# Alkylaminobis(difluorophosphines): Novel Bidentate Ligands for Stabilizing Low Metal Oxidation States and Metal–Metal Bonded Systems

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The coordination chemistry of transition metals in low, zero, and even negative oxidation states has been developed extensively during the past two decades and is becoming increasingly important because of applications of metal complexes in homogeneous catalysis. In this connection the preparation of stable complexes of transition metals in low oxidation states depends to a large extent upon the use of strong π-acceptor (i.e., "back bonding") ligands which can remove electron density from the metal atom through overlap of filled metal d orbitals with appropriate ligand antibonding orbitals of π^* symmetry. Examples of ligands of this type include carbon monoxide[1] and organic isocyanides[2] which have appropriate antibonding π^* orbitals and phosphorus trifluoride[3] in which the empty phosphorus 3d orbitals can play an analogous role as represented schematically below:
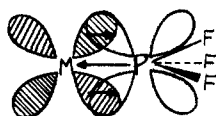
Factors influencing the π-acceptor strength of various ligands have been discussed elsewhere.[4]

Despite this extensive work on the transition-metal coordination chemistry of *monodentate* strong π-acceptor ligands, the development of *chelating* strong π-acceptor ligands has received relatively little attention even though the chelate effect[5] should add considerable stability to the resulting low oxidation state transition-metal complexes. The research outlined in the present Account arose from our interest in developing the coordination chemistry of chelating ligands with sufficiently strong π-acceptor properties to stabilize zerovalent transition-metal derivatives.

The design of chelating ligands containing multiple strong π-acceptor donor sites poses some clear difficulties. Carbon monoxide clearly has no "handle" for incorporation into a polydentate ligand. Alkyl and aryl isocyanides on the other hand can be incorporated into a polyfunctional ligand using the alkyl or aryl group as a handle. Thus, a ligand such as $CNCH_2CH_2CH_2NC$ contains two isocyanide donor groups.[6] However, the nearly linear hybridization of the isocyanide carbon atoms prevents such poly(isocyanides) from functioning

as chelating ligands (i.e., all of the isocyanide carbon atoms coordinating to the same transition-metal atom) except in macrocyclic chelate rings.[7]

These rather elementary considerations suggested that the most promising approach to chelating strong π-acceptor ligands would be the design of a poly(fluorophosphine) containing several PF_2 donor units so situated that two or more of these trivalent phosphorus atoms can bond to a single transition-metal atom. Ideally, the donor trivalent phosphorus atoms in such a chelating ligand would mimic as closely as possible the strong π-acceptor phosphorus trifluoride.

In this connection the electronegativity of the bridge separating the PF_2 donors should be maximized. This suggests fluorocarbon bridges between the PF_2 donor groups in order to maximize the phosphorus π-acceptor properties and hence the ability of the ligands to stabilize low transition-metal oxidation states. A bidentate ligand of this type, $F_2PCF_2CF_2PF_2$, has been prepared by Morse and Morse[8] by the photochemical addition of P_2F_4 across the carbon–carbon double bond of tetrafluoroethylene. However, the difficulty of performing this reaction on a large scale coupled with the rather low yields ($\sim 10\%$) makes $F_2PCF_2CF_2PF_2$ unavailable in sufficient quantities for a detailed study of its transition-metal coordination chemistry. Furthermore, in general, ligands with a carbon bridge separating two PF_2 donor sites prepared by reactions of P_2F_4 with olefins appear to be unstable upon standing at room temperature,[8] thereby restricting the conditions under which they can be used for preparative reactions with transition-metal derivatives.

These considerations led to our interest in the coordination chemistry of the alkylaminobis(difluorophosphines) $RN(PF_2)_2$. Such ligands are readily accessible in quantities of 100 g or larger through a simple two-step synthesis developed by Nixon and co-workers

(1) For a summary of metal carbonyl chemistry, see R. B. King, "Transition Metal Organometallic Chemistry: An Introduction", Academic Press: New York, 1969.

(2) L. Malatesta and F. Bonati, "Isocyanide Complexes of Metals", Wiley, London, 1969.

(3) T. Kruck, *Angew. Chem., Int. Ed. Engl.*, **6**, 53 (1967); J. F. Nixon, *Adv. Inorg. Chem. Radiochem.*, **13**, 363 (1970).

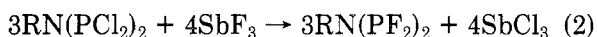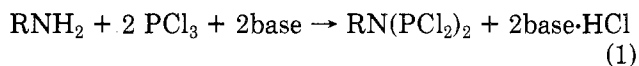(4) G. R. Dobson, I. W. Stolz, and R. K. Sheline, *Adv. Inorg. Chem. Radiochem.*, **8**, 1 (1966).

(5) For a discussion of the chelate effect, see G. Anderegg in "Coordination Chemistry", Vol. I, A. E. Martell, Ed., American Chemical Society Monograph 168, van Nostrand-Reinhold, New York, 1971, pp 427–490.

