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Contribution from the Department of Chemistry and Biochemistry,
Utah State University, Logan, Utah 84322

Coordination Chemistry of Bidentate Difluorophosphines. 3. Complexes of 1,2-Bis(difluorophosphino)cyclohexane with Molybdenum(0), Manganese(I), and Iron(0)[1]

DARRELL L. GALLUP and JOSEPH G. MORSE*

Received April 3, 1978

1,2-Bis(difluorophosphino)cyclohexane, $F_2PC_6H_{10}PF_2$ (L), has been found to react with pentacarbonyliron(0), $Fe(CO)_5$, and with pentacarbonylmanganese(I) bromide, $Mn(CO)_5Br$, in hexane, displacing 2 mol of carbon monoxide/mol of ligand. The resulting products, $LFe(CO)_3$, $L_2Fe(CO)$, $LMn(CO)_3Br$, and $L_2Mn(CO)Br$, are all air-stable solid monomers indicating that L is an effective chelating agent. A slight excess of L also reacts readily with bis(toluene)molybdenum(0) displacing the toluene to give L_3Mo, also an air-stable monomer. This result contrasts with the formation of bridged species on reaction of L with $Mo(CO)_6$ and the other 6B metal hexacarbonyls. All new compounds were characterized by elemental analysis and osmometric molar mass and by IR, NMR, and mass spectra. Analysis of the IR and NMR data supports the conclusion that L functions as a strong π acceptor and assists in assigning structures.

We have recently presented evidence that *trans*-1,2-bis(difluorophosphino)cyclohexane functions as an unusually strong π acceptor in its complexes with the group 6B metals[2a] and with Ni.[2b] It functions as a bidentate and/or as a bridging bifunctional ligand in these compounds. Analysis of the Cotton–Kraihanzel CO force constants[3] and NMR parameters resulted in assignment of π acidity comparable to that of PCl_3 and slightly greater than that of $CH_3N(PF_2)_2$. The latter is the only other bidentate, strong π-acid ligand to have received substantial attention.[4-8] Both of these ligands are of interest because the chelate effect is expected to render their complexes with metals in low oxidation states even more stable than can monodentates such as CO. One noteworthy contrast between these two ligands is the nature of the reaction products resulting from photoreaction with the group 6B metal carbonyls. While $CH_3N(PF_2)_2$ readily displaces the CO to give chelates,[4] $F_2PC_6H_{10}PF_2$ gives bridged complexes[2a] though it chelates readily with Ni(0). In order to characterize further the coordinating behavior of $F_2PC_6H_{10}PF_2$ we have studied its reactions with metals having different stereochemical demands, specifically with Mn(I) and Fe(0). In addition, we report evidence that the formation of bridged complexes of Mo(0) observed previously is not indicative of an inability of this ligand to form chelates about a six-coordinate metal.

Experimental Section

General Techniques. Standard high-vacuum techniques were employed throughout[9], and manipulations of the reaction products were carried out under dry nitrogen. Infrared spectra of the complexes in hexane and chloroform were recorded on a Beckman IR-20A spectrometer. Values reported are correct to $\pm 3\ cm^{-1}$. Proton NMR spectra were obtained at 60 MHz with a Varian Associates EM-360 instrument. ^{19}F NMR spectra were obtained at 94.1 MHz with a Varian Associates XL-100-12 instrument. ^{31}P NMR spectra were obtained at 40.5 MHz with a Varian Associates XLFT-100-15 instrument in the Fourier transform mode with proton noise decoupling and a deuterium lock. The ^{13}C NMR spectrum was obtained at 25.2 MHz with a Varian Associates XLFT-100-15 instrument in the Fourier transfer mode with fluorine noise decoupling and a deuterium lock. Chemical shift values are given in ppm from benzene (internal standard), CCl_3F and 85% orthophosphoric acid (external standards), and Me_4Si (corrected from $CDCl_3$, $\delta_{Me_4Si} = \delta_{CDCl_3} + 77$), respectively. (Chemical shifts are given as + = downfield.) Mass spectra were obtained at 70 eV with an Hitachi Perkin-Elmer RMU-6E spectrometer applying a solid inlet system. Molecular weights were determined osmometrically in benzene or chloroform with a Mechrolab vapor pressure osmometer, Model 301A. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. A Rayonet photochemical reactor (Southern NE Ultraviolet Co., Middleton, Conn.) containing RPR-3000 A reactor lamps was used as the energy source for the photoreactions.

Materials. All organic solvents were dried over Linde Molecular Sieves, no. 3A, and degassed before use. *trans*-$PF_2C_6H_{10}PF_2$[10] and $Mo(C_6H_5CH_3)_2$[11] were prepared according to the literature. $Mn(CO)_5Br$ was purchased from Strem Chemicals, Inc., Danvers, Mass., and was purified by high-vacuum sublimation immediately before use. $Fe(CO)_5$ was purchased from Ventron Corp., Beverly, Mass., and was filtered and vacuum distilled before use.

Preparation of Tris[1,2-bis(difluorophosphino)cyclohexane]molybdenum(0), $(PF_2C_6H_{10}PF_2)_3Mo$. A 0.688-g (3.13-mmol) sample of $PF_2C_6H_{10}PF_2$ was condensed onto 0.261 g (0.932 mmol) of $Mo(C_6H_5CH_3)_2$ at −196 °C. Upon warming to room temperature, the mixture turned red-brown indicating the occurrence of a reaction. The mixture was heated to 140 °C for several hours to ensure reaction completion. No change was observed in the mixture during heating. The solid was extracted with hexane and filtered on a medium-porosity glass frit. The filtrate was applied to a Florisil column. A light yellow band was eluted from the column with hexane. Light yellow crystals were obtained after solvent removal [mp 76–80 °C (uncor); 22% yield]. Anal. Calcd for $MoP_6F_{12}C_{18}H_{30}$: C, 28.57; H, 3.97; P, 24.60; mol wt 756. Found: C, 30.36; H, 4.18; P, 24.07; mol wt 772.

