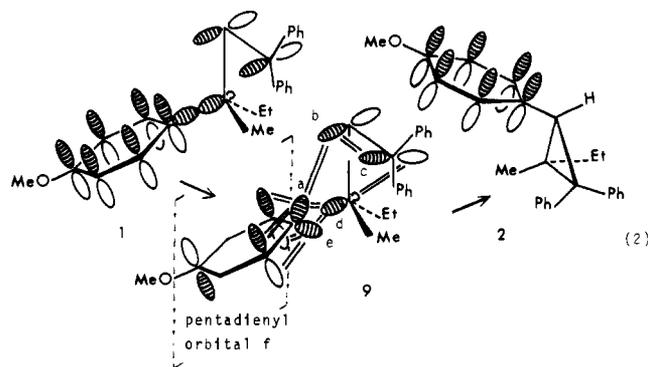


Figure 1. Optical purity of photoproduct **2** vs. percent conversion.

Hence our conclusion is that the reaction proceeds totally stereospecifically within experimental error. This is in agreement with our study of the stereochemistry of the "diene version" of the di- $\pi$ -methane rearrangement where inversion of the methane carbon configuration was also observed.<sup>5c</sup> Thus, the hydrocarbon di- $\pi$ -methane rearrangement contrasts with the oxa-di- $\pi$ -methane variation.

The rationale that we have used<sup>5</sup> for inversion of configuration has been the requirement for a Möbius array with six delocalized electrons in the excited state. Presently there is no such simple array of atomic and hybrid orbitals. The truncated set of orbitals, consisting only of those in bonds being formed or dissipated, is given in eq 2. There is still a Möbius array<sup>5,9</sup>



in the half-reacted species **9** which provides an excited-state-allowed<sup>10</sup> pathway. However, in this case, the nonbonding MO of the pentadienyl moiety left in the originally aromatic ring is one of the six basis orbitals a-f comprising the Möbius array. It has been noted<sup>10,11</sup> that MOs as well as AOs can be taken as basis orbitals in constructing such cyclic arrays.

Thus eq 2 illustrates use of the Möbius-Hückel treatment where one moiety is complex.

We conclude by noting that arylvinylmethane stereochemistry parallels that of the divinylmethane version rather than the oxa-di- $\pi$ -methane variety and that singlet vs. triplet factors seem dominant.

**Acknowledgment.** Support of this research by National Institutes of Health Grant GM07487, the National Science Foundation, and the U.S. Army Research Office is gratefully acknowledged.

## References and Notes

- (1) This is paper 109 of our Photochemical Series.
- (2) For paper 108, see H. E. Zimmerman, *Pure Appl. Chem.*, **49**, 389 (1977).
- (3) (a) H. E. Zimmerman and G. L. Grunewald, *J. Am. Chem. Soc.*, **88**, 183 (1966); (b) H. E. Zimmerman, R. M. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967); (c) see S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973), for a review; (d) R. S. Givens and W. F. Oettle, *Chem. Commun.*, 1164 (1969); (e) W. G. Dauben, M. S. Kellogg, J. I. Seeman, and W. A. Spitzer, *J. Am. Chem. Soc.*, **92**, 1786 (1970).
- (4) H. E. Zimmerman and M. G. Steinmetz, *J. Chem. Soc., Chem. Commun.*, in press.

- (5) (a) H. E. Zimmerman and A. C. Pratt, *J. Am. Chem. Soc.*, **92**, 6267 (1970); (b) H. E. Zimmerman, P. Baeckstrom, T. Johnson, and D. W. Kurtz, *ibid.*, **96**, 1459 (1974); (c) H. E. Zimmerman, J. D. Robbins, R. D. McKelvey, C. J. Samuel, and L. R. Sousa, *ibid.*, **96**, 4630 (1974); (d) H. E. Zimmerman and J. A. Pincock, *ibid.*, **95**, 2957 (1973).
- (6) W. G. Dauben, G. Lodder, and J. D. Robbins, *J. Am. Chem. Soc.*, **98**, 3030 (1976).
- (7) (a) B. Winter and K. Schaffner, *J. Am. Chem. Soc.*, **98**, 2022 (1976); (b) S. Domb and K. Schaffner, *Helv. Chim. Acta*, **53**, 677 (1970).
- (8) Complete experimental details will be given in our full paper. All new compounds analyzed satisfactorily.
- (9) H. E. Zimmerman and P. S. Mariano, *J. Am. Chem. Soc.*, **91**, 1718 (1969).
- (10) (a) H. E. Zimmerman, *Acc. Chem. Res.*, **4**, 272 (1971); (b) H. E. Zimmerman, *J. Am. Chem. Soc.*, **88**, 1564 (1966).
- (11) H. E. Zimmerman, "Quantum Mechanics for Organic Chemists", Academic Press, New York, N.Y., 1975.

