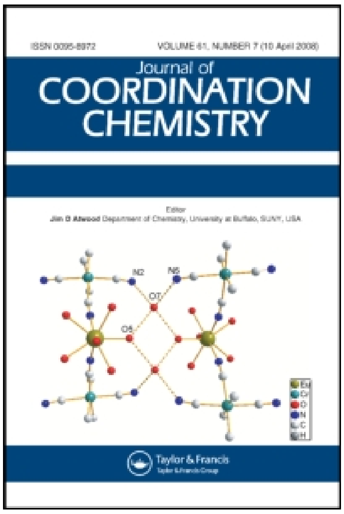

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THE STRUCTURE OF IRON-PHOSPHONATE COMPLEX IN A SOLID AND IN A SOLUTION

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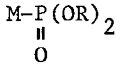
INTRODUCTION



$\underset{\overset{\|}{O}}{M-P}(OR)_2$

phosphonate complex

Many kinds of complexes with phosphine or phosphite which bonds datively to a transition-metal through its lone-pair have been reported. In contrast, the chemistry of complexes with covalent bond between transition-metal and phosphorus, such as phosphonate complexes, has not been well established.[1] We report the structural information of $[Cp(CO)_2FeP(O)(OEt)_2]$ in single crystal and in solution, where Cp stands for cyclopentadienyl group.

CRYSTAL STRUCTURE OF $[Cp(CO)_2FeP(O)(OEt)_2]$

The complex, $[Cp(CO)_2FeP(O)(OEt)_2]$, was prepared from $[Cp(CO)_2FeCl]$ and $P(OEt)_3$ according to the literature method[2] with some modification. The single crystals were obtained from the hexane solution. The X-ray diffraction data were collected on a Rigaku AFC-5 automated four-circle diffractometer by the use of an ω-2θ scan method. The final R index was 0.063. The molecular structure, together with the selected bond distances, is shown in Figure 1.

The X-ray analysis reveals two interesting features. The first point noted is that one of the carbonyl groups (C1 and O1), Fe atom, and phosphoryl group (P and O3) are situated almost on

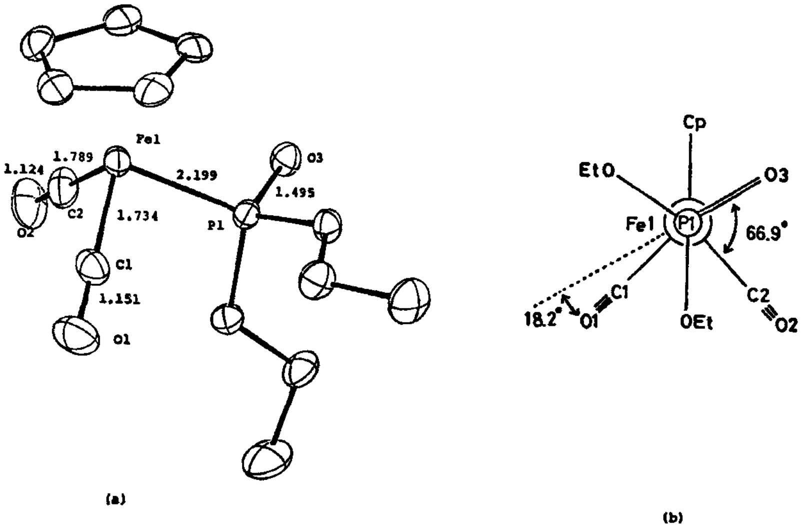


FIGURE 1 (a) ORTEP drawing of $[Cp(CO)_2FeP(O)(OEt)_2]$ showing selected bond distances. (b) Newman projection along the P-Fe bond.

the same plane. In other words, one carbonyl group (C1 and O1) is trans and the other one (C2 and O2) is gauche to the P=O bond. The second point noted is that the Fe-CO bond lengths for the two carbonyls are different and the FeC-O bond distances are also different. Comparison with the results of the X-ray analyses of the related iron complexes,[3] $[Cp(CO)_2FeP(O)(CF_3)_2]$ and $[Cp(CO)_2FeP(CF_3)_2]$, revealed that the Fe-CO bond distance is shorter in the trans CO than in the gauche CO, and the FeC-O bond length is longer in the trans CO than in the gauche CO. Since the increase of the back donation from a central metal atom to a carbonyl group causes a shortening of the Fe-CO bond and a lengthening of the FeC-O bond, it can be considered that the phosphoryl group promotes a back donation from the iron atom to the carbonyl group trans to the P=O, and does not affect the carbonyl group gauche to the P=O.

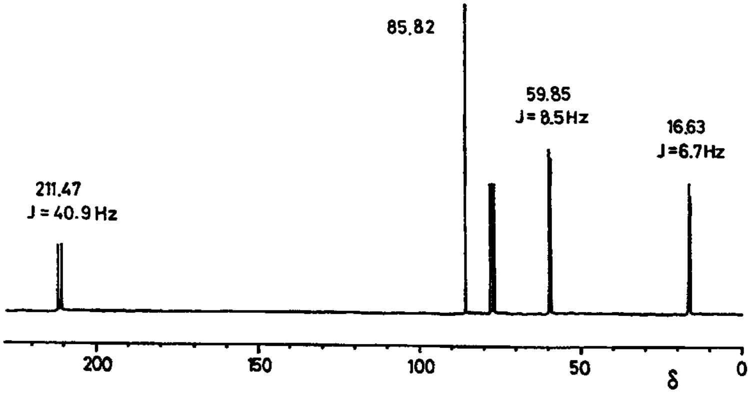


FIGURE 2 The ^{13}C NMR spectrum in $CDCl_3$.

STRUCTURE IN SOLUTION

In order to examine whether the effect of the phosphoryl group is observed even in solution or not, the ^{13}C NMR spectrum was measured in $CDCl_3$. The observed spectrum shown in Figure 2 consists of a doublet at 16.63ppm (J=6.7Hz) due to the methyl groups, a doublet at 59.85ppm (J=8.5Hz) due to the methylene groups, a singlet at 85.82ppm due to the cyclopentadienyl group, and a doublet at 211.47ppm (J=40.9Hz) due to the carbonyl groups. The observation indicates that the two carbonyl groups are magnetically equal, that is, the phosphonate group rotates freely along the Fe-P bond in solution at room temperature on the NMR time scale. The ^{13}C NMR spectra of the CD_2Cl_2 solution was measured at several temperatures from 25°C to -85°C, which showed no significant signal changes. Therefore, the rotation barrier along the Fe-P bond in solution can be considered to be very low.

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