09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

09.3-07 STRUCTURES OF TWO TRANSITION-METAL COMPLEXES OF STRONG σ-ACCEPTOR LIGANDS: (1) TRICARBOXYL(TRANS)PHENYL(DFLUOROPHOSPHINO)(DIETHOXYPHOSPHINO)CARBONYLCARBONYL-M-\(N,N\)-BIS(DIMETHOXYPHOSPHINO)METHYLAMINE]BIS(TRICARBOXYLIRON) and (2) TRICARBOXYL-\(N,N\)-BIS(DIMETHOXYPHOSPHINO)METHYLAMINE]BIS(TRICARBOXYLIRON)

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Compound 1 (see Title and Figure) is an unexpected product from reaction of fac-(CH\(_2\)CH)\(_2\)Mo(CO)\(_5\), and N,N-bis(difluorophosphino)antiline, C\(_2\)H\(_4\)(PF\(_2\))\(_2\), in 1 is the first example of a tridentate chelating strongly σ-acceptor ligand containing three σ-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 σ-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 Fe\(_2\)(CO)\(_5\), in boiling hexane, is structurally similar to \(\text{MoCO(NHPh)}\)(N\(_2\))(PF\(_2\))\(_2\), \(\text{FeCO}(\text{PF\(_2\)})\)\(_2\), \(\text{FeCO}(\text{ND\(_2\)})\)\(_2\), and \(\text{FeCO}(\text{N\(_2\)})\)\(_2\). The ligand \(\text{PF\(_2\)}\)\(_2\) is dominated by segregated columns of (PrFcFcPr)\(^{+}\) cations and \(I\(_3\)\) anions along c. Each iron atom is sandwiched between five-membered rings in trans configuration at both temperatures. The (PrFcFcPr)\(^{+}\) cation at 298 K is on the symmetry centre and exhibits disorder. The Fe 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 A. On the other hand, at 110 K one Fe 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 Fe 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 Fe unit. The \(I\(_3\)\) anion exhibits positional disorder at 110 K.

Crystal Data for 1

Monoclinic, P2\(_{1}/c\)

\(a = 8.683(7)\) A
\(b = 28.218(7)\)
\(c = 15.332(2)\)
\(\beta = 116.12(1)\)

\(Z = 4\)

Molecule in gen. pos.

filtered Mo Kα rad.

\(R = 0.052\) for 3079 rfrns.

with \(P^2 > 2\sigma\)

Crystal Data for 2

Monoclinic, P2\(_1)/m\)

\(a = 9.143(2)\) A
\(b = 15.977(5)\)
\(c = 6.876(1)\)
\(\beta = 101.00(1)\)

\(Z = 2\)

Molecule on mirror

Filtered Mo Kα rad.

\(R = 0.039\) for 2533

rfrns.

with \(P^2 > 2\sigma\)


09.3-08 CRYSTAL STRUCTURES AND PHASE TRANSITION OF A MIXED-VALENCE BINUCLEAR FERROCENE COMPOUND.

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The crystal structures of 1',1''-dipropyl-

biferrocene[-Fe(II)Fe(III)]; \(1\)^{+}\: \((\text{PrFcFcPr})^{+}\) \(I\(_3\)\) with intervalence type ions at 298 K and with trapped-valence type ions at 110 K were determined by X-ray diffractions using Ag Kα radiation. Crystallographic data for 298 K are triclinic with space group P1, \(a=8.5148(8)\), \(b=8.5482(5)\), \(c=10.9032(13)\), \(\alpha=89.546(9)\), \(\beta=115.582(9)\), \(\gamma=108.488(7)\), \(\nu=617.10(9)\) A\(^3\) and \(Z=1\); at 110 K, \(a=8.431(2)\), \(b=8.478(2)\), \(c=10.816(3)\), \(\alpha=88.58(3)\), \(\beta=117.39(2)\), \(\gamma=108.65(2)\), \(\nu=643.4(3)\) A\(^3\) and \(Z=1\). Refinements by block-diagonal least-squares method reduced the \(R\) values to 0.043 and 0.055 for 1928 and 2062 reflections at 298 and 110 K, respectively. The structure is dominated by segregated columns of (PrFcFcPr)\(^{+}\) cations and \(I\(_3\)\) anions along c. Each iron atom is sandwiched between five-membered rings in trans configuration at both temperatures. The (PrFcFcPr)\(^{+}\) cation at 298 K is on the symmetry centre and exhibits disorder. The Fe 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 A. On the other hand, at 110 K one Fe 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 Fe 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 Fe unit. The \(I\(_3\)\) anion exhibits positional disorder at 110 K.