853(46)
C(1)-C(2)	1.437(22)	C(4)-C(4A)	0.537(55)
C(2)-C(3)	1.408(27)	C(5)-C(5A)	0.572(39)
C(3)-C(4)	1.511(28)	Re-C(6)	1.891(11)
C(4)-C(5)	1.349(31)	Re-P(1)	2.223(2)
C(5)-C(1)	1.446(30)	Re-P(2)	2.215(2)
Re-C(1A)	2.250(30)	P(1)-C(7)	1.803(8)
Re-C(2A)	2.248(31)	P(2)-C(8)	1.817(9)
Re-C(3A)	2.210(42)	C(7)-C(8)	1.473(15)
Re-C(4A)	2.309(38)	C(6)-O	1.144(14)
Re-C(5A)	2.264(21)	P(1)-F(1)	1.583(10)
C(1A)-C(2A)	1.538(56)	P(1)-F(2)	1.568(6)
C(2A)-C(3A)	1.375(59)	P(2)-F(3)	1.580(7)
C(3A)-C(4A)	1.121(56)	P(2)-F(4)	1.579(7)
C(2)-C(1)-C(5)	108.3(16)	C(6)-Re-P(1)	87.9(3)
C(1)-C(2)-C(3)	107.5(15)	C(6)-Re-P(2)	88.8(2)
C(2)-C(3)-C(4)	106.9(15)	P(1)-Re-P(2)	79.9(1)
C(3)-C(4)-C(5)	108.0(20)	Re-P(1)-C(7)	116.3(4)
C(4)-C(5)-C(1)	109.3(16)	Re-P(2)-C(8)	114.8(3)
C(1)-Re-C(2)	36.3(5)	P(1)-C(7)-C(8)	112.2(6)
C(2)-Re-C(3)	35.4(7)	P(2)-C(8)-C(7)	111.3(6)
C(3)-Re-C(4)	37.6(7)	Re-P(1)-F(1)	119.5(3)
C(4)-Re-C(5)	33.6(7)	Re-P(1)-F(2)	120.1(3)
C(5)-Re-C(1)	36.4(7)	Re-P(2)-F(3)	117.2(2)
C(2A)-C(1A)-C(5A)	95.1(32)	Re-P(2)-F(4)	122.6(2)
C(1A)-C(2A)-C(3A)	102.4(29)	C(7)-P(1)-F(1)	99.5(5)
C(2A)-C(3A)-C(4A)	116.8(45)	C(7)-P(1)-F(2)	101.7(4)
C(3A)-C(4A)-C(5A)	110.9(44)	C(8)-P(2)-F(3)	103.5(4)
C(4A)-C(5A)-C(1A)	114.4(30)	C(8)-P(2)-F(4)	101.2(4)
C(1A)-Re-C(2A)	40.0(14)		
C(2A)-Re-C(3A)	35.9(15)	F(1)-P(1)-F(2)	95.7(5)
C(3A)-Re-C(4A)	28.6(15)	F(3)-P(2)-F(4)	94.0(4)
C(4A)-Re-C(5A)	32.1(14)		
C(5A)-Re-C(1A)	37.1(13)	Re-C(6)-O	177.8(7)

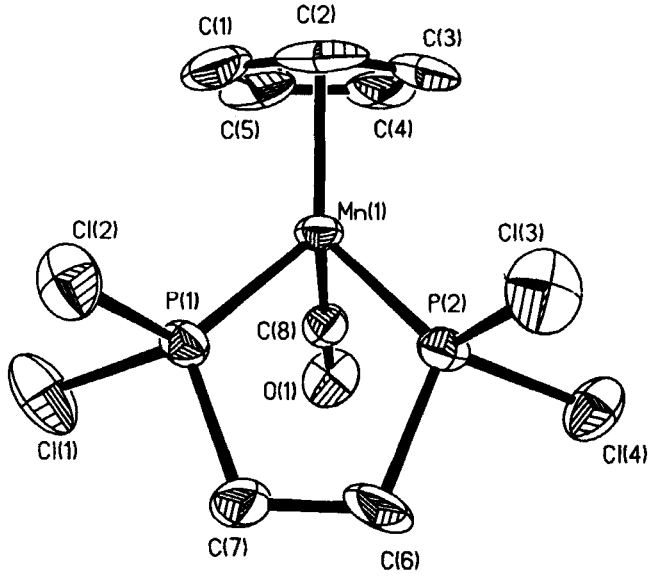

FIGURE 1 ORTEP drawing of **1** with numbering. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