Preparation of *fac*-[1,2-Bis(difluorophosphino)cyclohexane]tricarbonylmanganese(I) Bromide, $(PF_2C_6H_{10}PF_2)Mn(CO)_3Br$, and Bis[1,2-bis(difluorophosphino)cyclohexane]carbonylmanganese(I) Bromide, $(PF_2C_6H_{10}PF_2)_2Mn(CO)Br$. An equimolar amount (approximately 1 mmol) of $PF_2C_6H_{10}PF_2$ was condensed onto a suspension of $Mn(CO)_5Br$ in ca. 35 mL of dry, air-free hexane in a 50-mL Pyrex vessel. The mixture was allowed to warm to room temperature and was irradiated with magnetic stirring for 20 h. At periodic intervals, the CO liberated during the reaction was removed while the reaction mixture was held at −196 °C. We recovered 1.8 equiv of CO/equiv of $Mn(CO)_5Br$. The solvent was removed under reduced pressure, and the resultant yellow-white solid was charged into a sublimation apparatus. A small amount of unreacted $Mn(CO)_5Br$ was recovered by careful sublimation below 60 °C. Yellow-orange crystals were obtained which sublimed at 70 °C [mp 96–98 °C (uncor); 21% yield] and were identified as the tricarbonyl. Anal. Calcd for $MnP_2F_4C_9H_{10}O_3Br$: C, 24.60; H, 2.28; P, 14.12; mol wt 439. Found: C, 24.80; H, 2.48; P, 13.96; mol wt 436. Light yellow crystals identified

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as the monocarbonyl remained in the apparatus which did not sublime up to 150 °C [mp 252–258 °C (uncor); 20% yield]. Molecular weight: calcd, 603; found, 630. Elemental analyses for the complex were inconclusive, but infrared, NMR, mass spectral, and molecular weight data all indicate that this formulation is correct.

Preparation of *cis*-[1,2-Bis(difluorophosphino)cyclohexane]tricarbonyliron(0), $Fe(CO)_3(PF_2C_6H_{10}PF_2)$, and Bis[1,2-bis(difluorophosphino)cyclohexane]carbonyliron(0), $Fe(CO)(PF_2C_6H_{10}PF_2)_2$. An equimolar amount (1 mmol) of $PF_2C_6H_{10}PF_2$ was condensed onto a suspension of $Fe(CO)_5$ in ca. 25 mL of dry, air-free hexane in a 50-mL Pyrex vessel at −196 °C. Upon warming to room temperature, the mixture was irradiated for 17 h with magnetic stirring. The CO which was displaced during the reaction was removed at intervals of several hours while the mixture was held at −196 °C. We recovered 1.74 equiv of CO/equiv of $Fe(CO)_5$. The hexane was removed under reduced pressure leaving a reddish brown solid. Sublimation of the solid under high vacuum at 55 °C gave beige crystals [mp 75–77 °C (uncor); 16% yield] identified as the tricarbonyl. Anal. Calcd for $FeP_2F_4C_9H_{10}O_3$: C, 30.00; H, 2.77; P, 17.22; mol wt 360. Found: C, 29.99; H, 3.03; P, 16.66; mol wt 344. The solid which did not sublime was chromatographed on a Florisil column in hexane giving yellow crystals [mp 105–109 °C (uncor); 16% yield] identified as the monocarbonyl. Anal. Calcd for $FeP_4F_8C_{13}H_{20}O$: C, 29.77; H, 3.82; P, 23.66; mol wt 524. Found: C, 29.78; H, 3.99; P 23.35; mol wt 518.

Results and Discussion

Molybdenum Complex. In the previous study of this series we reported that our attempts to prepare the complexes $M(CO)_2(PF_2C_6H_{10}PF_2)_2$ and $M(PF_2C_6H_{10}PF_2)_3$ (where M = Cr, Mo, and W) by the photoreaction of $M(CO)_6$ and excess $PF_2C_6H_{10}PF_2$ were unsuccessful.[2a] King and Gimeno[4] have obtained the carbonyl-free complexes $M[CH_3N(PF_2)_2]_3$ by irradiating $M(CO)_6$ with fivefold excesses of the bidentate fluorophosphine ligand. Complete substitution of CO in the group 6B metal carbonyls by bidentate organophosphine ligands, such as $Ph_2PC_2H_4PPh_2$, has not been achieved, although the $M(diphos)_3$ compounds can be prepared directly.[12,13] The complexes $M(Me_2PC_2H_4PMe_2)_3$ were prepared by reducing metal halides with $LiAlH_4$ or sodium naphthalenide in tetrahydrofuran.[12] Several molybdenum(0) complexes (formula MoL_3) of bidentate organophosphine ligands have been obtained by heating $Mo(C_6H_6)_2$ with the ligand in a sealed tube.[13]

The attempted reduction of $MoCl_5$ with $LiAlH_4$ in THF in the presence of a threefold excess of $PF_2C_6H_{10}PF_2$ resulted in a very dirty reaction, and only unreacted ligand was recovered from the reaction mixture. In a further effort to obtain the complex $Mo(PF_2C_6H_{10}PF_2)_3$ the ligand was allowed to react with bis(toluene)molybdenum(0). Although the mixture was heated to temperatures as high as 140 °C to ensure reaction completion, the reaction appeared to proceed readily at room temperature as evidenced by an immediate color change of the green molybdenum compound. The complex $Mo(PF_2C_6H_{10}PF_2)_3$ was obtained as an air-stable, light yellow solid which is oxidized slowly in the presence of solvent.

