Truter's cell compared to those of the $P4_2/n$ cell of $Co(tu)_4Cl_2$ are $a = b = 13.524$ (5) Å, $c = 8.981$ (5) Å and $a = b = 13.508$ (7) Å, $c = 9.106$ (5) Å, respectively.

Upon examination of the data for $Co(tu)_4Cl_2$ it was noted that of the 885 observed reflections 499 were consistent with the diffraction pattern for $Ni(tu)_4Cl_2$ (compare with 404 reflections observed for $Ni(tu)_4Cl_2$ by Truter[6]). However, the other 386 reflections that changed the cell represent 43.6% of the total number of reflections but account for only 28.6% of the sum of structure amplitudes. Hence, all five compounds appear to be crystallographically isomorphous if one examines only the *hk*0 Weissenberg photographs and the oscillation photograph rotating about the symmetry axis. However, the symmetry axis is ~0.1 Å longer in the Co type of complex.

The $Co(tu_4)Cl_2$ structure is thus a representative structure for $Mn(tu)_4Cl_2$, $Fe(tu)_4Cl_2$, and $Cd(tu)_4Cl_2$. It is safe to say that these are all *trans* octahedral with both metal–chlorine distances equal in length. On the other hand, *trans*-$Ni(tu)_4Cl_2$ can be viewed as a distortion toward a tetragonal-pyramid configuration. It should be possible with the right combination of sulfur ligands and halogen to form a NiR_4X tetragonal pyramid. It is to be noted that tetrakis(thioacetamide)-nickel(II) chloride is *trans* octahedral with equal Ni–Cl distances at 2.44 ± 0.02 Å[25] and tetrakis(thioacetamide)-nickel(II) bromide is also *trans* octahedral but with a long Ni–Br distance of 3.599 ± 0.004 Å.[26] The structure of tetrakis(dimethylthiourea)nickel(II) bromide is definitely square planar since the bromine is no longer axial and the Ni–Br distance is 4.561 ± 0.003 Å.[27]

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[25] J. E. O'Connor, R. L. Girling, and E. L. Amma, to be submitted for publication.

[26] W. A. Spofford, III, and E. L. Amma, to be submitted for publication.

[27] M. S. Weininger and E. L. Amma, to be submitted for publication.

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Complexes of Trivalent Phosphorus Derivatives. XI. Reactions of Cyclopentadienylmanganese Dicarbonyl Nitrosyl Hexafluorophosphate with Various Tertiary Phosphines and Related Ligands[1]

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The manganese salt $[C_5H_5Mn(CO)_2NO][PF_6]$ reacts with various tertiary phosphines and related ligands upon heating in methanol without ultraviolet irradiation to form yellow to orange substitution products $[C_5H_5Mn(CO)(NO)L][PF_6]$ ($L = (C_6H_5)_3P$, $(C_6H_5)_3As$, $(C_6H_5)_3Sb$, and $(C_6H_5)_2PC{\equiv}CC_6H_5$ but not $(C_6H_5)_3Bi$ or $(C_6H_5O)_3P$). The ditertiary phosphine *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ reacts with $[C_5H_5Mn(CO)_2NO][PF_6]$ to form the red-orange bidentate monometallic (chelate) derivative $[C_5H_5Mn(NO)(diphos)][PF_6]$. The other ditertiary phosphines $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$, $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$, and $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2$ may form monodentate monometallic derivatives of the type $[C_5H_5Mn(CO)(NO)(diphos)][PF_6]$ and/or bidentate bimetallic (bridging) derivatives of the type $[C_5H_5Mn(CO)(NO)]_2(diphos)[PF_6]_2$ depending on the ligand and the reaction conditions. The triteriary phosphine $CH_3C[CH_2P(C_6H_5)_2]_3$ reacts with $[C_5H_5Mn(CO)_2NO][PF_6]$ to form $[(C_5H_5)_2Mn_2(CO)(NO)_2(triphos)][PF_6]_2$ in which two of the phosphorus atoms are bonded to one manganese atom and the third phosphorus atom is bonded to the other manganese atom. The infrared and proton nmr spectra of the new compounds are discussed.

Introduction

Within the past few years reactions of a variety of neutral metal carbonyls with numerous tricovalent phosphorus derivatives have been investigated.[4] However, corresponding reactions of metal carbonyl cations with tricovalent phosphorus derivatives have received relatively little attention. A few reactions of $Re(CO)_6^+$ with chelating tertiary phosphines have been reported to give various substitution products.[5] However, no reactions of cyclopentadienylmetal carbonyl cations with tertiary phosphines have been reported although phosphine-substituted derivatives of $C_5H_5Fe(CO)_3^+$ and $C_5H_5M(CO)_4^+$ (M = Mo and W) have been prepared by other methods.[6,7] This paper reports the reactions of the salt $[C_5H_5Mn(CO)_2NO][PF_6]$ with a variety of tertiary phosphines and related ligands. These reactions could be effected thermally in contrast to the corresponding reactions of the isoelectronic $C_5H_5Mn(CO)_3$ with tertiary phosphines which require ultraviolet irradiation.[8]

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[1] Part X: R. B. King, L. W. Houk, and P. N. Kapoor, *Inorg. Chem.*, **8**, 1792 (1969).

[2] Fellow of the Alfred P. Sloan Foundation, 1967–1969.

[3] Postdoctoral Research Associate, 1968–1970.

[4] For a review on metal carbonyl derivatives of tertiary phosphines see T. A. Manuel, *Advan. Organometal. Chem.*, **3**, 181 (1965).