(6) W. P. Weber, G. W. Gokel, and I. K. Ugi, *Angew. Chem. Int. Ed. Engl.*, **11**, 530 (1972); K. R. Mann, N. S. Lewis, V. M. Miskowski, D. K. Erwin, G. S. Hammond, and H. B. Gray, *J. Am. Chem. Soc.*, **99**, 5525 (1977).

(7) R. J. Angelici, M. H. Quick, and G. A. Kraus, *Inorg. Chim. Acta*, **44**, L137 (1980).

(8) J. G. Morse and K. W. Morse, *Inorg. Chem.*, **14**, 565 (1975).

Robert Bruce King was born in Rochester, NH, in 1938. He received his chemical education at Oberlin College (B.A.) and Harvard University (Ph.D.). After 1 year at Du Pont and 4.5 years at The Mellon Institute, he joined the chemistry faculty of the University of Georgia where he is now Regents' Professor. He held an Alfred P. Sloan Fellowship (1967–1969) and received the 1971 American Chemical Society Award in Pure Chemistry. His current research interests include the synthesis and reactivity of transition-metal organometallic and organophosphorus compounds, molecular catalysis, applications of group theory and graph theory in inorganic chemistry, and the mathematical analysis of oscillating and bifurcating dynamic systems.

using primary amines, phosphorus trichloride, and antimony trifluoride as raw materials according to eq 1 and 2 (R = CH_3,[9] C_2H_5,[9] and C_6H_5[10]).

$$RNH_2 + 2\ PCl_3 + 2base \rightarrow RN(PCl_2)_2 + 2base \cdot HCl \quad (1)$$

$$3RN(PCl_2)_2 + 4SbF_3 \rightarrow 3RN(PF_2)_2 + 4SbCl_3 \quad (2)$$

The following features of this synthetic scheme are of interest: (1) Pyridine or conceivably a tertiary amine can be used for the base in the first step (eq 1). Alternatively, the base can be omitted entirely and the primary amine introduced as the hydrochloride provided relatively vigorous reaction conditions are used (e.g., boiling *sym*-tetrachloroethane (bp 146 °C) for 1 week). (2) The reaction fails if the R group of the primary amine is too bulky (e.g., isopropyl,[10] *tert*-butyl,[10] and neopentyl[11]). Such primary amines instead react with PCl_3 to form cyclophosphazanes of the type $(RNPCl)_2$ containing a four-membered phosphorus–nitrogen ring.

This Account summarizes the highlights of our research at the University of Georgia on the coordination chemistry of alkylaminobis(difluorophosphines), RN-$(PF_2)_2$. For further details on the individual features of what has proven to be a very rich and exciting area of chemistry, the interested reader is directed to the cited literature references.

Chelate Derivatives of RN(PF$_2$)$_2$ Ligands

Alkylaminobis(difluorophosphines) can function as bidentate ligands in transition-metal chemistry by forming four-membered chelate rings in which both phosphorus atoms coordinate to the same metal atom (structure I). The first examples of such chelates were
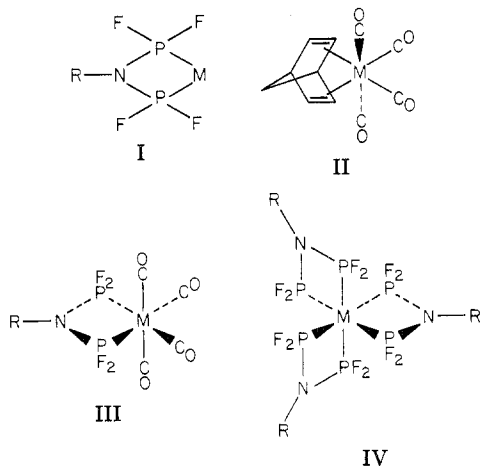
prepared by Johnson and Nixon[12] shortly after the discovery of the alkylaminobis(difluorophosphines). These workers showed that the ethyl derivative C_2H_5-$N(PF_2)_2$ could easily displace the coordinated norbornadiene ligand in $C_7H_8M(CO)_4$ (II: M = Cr, Mo, and W) to form the chelates $C_2H_5N(PF_2)_2M(CO)_4$ (III: R = C_2H_5; M = Cr, Mo, and W) in a reaction of a type long known[13] to be useful for the preparation of *cis*-

$L_2M(CO)_4$ complexes. However, these workers apparently did not extend the coordination chemistry of $RN(PF_2)_2$ ligands to other transition-metal systems. Nevertheless, their early results were significant in indicating that stable transition-metal complexes could be prepared containing four-membered chelate rings of type I.