Manganese Carbonyl Complexes. The photoreaction of $PF_2C_6H_{10}PF_2$ and Mn(I) in the form of $Mn(CO)_5Br$ results in the formation of two substitution products, $(PF_2C_6H_{10}PF_2)Mn(CO)_3Br$ and $(PF_2C_6H_{10}PF_2)_2Mn(CO)Br$. Both complexes are colored and exceptionally air stable. No decomposition or oxidation of either complex in solution when exposed to the air was observed, in direct contrast to the rapid oxidation of the group 6B metal carbonyl complexes in solution.[2a] The monocarbonyl is somewhat soluble in the more polar solvents, while the tricarbonyl is readily soluble in nonpolar solvents.

Iron Carbonyl Complexes. The photoreaction of $Fe(CO)_5$ and $PF_2C_6H_{10}PF_2$ in hexane also results in the formation of two air-stable substitution products, $(PF_2C_6H_{10}PF_2)Fe(CO)_3$ and $(PF_2C_6H_{10}PF_2)_2Fe(CO)$. These products were found to be very soluble in nonpolar solvents and to oxidize in solution upon exposure to air for prolonged periods. Precautions were taken to avoid exposure of $Fe(CO)_5$ to any light source until irradiation of the carbonyl with $PF_2C_6H_{10}PF_2$ was initiated. A trace of red-brown insoluble (in hexane) material appeared during the photoreaction which was not identified.

Table I. Assignments, Mass Numbers, and Relative Intensities of Some Ions in the Mass Spectra of the Manganese and Iron Carbonyl Complexes of $PF_2C_6H_{10}PF_2$

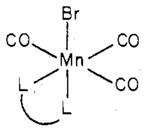
ion	mass	intens	ion	mass	intens
$(PF_2C_6H_{10}PF_2)Mn(CO)_3Br$			$(PF_2C_6H_{10}PF_2)_2Mn(CO)Br$		
$LMn(CO)_3{}^{81}Br^+$	440	34	$L_2Mn(CO){}^{81}Br^+$	604	18
$LMn(CO)_3{}^{79}Br^+$	438	34	$L_2Mn(CO){}^{79}Br^+$	602	19
$LMn(CO){}^{81}Br^+$	384	9	$L_2Mn{}^{81}Br^+$	576	43
$LMn(CO){}^{79}Br^+$	382	9	$L_2Mn{}^{79}Br^+$	574	43
$LMn{}^{81}Br^+$	356	100	$LMn{}^{81}Br^+$	356	55
$LMn{}^{79}Br^+$	354	100	$LMn{}^{79}Br^+$	354	54
LMn^+	275	25	Br^+	79, 81	100
Br^+	79, 81	53	Mn^+	55	48
Mn^+	55	66			
$Fe(CO)_3(PF_2C_6H_{10}PF_2)$			$Fe(CO)(PF_2C_6H_{10}PF_2)_2$		
$Fe(CO)_3L^+$	360	16	$Fe(CO)L_2{}^+$	524	32
$Fe(CO)_2L^+$	332	12	$FeL_2{}^+$	496	100
$Fe(CO)L^+$	304	27	FeL^+	276	18
FeL^+	276	100	Fe^+	56	4
Fe^+	56	19			

Mass Spectra and Molar Masses. Our previous study of the coordination of $PF_2C_6H_{10}PF_2$ with the group 6B metal carbonyls gave unexpectedly high molecular weight species attributed to bridging ligands across at least two metal centers.[2a] Mass spectra of the polymeric species gave only the apparent spectra of the monomers due to fragmentation. That $Mo(PF_2C_6H_{10}PF_2)_3$ is a monomeric complex was verified by its osmometric molar mass (calcd 756, found 772). The mass spectrum (70 eV) consisted of an intense molecular ion signal clustered between *m/e* 752 and *m/e* 760 in a pattern characteristic of the Mo isotopic distribution. Ligand fragmentation peaks were present as expected and no peaks of mass higher than that of the molecular ion were observed. A weak set of signals corresponding to $Mo(PF_2C_6H_{10}PF_2)_2{}^+$ was discernible between *m/e* 532 and 540.

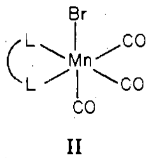
Osmometric molar masses of the manganese and iron complexes are consistent with monomeric formulations. Relative intensities and assignments of the peaks in the mass spectra are presented in Table I. Stepwise removal of the CO ligands from the molecular ions is indicated by intense peaks at *m/e* −28 intervals. Isotope peaks due to bromine in the manganese complexes are easily distinguishable. Metal isotope peaks and ligand fragmentation peaks are present in each as expected. No peaks of mass higher than that of the molecular ion peak were observed.

Infrared Spectra. The solid-phase infrared spectrum of $Mo(PF_2C_6H_{10}PF_2)_3$ gives the following bands with some tentative assignments as shown (in cm^{-1}): 2941 m (ν(CH)); 2868 w (ν(CH)); 1440 m (δ(CH$_2$)); 1386 w, 1066 m, 1038 w, 983 m, 789 vs, br (ν(PF)). No bands in the aromatic C–H stretching region attributable to unreacted $(C_6H_5CH_3)_2Mo$ were obtained.