[5] R. S. Nyholm, M. R. Snow, and M. H. B. Stiddard, *J. Chem. Soc.*, 6564 (1965).

[6] A. Davison, M. L. H. Green, and G. Wilkinson, *ibid.*, 3172 (1961).

[7] P. M. Treichel, K. W. Barnett, and R. L. Shubkin, *J. Organometal. Chem.* (Amsterdam), **7**, 449 (1967).

[8] R. G. Hayter and L. F. Williams, *J. Inorg. Nucl. Chem.*, **26**, 1977 (1964).

TABLE I
NEW COMPOUNDS PREPARED IN THIS WORK

			Analyses, %							
			C		H		N		Mn	
Compound[a]	Color	Mp, °C	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[C_5H_5Mn(CO)(NO)(P(C_6H_5)_3)][PF_6]$	Orange	180–183 dec	48.9	49.4	3.4	3.3	2.4	2.3	9.2	9.4
$[C_5H_5Mn(CO)(NO)(As(C_6H_5)_3)][PF_6]$	Orange	157–160 dec	45.9	46.1	3.2	3.3	2.2	2.1	8.7	8.7
$[C_5H_5Mn(CO)(NO)(Sb(C_6H_5)_3)][PF_6]$	Pale orange	169–170 dec	42.7	42.8	3.0	3.2	2.1	2.0	8.1	8.3
$[C_5H_5Mn(CO)(NO)((C_6H_5)_2PC_2C_6H_5)][PF_6]$	Light yellow	79–80	51.4	53.3	3.3	3.6	2.3	2.1	9.0	8.5
$[C_5H_5Mn(CO)(NO)(Pf{-}Pf)][PF_6]$	Orange	165–166	53.2	53.2	4.1	4.2	1.9	1.9	7.6	7.5
$[C_5H_5Mn(CO)(NO)]_2(Pf{-}Pf)[PF_6]_2$	Deep yellow	209–210 dec	43.7	44.0	3.3	3.6	2.7	2.6	10.5	10.2
$[C_5H_5Mn(NO)(cPf{=}Pf)][PF_6]$	Red-orange	227–228 dec	53.9	54.1	3.9	4.5	2.0	1.8	7.9	7.5
$[C_5H_5Mn(CO)(NO)(tPf{=}Pf)][PF_6]$	Deep yellow	192–194 dec	53.4	53.3	3.8	3.7	1.9	1.9	7.6	7.9
$[C_5H_5Mn(CO)(NO)]_2(tPf{=}Pf)[PF_6]_2$	Yellow	219–221 dec	43.7	44.1	3.1	3.3	2.6	2.6	10.7	10.7
$[C_5H_5Mn(CO)(NO)(Pf{\equiv}Pf)][PF_6]$	Yellow-orange	143–144	53.6	53.6	3.5	3.5	1.9	1.9	7.7	8.1
$[C_5H_5Mn(CO)(NO)]_2(Pf{\equiv}Pf)[PF_6]_2$	Orange	213–215 dec	43.8	44.3	2.9	2.5			10.5	10.8
$[C_5H_5Mn(CO)(NO)]_2(PfC{\equiv}CPf)[PF_6]_2$	Pale orange	203–205 dec	45.0	45.5	3.2	3.2	2.6	2.5	10.3	10.5
$[(C_5H_5)_2Mn_2(CO)(NO)_2(triphos)][PF_6]_2$	Yellow	214–215 dec	50.3	50.3[b]	4.0	4.2[b]	2.3	2.1		

[a] For the abbreviations of the ligands used see the Experimental Section. [b] Average of analyses on two independently prepared samples.

Experimental Section

Microanalyses (Table I) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Tungsten(VI) oxide was added as a catalyst during the combustions to determine carbon and hydrogen. This expedient assured complete oxidation of the carbon to CO_2 eliminating the previously observed tendencies[9] for low carbon analyses in organophosphorus derivatives of transition metals. Melting and decomposition points were taken of samples in capillaries and are uncorrected. A nitrogen atmosphere was always provided for the following three operations: (a) carrying out reactions, (b) handling all filtered solutions of metal complexes, and (c) admitting to evacuated vessels.

Triphenylphosphine and diphenylchlorophosphine were purchased from Eastern Chemical Corp., Pequannock, N. J. Triphenylarsine, triphenylstibine, and triphenylbismuth were generous gifts of M and T Chemicals, Inc. The remaining tricovalent phosphorus derivatives were prepared by one of the following two general methods: (1) reaction of diphenylchlorophosphine with an organolithium or organomagnesium derivative: $(C_6H_5)_2PC{\equiv}CC_6H_5$[10] and $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$ (Pf≡Pf);[11] (2) reaction of lithium diphenylphosphide with an organic halide: $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (Pf—Pf),[12] *cis*- and *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ (cPf=Pf and tPf=Pf, respectively),[13] $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2$ (PfC≡CPf),[14] and $CH_3C[CH_2P(C_6H_5)_2]_3$ (triphos).[12] The salt $[C_5H_5Mn(CO)_2NO][PF_6]$ was prepared by the previously described procedure.[15]

Reactions of $[(C_5H_5Mn(CO)_2NO][PF_6]$ with Monodentate Ligands.—A mixture of 2.0 g (5.7 mmol) of $[C_5H_5Mn(CO)_2NO][PF_6]$, 1.5 g (5.7 mmol) of triphenylphosphine, and 50 ml of methanol was boiled under reflux for 1.5 hr. The reaction mixture was cooled to room temperature. The resulting orange precipitate was filtered off, washed with methanol, and then recrystallized twice from a mixture of methanol and dichloromethane to give 1.98 g (60% yield) of orange $[C_5H_5Mn(CO)(NO)P(C_6H_5)_3][PF_6]$.