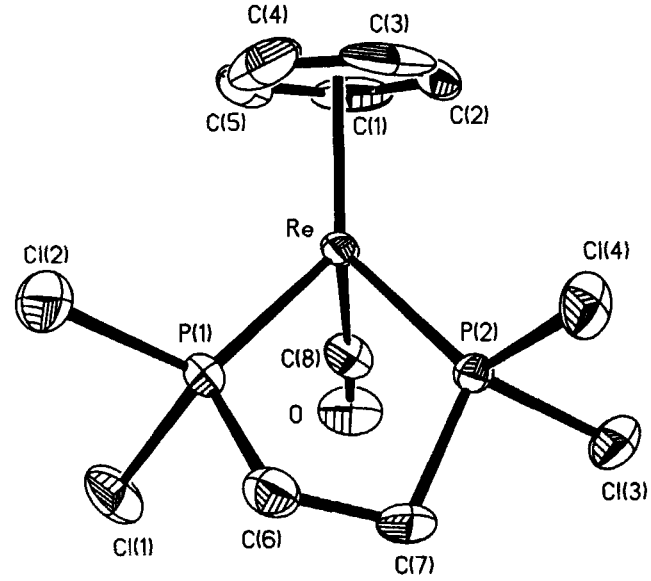

FIGURE 2 ORTEP drawing of **2** with numbering. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

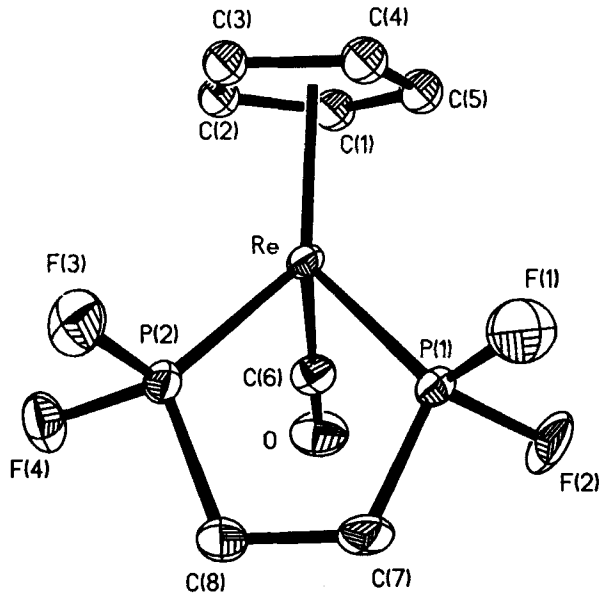

FIGURE 3 ORTEP drawing of **6** with numbering. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

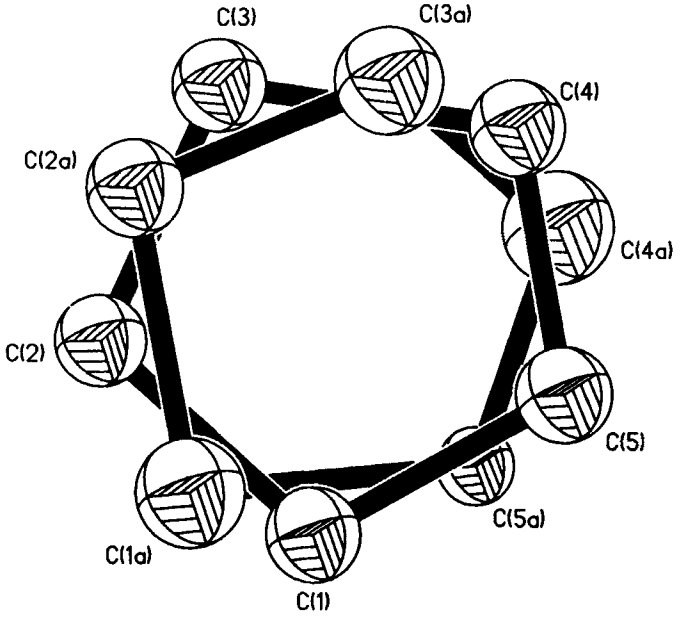

FIGURE 4 ORTEP drawing of disordered bicyclopentadienyl ring in **6**.

Complete X-ray data were deposited as Supplementary Materials with CCDC. The ORTEP drawings are shown in Figures 1–4.