An early objective of our work on the coordination chemistry of $RN(PF_2)_2$ was the preparation of zerovalent metal complexes containing exclusively $RN(PF_2)_2$ ligands. This objective was soon achieved when we found that ultraviolet irradiation of the metal hexacarbonyls $M(CO)_6$ (M = Cr, Mo, and W) with excess $CH_3N(PF_2)_2$ in diethyl ether solution results in complete substitution of all six metal carbonyl groups to give the corresponding tris(bidentate) zerovalent metal complexes $[CH_3N(PF_2)_2]_3M$ (IV, R = CH_3; M = Cr, Mo, and W).[14,15] Later the phenyl analogues $[C_6H_5N-(PF_2)_2]_3M$ (IV, R = C_6H_5; M = Cr, Mo, and W) were analogously prepared.[16] The ligands $RN(PF_2)_2$ (R = CH_3 and C_6H_5) are in fact the first known examples of bidentate ligands which can displace all of the six carbonyl groups in the metal hexacarbonyls in photochemical reactions to form fully substituted zerovalent metal complexes. Previously reported examples of the complete displacement of all six carbonyl groups in the metal hexacarbonyls upon reaction with a trivalent phosphorus ligand are limited to the monodentate ligands PF_3,[17] $CH_3CH_2CH_2OPF_2$,[18] $(CH_3O)_2PF$,[18] and $(CH_3O)_3P$.[18]

The complexes $[RN(PF_2)_2]_3M$ (III, R = CH_3 and C_6H_5; M = Cr, Mo, and W) are white volatile solids which exhibit high thermal and oxidative stabilities for zerovalent metal derivatives. Thus, the complexes $[CH_3N(PF_2)_2]_3M$ are stable toward air oxidation in the solid state, in contrast, for example, to the very air-sensitive known octahedral zerovalent metal derivatives $(diphos)_3M$ (e.g., diphos = $(CH_3)_2PCH_2CH_2P(CH_3)_2$).[19] Solutions of $[CH_3N(PF_2)_2]_3Cr$ begin to decompose in air over a period of 1 week whereas solutions of the molybdenum and tungsten derivatives decompose somewhat more rapidly. The $[CH_3N(PF_2)_2]_3M$ (M = Cr, Mo, and W) derivatives melt to clear yellow liquids without apparent decomposition at temperatures ranging from 182–183 °C for the chromium derivative to 221–223 °C for the tungsten derivative. The chromium derivative even appears to distill unchanged at atmospheric pressure at 256 °C. Thus, the strong π-acceptor chelating ability of the $RN(PF_2)_2$ ligands leads to unusually stable zerovalent metal complexes in these cases.

The photochemical reactions of other metal carbonyl derivatives have also been investigated. Among the least complicated such reactions are the ultraviolet irradiations of $CH_3N(PF_2)_2$ with the cyclopentadienyl-metal carbonyls $C_5H_5M(CO)_4$ (M = V[20] and Nb[21]) which result in pairwise substitution of the four carbonyls to

(9) J. F. Nixon, *J. Chem. Soc. A*, 2689 (1968).

(10) R. Jefferson, J. F. Nixon, T. M. Painter, R. Keat, and L. Stobbs, *J. Chem. Soc., Dalton Trans.*, 1414 (1973).

(11) R. B. King and S. Goel, unpublished results, 1977.

(12) T. R. Johnson and J. F. Nixon, *J. Chem. Soc. A*, 2518 (1969).

(13) R. B. King, *Inorg. Chem.*, 2, 936 (1963).

(14) R. B. King and J. Gimeno, *J. Chem. Soc., Chem. Commun.*, 142 (1977).

(15) R. B. King and J. Gimeno, *Inorg. Chem.*, 17, 2390 (1978).

(16) R. B. King and S. Goel, *Synth. React. Inorg. Metalorg. Chem.*, 9, 139 (1979).

(17) R. J. Clark and P. I. Hoberman, *Inorg. Chem.*, 4, 1771 (1965).

(18) R. Mathieu and R. Poilblanc, *Inorg. Chem.*, 11, 1858 (1972).

(19) J. Chatt and H. R. Watson, *J. Chem. Soc.*, 2545 (1962).

(20) R. B. King and K.-N. Chen, *Inorg. Chim. Acta*, 23, L19 (1977).

(21) R. B. King and C. D. Hoff, unpublished results, 1979.

give successively $C_5H_5M(CO)_2(PF_2)_2NCH_3$ (V) and $C_5H_5M[(PF_2)_2NCH_3]_2$ (VI). The compounds VI (M =