A similar reaction between $[C_5H_5Mn(CO)_2NO][PF_6]$ and triphenylarsine gave a 36% yield of orange $[C_5H_5Mn(CO)(NO)As(C_6H_5)_3][PF_6]$.

A mixture of 1.0 g (2.85 mmol) of $[C_5H_5Mn(CO)_2NO][PF_6]$, 2.0 g (5.65 mmol) of triphenylstibine, and 75 ml of methanol was boiled under reflux for 6 hr. Solvent was removed from the reaction mixture at ~35 mm. The product was extracted from the residue with several portions of dichloromethane. The filtered extracts were treated with benzene and then concentrated at ~35 mm. The product which separated was recrystallized from a mixture of dichloromethane and benzene to give 0.52 g (27% yield) of pale orange $[C_5H_5Mn(CO)(NO)Sb(C_6H_5)_3][PF_6]$.

A mixture of 1.5 g (4.27 mmol) of $[C_5H_5Mn(CO)_2NO][PF_6]$, 1.0 g (3.57 mmol) of $(C_6H_5)_2PC{\equiv}CC_6H_5$, and 75 ml of methanol was boiled under reflux for 1.5 hr. The methanol was then removed at ~35 mm and the dry residue was washed with benzene. The product was extracted from this residue with several portions of dichloromethane. Ethanol was added to the filtered dichloromethane extracts. Upon concentrating and cooling 0.73 g (28% yield) of light yellow $[C_5H_5Mn(CO)(NO)(C_6H_5)_2PC{\equiv}CC_6H_5][PF_6]$ was obtained.

Reaction of $[C_5H_5Mn(CO)_2NO][PF_6]$ with $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$.—A mixture of 0.44 g (1.25 mmol) of $[C_5H_5Mn(CO)_2NO][PF_6]$, 0.50 g (1.25 mmol) of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, and 100 ml of methanol was boiled under reflux for 1 hr. The reaction mixture was filtered hot to give 0.065 g (10% yield) of deep yellow $[C_5H_5Mn(CO)(NO)]_2(Pf{-}Pf)[PF_6]_2$. The filtrate was evaporated to dryness at ~35 mm. The residue was extracted with several portions of dichloromethane. Treatment of the filtered dichloromethane extracts with ethanol followed by concentration at ~35 mm gave 0.44 g (49% yield) of orange $[C_5H_5Mn(CO)(NO)(Pf{-}Pf)[PF_6]$.

A similar reaction between 0.806 g (2.30 mmol) of $[C_5H_5Mn(CO)_2NO][PF_6]$ and 0.46 g (1.15 mmol) of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ gave 0.475 g (40% yield) of $[C_5H_5Mn(CO)(NO)]_2(Pf{-}Pf)[PF_6]_2$ and 0.148 g (18% yield) of $[C_5H_5Mn(CO)(NO)(Pf{-}Pf)][PF_6]$.

Reaction of $[C_5H_5Mn(CO)_2NO][PF_6]$ with *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$.—A mixture of 2.0 g (5.70 mmol) of $[C_5H_5Mn(CO)_2NO][PF_6]$, 2.0 g (5.06 mmol) of *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$, and 100 ml of acetone was boiled under reflux for 17.5 hr. Solvent was then removed from the reaction mixture at ~35 mm. The oily residue was washed with several portions of benzene to remove unchanged phosphine. The residue was then extracted with several portions of boiling methanol. The filtered red solution was allowed to cool to room temperature and finally concentrated at ~35 mm. The crystals which separated were recrystallized from a mixture of dichloromethane and ethanol to give 0.87 g (22% yield) of red-orange $[C_5H_5Mn(NO)(cPf{=}Pf)][PF_6]$.

Reaction of $[C_5H_5Mn(CO)_2NO][PF_6]$ with *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$.—A mixture of 2.0 g (5.72 mmol) of $[C_5H_5Mn(CO)_2NO][PF_6]$, 1.2 g (3.03 mmol) of *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$, and 75 ml of methanol was boiled under reflux for 2.0 hr. Solvent was then removed from the reaction mixture at ~35 mm. The residue was extracted with several portions of dichloro-

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[9] R. B. King, K. H. Pannell, C. A. Eggers, and L. W. Houk, *Inorg. Chem.*, **7**, 2353 (1968); R. B. King, L. W. Houk, and K. H. Pannell, *ibid.*, **8**, 1042 (1969).

[10] W. Chodkiewicz, P. Cadiot, and A. Willemart, *Compt. Rend.*, **250**, 866 (1960).

[11] H. Hartmann, C. Beerman, and H. Czempik, *Z. Anorg. Allgem. Chem.*, **287**, 261 (1956).

[12] J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

[13] A. M. Aguiar and D. Daigle, *J. Am. Chem. Soc.*, **86**, 2299 (1964).

[14] R. B. King and A. Efraty, to be submitted for publication.

[15] R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 791 (1964).

methane. The filtered dichloromethane extracts were evaporated at ~35 mm and the residue recrystallized from a mixture of dichloromethane and benzene to give 0.67 g (17% yield) of deep yellow $[C_5H_5Mn(CO)(NO)(tPf{=}Pf)][PF_6]$.