RESULTS AND DISCUSSION

Syntheses of "Piano Stool" Halophosphine Complexes

Photolysis of $CpMn(CO)_3$ and $Cl_2PCH_2CH_2PCl_2$ in hexane gave the chelate complex **1** as the only isolated product. Neither the η^1 compound nor the bridged, dinuclear product was obtained. While **1** can be obtained by photoreaction in other solvents (THF, Et_2O, methylcyclohexane, and benzene were tried) yields were significantly lower (24–8%, respectively). No reaction was observed over three days in the absence of UV light.

Compound **2** is the first bidentate phosphine derivative of $CpRe(CO)_3$ reported. Treatment of $CpRe(CO)_3$ with dcpe in Et_2O gave **2** in low but useful yield. The reaction gave only chelate complex when the concentration of $CpRe(CO)_3$ was less than 1.4×10^{-3} M. As the concentration increased, formation of the ligand-bridged compound **10** increased as well.

Similarly **3** is the first reported bidentate phosphine derivative of $Cp^*Mn(CO)_3$. In this case, photolysis of $Cp^*Mn(CO)_3$ with dcpe in hexane gave both the η^1 phosphine complex and the chelate, η^2, compound. The presence of the η^1 compound was determined by ir and ^{31}P nmr spectroscopy. Compound **3** can also be synthesized in Et_2O in comparable yield, but workup is complicated by greater breakage of Cp^*-Mn bonding, as shown by ^1H nmr spectroscopy. Similar lability of the C_5Me_5 group has been observed in reactions of Ni, Ir, W, Y, and Th complexes, each giving small quantities of C_5Me_5H and its dimer.[22]

Attempts to synthesize $Cp^*Re(CO)$ dcpe by analogous means failed.

Photolysis of $CpMn(CO)_3$ in THF solution generates a solvento complex, $CpMn(CO)_2(THF)$. The lability of the THF ligand can often be used to accomplish synthesis of monodentate or η^1 complexes.[23,24] In the present instance photolytic treatment of the THF complex with dcpe permits preparation of the "dangling" compound **7**, though repeated attempts to purify the compound failed. As the concentration of dcpe was reduced, the production of ligand-bridged compound **9** increased. Neither **7** nor **9** was completely separable under conditions which we discovered. By contrast, when P_2H_4 was used as a ligand under comparable and varying conditions, only the ligand-bridged compound was obtained.[24]

The same general approach, that of first forming the solvento complex, was successful in the preparation of $CpRe(CO)_2(\eta^1$-dcpe) (**8**). Both **7** and **8** proved to be useful precursors for the synthesis of bimetallic ligand-bridged compounds.

The symmetric bimetallic compound $CpMn(CO)_2(\mu$-dcpe$)Mn(CO)_2Cp$, **9**, can be synthesized in either of two ways—the treatment of $CpMn(CO)_2(THF)$ with **7** or with less than 1 equivalent of dcpe. The yield is significantly better by the first route (44% to 32%). The corresponding Re compound **10** can be synthesized either by treatment of $CpRe(CO)_2(THF)$ with **8**, with less than 1 equivalent of dcpe, or the photochemical treatment of $CpRe(CO)_3$ with dcpe in diethylether solution. Yields declined from 18% to 15% to 5%, respectively, for the three methods. The

hetero-bimetallic compound **11** was synthesized either by means of addition of **7** to $CpRe(CO)_2(THF)$ or addition of **8** to $CpMn(CO)_2(THF)$.

Reactions of 1 and 2 with Nucleophiles

The compounds prepared have the potential for nucleophilic attack at the Cp ring, at CO, or at PCl sites. Significant reaction was observed only at the PCl bond sites. The reaction of **1** with excess $KF \cdot 2H_2O$ in the presence of the phase-transfer catalyst $(n\text{-}Bu)_4N^+Cl^-$, gave the fully fluorinated compound **4** in excellent yield (95%). With 18-crown-6 as the phase-transfer catalyst, either in benzene or acetonitrile solution, the fluorination appeared successful from the ^{31}P and ^{19}F nmr data, but neither other spectral nor elemental analysis data was consistent with **4**. Further characterization of the product was not pursued. Fluorination of **2** was similarly successful using excess $KF \cdot 2H_2O$ and $(n\text{-}Bu)_4N^+Cl^-$ in CH_3CN. The yield of 85% **6** was somewhat less than for **4**, a result consistent with the generally lower recovered yields of Re compounds.

Reaction of **1** with excess NaOMe gave the fully substituted phosphine complex **5** in 94% yield. The corresponding reaction with the rhenium compound **2** was less successful. In this case the compound decomposed sufficiently rapidly at room temperature to preclude ready purification or obtaining elemental analysis, though the spectral data are consistent with the fully substituted compound in yield of approximately 70%.

