

- man, T. R. Halbert, and K. S. Suslick, *Proc. Natl. Acad. Sci. U.S.A.*, **73**, 3333 (1976); (c) E. Bayer and G. Holzbach, *Angew. Chem., Int. Ed. Engl.*, **16**, 117 (1977); (d) J. P. Collman, *Acc. Chem. Res.*, **10**, 265 (1977); (e) B. R. James in "The Porphyrins", Vol. V, D. Dolphin, Ed., Academic Press, New York, N.Y., in press.
- (2) C. K. Chang, D. Powell, and T. G. Traylor, *Croat. Chem. Acta*, **49**, 295 (1977).
- (3) B. R. James, L. D. Markham, A. D. Rattray, and D. K. W. Wang, *Inorg. Chim. Acta*, L25 (1976).
- (4) F. R. Hopf and D. G. Whitten, *J. Am. Chem. Soc.*, **98**, 7422 (1976).
- (5) The ruthenium complexes reported here gave elemental analyses and spectroscopic data consistent with their proposed structures: ν^{KBr} for $Ru^{II}OEP(CH_3CN)_2$, 2260 cm^{-1} ; for $Ru^{II}TPP(CH_3CN)_2$, 2265 cm^{-1} .
- (6) J. J. Bonnet, S. S. Eaton, G. R. Eaton, R. H. Holm, and J. A. Ibers, *J. Am. Chem. Soc.*, **95**, 2141 (1973).
- (7) The exact nature of the species in solution is under investigation.
- (8) Exposure of $Ru(OEP)(DMF)_2$ solution to N_2 (pretreated with chromous) gave visible spectral changes similar to those observed during oxygenation, and is likely due to formation of a dinitrogen complex (cf. ref 4).
- (9) G. M. Brown, F. R. Hopf, J. A. Ferguson, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **95**, 5939 (1973).
- (10) J. P. Collman, R. R. Gagné, and C. A. Reed, *J. Am. Chem. Soc.*, **96**, 2629 (1974).

N. Farrell, D. H. Dolphin,* B. R. James*

Department of Chemistry, University of British Columbia
Vancouver, Canada V6T 1W5

Received September 6, 1977

Tetrakis[methylaminobis(difluorophosphine)]-carbonyldiiron: Unsymmetrical Bonding of Methylaminobis(difluorophosphine) to a Pair of Transition Metals Involving Phosphorus-Nitrogen Bond Cleavage

Sir:

The bidentate ligand $CH_3N(PF_2)_2$ is now well established to be very effective in replacing pairwise the maximum number of carbonyl groups in a variety of metal carbonyls. For example, ultraviolet irradiations of $CH_3N(PF_2)_2$ with the metal hexacarbonyls $M(CO)_6$ ($M = Cr, Mo, \text{ and } W$) give the carbonyl-free complexes¹ $[CH_3N(PF_2)_2]_3M$ ($M = Cr, Mo, \text{ and } W$). Similarly, reactions of $CH_3N(PF_2)_2$ with $Co_2(CO)_8$ under various conditions give $[CH_3N(PF_2)_2]_3Co_2L_2$ ($L = CO$,² CH_3NHPF_2 ,² and monodentate $CH_3N(PF_2)_2$).³ This communication describes the preparation and structure of $[CH_3N(PF_2)_2]_4Fe_2CO$, suggested by its stoichiometry to be derived from $Fe_2(CO)_9$ by pairwise replacement of the maximum number of carbonyl groups with bidentate $CH_3N(PF_2)_2$ ligands. However, x-ray crystallography shows this complex to have a totally unexpected structure in which a phosphorus-nitrogen bond in one of the $CH_3N(PF_2)_2$ ligands is broken completely to give separate CH_3NPF_2 and PF_2 units both of which are bonded to iron atom(s).