The residue from the original dichloromethane extraction was the binuclear derivative $[C_5H_5Mn(CO)(NO)]_2(tPf{=}Pf)[PF_6]_2$. This residue was washed with dichloromethane and benzene. Recrystallization from boiling acetone gave 1.28 g (43% yield) of yellow $[C_5H_5Mn(CO)(NO)]_2(tPf{=}Pf)[PF_6]_2$.

Reaction of $[C_5H_5Mn(CO)_2NO][PF_6]$ with $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$.—A mixture of 0.9 g (1.7 mmol) of $[C_5H_5Mn(CO)_2NO][PF_6]$, 2.0 g (5.08 mmol) of $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$, and 75 ml of methanol was boiled under reflux for 1.5 hr. Solvent was removed at ~35 mm. The residue was extracted with dichloromethane. The filtered dichloromethane extracts were evaporated at ~35 mm and the residue was washed with benzene to remove excess ligand. Recrystallization from methanol or a mixture of methanol and dichloromethane gave 1.23 g (52% yield) of yellow-orange $[C_5H_5Mn(CO)(NO)(Pf{\equiv}Pf)][PF_6]$.

For the preparation of the binuclear derivative a different ratio of reactants was used. A mixture of 1.0 g (2.85 mmol) of $[C_5H_5Mn(CO)_2NO][PF_6]$, 0.46 g (1.17 mmol) of $(C_6H_5)_2P{\equiv}CP(C_6H_5)_2$, and 100 ml of methanol was boiled under reflux for 2 hr. Solvent was removed at ~35 mm. The residue was extracted with dichloromethane. The filtered dichloromethane extracts were evaporated at ~35 mm. The residue was recrystallized from a mixture of dichloromethane and ethanol to give 0.025 g (2.1% yield) of orange $[C_5H_5Mn(CO)(NO)]_2(Pf{\equiv}Pf)[PF_6]_2$.

Reaction of $[C_5H_5Mn(CO)_2NO][PF_6]$ with $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2$.—A mixture of 0.80 g (2.28 mmol) of $[C_5H_5Mn(CO)_2NO][PF_6]$, 1.05 g (2.50 mmol) of $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2$, and 150 ml of methanol was boiled under reflux for 2.5 hr. The reaction mixture was filtered hot and the filtrate was allowed to stand at room temperature for 2 days. The deep orange crystals which separated were purified by crystallization from a mixture of dichloromethane and ethanol to give 0.445 g (39% yield) of pale-orange $[C_5H_5Mn(CO)(NO)]_2(PfC{\equiv}CPf)[PF_6]_2$.

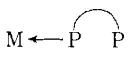
Reaction of $[C_5H_5Mn(CO)_2NO][PF_6]$ with $CH_3C[CH_2P(C_6H_5)_2]_3$.—A mixture of 2.0 g (5.72 mmol) of $[C_5H_5Mn(CO)_2NO][PF_6]$, 2.0 g (3.21 mmol) of $CH_3C[CH_2P(C_6H_5)_2]_3$, and 100 ml of methanol was refluxed for 1.5 hr. Solvent was removed at ~35 mm and the residue was washed with benzene to remove any excess ligand. The dry solid was extracted with dichloromethane. Ethanol was added to the filtered dichloromethane extracts. Concentration at ~35 mm gave a precipitate which was purified by recrystallization from a mixture of dichloromethane and ethanol to give 2.0 g (56% yield) of yellow $[(C_5H_5)_2Mn_2(CO)(NO)_2(triphos)][PF_6]_2$. In a repeat experiment a mixture of 1.0 g (2.85 mmol) of $[C_5H_5Mn(CO)_2NO][PF_6]$ and 0.59 g (0.95 mmol) of $CH_3C[CH_2P(C_6H_5)_2]_3$ gave 0.560 g (43% yield) of $[(C_5H_5)_2Mn_2(CO)(NO)_2(triphos)][PF_6]$, identical with the material prepared as described above.

Discussion

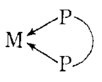
The reactions of $[C_5H_5Mn(CO)_2NO][PF_6]$ with the various ligands discussed in this paper did not require ultraviolet irradiation in contrast to similar reactions with the isoelectronic $C_5H_5Mn(CO)_3$.[8] Products of the type $[C_5H_5Mn(CO)(NO)L][PF_6]$ were obtained not only with the monodentate ligands but also with the ditertiary phosphines Pf—Pf, tPf=Pf, and Pf≡Pf. The monometallic derivatives of the type $[C_5H_5Mn(CO)(NO)L][PF_6]$ were readily soluble in dichloromethane and thus could be separated from any unchanged $[C_5H_5Mn(CO)_2NO][PF_6]$ which is insoluble in dichloromethane. The potential ligands triphenylbismuth, triphenyl phosphite, and hexakis(trifluoromethyl)-1,4-diphosphabicyclo[2.2.2]octatriene-2,5,7 failed to react with $[C_5H_5Mn(CO)_2NO][PF_6]$ in boiling methanol using techniques similar to those successfully employed for the compounds described in this paper. The presence of the hexafluorophosphate anion in all of the new compounds described in this paper was confirmed by the presence of a strong $\nu(PF)$ infrared frequency in the range 860–820 cm^{-1} in their infrared spectra.

The behavior of the ditertiary phosphines when treated with $[C_5H_5Mn(CO)_2NO][PF_6]$ is particularly interesting. Ditertiary phosphines can interact with metal atoms in the following three ways: (1) In the monodentate monometallic (Ia) case only one phosphine atom of the ditertiary phosphines is bonded to the metal atom with the other one remaining uncomplexed. (2) In the bidentate monometallic (Ib) case the ditertiary phosphine acts as a chelating agent. This type of behavior is only possible if the two phosphorus atoms are so situated spatially that they can form a ring with the metal atom. In the cases of the ditertiary phosphines used in this study this stereochemical condition is fulfilled only by the two ligands $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ and *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$. (3) In the bidentate bimetallic (Ic) case the ditertiary phosphine acts as a bridge between the two metal atoms.