The tricarbonylmanganese complex $(PF_2C_6H_{10}PF_2)Mn(CO)_3Br$ may exist in two isomeric forms: either meridional-cis (I) or facial-cis (II), with respect to the ligand en-



I



II

Table II. CO Frequencies and Force Constants for Some Manganese Tricarbonyl and Monocarbonyl Complexes

	freq, cm^{-1}			force const, mdyn/Å[18]			
compd	A^2	A^1	B	k_a	k_e	k_c'	k_c
fac-$(PF_2C_6H_{10}PF_2)Mn(CO)_3Br$	2059	1973	2017	15.81	16.73	0.24	0.30
fac-$(PPhCl_2)_2Mn(CO)_3Br$[a]	2058	1953	2004	15.63	16.55	0.33	0.41
fac-$[P(OPh_3)_3]_2Mn(CO)_3Br$[a]	2053	1947	2004	15.56	16.47	0.32	0.40
fac-$[P(OMe)_2Ph]_2Mn(CO)_3Br$[b]	2045	1927	1975	15.32	16.16	0.41	0.50
fac-$(Ph_2PC_2H_4PPh_2)Mn(CO)_3Br$[c]	2022	1918	1959	15.01	15.93	0.35	0.43
fac-$(PEt_2Ph)_2Mn(CO)_3Br$[d]	2021	1902	1954	14.90	15.81	0.39	0.48
fac-$(PMePh)_2Mn(CO)_3Br$[b]	2020	1903	1954	14.91	15.80	0.38	0.48
$(PF_2C_6H_{10}PF_2)_2Mn(CO)Br$		1945			15.26		
$(PF_3)_4Mn(CO)H$[e]		2038			16.75		

[a] R. J. Angelici, F. Basolo, and A. Poe, *J. Am. Chem. Soc.*, **85**, 2215 (1963). [b] R. H. Reimann and E. Singleton, *J. Chem. Soc., Dalton Trans.*, 841 (1973). [c] A. G. Osborne and M. H. B. Stiddard, *J. Chem. Soc.*, 4715 (1962). [d] R. J. Angelici, *J. Inorg. Nucl. Chem.*, **28**, 2627 (1966). [e] Reference 20.

vironment (C_s carbonyl symmetry). The two isomers can be distinguished through CO stretching band positions and intensities.[14] On the basis of these considerations, the tricarbonyl complex has been assigned to the facial-cis isomer. Table II shows the CO stretching frequencies obtained from the solution infrared spectrum of $(PF_2C_6H_{10}PF_2)Mn(CO)_3Br$, along with the frequencies of similar complexes for comparative purposes. A P–F stretching band is observed at 815 cm^{-1}.

Examination of the CO stretching frequencies in Table II supports our previous observation that $PF_2C_6H_{10}PF_2$ exhibits strong π-acceptor character.[2a] The CO stretching frequencies for $(PF_2C_6H_{10}PF_2)Mn(CO)_3Br$ are much higher than the frequencies reported for other phosphine-substituted tricarbonylmanganese(I) complexes, implying a greater contribution of the triply bonded resonance form $M—C{\equiv}O$ arising from greater back-bonding capabilities expected for a strong π-acid ligand.[15] A semiquantitative value can be assigned to this π-acceptor character by determination of the appropriate Cotton–Kraihanzel force constants for the CO stretching modes.[3,16] Some distinction between π-acceptor effects and σ-donor effects of the phosphine ligands on the CO stretching force constants can be made. Graham[17] has performed such an analysis for a series of $LMo(CO)_5$ complexes. For complexes of the type *fac*-$L_2Mn(CO)_3Br$ (structure II), Wuyts and Van der Kelen[18] express the overall changes in force constants between complexes as

$$\Delta k_a = 2\Delta(\sigma \rightarrow \pi^*) + 2(\Delta(\pi)/2)$$

$$\Delta k_e = \Delta(\sigma \rightarrow \pi^*) + 3(\Delta(\pi)/2)$$

where k_a and k_e are force constants for the axial and equatorial CO ligands, respectively, determined as described by Dalton et al.[19] The term $(\sigma \rightarrow \pi^*)$ relates to electron density transferred *to* the CO π^* orbitals by interaction with the σ-donor orbitals of the phosphine ligands while the $\Delta(\pi)$ term relates to the conventionally considered π-orbital interaction. The relative weights assigned to the effects are based on simple geometric considerations. The model assumes negligible change in any Mn–Br π bonding on varying L and also that changes in ligand–metal σ bonding are of minor importance in determining ν(CO). All values are taken relative to aniline as a ligand. The values of the appropriate force constants for the complexes prepared here are included in Table II with those for several other Mn(I) complexes for comparison. To the extent that decreasing values of the CO stretching force constants k_a and k_e correspond to increasing π-acceptor strength of the phosphine ligands it can be seen that the relative π acidities of these ligands follow the order $F_2PC_6H_{10}PF_2 > PPhCl_2 > P(OPh)_3 > Ph_2C_2H_4PPh_2 > Et_2PPh = Me_2PPh$, consistent with the qualitative assessment based upon stretching frequencies. When the possible σ-donor effects on the CO stretching force constants are included in the analysis, as outlined above,[18] the values shown in Table III are obtained, with those for several other phosphines included for comparison. Again, $F_2PC_6H_{10}PF_2$ stands in the same relative position as a π acceptor—substantially weaker than CO itself but stronger than the organophosphines. Both of these analyses assume regular octahedral geometry, i.e., no appreciable distortion due to the bidentate ligands. The $\sigma \rightarrow \pi^*$ parameters vary only slightly for similar ligands. They do not necessarily correspond to $\sigma(L \rightarrow M)$ donor strength but may better be viewed as a measure of the diffuseness of the σ orbital.[18] The relatively small values of the parameter for the phosphines with the more electronegative substituents are consistent with this view.

