halogenoacetonitrilerhodium(III) complexes with coordinated acetonitrile resonances all falling in the range δ 2.55–2.64 ppm, in agreement with our observations. No rhodium–hydrogen coupling was reported for their complexes which were studied on a lower resolution instrument.

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The Synthesis of Bis-μ-difluorophosphido-diiron Hexacarbonyl

BY W. M. DOUGLAS AND J. K. RUFF*[1]

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Although phosphorus trifluoride closely resembles carbon monoxide in many of its properties toward low-valent transition metals, it has not been observed to act as a bridging group. Instead, in only one example a PF_2 moiety has been found to bridge two metals. The compound $[Co(PF_3)_3PF_2]_2$ was prepared by Kruck and Lang[2] using forcing conditions (*e.g.*, cobalt(II) iodide, excess copper, and phosphorus trifluoride at 400 atm and temperatures above 170°). By use of nickel carbonyl, PF_2 bridging groups can be formed by a halogen-abstraction reaction. Thus with $BrPF_2Fe(CO)_4$,[3] $Ni(CO)_4$ affords the complex $[PF_2Fe(CO)_3]_2$. Criegee and Schroeder used a similar technique in the preparation of dichlorotetramethylcyclobutadienenickel dimer, $[(CH_3C)_4NiCl_2]_2$.[4]

Experimental Section

Materials.—Nickel carbonyl was used as obtained from J. T. Baker. $BrPF_2Fe(CO)_4$ was prepared according to the literature.[3]

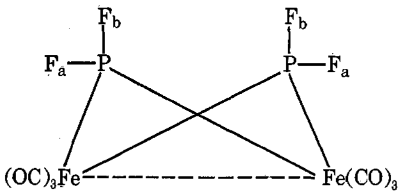
Analysis and Spectroscopic Measurements.—The mass, infrared, and nmr spectra were recorded on AEI MS-902, Perkin-Elmer 621, and Hitachi Perkin-Elmer R-20 spectrometers, respectively. Elemental analysis was obtained from Galbraith Laboratories, Knoxville, Tenn.

The Preparation of Bis-μ-difluorophosphido-diiron Hexacarbonyl.—A 9.51-g (30-mmol) sample of $BrPF_2Fe(CO)_4$ was added to 350 ml of deoxygenated hexane in a 500-ml flask. After degassing at −196°, nickel carbonyl (17.1 g, 100 mmol) was condensed into the flask. The flask was allowed to warm to ambient temperature under a nitrogen atmosphere and then fitted with a dewar condenser cooled to −78°. After refluxing until a metallic deposit was observed, the reaction mixture was allowed to cool to room temperature, and then the mixture was filtered through filter-aid. The solvent was removed *in vacuo*. The residue was extracted with four 50-ml portions of methylene chloride and the extracts were filtered. The filtrate was stripped dry, extracted with three 10-ml portions of pentane, and filtered again. The volume of the solution was then reduced to *ca.* 10 ml with a stream of dry nitrogen, and after cooling to −78°, orange-red to red crystals were obtained. Final purification was accomplished by sublimation (40–45° (0.1 mm)), yield 0.4 g (6.3%). *Anal.* Calcd for $P_2F_4Fe_2C_6O_6$: C, 17.21; H, 0.00; P, 14.85; F, 18.20; mol wt 418. Found: C, 17.44; H, 0.09; P, 14.85; F, 18.27; mol wt 418 (mass spectroscopy).

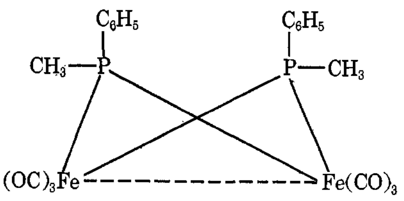
Results and Discussion

Nickel carbonyl has been found to react with $BrPF_2Fe(CO)_4$ in refluxing hexane to give the bis-μ-difluorophosphido complex $[F_2PFe(CO)_3]_2$. The new complex is an orange-red crystalline material, soluble in organic solvents, and easily sublimable. Though indefinitely stable under nitrogen, the complex decomposes upon exposure to the atmosphere.