V VI VII
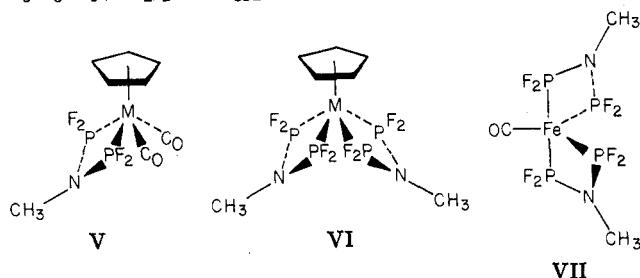
V and Nb) are the first known examples of compounds in which all four carbonyl groups of $C_5H_5M(CO)_4$ (M = V and Nb) have been completely replaced with other ligands.
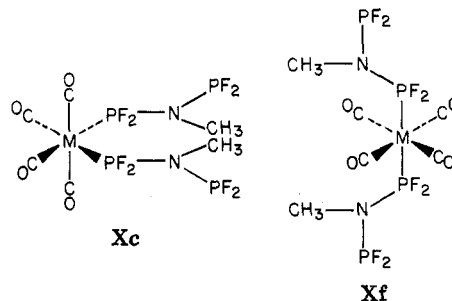
Photochemical reactions with metal carbonyls having an odd number of carbonyl groups are more complicated since pairwise substitution of carbonyl groups with *bidentate* $RN(PF_2)_2$ ligands clearly cannot proceed all of the way to carbonyl-free derivatives analogous to $[RN(PF_2)_2]_3M$ and $C_5H_5M[(PF_2)_2NCH_3]_2$. The photochemical reaction of $Fe(CO)_5$ with excess $CH_3N(PF_2)_2$ in tetrahydrofuran solution[15] can result in pairwise substitution of four of the five carbonyl groups to give $[CH_3N(PF_2)_2]_2FeCO$ (VII), but similar reactions in other solvents such as pentane or diethyl ether instead lead mainly to bimetallic derivatives discussed later. Photochemical reaction of $C_5H_5Mn(CO)_3$ with $CH_3N(PF_2)_2$ leads to successive formation of $C_5H_5Mn(CO)(PF_2)_2NCH_3$ (VIII) and $C_5H_5Mn[(PF_2)_2NCH_3]_2$ (IX).[22]

VIII IX
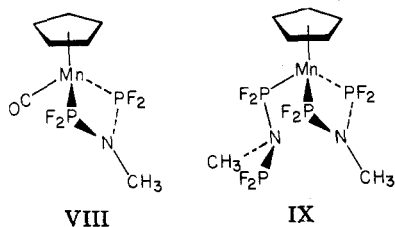
These results clearly indicate the existence of diverse transition-metal complexes containing four-membered chelate rings of type I formed by the $RN(PF_2)_2$ ligands. Although most of these metal complexes are quite stable, the potentially strained four-membered chelate rings can undergo ring-opening reactions upon treatment with Lewis base donor ligands according to eq 3.


$$R-N\begin{matrix}PF_2\\ \\PF_2\end{matrix}M \ + \ L \ \longrightarrow \ R-N\begin{matrix}PF_2\\ \\PF_2\end{matrix}M-L \qquad (3)$$
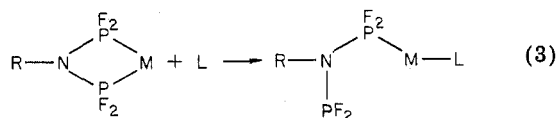
We have investigated reactions of this type by using the chromium complex $CH_3N(PF_2)_2Cr(CO)_4$.[23] Thus, treatment of $CH_3N(PF_2)_2Cr(CO)_4$ with excess $CH_3N(PF_2)_2$ at ~80 °C results in the formation of *trans*-$[CH_3N(PF_2)_2]_2Cr(CO)_4$ with two monodentate $CH_3N(PF_2)_2$ ligands. Compounds of this type can also be prepared in a single step from the norbornadiene complexes $C_7H_8M(CO)_4$ (II) by reaction with excess $RN(PF_2)_2$. This reaction gives the trans isomer Xt in the case of the chromium derivatives and the cis isomer Xc in the cases of the molybdenum and tungsten derivatives apparently because of the smaller size of chro-

(22) R. B. King and J. Gimeno, *Inorg. Chem.*, 17, 2396 (1978).
(23) R. B. King and T. W. Lee, *J. Organometal. Chem.*, in press.

Xc Xf

mium relative to molybdenum and tungsten. Stereospecific displacement of the coordinated norbornadiene in $C_7H_8M(CO)_4$ (II) by two monodentate $RN(PF_2)_2$ ligands should give initially the cis isomers Xc which in the case of the relatively small chromium atom undergo rearrangement to the less crowded trans isomers Xt. Johnson and Nixon apparently did not observe any of the $[C_2H_5N(PF_2)_2]_2M(CO)_4$ derivatives in their earlier studies[12] on the reactions of the norbornadiene complexes $C_7H_8M(CO)_4$[12] with $C_2H_5N(PF_2)_2$ because their reaction conditions (e.g., temperature and amount of $RN(PF_2)_2$ ligand) were not sufficiently forcing to open the chelate ring.