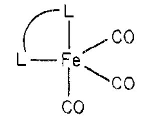
Table III. Bonding Parameters for *fac*-$L_2Mn(CO)_3Br$ Complexes (mdyn/Å)[a]

L	Δ-$(\sigma \rightarrow \pi^*)$	$\Delta(\pi)$	L	Δ-$(\sigma \rightarrow \pi^*)$	$\Delta(\pi)$
CO[a]	0.14	1.055	$Ph_2PC_2H_4PPh_2$[b,c]	−0.43	0.40
$PF_2C_6H_{10}PF_2$[b]	−0.23	0.80	PEt_2Ph[a]	−0.45	0.335
$PPhCl_2$[a]	−0.275	0.71	PMe_2Ph[a]	−0.44	0.32
$P(OPh)_3$[a]	−0.29	0.665	$C_6H_5NH_2$	0.00	0.00
$P(OMe)_2Ph$[a]	−0.31	0.475			

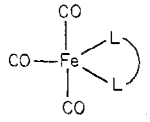
[a] Reference 19. [b] Bidentate. [c] Calculated from frequencies reported by A. G. Osborne and M. H. B. Stiddard, *J. Chem. Soc.*, 4715 (1962).

The existence of only one CO stretching frequency in the infrared spectrum of $(PF_2C_6H_{10}PF_2)_2Mn(CO)Br$ is consistent with this formulation and expected symmetry. Whether the lone CO ligand is cis or trans to Br in the molecule is not known, since only one isomer is detected in the spectrum. Both isomers have been observed for the monocarbonyl complex $(PF_3)_4Mn(CO)H$,[20] as two different CO stretching frequencies were observed. The CO stretching frequencies and corresponding force constants for these monocarbonyl complexes are given in Table II. Direct comparison of CO stretching frequencies and force constants is not possible because of the differences in ligand environment (Br vs. H). The P–F stretching frequency of $(PF_2C_6H_{10}PF_2)_2Mn(CO)Br$ was observed at 825 cm^{-1}.

The tricarbonyliron complex $Fe(CO)_3(PF_2C_6H_{10}PF_2)$ may also exist in two isomeric forms: cis (III), exhibiting C_s carbonyl symmetry, or *vic* (IV), exhibiting C_{2v} carbonyl symmetry. Although each isomer gives rise to three infrared-active bands in the CO stretching region,[21] band positions and intensities have been used to differentiate between the isomers of the tricarbonyliron complexes of PF_3[22,23]. Table IV shows the CO stretching frequencies obtained for the complex $Fe(CO)_3(PF_2C_6H_{10}PF_2)$ and similar complexes.



III



IV

Table IV. CO Frequencies for Some Iron Carbonyl Complexes

compd	freq, cm^{-1}
cis-$Fe(CO)_3(PF_2C_6H_{10}PF_2)$	2041, 1995, 1982
cis-$Fe(CO)_3(PF_3)_2$[a]	2071, 2019, 1992
cis-$Fe(CO)_3(Ph_2PC_4F_4PPh_2)$[b]	2008, 1947, 1927
cis-$Fe(CO)_3(Ph_2PC_2H_4PPh_2)$[b]	2007, 1946, 1928
$Fe(CO)(PF_2C_6H_{10}PF_2)_2$	1983
$Fe(CO)(PF_3)_4$[a]	2037 (axial), 2008 (equatorial)

[a] Reference 33. [b] Reference 32.

Since three CO stretching bands (no shoulders) were observed, only one isomer is present in solution. On the basis of experimental results reported for bidentate phosphine-substituted tricarbonyliron complexes,[24-27] we have assigned $Fe(CO)_3(PF_2C_6H_{10}PF_2)$ to the cis isomer. This allows the P–M–P bond to assume an angle of approximately 90° rather than the 120° angle required for the *vic* isomer, which would introduce much ring strain in the ligand. According to Reckziegel and Bigorgne,[28] considerable distortion of the trigonal bipyramid of iron tricarbonyl complexes occurs. Such distortions have been reported to give complexes which have structures intermediate between a trigonal bipyramid and a square pyramid.[24] This flexibility could account for the ready formation of iron chelates relative to the Cr(0) case.

Examination of the CO stretching frequencies of tricarbonyliron complexes (Table IV) obtained from solution infrared spectra supports the hypothesis that $PF_2C_6H_{10}PF_2$ is a good π-acceptor ligand. The frequencies given for the $PF_2C_6H_{10}PF_2$ complex are not as high as those reported for the complexes of PF_3 but are substantially higher than the frequencies reported for the tricarbonyl complexes of the bidentate organophosphines. These comparisons are made only through the CO frequency data, since force constants for the pentacoordinate metal carbonyls are difficult to obtain.[23] The results of these comparisons are nonetheless consistent with both expectations and previous results.[2a] The P–F stretching band for the tricarbonyliron complex was observed at 823 cm^{-1}.

For the complex $Fe(CO)(PF_2C_6H_{10}PF_2)_2$ only one CO stretching band was observed in the solution infrared spectrum indicating the presence of only one isomer. The infrared data alone cannot distinguish whether the lone carbonyl is located on an axial or equatorial position of the trigonal bipyramid (which may be distorted), although the equatorial isomer would be expected to be the preferred isomer due to the "bite" of the ligand. Both isomers were observed for the monocarbonyliron complex of PF_3, the isomer with the axial CO giving the higher CO frequency.[23] The CO stretching frequencies of these monocarbonyl complexes are found in Table IV. The isomers of the PF_3 complex exhibit higher CO frequencies and force constants than the $PF_2C_6H_{10}PF_2$ complex as expected. Two P–F stretching bands were observed at 822 and 841 cm^{-1}.