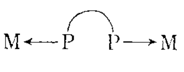
In the cases of metal carbonyl derivatives, formation of bidentate monometallic ("chelate") derivatives will be hindered by the increased resistance of carbonyl groups to substitution upon replacement of some carbonyl groups with tertiary phosphine ligands. This arises from the reduced π-acceptor ability of tertiary phosphines as compared with carbonyl groups, thereby increasing the electron density available for retrodative π bonding with the fewer remaining carbonyl groups, hence increasing the strength of the metal–carbon bond. This will increase the tendency for the second tricovalent phosphorus atom in a potentially chelating ditertiary phosphine to replace a carbonyl group attached to a second metal atom rather than a further carbonyl group attached to the metal atom to which the first phosphorus atom has bonded. Thus bidentate bimetallic (Ic) behavior will be favored over bidentate monometallic behavior (Ib) in metal carbonyl complexes relative to metal halide complexes; in metal halide complexes a potentially chelating ditertiary phosphine always acts as a chelating ligand (Ib) rather than a bridging ligand (Ic).[16]



Ia



Ib



Ic

The only ditertiary phosphine used in this study which acted as a chelating agent when allowed to react with $[C_5H_5Mn(CO)_2NO][PF_6]$ was *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)$ which formed red-orange $[C_5H_5Mn(NO)(cPf{=}Pf)][PF_6]$ (II). The absence of $\nu(CO)$ frequencies (Table II) in the infrared spectrum of II con-

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[16] For a review of tertiary phosphine complexes of metal halides see G. Booth, *Advan. Inorg. Chem. Radiochem.*, **6**, 1 (1964).

TABLE II

INFRARED SPECTRA OF SOME CYCLOPENTADIENYLMANGANESE NITROSYL DERIVATIVES IN THE 2200–1700-CM^{-1} REGION[a,b]

	Infrared spectrum, cm^{-1}		
Compound[c]	$\nu(CO)$	$\nu(NO)$	$\nu(C{\equiv}C)$
$[C_5H_5Mn(CO)_2NO][PF_6]$	2114, 2076	1865	. . .
$[C_5H_5Mn(CO)(NO)(P(C_6H_5)_3)][PF_6]$	2028	1787	. . .
$[C_5H_5Mn(CO)(NO)(As(C_6H_5)_3)][PF_6]$	2028	1788	. . .
$[C_5H_5Mn(CO)(NO)(Sb(C_6H_5)_3)][PF_6]$	2029	1789	. . .
$[C_5H_5Mn(CO)(NO)((C_6H_5)_2PC_2C_6H_5)][PF_6]$	2035	1798	2065
$[C_5H_5Mn(CO)(NO)(Pf\text{—}Pf)][PF_6]$	2038	1808	. . .
$[C_5H_5Mn(CO)(NO)]_2(Pf\text{—}Pf)[PF_6]_2$	2033 2010	1805 1779	. . .
$[C_5H_5Mn(NO)(cPf{=}Pf)][PF_6]$		1770	. . .
$[C_5H_5Mn(CO)(NO)(tPf{=}Pf)][PF_6]$	2040	1800	. . .
$[C_5H_5Mn(CO)(NO)]_2(tPf{=}Pf)[PF_6]_2$	2043	1803	. . .
$[C_5H_5Mn(CO)(NO)(Pf{\equiv}Pf)][PF_6]$	2041	1797	2106
$[C_5H_5Mn(CO)(NO)]_2(Pf{\equiv}Pf)[PF_6]_2$	2042 2020	1814 1789	Absent
$[C_5H_5Mn(CO)(NO)]_2(PfC{\equiv}CPf)[PF_6]_2$	2030	1803	Absent
$[(C_5H_5)_2Mn_2(CO)(NO)_2(triphos)][PF_6]_2$	2022	1790, 1742	. . .

[a] These spectra were taken in potassium bromide pellets on a Perkin-Elmer Model 257 grating spectrometer. [b] The infrared spectra of all of these compounds exhibited strong absorptions in the range 860–820 cm^{-1} from the $\nu(PF)$ of the PF_6^- anion. [c] For the abbreviations of the ligands used see the Experimental Section.

TABLE III

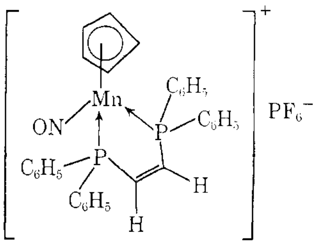
PROTON NMR SPECTRA OF SOME CYCLOPENTADIENYLMANGANESE NITROSYL DERIVATIVES[a]