Chelate ring-opening reactions on $CH_3N(PF_2)_2Cr(CO)_4$ can also be used to prepare novel mixed ligand complexes of the type *trans*-$LL'Cr(CO)_4$[23] which represent one of the least frequently encountered types of substituted octahedral metal carbonyls. Thus, reaction of $CH_3N(PF_2)_2Cr(CO)_4$ with $C_6H_5N(PF_2)_2$ gives a complex *trans*-$[CH_3N(PF_2)_2][C_6H_5N(PF_2)_2]Cr(CO)_4$ (XI),

XI XII
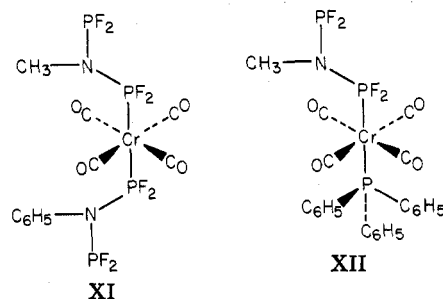
the first example of a complex containing two different $RN(PF_2)_2$ ligands. A related mixed ligand complex *trans*-$CH_3N(PF_2)_2Cr(CO)_4P(C_6H_5)_3$ of apparent structure XII is the major product from the reaction of $CH_3N(PF_2)_2Cr(CO)_4$ with triphenylphosphine.

$RN(PF_2)_2$ Ligands as Bridges across Metal–Metal Bonds

Alkylaminobis(difluorophosphines) can function as bidentate ligands in bimetallic systems by bridging a bonded pair of metal atoms to form a five-membered chelate ring (XIII). We have prepared extensive series

XIII XIV
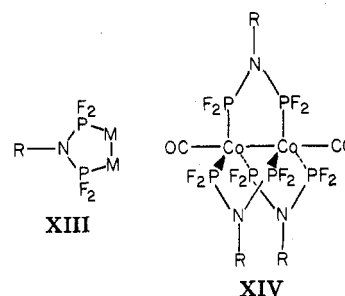
of compounds containing such structural units. Such

compounds are of interest because of the effect of the strong fluorophosphine bridges on the chemical reactivity of the metal–metal bond.

Bimetallic derivatives containing metal–metal bonds bridged by $RN(PF_2)_2$ (XIII) were first encountered in a study of the reactions of these ligands with $Co_2(CO)_8$. Thus, treatment of $Co_2(CO)_8$ with $RN(PF_2)_2$ (R = CH_3[24,25] and C_6H_5[16]) at room temperature results in rapid evolution of carbon monoxide to give the corresponding $[RN(PF_2)_2]_3Co_2(CO)_2$ derivatives as purple solids. These compounds may be regarded as formal substitution products of $Co_2(CO)_8$ in which six of the eight carbonyl groups have been replaced. In contrast to the air-sensitive $Co_2(CO)_8$, the $[RN(PF_2)_2]_3Co_2(CO)_2$ complexes appear to be stable to air. The structure XIV (R = CH_3) containing a cobalt–cobalt bond bridged by three $CH_3N(PF_2)_2$ ligands has been confirmed[24] by X-ray crystallography.

The $[CH_3N(PF_2)_2]_3Co_2$ unit in $[CH_3N(PF_2)_2]_3Co_2$-$(CO)_2$ is stable toward a variety of chemical transformations. Thus, ultraviolet irradiation of $[CH_3N(PF_2)_2]_3Co_2(CO)_2$ with the ligands $(CH_3)_2NPF_2$, $(C_2H_5O)_3P$, $(C_6H_5)_3P$, and $(CH_3)_3CNC$ (designated as L) results in the stepwise displacement of the two terminal carbonyl groups to give complexes of the types $[CH_3N(PF_2)_2]_3Co_2(CO)L$ and $[CH_3N(PF_2)_2]_3Co_2L_2$.[25] Related purple-black derivatives of the stoichiometry $[RN(PF_2)_2]_5Co_2$ (R = CH_3 and C_6H_5) can be obtained by ultraviolet irradiation of $Co_2(CO)_8$ with excess $RN(PF_2)_2$. The peculiar stoichiometry of the $[RN(PF_2)_2]_5Co_2$ complexes can be explained by structure XV. This structure is also supported by the observa-
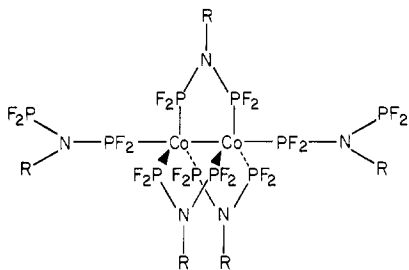

XV
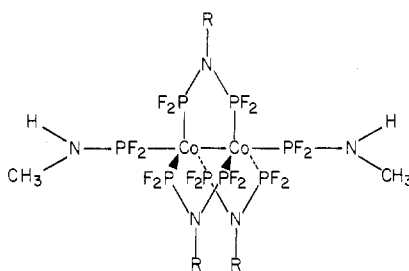
XVI

tion that chromatography of $[CH_3N(PF_2)_2]_5Co_2$ on Florisil results in hydrolytic removal of the uncomplexed PF_2 groups of the terminal $CH_3N(PF_2)_2$ ligands to give $[CH_3N(PF_2)_2]_3Co_2(PF_2NHCH_3)_2$, shown by X-ray crystallography[24] to have structure XVI.