NMR Spectra. The 60-MHz proton NMR spectra of complexes of Mo(0), Mn(I) (the monocarbonyl could not be dissolved sufficiently to produce a spectrum), and Fe(0) give complex multiplets centered near δ 2.0 with benzene as the internal reference. The chemical shift for the free unbound ligand (broad multiplet) was reported as δ 1.97.[10]

Fluorine NMR Spectra. The ^{19}F NMR spectrum of $Mo(PF_2C_6H_{10}PF_2)_3$ gives three broad doublets, a large doublet centered at −58 ppm and two smaller doublets of equal intensity at −54 and −50 ppm (Table V). The smaller doublets, which are less than half as intense as the large doublet, apparently result from the presence of coordinated difluorophosphino groups cis in the ligand, while the large doublet is assigned to the complex containing only the dominant trans diequatorial conformer.[2b] The fluorine coordination shifts for the doublets are +23, +27, and +31 ppm. The P–F coupling constants for the doublets span approximately 1150 Hz. Downfield fluorine coordination shifts and simultaneous decreases in $^1J_{P-F}$ have been reported for (fluorophosphine)metal complexes.[2a,29] The broadness of the signals (width at half-height spans 150–200 Hz) arises from longer range P–F couplings through the metal.[30]

Table V. ^{31}P and ^{19}F NMR Data for Metal Complexes of $PF_2C_6H_{10}PF_2$

complex	δ_P(complex),[a] ppm	$\Delta\delta_P$,[b] ppm	$^1J_{FP}$,[c] Hz	ϕ_F(complex),[d] ppm	$\Delta\phi_F$,[e] ppm
MoL_3	+281.5	+47.4	1121	−50	+31
				−54	+27
				−58	+23
$LMn(CO)_3Br$	+272.7	+38.6	1135	−60	+21
				−70	+11
				−79	+2
				−85	−4
$L_2Mn(CO)Br$	*f*	*f*	*g*	−58 ± 3	+23 ± 3
$Fe(CO)_3L$	+271.4	+37.3	1159	−58	+23
				−56	+25
$Fe(CO)L_2$	+272.6	+38.5	1140	−52	+29

[a] Because of second-order splitting patterns in the spectra, the chemical shifts and $^1J_{FP}$ values were measured from the centroids of the signals. [b] δ_P(ligand) +234.1. [c] $^1J_{FP}$(ligand) = 1218 Hz. [d] Shifts reported for the dominant doublets. [e] ϕ_F(ligand) −81.3. [f] No data. [g] J_{FP} could not be obtained, but J_{PF} from the ^{19}F NMR spectrum is 1125 ± 25 Hz.

The 94.1-MHz ^{19}F NMR spectrum (Table V) of $(F_2PC_6H_{10}PF_2)Mn(CO)_3Br$ is surprisingly complex. Four sets of doublets of equal intensity are observed; each member of these doublets is further split into complex patterns. Because the IR spectrum indicates only a single isomer is present and because all the doublets are of equal intensity, a single compound is likely the source of this spectrum. Carefully constructed models show two distinct fluorine environments—above and below the P–Mn–P plane. The further differentiation of fluorine environments is less obvious but is likely due to the difference between approximately equatorial and axial fluorine positions with respect to the chelate ring and the hydrocarbon ring. Very weak peaks downfield from the major peaks were observed which are again attributed to the presence of a small amount of coordinated cis ligand.

The ^{19}F NMR spectrum of $(PF_2C_6H_{10}PF_2)_2Mn(CO)Br$ consists of a very weak doublet barely discernible above the noise due to the small amount of sample that could be dissolved in $CDCl_3$. Table V includes the parameters obtained from the spectrum.

The complex $(F_2PC_6H_{10}PF_2)Fe(CO)_3$ gives two doublets of equal intensity in the ^{19}F spectrum (Table V). The positions and shapes of the lines are unchanged over the temperature range 25–65 °C. In a fashion similar to the $(F_2PC_6H_{10}PF_2)Mn(CO)_3Br$ case we interpret this pair of doublets as arising from two nonequivalent fluorine atom positions with respect to the chelate ring. The fluxional behavior of the molecule at ambient temperature (see below) prevents observations of further differentiation with respect to the axial and equatorial positions in the metal coordination sphere. The downfield coordination shifts and decreases in the P–F coupling constants for the resonances are consistent with previous reports.[2a,29] Again in this case, two weak doublets are observed just downfield from the major doublets.

The ^{19}F NMR spectrum of $Fe(CO)(PF_2C_6H_{10}PF_2)_2$ exhibits only one broad doublet (width at half-height spans 150 Hz) centered at −52.1 ppm. The broadness of the signal is likely due to longer range spin coupling of the nuclei across the metal. Weak-intensity doublets resulting from the coordinated cis ligand could not be seen in this case. The fluorine coordination shift of the monocarbonyl is downfield from the coordination shifts obtained for the tricarbonyl (Table V). A similar observation was noted for the dicarbonyl and tetracarbonylmolybdenum complexes of $PF_2C_6H_{10}PF_2$.[2a]

There are at least two noteworthy features of the ^{19}F spectra in general: the observation of chelate ring differentiation in the fluorine atom environment and the observation of small and varying quantities of a second compound in the samples assigned as the coordinated cis ligand. Chelate ring differentiation is observed for the Cr(0), Mn(I), and Fe(0) complexes but not for Mo(0) nor W(0) complexes.[2a] Differentiation in the Cr(0) case was initially ascribed to second-order coupling phenomena, but the appearance of the spectrum is entirely consistent with the Mn(I) and Fe(0) cases. That it is *not* observed for Mo(0) and W(0) suggests it is a function of the size of the central atom. This is also consistent with its absence from the Ni(0) spectrum[2b] where the "tetrahedral bite" may be expected to have a similar effect on ligand conformation. The difference is ~1–2 ppm for the Cr(0) and Fe(0) complexes but ~6–10 ppm in the Mn(I) case (assuming the major differentiation to be due to the adjacent Br atom as opposed to CO moiety). This may be a secondary effect of the relationship of chelate ring axial or equatorial positions to the Br atom or it may be a further reflection of central atom size, assuming Mn(I) to have a still smaller effective radius than Cr(0) or Fe(0). We know of no truly comparable situation with which to compare these data.