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## Reversible Binding of Dioxygen to Ruthenium(II) Porphyrins

Sir,

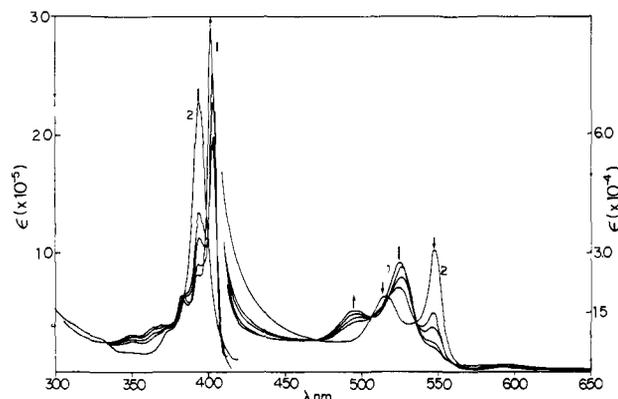
We are presently concerned with the interaction of dioxygen and carbon monoxide with metalloporphyrin complexes as models for biologically important heme proteins.<sup>1</sup> In the iron(II) systems that have been developed to mimic the reversible oxygenation of myoglobin, oxidation to iron(III), which is brought about by interaction of a second iron(II) moiety with an initially formed Fe<sup>II</sup>-O<sub>2</sub> species,<sup>2</sup> is prevented by (1) designing porphyrins of such a geometry (or supporting them on a rigid polymer backbone) so as to physically prevent such an interaction or (2) use of low temperatures (subzero) to retard such an interaction. An alternative approach to these problems using the more substitution-inert ruthenium(II) analogues has, in our hands, yielded significant results.

In this communication we report on reversible O<sub>2</sub> binding in solution under ambient conditions by solutions of ruthenium(II) complexes of *meso*-tetraphenylporphyrin (TPP) and octaethylporphyrin (OEP).

To our knowledge,<sup>3</sup> this is the first report of reversible dioxygen binding by a ruthenium(II) species in solution. Hopf and Whitten<sup>4</sup> have "activated" ruthenium(II) porphyrins to do similar chemistry to that described here by using surfactant complexes in monolayer assemblies; however, we find the "activation" of the porphyrins toward O<sub>2</sub> (and CO) can be accomplished by the use of labile axial ligands, especially acetonitrile.

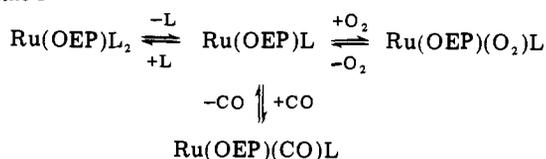
The complexes Ru(OEP)L<sub>2</sub> and Ru(TPP)L<sub>2</sub> (L = CH<sub>3</sub>CN) were synthesized as purple crystals<sup>5</sup> by photolysis of the corresponding Ru(porphyrin)(CO)(C<sub>2</sub>H<sub>5</sub>OH) complexes<sup>6</sup> in acetonitrile under argon over 8-10 h (Hanovia medium pressure 450-W mercury vapor bulb). Dilute solutions (~10<sup>-5</sup> M) of the bisnitrile species are also formed cleanly and rapidly (10 min) by photolysis of the carbonyl complexes using a Rayonet photochemical reactor. Figure 1 shows spectral data for such formation of Ru(OEP)(CH<sub>3</sub>CN)<sub>2</sub>; a number of isosbestic points are generated. Use of solvents such as dimethylacetamide (DMA), dimethylformamide (DMF), and pyrrole, gives similar in situ spectral changes attributable to formation of the corresponding Ru(OEP)(solvent)<sub>2</sub> species.

Solutions of Ru(OEP)(CH<sub>3</sub>CN)<sub>2</sub> in DMA, DMF, or pyrrole absorb 1.0 mol of O<sub>2</sub>/Ru reversibly at room temperature and 1-atm pressure.<sup>7</sup> At constant O<sub>2</sub> pressure, the reactions follow pseudo-first-order behavior: the uptake is almost instantaneous in DMA (*t*<sub>1/2</sub> ~ 1 min); *t*<sub>1/2</sub> is ~7 min in pyrrole and ~30 min in DMF. Figure 2 shows the accompanying



**Figure 1.** Spectral data showing photochemical formation of Ru(OEP)(CH<sub>3</sub>CN)<sub>2</sub>, curve 1, from dilute acetonitrile solutions of Ru(OEP)(CO)(C<sub>2</sub>H<sub>5</sub>OH), curve 2; total reaction time ~10 min.

