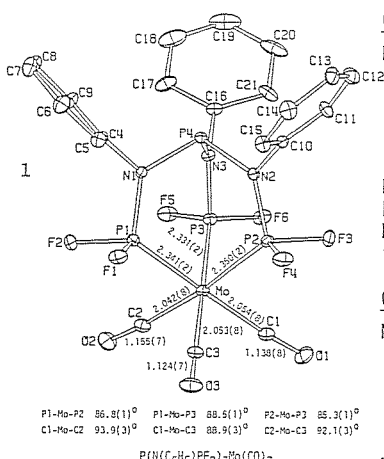


09.3-07 STRUCTURES OF TWO TRANSITION-METAL COMPLEXES OF STRONG π -ACCEPTOR LIGANDS: (1) TRICARBONYL[TRIS[PHENYL(DIFLUOROPHOSPHINO)AMINO]PHOSPHINE]MOLYBDENUM AND (2) μ -CARBONYL- μ -[N,N-BIS(DIMETHOXYPHOSPHINO)METHYLAMINE]-BIS(TRICARBONYLIRON)* G. M. Brown and J. E. Finholt, Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, and R. B. King, T. W. Lee, J. W. Bibber, and J. Kim, Chemistry Department, University of Georgia, Athens, Georgia 30602, U. S. A.

Compound 1 (see Title and Figure) is an unexpected product from reaction of $\text{fac}-(\text{CH}_3\text{CN})_3\text{Mo}(\text{CO})_3$ and N,N-bis(difluorophosphino)aniline, $\text{C}_6\text{H}_4\text{N}(\text{PF}_2)_2$. The ligand $\text{P}[\text{N}(\text{C}_6\text{H}_4)\text{PF}_2]_3$ in 1 is the first example of a tridentate chelating strong π -acceptor ligand containing three π -acceptor PF_2 groups. In the bicyclo[2,2,2]octane-like cage molecule of 1, the central P atom of the ligand and the Mo atom are the bridgehead atoms. The coordination polyhedron about Mo is distorted slightly from the ideal octahedron (see angles in Figure). The Mo-P and Mo-C bond lengths provide striking evidence of the strong π -acceptor character of the PF_2 groups. The Mo-P lengths are among the shortest ever observed for phosphino groups bound to Mo, and the Mo-C lengths are among the longest ever observed for CO groups similarly bound.

Compound 2, from the reaction of N,N-bis(dimethoxyphosphino)methylamine and $\text{Fe}_2(\text{CO})_9$ in boiling hexane, is structurally similar to μ -carbonyl- μ -[bis(diphenylphosphino)methane]bis(tricarbonyliron) (3) [F. A. Cotton and J. M. Troup, J. Am. Chem. Soc., 96, 4422 (1974)]. However, in 2 the Fe-Fe length is 0.05 Å shorter, the P...P intramolecular distance is 0.11 Å shorter, and the Fe-P length is 0.06 Å shorter than in 3. The atom N is only 0.018 Å from the exact plane of the group Fe_2P_2 , which makes an angle 89.3° with the best least-squares plane of the group $\text{Fe}_2(\text{C}1)(\text{C}3)(\text{C}4)_2$. The greatest deviation from the latter plane is 0.002 Å.



Crystal Data for 1

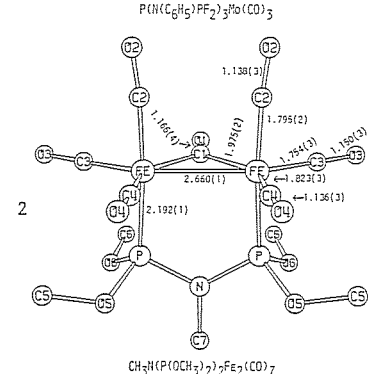
Monoclinic, $P2_1/c$
 $a = 8.683(1)$ Å
 $b = 28.218(7)$
 $c = 15.338(2)$
 $\beta = 118.12(1)$
 $Z = 4$

Molecule in gen. pos.
 Filtered Mo K α rad.
 $R = 0.052$ for 3079
 rflns. with $F^2 > 2\sigma$

Crystal Data for 2

Monoclinic, $P2_1/m$
 $a = 9.143(2)$ Å
 $b = 15.977(5)$
 $c = 6.876(1)$
 $\beta = 101.00(1)$ ^o
 $Z = 2$

Molecule on mirror
 Filtered Mo K α rad.
 $R = 0.039$ for 2533
 rflns. with $F^2 > 2\sigma$



*Research sponsored in part by the Division of Materials Sciences, Office of Basic Energy Sciences, U. S. Department of Energy, under contract W-7405-eng-26 with the Union Carbide Corporation.

09.3-08 CRYSTAL STRUCTURES AND PHASE TRANSITION OF A MIXED-VALENCE BINUCLEAR FERROCENE COMPOUND. By M. Konno, The Institute for Solid State Physics, The University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106, Japan.

The crystal structures of 1',1''-dipropylbiferrocene[Fe(II)Fe(III)]⁺ I_3^- : $(\text{PrFcFcPr})^+ \text{I}_3^-$ with intervalence type irons at 298 K and with trapped-valence type irons at 110 K were determined by X-ray diffraction using Ag K α radiation. Crystals at 298 K are triclinic with space group $P\bar{1}$, $a=8.5148(8)$, $b=8.5482(5)$, $c=10.9032(13)$ Å, $\alpha=89.546(9)$, $\beta=115.582(9)$, $\gamma=108.488(7)$ ^o, $V=671.10(9)$ Å³ and $Z=1$; at 110 K, $P\bar{1}$, $a=8.431(2)$, $b=8.478(2)$, $c=10.816(3)$ Å, $\alpha=88.58(3)$, $\beta=117.39(2)$, $\gamma=108.65(2)$ ^o, $V=643.4(3)$ Å³ and $Z=1$. Refinements by block-diagonal least-squares method reduced the R values to 0.043 and 0.050 for 1928 and 2062 reflections at 298 and 110 K, respectively. The structure is dominated by segregated columns of $(\text{PrFcFcPr})^+$ cations and I_3^- anions along c. Each iron atom is sandwiched between five-membered rings in trans configuration at both temperatures. The $(\text{PrFcFcPr})^+$ cation at 298 K is on the symmetry centre and exhibits disorder. The Fc unit takes eclipsed and staggered conformations randomly with a population ratio of about 8:2. The interplanar distance between five-membered rings is 3.330 Å. On the other hand, at 110 K one Fc unit shows the eclipsed conformation and the other shows the same disorder as that observed at 298 K. Spacings between the rings differ for the two Fc units. This seems to indicate that at 110 K ferrocene- and ferrocenium-like irons coexist. This change is accompanied by rotation of the propyl-group in one Fc unit. The I_3^- anion exhibits positional disorder at 110 K.