	Proton nmr spectra, τ[c]		
Compound[b]	C_6H_5	C_5H_5	Other
$[C_5H_5Mn(CO)_2NO][PF_6]$[d]	. . .	3.86 s	. . .
$[C_5H_5Mn(CO)(NO)(P(C_6H_5)_3)[PF_6]$	2.22	4.19 d (2)	. . .
$[C_5H_5Mn(CO)(NO)(As(C_6H_5)_3)][PF_6]$	2.28, 2.31	4.07 s	. . .
$[C_5H_5Mn(CO)(NO)(Sb(C_6H_5)_3)][PF_6]$	2.28	3.98 s	. . .
$[C_5H_5Mn(CO)(NO)((C_6H_5)_2PC_2C_6H_5)][PF_6]$	2.23, 2.33, 2.44	4.15 d (2)	. . .
$[C_5H_5Mn(CO)(NO)(Pf\text{—}Pf)][PF_6]$	2.37, 2.68	4.38 d (2)	7.15 b (CH_2)
$[C_5H_5Mn(CO)(NO)]_2(Pf\text{—}Pf)[PF_6]_2$	2.38	4.36 s	7.03 s (CH_2)
$[C_5H_5Mn(NO)(cPf{=}Pf)][PF_6]$	~2.4 br	4.80 t (2)	0.80, 1.80 (CH)
$[C_5H_5Mn(CO)(NO)(tPf{=}Pf)][PF_6]$	2.20, 2.43, 2.50	4.19 d (2)	[e]
$[C_5H_5Mn(CO)(NO)(Pf{\equiv}Pf)][PF_6]$	2.22, 2.40	4.17 d (2)	. . .
$[C_5H_5Mn(CO)(NO)]_2(Pf{\equiv}Pf)[PF_6]_2$	2.20	4.08 d (2)	. . .
$[C_5H_5Mn(CO)(NO)]_2(PfC{\equiv}CPf)[PF_6]_2$	2.36, 2.43	4.26 s	6.01 d (3) (CH_2)
$[(C_5H_5)_2Mn_2(CO)(NO)_2(triphos)][PF_6]_2$	~2.3 br	4.58 d (2)	~6.8 vbr (CH_2)
		4.82, 4.94	8.99 (CH_3)

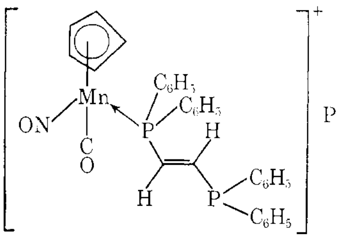
[a] These proton nmr spectra were taken in $(CD_3)_2CO$ solution either at 60 Mc on a Perkin-Elmer R-20 spectrometer or at 100 Mc on a Varian HA-100 spectrometer. A few compounds were checked at both frequencies to confirm the field strength independence of the splitting of the π-C_5H_5 resonances. [b] For the abbreviations of the ligands used see the Experimental Section. [c] Abbreviations: s, singlet; d, doublet; t, triplet; b, broad. Splittings indicated in cps. [d] Data of R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 791 (1964). [e] The resonances from the olefinic protons could not be observed in this complex probably because they were hidden under the strong phenyl resonances.

firms the absence of carbonyl groups in this compound. A more detailed comparison of the spectroscopic properties of II with the monodentate monometallic complex $[C_5H_5Mn(CO)(NO)(tPf{=}Pf)][PF_6]$ (III) provided further support of structure II. Thus the proton nmr spectrum of II with two phosphorus atoms bonded to the manganese atom exhibited a triplet π-cyclopentadienyl resonance whereas the proton nmr spectrum of III with but one phosphorus atom bonded to the manganese atom exhibited only a doublet π-cyclopentadienyl resonance (Table III). Furthermore, the $\nu(NO)$ frequency of II occurs at 1770 cm^{-1} whereas the $\nu(NO)$ frequency of III occurs at 1800 cm^{-1} consistent with the expected increase in the metal–nitrogen retrodative π bonding to the nitrosyl group upon replacing the carbonyl group with the more weakly π-accepting tertiary phosphine ligand.

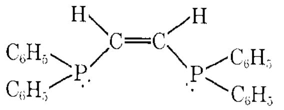
This work further indicates the tendency for *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ (IV) to act as a bidentate monometallic (chelating) ligand and not as a bidentate bimetallic (bridging) ligand, as had been suggested by the prior observation[1] that cPf=Pf reacts with the alkyls $RMo(CO)_3C_5H_5$ with loss of the cyclopentadienyl and alkyl groups to form the bidentate monometallic derivative $(cPf{=}Pf)_2Mo(CO)_2$ whereas all other ditertiary phosphines (including potentially chelating ones such as Pf—Pf) react with $RMo(CO)_3C_5H_5$ to form the bidentate bimetallic derivatives (diphos)$[Mo(CO)_2(COR)(C_5H_5)]_2$. The relatively large tendency for *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ to form chelate derivatives is consistent with the rigidity of the carbon–carbon double bond which holds the phosphorus atoms in excellent positions to form chelate derivatives but in poor positions to form bridging derivatives because of insufficient space to accommodate without excessive steric hindrance the other ligands on the metal atoms being bridged.