#### Scheme I

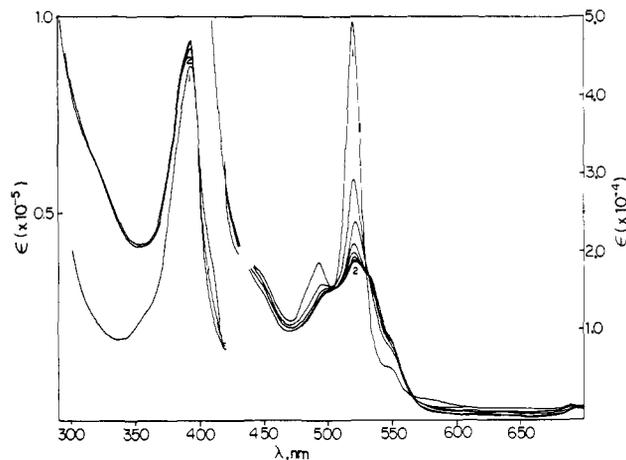


spectral changes for the pyrrole system which changes from purple to orange: the initial double maximum in the visible broadens out, and there is a small increase in intensity of the Soret band which also shows a very slight blue shift to 394 nm. Regeneration of the Ru(OEP)L<sub>2</sub> species by pumping is much slower than the forward reaction. About 24 h under vacuum are required to reverse the pyrrole system: no ruthenium(II) is lost to oxidation, and complete reoxygenation can be carried out. Addition of 1 atm of CO to the oxygenated system at 20 °C leads to slow formation of a monocarbonyl Ru(OEP)(CO)L with *no net change in the gaseous volume*,<sup>8</sup> the same species is also formed by carbonylation of Ru(OEP)(CH<sub>3</sub>CN)<sub>2</sub>, 1.0 mol of CO/Ru being absorbed. The spectra of all the Ru(OEP)(CO)L complexes are very similar to that shown in curve 1 of Figure 1. The data are readily interpreted in terms of Scheme I.

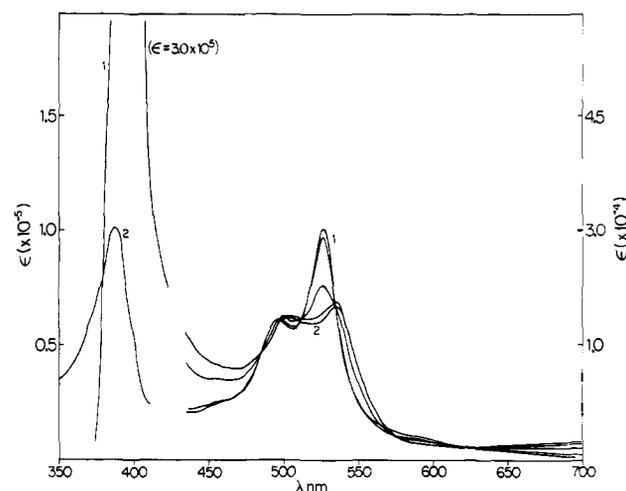
Interestingly, solutions of Ru(OEP)(CH<sub>3</sub>CN)<sub>2</sub> in toluene under O<sub>2</sub> undergo only a slow irreversible oxidation with consumption of ~0.25 mol of O<sub>2</sub>/Ru; the product is probably a bridged oxo dinuclear ruthenium(III) species, although a hydroxy complex formed with traces of water cannot be ruled out.<sup>1c</sup> Solutions of the Ru(OEP)(O<sub>2</sub>)L complexes do eventually oxidize to the same species over long periods at 20 °C. The electronic spectrum of the oxidized species resembles that of a ruthenium(III) species (Figure 3, see below).

The reactivity of the acetonitrile complexes according to Scheme I contrasts markedly with that of the Ru(OEP)L<sub>2</sub> complexes (L = pyridine) or *N*-methylimidazole; these systems in DMF undergo only a slow irreversible oxidation. Dissociation of L is much slower for the amines, as judged by formation of the monocarbonyl complexes from the Ru(OEP)L<sub>2</sub> complexes, but it is not clear why this allows an oxidation process (presumably via a Ru<sup>II</sup>O<sub>2</sub> + Ru<sup>II</sup> process) to dominate over reversible oxygenation.