Since the complex $[F_2PFe(CO)_3]_2$ is formally similar to the known complexes $[R_2PFe(CO)_3]_2$[5] ($R = CH_3$, C_6H_5), $[CH_3PC_6H_5Fe(CO)_3]_2$,[6,7] and $[C_2H_5SFe(CO)_3]_2$,[8,9] it is probable that it possesses the same generalized geometry. The complex $[C_2H_5SFe(CO)_3]_2$ has been shown by Dahl and Wei[9] to have a folded structure consisting of two octahedra sharing a common face whose three points of intersection consist of two bridging C_2H_5S units and a metal–metal bond. A recent structural determination of *sym*-$[CH_3PC_6H_5Fe(CO)_3]_2$[7] (II) has shown it to be isostructural with $[C_2H_5SFe(CO)_3]_2$, in which the $CH_3PC_6H_5$ moiety replaces the C_2H_5S units. Hence it is likely that $[FePFe(CO)_3]_2$ possesses a similar structure as shown in I.



I



II

The fluorine-19 nmr spectrum of $[F_2PFe(CO)_3]_2$ is consistent with the proposed structure. The observed spectrum consists of two sets of doublets, δ_a +46 ppm, $J_{F_aP} = 1260$ Hz, and δ_b +55 ppm, $J_{F_bP} = 1375$ Hz (*vs.* CCl_3F), whose areas integrate in a 1:1 ratio. Each member of the doublets is further split into a doublet by the adjacent fluorine atom, $J_{F_aF_b} = 285$ Hz. While it is not possible to assign the chemical shift values definitively, it is felt that the F_b fluorines [parallel to the principal (C_2) axis] are shifted upfield by a through-space interaction. This assignment is based on the relative shielding of the methyl groups in the complexes $[(CH_3)_2PFe(CO)_3]_2$[5] and *sym*-$[CH_3PC_6H_5Fe(CO)_3]_2$.[6] The proton nmr spectra of these complexes

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[8] W. Hieber and P. Spacu, *Z. Anorg., Allg. Chem.*, **233**, 353 (1937).

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show that the phosphorus atoms are virtually coupled, giving rise to 1:2:1 triplets. An X-ray structural determination of *sym*-$[CH_3PC_6H_5Fe(CO)_3]_2$[7] demonstrated that the phenyl groups are parallel to the C_2 axis (the phosphorus–phosphorus distance in this complex is 2.864 Å). The proton nmr of this sym isomer exhibits a methyl resonance at τ 8.08. In $[(CH_3)_2PFe(CO)_3]_2$, two methyl resonances occur at τ 8.07 and 8.48, respectively. The higher methyl resonance (τ 8.48) probably corresponds to those methyl groups parallel to the C_2 axis (occupying the position of the phenyl group in *sym*-$[CH_3PC_6H_5Fe(CO)_3]_2$) and corresponding to the F_b fluorines in this new complex. This shift to higher magnetic fields was explained on the basis of mutual through-space shielding of the methyl groups. The van der Waals radius of a methyl group (*ca.* 2.0 Å[10]) is sufficiently large to permit an electronic interaction at the distances involved (*ca.* 3.0 Å). In addition, it is noted that in a mixture of isomers of $[CH_3PC_6H_5Fe(CO)_2]_2$, the higher field of the two observed phenyl resonances (τ 3.10 and 2.57) belongs to the sym isomer described above. It is thus reasonable to assume that the higher of the two PF doublets (+55 ppm) arises from the F_b atoms. The van der Waals radius of fluorine (1.35 Å[10]) is sufficiently large to permit the postulated through-space interaction.

No coupling of the phosphorus atoms in $[F_2PFe(CO)_3]_2$ was observed in contrast to the methylphosphido complexes.

