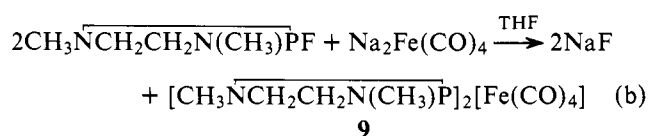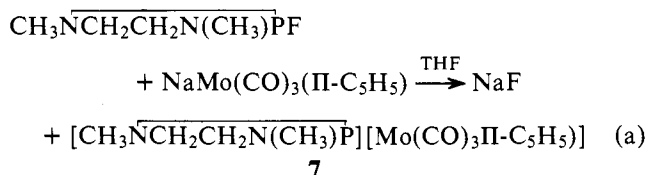(J_{HCNP} = 5.5 Hz) (rel intensity 4), and a cyclopentadienyl proton singlet at 4.57 ppm (rel intensity 5). Compound **9** shows ^{1}H resonances centered at 2.04 ppm with overlapping multiplet structure which has not been fully resolved. The ^{13}C{^{1}H} NMR spectrum (THF, 32 °C, Me$_4$Si external standard) of **7** shows a methyl doublet at 33.55 ppm (downfield) (J_{CNP} = 9.0 Hz), a methylene doublet at 57.70 ppm (J_{CPN} = 4.0 Hz), a Cp ring singlet at 87.73 ppm, and a carbonyl singlet at 215.22 ppm. The spectrum of **9** shows a methyl multiplet (unresolved) at 35.67 ppm, a methylene multiplet at 53.85 ppm, and a carbonyl singlet at 214.75 ppm.

The compositions of **7, 8,** and **9** are established by elemental analyses and/or mass spectra. Furthermore, the reaction stoichiometry and characterization data are consistent only with the following equations

$$CH_3\overline{NCH_2CH_2N(CH_3)}PF$$

$$+ NaMo(CO)_3(\Pi\text{-}C_5H_5) \xrightarrow{\text{THF}} NaF$$

$$+ [CH_3\overline{NCH_2CH_2N(CH_3)}P][Mo(CO)_3\Pi\text{-}C_5H_5)] \quad (a)$$

$$\mathbf{7}$$

$$2CH_3\overline{NCH_2CH_2N(CH_3)}PF + Na_2Fe(CO)_4 \xrightarrow{\text{THF}} 2NaF$$

$$+ [CH_3\overline{NCH_2CH_2N(CH_3)}P]_2[Fe(CO)_4] \quad (b)$$

$$\mathbf{9}$$

The structures of these unusual coordination complexes are now of central interest and the NMR and infrared data outlined here are consistent with the schematic arrangements shown here. We propose the structure of **7** in analogy to the

(7)   (9)
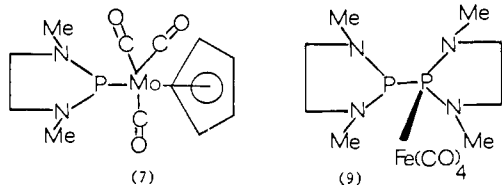
proposed structure of the mononuclear bis(pentafluorophenyl)phosphine–metal carbonyl complexes reported by Green and coworkers.[12] The structural possibilities for **9** are most interesting. The second-order ^{31}P NMR pattern and the coupling constant and chemical-shift parameters suggest that the iron center is asymmetrically positioned between the two phosphorus coordination sites of the condensed diphosphine, but it is not yet clear if the iron atom is primarily associated with only one phosphorus atom as schematically shown here. X-ray crystal structure analyses of these compounds are in progress, and their structures and photochemistry will be presented separately.