The $[CH_3N(PF_2)_2]_3Co_2$ unit in the formal cobalt(0) derivative $[CH_3N(PF_2)_2]_3Co_2(CO)_2$ even survives some redox reactions. Treatment with excess bromine at

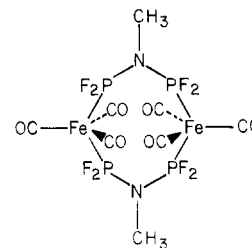room temperature gives the brown cobalt(II) derivative $[CH_3N(PF_2)_2]_3Co_2Br_4$, shown by X-ray crystallography to have structure XVII.[26] Electrochemical studies on
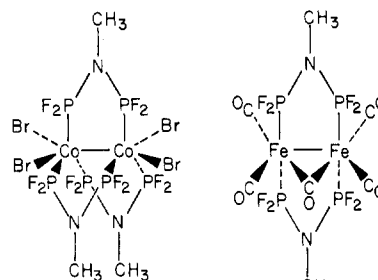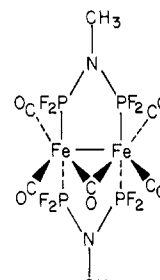
XVII   XVIII

XIX

$[CH_3N(PF_2)_2]_3Co_2(CO)_2$ in collaboration with Dr. N. El Murr of the University of Dijon in France[27] indicate both a reversible one-electron reduction to a green radical anion, $[CH_3N(PF_2)_2]_3Co_2(CO)_2^-$, and a reversible two-electron reduction to a pale yellow dianion, $[CH_3N(PF_2)_2]_3Co_2(CO)_2^{2-}$.

Studies on reactions of iron carbonyls with the $RN(PF_2)_2$ ligands have yielded several compounds containing an iron–iron bond bridged by one or two $RN(PF_2)_2$ ligands.[15,28] Ultraviolet irradiation of $Fe(CO)_5$ with $CH_3N(PF_2)_2$ in pentane or diethyl ether gives an orange bimetallic complex, $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$ (XVIII), in contrast to the reaction in tetrahydrofuran discussed above which leads to $[CH_3N(PF_2)_2]_2FeCO$ (VII). Reaction of $Fe_3(CO)_{12}$ with $CH_3N(PF_2)_2$ in boiling tetrahydrofuran gives yellow crystalline $[CH_3N(PF_2)_2Fe(CO)_3]_2$ (XIX) which readily loses carbon monoxide upon standing or heating in solution to form $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$ (XVIII). Structures of both XVIII and XIX have been determined by X-ray crystallography. The formation of XVIII from XIX involves displacement of a carbonyl ligand through formation of a metal–metal bond and suggests that $RN(PF_2)_2$ bridges hold pairs of metal atoms so close together that formation of a metal–metal bond is very facile, even if carbonyl loss is required. An unusual feature of XIX is the square-pyramidal rather than the usual trigonal-bipyramidal coordination for the five-coordinate iron(0) atoms. This unusual stereochemistry for a d^8 five-coordinate system may be a consequence of the constraints introduced by the two $CH_3N(PF_2)_2$ bridges combined with the fluxionality of five-coordinate complexes.[29]

The extensive series of bimetallic complexes in which $RN(PF_2)_2$ ligands bridge metal–metal bonds as exem-

(24) M. G. Newton, R. B. King, M. Chang, N. S. Pantaleo, and J. Gimeno, *J. Chem. Soc., Chem. Commun.*, 531 (1977).

(25) R. B. King, J. Gimeno, and T. J. Lotz, *Inorg. Chem.*, 17, 2401 (1978).

(26) M. G. Newton, N. S. Pantaleo, R. B. King, and T. J. Lotz, *J. Chem. Soc., Chem. Commun.*, 514 (1978).

(27) A. Chaloyard, N. El Murr, and R. B. King, *J. Organometal. Chem.*, in press.

(28) M. G. Newton, R. B. King, M. Chang, and J. Gimeno, *J. Am. Chem. Soc.*, 99, 2802 (1977).