A solution of 2.0 g (4 mmol) of $Fe_3(CO)_{12}$, 4.0 g (24 mmol) of $CH_3N(PF_2)_2$,⁴ and 250 mL of diethyl ether was exposed for 2 h to the ultraviolet irradiation from a 450-W Englehard-Hanovia lamp. Removal of diethyl ether from the filtered reaction mixture followed by chromatography of a concentrated dichloromethane solution on a Florisil column gave up to 1.78 g (37% yield) of yellow, crystalline, relatively air-stable $[CH_3N(PF_2)_2]_4Fe_2CO$, mp 181–183 °C, after elution with diethyl ether and crystallization from a mixture of dichloromethane and hexane. Anal. Calcd for $C_5H_{12}F_{16}Fe_2N_4OP_8$: C, 7.4; H, 1.5; N, 6.9. Found: C, 7.8; H, 1.6; N, 6.7.

The single carbonyl group in $[CH_3N(PF_2)_2]_4Fe_2CO$ exhibits a strong infrared frequency at 1990 cm^{-1} indicating that this carbonyl group is terminal rather than bridging. Since 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

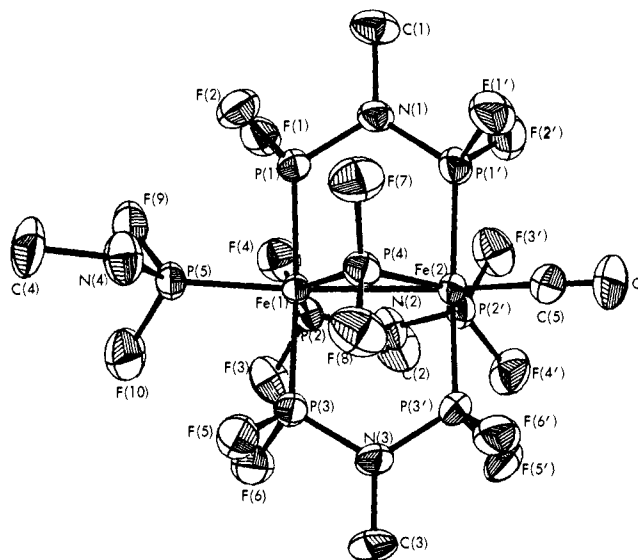
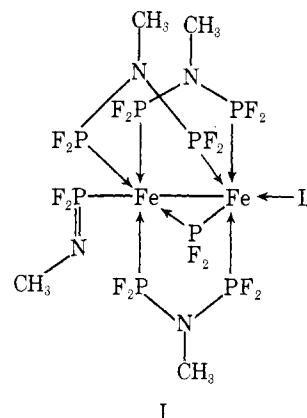


Figure 1. ORTEP drawing of the structure of $[CH_3N(PF_2)_2]_4Fe_2CO$.

complexes $R_4C_4Fe_2(CO)_6$,⁵ the structure of this unusual complex was determined by single-crystal x-ray diffraction.

The iron complex $[CH_3N(PF_2)_2]_4Fe_2CO$ forms monoclinic crystals by slow evaporation of an *n*-hexane solution at room temperature: space group $C2/c$; $a = 31.023$ (7) Å, $b = 9.273$ (3) Å, $c = 17.401$ (5) Å, $\beta = 96.57^\circ$, $Z = 8$. Least-squares refinement using the 2376 observed reflections (R 0.0489, R_w 0.0485) indicates the structure I ($L = CO$) depicted in detail



in Figure 1. The iron-iron distance is 2.725 (2) Å indicating an iron-iron bond. This iron-iron bond is bridged by three $CH_3N(PF_2)_2$ ligands and one PF_2 group, thereby providing a relatively rare example of a metal-metal bond bridged by four groups. The terminal CH_3NPF_2 ligand bonded to $Fe(1)$ functions as a one-electron donor. Alternatively the unit $FePF_2NCH_3$ may be regarded as a metal-substituted phosphinimine containing a phosphorus-nitrogen double bond. In support of this latter idea is the relatively short $P(5)-N(4)$ bond length of 1.590 (10) Å as compared with bond lengths in the range of 1.647 to 1.676 Å for the six phosphorus-nitrogen bonds in the three bridging $CH_3N(PF_2)_2$ ligands.