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(7) Analyses of **8** and **9** were plagued by minor decomposition impurities. The analytical composition of these compounds must for now be deduced from the mass spectra.
(8) The characterization data for **8** resembles those of **7**; so this data has not been presented.
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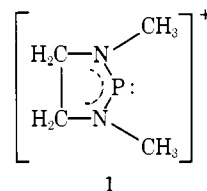
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Iron Carbonyl Complexes Containing Positively Charged Phosphorus Ligands

Sir:

A 1972 paper by Fleming, Lupton, and Jekot[1] described a cyclic cationic phosphorus species **1**. A more recent paper from


1

this laboratory[2] described the related noncyclic cations, [[(CH$_3$)$_2$N]$_2$P]$^+$ and [(CH$_3$)$_2$NPCl]$^+$. It was recognized in very early studies of these systems that the presence on phosphorus of (1) a free-electron pair, (2) a positive charge, and (3) a vacant p orbital should make ligands of this type effective π-type Lewis acids as well as weak σ-type Lewis bases. These arguments are supported by the observation that the cyclic cation (**1**) will slowly displace CO from Fe(CO)$_5$ in accordance with eq 1.

$$\mathbf{2}$$
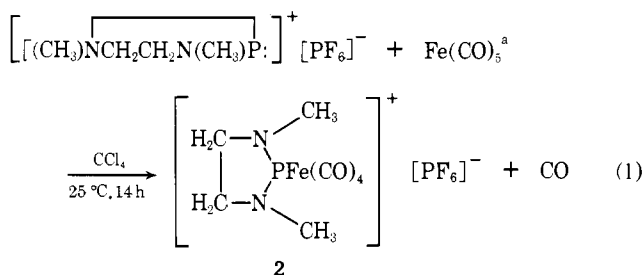
^{a} Fe$_2$(CO)$_9$ can also be used.

An alternative procedure for generating **2** involves the preparation of the easily characterized, stable compound, **3**. Fluoride can be removed from this species by a Lewis acid such as PF$_5$ to give **2**. The appropriate reaction is given in eq 2. The

3   2
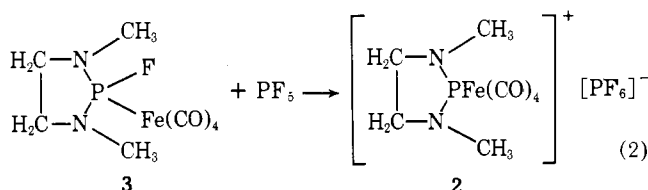
process is equally effective for preparing the analogous non-cyclic[3] cationic species [[(CH$_3$)$_2$N]$_2$PFe(CO)$_4$]$^+$ (**4**). A recent x-ray study of **3** in this laboratory[4] has shown unambiguously that the molecule has trigonal–bipyramidal geometry and that the phosphine is in the axial position around Fe. The structure

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Table I. Vibrational Spectral Data for Bis(dimethylamido)fluorophosphine Iron Tetracarbonyl (Cyclic and Noncyclic) and the Phosphine Iron Carbonyl Cations Derived from Them (C–O Stretching Region and P–F Stretching and Bending Region)

Fe(CO)$_5$	Substituted metal carbonyls (neutral)		Metal carbonyl cations		
	Cyclic ligand[a] iron carbonyl, cm^{-1}	Noncyclic ligand[b] iron carbonyl, m^{-1}	Cyclic ligand[c] cation carbonyl, cm^{-1}	Noncyclic ligand[d] cation carbonyl, cm^{-1}	Assignment (see ref 6)
(2114)[e]	2061	2055	2121	2123	A$_1$ $\nu_{CO(sym)}$ equatorial
(2031)	1996	1983	2070	2063	A$_1'$ $\nu_{CO(sym)}$ axial
2027	f	f	f	f	A$_2$ $\nu_{CO(asym)}$ axial
1994	1949 1956[g]	1951 1957[g]	2018, 1955[h]	2014, 1973[h]	E$\nu_{CO(asym)}$ equatorial
(1984)	1931[g]	1941 1938[g]			
	780	805			ν_{PF} of ligand
			840[h]	847[h] (vs)	ν_{PF} [PF$_6$]$^-$
			560[h]	563[h]	δ_{PF} [PF$_6$]$^-$

[a] Formula of compound is (CH$_3$)NCH$_2$CH$_2$N(CH$_3$)P(F)Fe(CO)$_4$. [b] Formula of compound is [(CH$_3$)$_2$N]$_2$P(F)Fe(CO)$_4$. [c] Formula [(CH$_3$)NCH$_2$CH$_2$N(CH$_3$)PFe(CO)$_4$]$^+$. [d] Formula [((CH$_3$)$_2$N)$_2$PFe(CO)$_4$]$^+$. [e] Values in parentheses were seen in Raman. [f] The A$_2$ mode does not exist for LFe(CO)$_4$ [g] Spectra of dry solid films [h] A Nujol mull sample of KPF$_6$ gave peaks at 840 and 560 cm^{-1}.