Unlike the organophosphorus and organosulfur complexes cited above which show only three or four bands in the terminal carbonyl region of the infrared, the infrared spectrum of $[PF_2Fe(CO)_3]_2$ in cyclohexane solution shows five carbonyl bands (ν_{CO} 2104 (m), 2065 (m), 2042 (s), 2031 (s), and 2018 (s) cm^{-1}). There are also two PF stretching frequencies at 867 (m) and 853 (m) cm^{-1}. This number of bands agrees with the maximum number allowed by simple symmetry arguments, since under C_{2v} symmetry five carbonyl bands are infrared active (*i.e.*, $2\ A_1 + 2\ B_1 + B_2$). The occurrence of these five bands supports the contention that the stretching frequencies of the carbonyl groups are strongly coupled through the metal–metal bond and/or the PF_2 groups.

The mass spectrum of $[F_2PFe(CO)_3]_2$ gave a peak corresponding to the parent molecular ion at 418 (based on the most abundant isotope) which agrees with the calculated value. The fragmentation pattern is similar to that of other carbonyl species, namely, loss of six carbon monoxide groups followed by a breakup of the $F_4P_2Fe_2$ framework. The degradation of the $F_4P_2Fe_2$ framework occurs by two pathways. The first is the loss of fluorine, followed by symmetric cleavage of P_2Fe_2 moiety. The second path is the symmetric cleavage of $F_2P_2F_4$, followed by the loss of fluorine.

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[Alkyl(fluorocarbon)phosphine]nickel Carbonyls. Effect of Bond Competition upon Ligand-Exchange Equilibria[1]

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It has been considered for many years that phosphorus(III) compounds may participate in both σ-donor and π-acceptor bonding in transition metal complexes. However, the relative importance of the σ and π bonds in any specific case has been controversial and difficult to judge.[2] For improved understanding of such bonding situations, there is a need for many further examples of ligand-displacement equilibria, so chosen as to contribute efficiently to the development of general principles.

The equilibria here studied were of the types

$$2LNi(CO)_3 \leftrightarrows L_2Ni(CO)_2 + Ni(CO)_4 \qquad (1)$$

$$[(CF_3)_3P]_2Ni(CO)_2 + L \leftrightarrows L(CF_3)_3PNi(CO)_2 + (CF_3)_3P \qquad (2)$$

$$L(CF_3)_3PNi(CO)_2 + L \leftrightarrows L_2Ni(CO)_2 + (CF_3)_3P \qquad (3)$$

wherein for (1) the ligand L was $(CF_3)_3P$, $CH_3P(CF_3)_2$, or $C_2H_5P(CF_3)_2$, and for (2) and (3) L was $CH_3P(CF_3)_2$, $C_2H_5P(CF_3)_2$, *i*-$C_4H_9P(CF_3)_2$, or $(C_2H_5)_2PCF_3$. The steric effects of these ligands were such as to minimize displacement of CO from the dicarbonyls, but the constants for (2) and (3) seemed not to be sterically affected except when L was *i*-$C_4H_9P(CF_3)_2$.

From the general lore of phosphine bases, it was expected that substitution of an alkyl group for CF_3 on P would increase the σ-bond energy by more than the decrease of π-bond energy, but there was a possibility that one of the mixed phosphines would show a maximum overall bonding power. Actually, K_2 and K_3 increased regularly with replacement of CF_3 by ethyl groups.

More interesting is the idea that equilibria of the type

$$L_2M(CO)_n + L'_2M(CO)_n \leftrightarrows 2LL'M(CO)_n \qquad (4)$$

normally will favor the product, because the competition among different ligands for σ- and π-bonding opportunities will not decrease the total bond energy as seriously as such competition between the same ligands will do. This idea, which may be regarded as a generalization of the "ROQ rule,"[3] contributes to the argument against any exact arrangement of ligands in their order of σ- or π-bonding power, even for the same central atom. The present results are confirmatory, for we can write $K_4 = K_2/K_3$ and so obtain K_4 values of 30, 20, and 20 for three different L's, with $L' = (CF_3)_3P$.

Such bond competition may concern the ligand→metal dative σ bonds to the extent that more variety of hybridization in these bonds may be advantageous, but competition for the use of the metal d electrons

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(1) We are grateful to the National Science Foundation for support of this research through Grant No. GP-17472.

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