(29) R. R. Holmes, *Acc. Chem. Res.*, 5, 296 (1972).

plified by those discussed above suggests the synthesis of metal cluster compounds in which $RN(PF_2)_2$ ligands bridge metal–metal bonds. In this connection the reaction of $Co_4(CO)_{12}$ with $CH_3N(PF_2)_2$ gives products of the type $[CH_3N(PF_2)_2]_nCo_4(CO)_{12-n}$ in which the cobalt tetrahedron is apparently maintained intact.[25] The products in which $n = 2, 3, 4,$ and 5 have been isolated in the pure state.
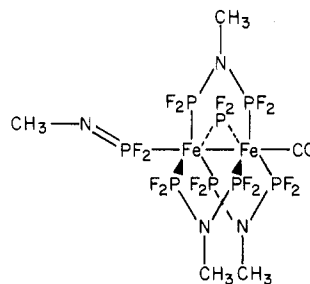
Phosphorus–Nitrogen Bond Cleavage Reactions in the Coordination Chemistry of $RN(PF_2)_2$ Ligands

Some reactions of $CH_3N(PF_2)_2$ with transition-metal derivatives lead to products in which one of the PF_2 groups has been removed through cleavage of the phosphorus–nitrogen bond. Most such reactions appear to fall into one of the following two types: (1) solvolytic removal of the uncoordinated PF_2 group of a monodentate $CH_3N(PF_2)_2$ ligand in the presence of a proton source to give a metal complex of CH_3NHPF_2, a ligand which is known[30] but unstable when not complexed to transition metals; (2) cleavage of a $CH_3N(PF_2)_2$ ligand to form separate CH_3NPF_2 and PF_2 units, both of which remain complexed to the transition-metal system. At the present time we have no evidence for analogous reactions of metal complexes of $C_6H_5N(PF_2)_2$.

Reactions of type I appear to be fairly general as indicated by the following examples: (1) The solvolysis of $[CH_3N(PF_2)_2]_5Co_2$ (XVI, R = CH_3) upon chromatography on Florisil as discussed earlier gives $[CH_3N(PF_2)_2]_3Co_2(PF_2NHCH_3)_2$ (XVI).[24,25] This example illustrates very nicely the much greater susceptibility of uncomplexed PF_2 groups relative to complexed PF_2 groups toward solvolytic cleavage since the bridging $CH_3N(PF_2)_2$ ligands remain intact under conditions where the monodentate $CH_3N(PF_2)_2$ ligands are converted to CH_3NHPF_2 ligands. (2) Reaction of $Fe_2(CO)_9$ with *excess* $CH_3N(PF_2)_2$ in diethyl ether at room temperature gives yellow liquid $CH_3N(PF_2)_2Fe(CO)_4$ containing a monodentate $CH_3N(PF_2)_2$ ligand.[31] This complex undergoes solvolysis upon chromatography on Florisil to give pale yellow volatile crystals of CH_3NH-$PF_2Fe(CO)_4$. (3) Reactions of $C_5H_5Mo(CO)_3Cl$ and $C_5H_5Fe(CO)_2Cl$ with $CH_3N(PF_2)_2$ in the presence of methanol give the complexes $C_5H_5Mo(CO)_2(PF_2NHC$-$H_3)Cl$ and $C_5H_5Fe(CO)(PF_2NHCH_3)Cl$, respectively.[22] In the absence of methanol these same reactions give the unsolvolyzed complexes $C_5H_5Mo(CO)_2[(PF_2)_2NC$-$H_3]Cl$ and $C_5H_5Fe(CO)[(PF_2)_2NCH_3]Cl$ containing monodentate $CH_3N(PF_2)_2$ ligands.

The phosphorus–nitrogen bond cleavage reactions of $CH_3N(PF_2)_2$ which lead to complexes containing separate CH_3NPF_2 and PF_2 units are somewhat more unusual. The first such complex arose in a study of complexes apparently derived from $Fe_2(CO)_9$ through pairwise displacement of its carbonyl groups by CH_3N-$(PF_2)_2$ ligands. Thus, the complexes $CH_3N(PF_2)_2Fe_2$-$(CO)_7$ and $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$ (XVIII), which are formally $Fe_2(CO)_{9-2n}$ derivatives ($n = 1$ and 2, respectively), have been prepared.[15,28] Ultraviolet irradiation of $Fe_3(CO)_{12}$ with excess $CH_3N(PF_2)_2$ in diethyl ether was found to give a yellow solid of stoichiometry

$[CH_3N(PF_2)_2]_4Fe_2CO$, apparently corresponding to another $Fe_2(CO)_{9-2n}$ derivative in which $n = 4$.[32] However, the infrared spectrum of $[CH_3N(PF_2)_2]_4Fe_2CO$ clearly indicates that the single carbonyl group is terminal rather than bridging. There is no way of formulating a $[CH_3N(PF_2)_2]_4Fe_2CO$ with a terminal carbonyl group and all eight donor phosphorus atoms each bonded to a single iron atom without either violating the rare gas electronic configuration for one or both iron atoms or introducing an iron–iron dative bond as found in the complexes $R_4C_4Fe_2(CO)_6$.[33] The structure of $[CH_3N$-$(PF_2)_2]_4Fe_2CO$ was therefore determined by X-ray diffraction[32] and found to be XX in which the phos-

XX

phorus–nitrogen bond in one of the $CH_3N(PF_2)_2$ units has been broken to give a terminal CH_3NPF_2 ligand and a bridging PF_2 group.