Table II. NMR Data[a] for Cyclic[b] and Noncyclic[c] (R$_2$N)$_2$(F)P–Fe(CO)$_4$ and [(R$_2$N)$_2$PFe(CO)$_4$]$^+$ [PF$_6$]$^-$

Nucleus	Temp, °C	Cyclic[d]	Noncyclic[e]	Cyclic[b]	Noncyclic[c]	Assignment
^{31}P (relative to H$_3$PO$_4$)	−70	d, −185 (J_{PF} = 1162)	d, −193 J_{PF} = 1073)	s, −300	s, −311	P coordinated to Fe(CO)$_4$ group
	−70			sept, 144 (J_{PF} = 715)	sept, 144 (J_{PF} = 715)	P of [PF$_6$]$^-$
^{19}F (relative to CFCl$_3$)	25	d, 7.3 (J_{PF} = 1165)	d, −48.7 (J_{PF} = 1085)			F on coordinated (R$_2$N)$_2$PF
	Below −80°			d, 71.3 (J_{PF} = 715)	d, 71.2 (J_{PF} = 715)	F of [PF$_6$]$^-$
^{1}H (relative to Me$_4$Si)	−10	d of d, 2.86 (J_{PH} = 13.3, J_{FH} = 2.5) m, 3.33	d of d, 2.71 (J_{PH} = 10.8, J_{FH} = 2.5)	d, 3.05 (J_{PH} = 14.0)	d, 3.10 (J_{PH} = 11.1)	H of –CH$_3$
				d, 3.83 (J_{PH} = 8.0)		–CH$_2$ of cyclic system

[a] In δ (parts per million) (*J* in hertz). [b] The formula of the cyclic cation is [(CH$_3$)NCH$_2$CH$_2$N(CH$_3$)PFe(CO)$_4$]$^+$. [c] The formula of the noncyclic cation is [((CH$_3$)$_2$N)$_2$PFe(CO)$_4$]$^+$. [d] The formula is (CH$_3$)NCH$_2$CH$_2$N(CH$_3$)P(F)Fe(CO)$_4$. [e] The formula is ((CH$_3$)$_2$N)$_2$P(F)-Fe(CO)$_4$.
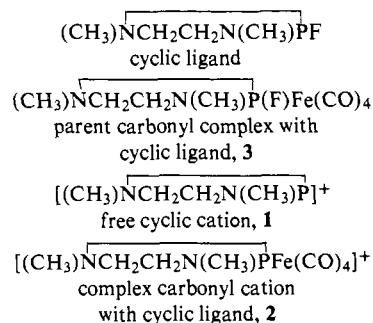
resembles that published for Ph$_2$HPFe(CO)$_4$ by Kilbourn, Raeburn, and Thompson.[5] Similarities between solid-state and solution IR spectra for **3** indicate that the structures in solution and in the solid state are the same.

This same structural conclusion for LFe(CO)$_4$ (L is either the cyclic or noncyclic amidofluorophosphine ligand) is reached on the basis of an infrared spectral analysis which uses the excellent paper of Darensbourg, Nelson, and Hyde[6] as a key. An earlier study[3] had assigned equatorial phosphine geometry to [(C$_2$H$_5$)$_2$N]$_2$P(F)Fe(CO)$_4$, on the basis of preliminary infrared data. Tis conclusion is no longer tenable. It is of interest that the degeneracy of the E mode for the equatorial C–O stretching frequencies in LFe(CO)$_4$ in solution has been lifted for the noncyclic ligand complex [(CH$_3$)$_2$N]$_2$P(F)-Fe(CO)$_4$; when spectra were run on dry solid samples of both complexes (cyclic and noncyclic), the degeneracy of the E mode was lifted in both cases. Detailed spectral characteristics will be considered elsewhere.