No explanation for the observation of weak downfield signals relative to the major signal other than the presence of coordinated cis ligand has been suggested which seems reasonable to us. At the same time no signal attributable to the cis ligand is observed in the fluorine or phosphorus spectra of the neat ligand.[10] Consequently its apparent presence in the complexes is somewhat surprising. It would seem either that what cis isomer is present in the neat ligand is preferentially coordinated in order to enhance its signal or that some isomerism occurs under the reaction conditions. This question is under investigation at present in our laboratory.

Phosphorus NMR Spectra. The PF_2 groups of the ligand $PF_2C_6H_{10}PF_2$ are responsible for the triplets observed in the 40.5-MHz phosphorus-31 NMR spectra of the complexes obtained in the study. A ^{31}P NMR spectrum of $(PF_2C_6H_{10}PF_2)_2Mn(CO)Br$ could not be obtained due to the insufficient solubility of the complex. Large P–F coupling constants on the order of 1150 Hz result from the fluorine nuclei adjacent to the phosphorus atoms in the molecules. Table V summarizes the chemical shift and coupling constant data obtained from the spectra. Phosphorus coordination shifts calculated from the difference between chemical shifts of the complex and the free ligand are all downfield, consistent with the coordination shifts reported for the $PF_2C_6H_{10}PF_2$ complexes of the group 6B metal carbonyls.[2a] The anticipated decrease in $^1J_{F-P}$ is also observed upon coordination.

The ^{31}P NMR spectrum of $Mo(PF_2C_6H_{10}PF_2)_3$ consists of a broad triplet centered at 281.5 ppm. The width of the resonances at half peak height spans approximately 155 Hz. This signal broadening has been attributed to longer range P–F coupling through the metal.[30] The phosphorus coordination shift of +47.4 ppm is larger than the coordination shifts of $Mo(CO)_2(PF_2C_6H_{10}PF_2)_2$ (+40.6 and +37.1 ppm) and $Mo(CO)_4(PF_2C_6H_{10}PF_2)$ (+29.0 ppm).[1]

The ^{31}P NMR spectrum of $(PF_2C_6H_{10}PF_2)Mn(CO)_3Br$ consists of a broad, weak-intensity triplet centered near +272.7 ppm. The chemical shift and coupling constant (Table V) were obtained with difficulty due to the broadness of the signals arising from the quadrupole coupling of ^{31}P to ^{55}Mn ($I = ^5/_2$).

The ^{31}P NMR spectrum of $Fe(CO)_3F_2PC_6H_{10}PF_2$, assigned structure III on IR evidence, exhibits a single triplet at 271.4 ppm. Each member of the triplet is complex, as expected. The presence of a single triplet implies a single phosphorus environment inconsistent with III unless the molecule is stereochemically nonrigid resulting in a time-averaged equivalence of the two positions. This is now well established for several bidentate $Fe(CO)_3$ molecules including some known to assume structure III in the crystal.[25–27] The rigidity afforded $F_2PC_6H_{10}PF_2$ by the cyclohexane ring renders rearrangement mechanisms for $LFe(CO)_3$ which require simultaneous rearrangement of the ligand ring unlikely. Of interest in this regard is a recent theoretical treatment of this question[31] which suggests that there may be essentially free rotation about the metal–bidentate ligand axis yielding effective equivalence of the monodentate ligands, hence of the two ends of the bidentate ligand. This model considers the bidentate bite to be quite rigid and is thus consistent with our data and with those of others who have studied the NMR spectra of similar bidentate $Fe(CO)_3$ complexes.[26,27,32] This is quite similar to the mechanism proposed for the molecule $Fe[(Ph_2P)_2CH_2](CO)_3$.[24]

The complex $Fe(CO)(PF_2C_6H_{10}PF_2)_2$ gives the characteristic triplet expected for a PF_2-containing species in the ^{31}P NMR spectrum but differs from the triplet observed for the tricarbonyl complex in that the resonance is broadened considerably. The width of the signals at half-height spans approximately 100 Hz. This phenomenon has been attributed to longer range P–F coupling and is common to the higher phosphine-substituted metal carbonyls.[30] The triplet is centered at 272.6 ppm which is slightly downfield from the triplet reported for the tricarbonyl complex.

The absence of well-defined signals in this case masks any detailed structural information, though it is anticipated that the bulk of the cyclohexane ring of the ligand may hamper ready rearrangement such as that discussed above for the tricarbonyl.

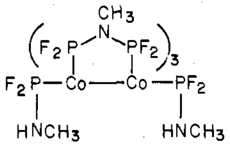
Carbon-13 NMR Spectrum. The broadening of the ^{31}P NMR signal of $Fe(CO)(PF_2C_6H_{10}PF_2)_2$ has made assignment of the monocarbonyl to the axial or equatorial position impossible from the standpoint of ^{31}P NMR since phosphorus equivalence in the molecule cannot be established. A carbon-13 NMR study of all possible isomers and substitution products of the $Fe(CO)_5$–PF_3 system has shown that for $Fe(CO)(PF_3)_4$ formation of the more symmetrical axial isomer prevails.[33,34] The 25.2-MHz carbon-13 NMR spectrum of $Fe(CO)(PF_2C_6H_{10}PF_2)_2$ was obtained in an effort to determine the structure of the complex. Three signals were obtained: a broad, weak resonance (due to CO) centered at δ 189 ± 8, a complex multiplet (due to the cyclohexane ring) centered at δ 51, and a singlet (cyclohexane ring) at δ 25. Like the ^{31}P NMR spectrum, the broadness of the CO resonance does not allow assignment of a specific structure.