II



III

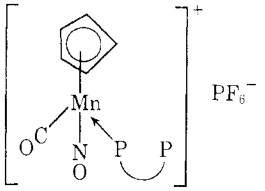


IV

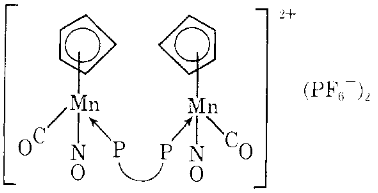
The remaining ditertiary phosphines with two-carbon bridges between the phosphorus atoms (Pf—Pf, tPf=Pf, and $\mathrm{Pf{\equiv}Pf}$) formed both the monodentate monometallic complexes $[\mathrm{C_5H_5Mn(CO)(NO)(diphos)}][\mathrm{PF_6}]$ (V) and the bidentate bimetallic complex $[\mathrm{C_5H_5Mn(CO)(NO)}]_2(\mathrm{diphos})[\mathrm{PF_6}]_2$ (VI). In the case of Pf—Pf and tPf=Pf the two products could be separated easily because of the much lower solubility of the bimetallic derivative. In the case of the acetylenic ditertiary phosphine $\mathrm{Pf{\equiv}Pf}$ formation of either the monodentate monometallic or bidentate bimetallic derivatives was controlled by varying the mole ratio of the reactants. The monodentate monometallic derivative $[\mathrm{C_5H_5Mn(CO)(NO)(Pf{\equiv}Pf)}][\mathrm{PF_6}]$ exhibited a $\nu(\mathrm{C{\equiv}C})$ frequency at 2106 cm^{-1} in its infrared spectrum whereas the bidentate bimetallic derivative $[\mathrm{C_5H_5Mn(CO)(NO)}]_2(\mathrm{Pf{\equiv}Pf})[\mathrm{PF_6}]_2$ failed to exhibit a $\nu(\mathrm{C{\equiv}C})$ frequency in its infrared spectrum. This is consistent with the expected infrared activity of the $\nu(\mathrm{C{\equiv}C})$ frequency in a $\mathrm{(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2}$ complex with only one phosphorus atom coordinated to a metal atom resulting in an unsymmetrically substituted carbon–carbon triple bond and with the expected infrared inactivity of the $\nu(\mathrm{C{\equiv}C})$ frequency in a $\mathrm{(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2}$ complex with both phosphorus atoms coordinated to metal atoms resulting in a symmetrically substituted carbon–carbon triple bond. Although numerous complexes of $\mathrm{Pf{\equiv}Pf}$ have been prepared,[17] this is the first time that this effect has been observed owing to prior difficulties in obtaining monodentate monometallic $\mathrm{Pf{\equiv}Pf}$ complexes.

The infrared spectra of solid $[\mathrm{C_5H_5Mn(CO)(NO)}]_2(\mathrm{diphos})[\mathrm{PF_6}]_2$ (diphos = Pf—Pf and $\mathrm{PfC{\equiv}CPf}$) in KBr pellets (Table II) exhibited *two* ν(CO) frequencies and two ν(NO) frequencies suggesting different environments of the two $\mathrm{C_5H_5Mn(CO)(NO)}$ groups in the solid state. This effect was not exhibited in spectra obtained in solution.

The reaction of $[\mathrm{C_5H_5Mn(CO)_2(NO)}][\mathrm{PF_6}]$ with the ditertiary phosphine $\mathrm{(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2}$ with a four-carbon bridge between the two phosphorus atoms gave no monodentate monometallic derivative but only the bidentate bimetallic derivative $[\mathrm{C_5H_5Mn(CO)(NO)}]_2(\mathrm{PfC{\equiv}CPf})[\mathrm{PF_6}]_2$. The failure to obtain a mondentate monometallic derivative from $[\mathrm{C_5H_5Mn(CO)_2NO}][\mathrm{PF_6}]$ and $\mathrm{PfC{\equiv}CPf}$ may relate to the greater separation of the two phosphorus atoms in the ligand making it difficult to coordinate selectively one and not the other with metal atoms.

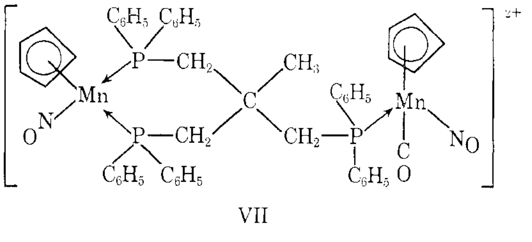


V

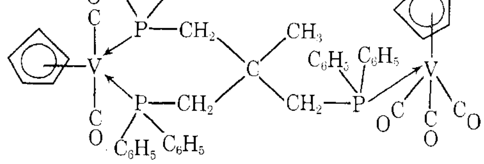


VI

The tritertiary phosphine $\mathrm{CH_3C[CH_2P(C_6H_5)_2]_3}$ reacts with $[\mathrm{C_5H_5Mn(CO)_2NO}][\mathrm{PF_6}]$ to form the complex $[\mathrm{(C_5H_5)_2Mn_2(CO)(NO)_2(triphos)}][\mathrm{PF_6}]_2$ formulated as VII in which two of the phosphorus atoms of the tritertiary phosphine are bonded to one manganese atom in a bidentate monometallic (chelating) manner and the third phosphorus atom is bonded to the second manganese atom. The spectroscopic properties of this



VII



VIII

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(17) A. J. Carty and A. Efraty, *Can. J. Chem.*, **46**, 1598 (1968); *Inorg. Nucl. Chem. Letters*, **4**, 427 (1968); *Chem. Commun.*, 1559 (1968); *Inorg. Chem.*, **8**, 543 (1969); A. J. Carty, A. Efraty, and T. W. Ng, *Can. J. Chem.*, **47**, 1429 (1969).

complex support this formulation. The infrared spectrum exhibits bands at 2022 and 1790 cm^{-1} from the ν(CO) and ν(NO) frequencies, respectively, of the $[C_5H_5Mn(CO)(NO)L][PF_6]$ portion of VII and a band at 1742 cm^{-1} from the ν(NO) frequency of the $[C_5H_5Mn(NO)L_2][PF_6]$ portion of VII. The proton nmr spectrum of VII exhibits resonances arising from nonequivalent π-cyclopentadienyl protons; the reasons for the additional complexities in this region are not clear. Recently, Behrens and Brandl have reported a related compound $(C_5H_5)_2V_2(CO)_5$(triphos) (VIII) which they prepared from the tritertiary phosphine and $C_5H_5V(CO)_4$.[18]