Addition of PF$_5$ to the complex results in removal of the fluoride ion from the axial amidofluorophosphine ligand of LFe(CO)$_4$ and generation of a compound with a cationic group in the *axial* position. The infrared data in the C–O stretching region and in the P–F stretching and bending region are shown in Table I for the neutral and cationic complexes as well as for Fe(CO)$_5$. The similarity in spectra of the system before and after fluoride removal provides proof that the cationic ligand is still axial. From the data of Table I it is clear that the P–F stretching frequency of the parent ligand disappears when PF$_5$

is added and that frequencies for the [PF$_6$]$^-$ ion appear. Fluoride transfer to PF$_5$ is unambiguously indicated. As expected, introduction of a positively charged ligand into a metal carbonyl brings about a sharp increase in C–O stretching frequencies. This fact is attributable to a reduction in Fe–C back-bonding. More detailed analysis of frequency shifts will be presented in the full paper. The reduction in Fe–C back-bonding suggests that weakening of the metal–carbon bond has occurred. Preliminary data support this premise which is being tested further. It is of obvious interest and significance.

The NMR data on the parent amidofluorophosphine iron carbonyls and on the cationic carbonyls derived from them are displayed in Table II. Conclusions based on the IR data are reinforced by the NMR results. In the ^{19}F spectrum the dou-

Chart I

(CH$_3$)NCH$_2$CH$_2$N(CH$_3$)PF
cyclic ligand

(CH$_3$)NCH$_2$CH$_2$N(CH$_3$)P(F)Fe(CO)$_4$
parent carbonyl complex with
cyclic ligand, **3**

[(CH$_3$)NCH$_2$CH$_2$N(CH$_3$)P]$^+$
free cyclic cation, **1**

[(CH$_3$)NCH$_2$CH$_2$N(CH$_3$)PFe(CO)$_4$]$^+$
complex carbonyl cation
with cyclic ligand, **2**

blet attributable in both cyclic and noncyclic cases to the F bound to the phosphorus of the ligand disappears and the doublet characteristic of $[PF_6]^-$ appears clearly at low temperature. The low temperature ^{31}P spectrum also shows the septet characteristic of $[PF_6]^-$. The ^{31}P chemical shift values further show a significant trend in the series shown in Chart I. The ^{31}P ∂ values relative to H_3PO_4 are $-138, -182, -264$, and -294 ppm, respectively. Comparable values for the noncyclic ligand series are $-153, -192, -264$, and -308 ppm. Increasingly negative values indicate that the phosphorus is becoming more deshielded, and more acidic through each series. In all cases this increased acidity shows up as more facile exchange of fluoride between the PF_6^- ion and the phosphorus of the cation. For cation **2** and $[PF_6]^-$ the fluoride doublet of $[PF_6]^-$ collapses at about -60 °C, indicating rapid exchange of fluoride between $[PF_6]^-$ and cation **2**. In contrast the ^{19}F doublet of the $[PF_6]^-$ associated with the simple, noncoordinated cyclic cation **1** shows *no* collapse up to above 60 °C. Corresponding temperatures for the noncyclic case are -72 and 10 °C. In studying this phenomenon of fluoride lability, purity of the system is extremely important. Small traces of base have dramatic effects in raising collapse temperatures.[7]

Amidofluorophosphine metal carbonyls involving Ni, Pt, P, Cr, W, Mn, Co, Cu, and Ag, have been prepared.[7,8] Most react with PF_5 to generate $[PF_6]^-$ and the corresponding cationic carbonyl complex.