The structure of $[CH_3N(PF_2)_2]_4Fe_2CO$ ($I, L = CO$) indicates that the phosphorus-nitrogen bond in one of the $CH_3N(PF_2)_2$ units has been broken in the formation of this complex from iron carbonyls and $CH_3N(PF_2)_2$. Such cleavage of a $CH_3N(PF_2)_2$ unit to a one-electron donor terminal CH_3NPF_2 ligand and a bridging PF_2 unit donating two electrons to the metal atom bearing the CH_3NPF_2 ligand and a single electron to the other metal atom is a method for $CH_3N(PF_2)_2$ to bridge a metal-metal bond by donating three electrons to one of the metal atoms and a single electron to the

other metal atom. This type of unsymmetrical bonding of $\text{CH}_3\text{N}(\text{PF}_2)_2$ to a pair of bonded metal atoms must be contrasted with the more usual symmetrical bonding exhibited by the other three $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands in $[\text{CH}_3\text{N}(\text{PF}_2)_2]_4\text{Fe}_2\text{CO}$ (1, L = CO) where all phosphorus-nitrogen bonds in the ligands are retained and each phosphorus atom donates a single electron pair to a single metal atom. Such unsymmetrical bonding of one $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligand is required in $[\text{CH}_3\text{N}(\text{PF}_2)_2]_4\text{Fe}_2\text{CO}$ to give each iron atom the favored rare gas electronic configuration without requiring an iron-iron dative bond.

The single carbonyl group in $[\text{CH}_3\text{N}(\text{PF}_2)_2]_4\text{Fe}_2\text{CO}$ (1, L = CO) has the expected reactivity toward photochemical replacement by trivalent phosphorus ligands to give $[\text{CH}_3\text{N}(\text{PF}_2)_2]_4\text{Fe}_2\text{PR}_3$ derivatives (1, L = PR_3) which are the first known compounds where a pair of bonded iron atoms is surrounded by nine phosphorus atoms, i.e., a formal although not a structural analogue of $\text{Fe}_2(\text{CO})_9$. For example, ultraviolet irradiation of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_4\text{Fe}_2\text{CO}$ with triphenylphosphine or trimethyl phosphite in diethyl ether followed by chromatography on Florisil gives the corresponding solid $[\text{CH}_3\text{N}(\text{PF}_2)_2]_4\text{Fe}_2\text{PR}_3$ (R = OCH_3 and C_6H_5) derivatives⁶ where apparently the unusual structure I is retained.

Acknowledgment. We are indebted to the Air Force Office of Scientific Research for partial support of this work under Grant AFOSR-75-2869. One of us (J.G.) is indebted to the Program of Cultural Cooperation between the United States of America and Spain administered by the Fulbright Commission of Spain for a Fellowship.

References and Notes

- (1) R. B. King and J. Gimeno, *J. Chem. Soc., Chem. Commun.*, 142 (1977).
- (2) M. G. Newton, R. B. King, M. Chang, N. S. Pantaleo, and J. Gimeno, *J. Chem. Soc., Chem. Commun.*, 531 (1977).
- (3) R. B. King and J. Gimeno, unpublished results, 1977.
- (4) J. F. Nixon, *J. Chem. Soc. A*, 2689 (1968).
- (5) A. A. Hock and O. S. Mills, *Proc. Chem. Soc.*, 223 (1958); *Acta Crystallogr.*, **14**, 139 (1961).
- (6) These compounds were characterized by correct C, H, and N analyses and ^1H NMR spectra.
- (7) University of Georgia Graduate Fellow, 1976-1978.
- (8) Departamento de Química Inorgánica, Universidad de Zaragoza, Spain.