Reaction of $[C_5H_5Fe(CO)_2]_2$ with $CH_3N(PF_2)_2$ yields another type of product in which phosphorus–nitrogen bond cleavage has taken place. Ultraviolet irradiation of $[C_5H_5Fe(CO)_2]_2$ with $CH_3N(PF_2)_2$ in tetrahydrofuran or pentane was found to result in pairwise substitution of the four carbonyl groups to give low yields of purple $[C_5H_5FeCO]_2(PF_2)_2NCH_3$ and red $[C_5H_5Fe(PF_2)_2N$-$CH_3]_2$.[34] The proton NMR spectrum of the carbonyl-free complex indicates nonequivalence of the two cyclopentadienyl rings and hence the two iron atoms. Since this observation could not be readily explained without invoking something unusual and unprecedented, the structure was determined by X-ray diffraction and found to be XXI. The bonding of the

XXI   XXII
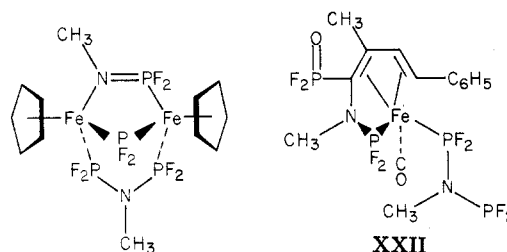
CH_3NPF_2 unit to the bimetallic system in XXI is unusual since it is attached to one iron through phosphorus and to the other iron through nitrogen. This is the only well-characterized compound where a ligand derived from an aminodifluorophosphine is bonded to

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a transition metal through nitrogen.

One of the most bizarre complexes containing RN-$(PF_2)_2$ ligands and incidentally involving phosphorus–nitrogen bond cleavage arose from an unsuccessful attempt to prepare a simple monomeric $RN(PF_2)_2Fe(CO)_3$ derivative, a complex type that still eludes us. The reagent (benzalacetone)tricarbonyliron, $[C_6H_5CH=CHC(O)CH_3]Fe(CO)_3$, is known to be a source of Fe-$(CO)_3$ groups under mild conditions.[35,36] It therefore appeared that reaction with $CH_3N(PF_2)_2$ might provide a route to $CH_3N(PF_2)_2Fe(CO)_3$. However, the reaction was found instead to give a yellow crystalline product indicated by elemental analyses and NMR spectra still to contain the benzalacetone moiety in some form.[37] A structure determination by X-ray diffraction on this complex indicates structure XXII. This complex contains a highly exotic ligand derived from 1 equiv each of $CH_3N(PF_2)_2$ and benzalacetone, which bonds to the iron through both a tetrahaptodiene unit and a trivalent phosphorus atom. Despite the bizarre structure of XXII a scheme can be conceived for a mechanism of its formation in which every step has a reasonable precedent.[37]

Summary and Future Prospects

In this Account I have attempted to indicate the richness of the transition-metal coordination chemistry of $RN(PF_2)_2$ which appears to rival that of the most versatile unsaturated hydrocarbon ligands in transition-metal organometallic chemistry (e.g., cyclopentadienyl, cyclooctatetraene, etc.). However, the chemistry outlined here is undoubtedly just the beginning of a field which is likely to be a productive area of investigation for many years to come. The ability of $RN(PF_2)_2$ ligands to form strong bridges across metal–metal bonds creates numerous unusual bimetallic systems and the possibility for devising novel catalyst systems involving two metal sites held at a close well-defined distance by the $RN(PF_2)_2$ bridges. The preliminary results outlined above on complexes derived from $CH_3N(PF_2)_2$ and $Co_4(CO)_{12}$ retaining the Co_4 tetrahedron suggest the use of $RN(PF_2)_2$ as ligands to hold metal–metal bonds together to stabilize novel metal cluster types.

Also, little work has yet been done on $RN(PF_2)_2$ complexes of the platinum metals despite the importance of these metals in numerous catalytic processes. The ability of related small bite bidentate trivalent phosphorus ligands such as $(C_6H_5)_2PCH_2P(C_6H_5)_2$ to stabilize unusual bimetallic palladium[38] and platinum[39] complexes with the unusual +1 formal oxidation state suggests that $RN(PF_2)_2$ complexes of platinum metals might prove to be a fertile field of investigation.

Finally, a tridentate analogue of the $RN(PF_2)_2$ ligands is $N(PF_2)_3$, which might form even more stable zerovalent metal complexes and which might be very effective at bridging triangular faces of metal clusters. Although the presently known preparations of $N(PF_2)_3$ are rather difficult,[40,41] particularly when compared with the easy preparations of the $RN(PF_2)_2$ ligands (R = CH_3, C_2H_5, and C_6H_5), further development of the preparation of $N(PF_2)_3$ should ultimately make this interesting ligand available in at least sufficient quantities for an exploration of its fundamental coordination chemistry.

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