Conclusion

The results presented here confirm our conclusion[2a] that $F_2PC_6H_{10}PF_2$ has strong π-acceptor character and functions as a bidentate ligand. This is the only ligand having a four-atom skeleton which has been shown clearly to exhibit this combination of characteristics and represents a class of ligands accessible through the photoaddition of P_2F_4 to olefins.[10] Unlike monofunctional alkyldifluorophosphines which, as a class, disproportionate very rapidly,[35] these ligands display relatively slow decomposition at room temperature but are susceptible to hydrolysis. As a consequence, wet solvents or alcohols as solvents are avoided of necessity in preparative reactions. Qualitative observation indicates that this sensitivity to hydrolysis is diminished dramatically on coordination. Complexes of $F_2PC_6H_{10}PF_2$ are particularly stable, many being air-stable over extended periods. In those instances where reaction is observed (mostly the solvent-wet complexes) it appears to be by way of metal oxidation rather than by a hydrolytic process.

The ligand $CH_3N(PF_2)_2$, a three-atom skeleton, also functions as a bidentate ligand in a bridging or chelating fashion[4-8] and is only a little weaker in π acidity than is $F_2PC_6H_{10}PF_2$;[1] vide supra. At least one noteworthy difference in the chemistry of the two ligands has appeared. While $F_2PC_6H_{10}PF_2$ forms chelates with the group 6B metals only with special precaution,[2a] $CH_3N(PF_2)_2$ has been shown to do so readily.[4] On the other hand displacement of CO from $Fe(CO)_5$[5] by $CH_3N(PF_2)_2$ gives bridged dimetal species while $F_2PC_6H_{10}PF_2$ readily gives chelates. This probably reflects the difference in bite between the three- and four-atom skeletons. It appears, however, to be a subtle factor in that in either Cr(0) or Fe(0) complexes a 90° PMP bond angle is expected.

A second feature of $CH_3N(PF_2)_2$ chemistry, which has not yet been identified for $F_2PC_6H_{10}PF_2$, is apparent hydrolysis of a P–N bond on a monodentate ligand to give a coordinated F_2PNCH_3H molecule (structure V).[7] The equivalent reaction of $F_2PC_6H_{10}PF_2$ would require hydrolysis of a P–C bond, a process much less facile as a rule than that of a P–N bond. The implication is that in comparable circumstances $F_2PC_6H_{10}PF_2$ might be expected to give higher polymers (e.g. VI). This may account in part for the insolubility of product obtained in our preliminary investigation of the reaction with $Co_2(CO)_8$.[36]



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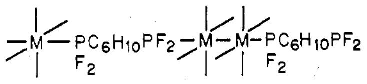

VI

Acknowledgment. We gratefully acknowledge the financial support of this study from the U.S. Army Research Office, Research Triangle Park, N.C. We appreciate the efforts of Mr. D. Hamill and Mr. G. Silcox and the University of Utah Department of Chemistry for assistance in obtaining ^{31}P FT NMR spectra. We greatly appreciate the many valuable suggestions from, and discussions with, Dr. Karen W. Morse.

Registry No. $(PF_2C_6H_{10}PF_2)_3Mo$, 67858-57-5; *fac*-$(PF_2C_6H_{10}PF_2)Mn(CO)_3Br$, 67858-58-6; $(PF_2C_6H_{10}PF_2)_2Mn(CO)Br$, 67858-59-7; *cis*-$Fe(CO)_3(PF_2C_6H_{10}PF_2)$, 67858-60-0; $Fe(CO)(PF_2C_6H_{10}PF_2)_2$, 67858-61-1; $Mo(C_6H_5CH_3)_2$, 12131-22-5; $Mn(CO)_5Br$, 14516-54-2; $Fe(CO)_5$, 13463-40-6.

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Contribution from the Gibbs Chemical Laboratory,
Harvard University, Cambridge, Massachusetts 02138

Molecular Orbital Studies on Large Closo Boron Hydrides

JOZEF BICERANO, DENNIS S. MARYNICK, and WILLIAM N. LIPSCOMB*

Received August 4, 1978

Wave functions calculated in the partial retention of diatomic differential overlap (PRDDO) approximation are presented for hypothetical closo boron hydrides $B_nH_n^c$ with n ranging from 13 to 24. Some structures are free of distortions due to incomplete occupancy only if $c = 0$, rather than the usual -2. Selected doubly negative and three neutral structures are discussed in terms of charge stability, static reactivity indices, degrees of bonding, overlap populations, and localized molecular orbitals obtained by the Boys criterion. Observations and speculations are made on stability, relations to metallocarborane chemistry, and synthesis.

I. Introduction

Closo boron hydrides[1] and metallocarboranes[2] are among the simplest metal cluster systems. Among the wide variety of known boron hydrides, the closed-polyhedral class is well-known for its high stability.[1] Recent experimental advances in metallocarborane chemistry,[2] especially the observation of polyhedra with up to 14 vertices for a wide variety of metals, have opened the new field of supraicosahedral boron chemistry. Recently, a broad outline was presented[3] for future theoretical studies on closo boron hydrides $B_nH_n^c$ for n ranging