M. G. Newton, R. B. King,* M. Chang,⁷ J. Gimeno⁸

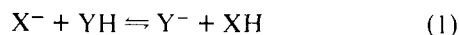
Department of Chemistry, University of Georgia
Athens, Georgia 30602

Received September 12, 1977

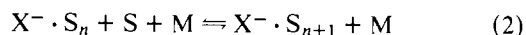
Bridging the Gap between the Gas Phase and Solution: Transition in the Relative Acidity of Water and Methanol at 296 ± 2 K

Sir:

For the past half decade the application of a variety of gas-phase experimental techniques to the measurement of rate and equilibrium constants for proton-transfer ion-molecule reactions of the type



has provided much quantitative information about their intrinsic kinetics and energetics.^{1,2} Furthermore, ion-solvent interactions have been examined extensively through gas-phase equilibrium measurements of the stepwise solvation of ions by three-body ion association reactions of the type



where S represents the solvent molecule and M is a stabilizing third body.³ Such studies have proven to be extremely valuable

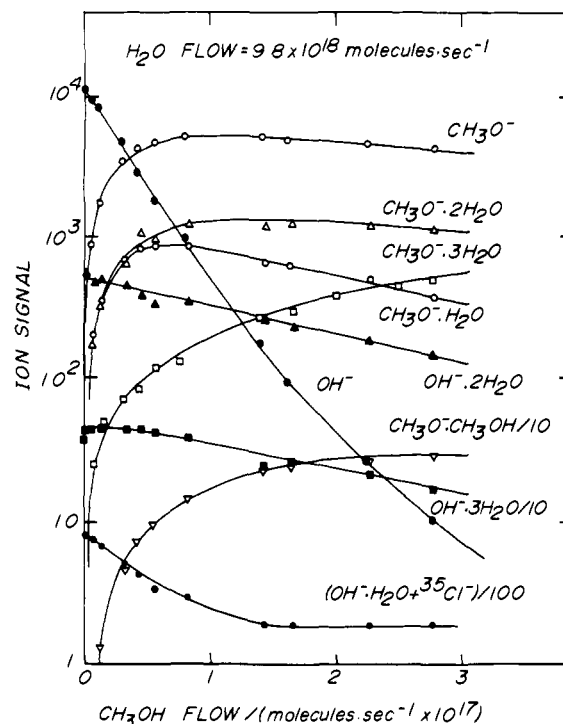


Figure 1. The observed variation of ion signals recorded upon the addition of CH_3OH into a H_2O -He plasma in which unhydrated and hydrated hydroxide ions are initially present. $P = 0.379$ Torr, $T = 294$ K, $L = 85$ cm, $\bar{v} = 8.4 \times 10^3$ cm s^{-1} .

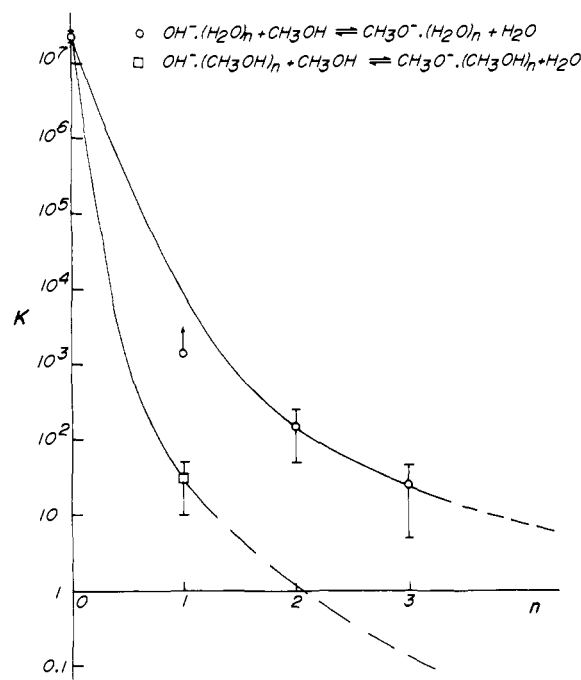


Figure 2. The shift in the position of equilibrium for the proton transfer between CH_3OH and OH^- as a function of the extent of solvation at 296 ± 2 K.

for the elucidation of the influence of intrinsic molecular parameters and ion-solvent interactions on proton-transfer kinetics and energetics and thus for the evolution of a unified model for acid-base chemistry.⁴ We report here gas-phase equilibrium measurements for solvated proton-transfer reactions of the type