The site of oxidation of ruthenium(II) porphyrins (metal or porphyrin) is dependent on the nature of the axial ligand. In a manner similar to the Ru(OEP)py<sub>2</sub> and Ru(TPP)py<sub>2</sub> systems,<sup>9</sup> the first reversible oxidation of our nitrile complexes occurs at the ruthenium to give red-orange solutions of the ruthenium(III) cation; for Ru(OEP)(CH<sub>3</sub>CN)<sub>2</sub>, E<sub>1/2</sub> = 0.23 V in acetonitrile/tetrabutylammonium hexafluorophosphate (0.1 M) relative to Ag/AgCl at 25 °C. Figure 3 shows the development of the [Ru(OEP)(CH<sub>3</sub>CN)<sub>2</sub>]<sup>+</sup> cation spectrally:



**Figure 2.** Spectral data as a function of time for oxygenation of Ru(OEP)(pyrrole)<sub>2</sub>, curve 1, in pyrrole at 20 °C and 1 atm of O<sub>2</sub> to give Ru(OEP)(O<sub>2</sub>)(pyrrole), curve 2; t<sub>1/2</sub> ~ 7 min.



**Figure 3.** Spectral data showing electrochemical production of the Ru(OEP)(CH<sub>3</sub>CN)<sub>2</sub><sup>+</sup> cation, curve 2, from Ru(OEP)(CH<sub>3</sub>CN)<sub>2</sub>, curve 1.

compared with the ruthenium(II) species, the two bands in the visible are more separated and the Soret peak lies further to the blue and is reduced in intensity by a factor of 2.

We have not yet been able to isolate a dioxygen complex since, during workup, the oxidation to ruthenium(III) is enhanced. A similar phenomenon has been noted for the corresponding chemistry of iron(II) species.<sup>10</sup> Indeed, the chemistry of our systems, not surprisingly, parallels closely that of corresponding iron(II) systems, *but* at more convenient temperatures. The enhanced oxygenation in the polar aprotic solvents, as in the iron systems, may be rationalized in terms of stabilization of a superoxide formulation Ru<sup>III</sup>O<sub>2</sub><sup>-</sup>, but detection of the coordinated dioxygen moiety by infrared will likely require difference techniques.<sup>1b</sup> ESR measurements on DMF solutions of oxygenated species frozen to liquid temperatures have yielded no signals.

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#### References and Notes

- (1) Recent studies in this area can be traced through the following references: (a) L. Vaska, *Acc. Chem. Res.*, **9**, 175 (1976); (b) J. P. Collman, J. I. Brau-

- 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:  $\nu^{KBr}$  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).

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### 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 complexes<sup>1</sup>  $[CH_3N(PF_2)_2]_3M$  ( $M = Cr, Mo, \text{ and } W$ ). Similarly, reactions of  $CH_3N(PF_2)_2$  with  $Co_2(CO)_8$  under various conditions give  $[CH_3N(PF_2)_2]_3Co_2L_2$  ( $L = CO$ ,<sup>2</sup>  $CH_3NHPF_2$ , and monodentate  $CH_3N(PF_2)_2$ ).<sup>3</sup> 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  $CH_3N(PF_2)_2$ ,<sup>4</sup> 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

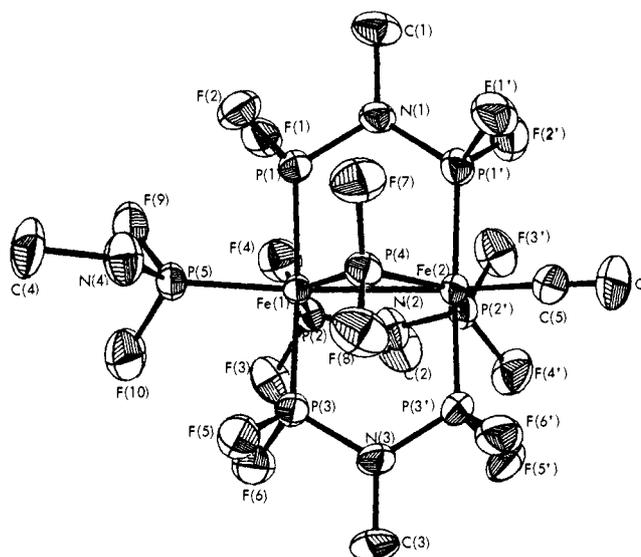
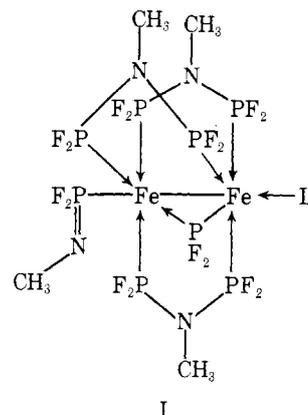


Figure 1. ORTEP drawing of the structure of  $[CH_3N(PF_2)_2]_4Fe_2CO$ .

complexes  $R_4C_4Fe_2(CO)_6$ ,<sup>5</sup> 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