The substituted phosphine products might also be accessible by means of substitution first on the free ligand then ligand substitution for carbonyl, that is by the alternate sequence to that used here. In the case of fluorination, however, the fluorinated ligand is obtained in 47% yield from dcpe.[4] Coupled with a comparable yield of Mn complex to that obtained with dcpe (44%) there is clear advantage to the present sequence (44% followed by 95% vs. 47% followed by 44%). Further, $F_2PCH_2CH_2PF_2$ is exceedingly air and heat-sensitive so that its handling even in vacuum apparatus is tedious.

Spectral Data

Several features of these data are noteworthy. The cyclopentadienyl protons in the chelate bisphosphine manganese complexes appear as triplets with a small P—H coupling constants. Corresponding Re spectra appeared as singlets reflecting inefficient transfer of coupling via Re as compared with Mn. Cyclopentadienyl protons on Re consistently appear downfield from those of the corresponding Mn complexes. The Cp protons are not sensitive to subtle changes in the ligand environment, their chemical shifts being indistinguishable in the "dangling" and ligand-bridged compounds for the same metal.

No signal could be observed corresponding to the carbonyl groups terminally bound to manganese. This has been attributed to quadrupolar broadening of this signal by coupling to the ^{55}Mn nucleus.[25,26] The shiftless relaxation reagent $Cr(acac)_3$ has been used to observe the carbonyl signal in other manganese carbonyl compounds.[26]

The ^{31}P signals of the rhenium derivatives appeared as doublets while those

of manganese derivatives appeared as singlets. This is consistent with the observation of Andrews and coworkers who observed the coupling constants decrease in the order of W > Mo > Cr for their metal carbonyl-diphosphine complexes.[27] Upon coordination, there is usually a downfield shift in the ^{31}P signal.[28,29] This was observed for most of the Mn complexes, but the Re complexes showed an upfield coordination shift. This was also observed by Edwards and Marshalsea for Re complexes[28] and by King and Raghuveer for $(CO)_4W(Me_2PCH_2PMe_2)$.[19] This is, presumably, due to the relative electron richness of the third row transition metals, though ^{31}P chemical shifts are not simply assigned to electronic factors.

The proton decoupled ^{19}F spectra of **4** and **6** showed two doublets due to coupling with phosphorus and to slightly different chemical environments on the chelate ring.

Carbonyl stretching frequencies in mixed carbonyl-phosphine compounds have been extensively utilized to indicate the relative extent of π-bonding in the M—P bonds. The ability of the phosphine ligand to reduce electron density on the metal appeared to decrease as the substituents on phosphorus changed from Cl to F to OMe: for **1**, ν = 1924 cm^{-1}; for **4**, ν = 1915 cm^{-1}; for **5**, ν = 1853 cm^{-1}. This is neither the sequence expected on relative electronegativity grounds nor Tolman's electronic parameters.[30] Nor is it consistent with the sequence seen in the Group 6 metal compounds of the same ligands.[4] The reversal of Cl and F has been observed in other compounds, however.[31] It may be a consequence of F → P π-donation, but it is not obvious why that should be seen in one instance and not in another.

X-ray Crystallography

Crystallographic data for **1**, **2**, and **6** are summarized in Tables I–VII and the structures are illustrated in Figures 1–4. Crystal data were obtained primarily to confirm characterization of the compounds because analytical data were not always unambiguous. There are few obvious unusual features of these structures compared with the structures of the starting materials. The Mn—P distances in **1** are shortened significantly (>0.1 Å) relative to alkylphosphine complexes,[32] consistent with the somewhat stronger bond expected if π-acceptor character is a significant bonding factor. (It is also consistent, however, with the small Cl—P—Cl cone angle and increased σ-bond strength resulting from greater s-character in the phosphorus donor orbital.[33]) Both **1** and **2** show a distinction between the pair of chlorine atoms on the side of the chelate ring toward the Cp ring relative to that opposite the Cp ring, as suggested by molecular models. This is consistent with the chemical shift distinction shown in the ^{19}F nmr spectra for the same pairs of substituent sites and apparent also in the structure of **6**. Whether the distinction is sufficient to differentiate between the two sites in their chemical reactions was not demonstrated under the reaction conditions of this work. Preliminary work with varying stoichiometric mixtures of nucleophiles to complexes is suggestive of such a difference, but it is not sharp and the data remain ambiguous at this time.

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