The proton nmr spectra of the new compounds prepared in this work (Table III) exhibited several features of interest. The phenyl region in the nmr spectra of the monodentate monometallic derivatives of any of the ditertiary phosphines Pf—Pf, tPf=Pf, or Pf≡Pf had an extra line toward the upper portion of this region as compared with the corresponding spectra of the more symmetrical bidentate bimetallic derivative of the same ligand. This suggests a partial ability to separate coordinated and noncoordinated diphenylphosphino groups in the nmr spectra of these complexes. The chemical shifts of the π-cyclopentadienyl nmr resonances increase upon increasing substitution of carbonyl groups with the more weakly π-accepting tertiary phosphines thereby parallelling decreases in the ν(CO) and ν(NO) infrared frequencies in a manner similar to that reported for neutral cyclopentadienylmetal carbonyl derivatives of the first-row transition metals.[19] The π-cyclopentadienyl resonances of the tertiary phosphine derivatives generally exhibited the characteristic splitting ($J_{PH} \approx 2$ cps) into doublets or triplets consistent with the number of phosphorus atoms coordinated to the manganese atom.

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[18] H. Behrens and H. Brandl, *Z. Naturforsch.*, **22b**, 1353 (1967).

[19] R. B. King, *Inorg. Chim. Acta*, **2**, 454 (1968).

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Dipole Moments and Electric Field Effects on the Proton Chemical Shifts of Halo(acetylacetonato) Complexes of Group IV Metals[1]

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Dipole moments for several dihalobis(acetylacetonato) complexes of tin, titanium, zirconium, and hafnium (6.19–8.15 D) and halotris(acetylacetonato) complexes of zirconium and hafnium (4.90–6.07 D) have been measured in dilute benzene solution at 25.0°. The results strongly support a *cis*-octahedral structure for the $M(acac)_2X_2$ complexes and are consistent with a seven-coordinate structure for the $M(acac)_3X$ compounds. Low-field shifts, $\Delta\sigma$, of the $-CH=$ and $-CH_3$ proton resonances of the $M(acac)_2X_2$ complexes have been computed from the dipole moments on the basis of an electric field model. Calculated and observed values of $\Delta\sigma$ are in good agreement for the $-CH_3$ protons and for the $-CH=$ proton of the tin complexes, but when M = Ti, Zr, or Hf, only ~50–60% of the observed $\Delta\sigma$ for the $-CH=$ proton can be accounted for by electric field effects. The discrepancy in the case of the transition metal compounds may be due to metal–ligand π bonding.

Introduction

The stereochemistry of dihalobis(acetylacetonato) complexes of group IV metals, $M(acac)_2X_2$, has been the subject of a number of recent papers.[3–18] Although Kawasaki and co-workers have proposed for the dichloro-, dibromo-, and diiodotin complexes a distorted *trans* structure containing somewhat localized double bonds within the chelate rings,[3–5] nmr,[6–8] infrared,[8–10] Raman,[8] and dipole moment[11–13] results overwhelmingly support a *cis*-octahedral structure. Spectroscopic evidence also points to a *cis* structure for the analogous titanium,[9,14–16] zirconium,[17,18] and hafnium[17,18] complexes, but this has not yet been confirmed by dipole moment studies.

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[2] National Research Council of Canada predoctoral fellow, 1966–1968.

[3] Y. Kawasaki and T. Tanaka, *J. Chem. Phys.*, **43**, 3396 (1965).

[4] Y. Kawasaki, T. Tanaka, and R. Okawara, *Spectrochim. Acta*, *A*, **22**, 1571 (1966); Y. Kawasaki, R. Ueeda, and T. Tanaka in "International Symposium on Nuclear Magnetic Resonance," Preliminary Report, Tokyo, Sept 1965. These papers state that a *trans* configuration is suggested for $Sn(acac)_2Cl_2$ by a dipole moment measurement in benzene solution; however, no experimental data are presented.

[5] Y. Kawasaki and T. Tanaka, *Inorg. Nucl. Chem. Letters*, **3**, 13 (1967).

[6] J. A. S. Smith and E. J. Wilkins, *Chem. Commun.*, 381 (1965).

[7] J. A. S. Smith and E. J. Wilkins, *J. Chem. Soc.*, *A*, 1749 (1966).

[8] J. W. Faller and A. Davison, *Inorg. Chem.*, **6**, 182 (1967).

[9] M. Cox, R. J. H. Clark, and H. J. Milledge, *Nature*, **212**, 1357 (1966).

[10] I. Douek, M. J. Frazer, Z. Goffer, M. Goldstein, B. Rimmer, and H. A. Willis, *Spectrochim. Acta*, *A*, **23**, 373 (1967).

[11] M. Cox, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 6113 (1964).

[12] W. H. Nelson, *Inorg. Chem.*, **6**, 1509 (1967).

[13] V. Doron and C. Fischer, *ibid.*, **6**, 1917 (1967).

[14] D. C. Bradley and C. E. Holloway, *Chem. Commun.*, 284 (1965).

[15] R. C. Fay and R. N. Lowry, *Inorg. Nucl. Chem. Letters*, **3**, 117 (1967).

[16] R. C. Fay and R. N. Lowry, *Inorg. Chem.*, **6**, 1512 (1967).

[17] T. J. Pinnavaia and R. C. Fay, *ibid.*, **7**, 502 (1968).

[18] R. C. Fay and T. J. Pinnavaia, *ibid.*, **7**, 508 (1968).