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A Donor–Acceptor Structure for the Acetyl Chloride–Aluminum Chloride Complex in Methylene Chloride from Aluminum-27 Nuclear Magnetic Resonance

Sir:

Although the Friedel–Crafts reaction is a familiar one,[1-3] the structure of the 1:1 complex between acetyl chloride and aluminum chloride in solvents relevant to usual synthetic practice is not well defined. An ion-pair structure for the solid was determined by x-ray diffraction[4] after many conflicting solid-state IR studies had been reported.[4,5] The ^1H, ^{19}F, and ^{13}C NMR studies of Olah and coworkers[6] on acetyl halides and Lewis acids indicate that either the ion-pair or donor–acceptor form may be present, depending on the solvent system. The donor–acceptor form is indicated for the 1:1 acetyl chloride–aluminum chloride complex in 1,2-dichloroethane from the
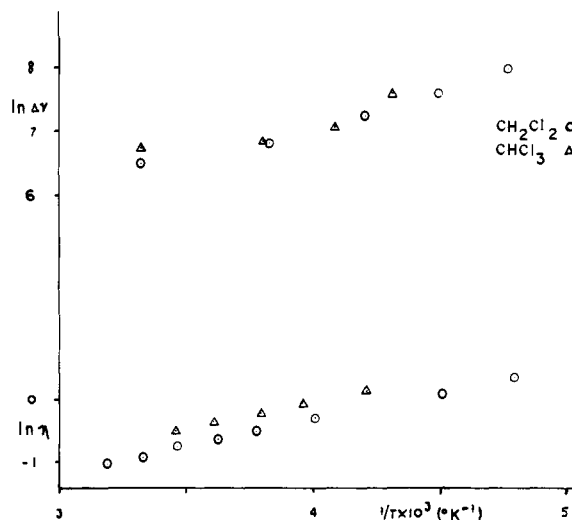
Figure 1. Logarithmic plot of aluminum-27 line widths, $\Delta\nu$, for the 1:1 acetyl chloride–aluminum chloride complex and solvent viscosities,[15] η, vs. reciprocal temperature. Concentrations are 1.4 M for methylene chloride, 0.118 M for chloroform.
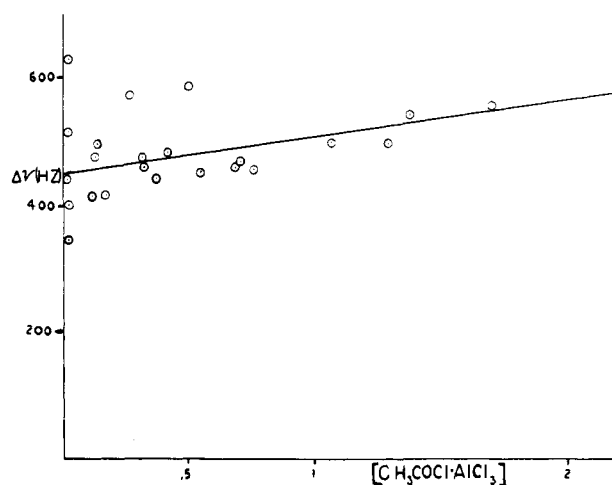

Figure 2. Aluminum-27 line widths, $\Delta\nu$, for the 1:1 acetyl chloride–aluminum chloride complex in methylene chloride vs. concentration. Temperature is 28 °C.

^1H NMR spectrum.[6a] The ^{27}Al NMR spectrum of this 1:1 complex has not been reported to our knowledge, although the ^{27}Al NMR parameters for aluminum chloride in acetyl chloride have been interpreted[7] to favor an ion-pair structure.

The ^{27}Al and ^1H NMR results reported here demonstrate that the 1:1 complex between acetyl chloride and aluminum chloride has a donor–acceptor structure in methylene chloride solution; only a minor fraction, if any at all, is present as the ion-pair form. Our conclusions come from two aspects of this study: the temperature and concentration dependence of the ^{27}Al NMR spectra of the 1:1 complex; the products shown by ^{27}Al and ^1H NMR to be formed on addition of halide ion to acetyl chloride–aluminum chloride and to acetyl bromide–aluminum chloride complexes.

^{27}Al FT NMR spectra (at 15.636 MHz) of the 1:1 complex[8] showed the following features: the line width, greater than that of tetrachloroaluminate by at least two orders of magnitude, showed a slight temperature and concentration dependence (Figure 1, 2); the chemical shift, 92.4 ppm,[9] did not change over a temperature range of -60 to 40 °C and over a concentration range of 10^{-3} to 2 M. The large line width and the chemical shift show that the complex does not exist as separated ion pairs in methylene chloride.[10] The temperature dependence of the ^{27}Al line width can be accounted for by vis-