Journal of Organometallic Chemistry, 69 (1974) C4—C6
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Preliminary communication

COMPARISON OF THE MOLECULAR STRUCTURES OF (π-C_5H_5)$Fe(CO)_2$-$P(CF_3)_2$ AND (π-C_5H_5)$Fe(CO)_2P(O)(CF_3)_2$

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(Received February 1st, 1974)

Summary

On oxidation of (π-C_5H_5)$Fe(CO)_2P(CF_3)_2$ at phosphorus the Fe—P bond length decreases from 2.265(3) to 2.191(3) Å, while the mean Fe—CO bond length increases from 1.768(7) to 1.780(7) Å and the C—O stretching bands shift from 2046 and 2000 cm^{-1} to 2062 and 2019 cm^{-1}.

The shift in the C—O stretching bands from 2046 and 2000 cm^{-1} in (π-C_5H_5)$Fe(CO)_2P(CF_3)_2$ (I) to 2062 and 2019 cm^{-1} in (π-C_5H_5)$Fe(CO)_2P(O)$-$(CF_3)_2$ (II), has been interpreted in terms of reduced Fe→CO, and hence presumably increased Fe→P, π back bonding in the phosphine oxide complex [1]. We have now carried out X-ray crystallographic studies of the compounds (I) and (II) in order to determine directly the changes in molecular geometry which arise as a consequence of the oxidation of the phosphorus atom: The pertinent bond lengths and valency angles, with standard deviations in parentheses, are listed in Table 1. Figures 1 and 2 show that the molecular conformations in the crystals are almost identical.

The principal structural change on oxidation of the phosphorus atom is a shortening of the Fe—P bond by 0.074(4) Å. We interpret this in terms of increased Fe→P d_π—d_π back bonding for two reasons: Firstly, the shift in the C—O stretching bands and, secondly, the similarity of the P—C bond lengths in (I) and (II) argues against any notable decrease in the σ-bonding covalent radius of phosphorus. The downfield shift of the cyclopentadienyl resonance in the ^1H NMR spectrum of (II) (τ 4.36) compared to (I) (τ 4.60) is also consistent with increased back donation to phosphorus in the former. The expected concomitant lengthening of the Fe—CO bonds and shortening of the C—O bonds is also shown

TABLE 1

Bond or angle	$(\pi\text{-C}_5\text{H}_5)\text{Fe-}(\text{CO})_2\text{P}(\text{CF}_3)_2$	$(\pi\text{-C}_5\text{H}_5)\text{Fe-}(\text{CO})_2\text{P}(\text{O})(\text{CF}_3)_2$
Fe—P	2.265(3) Å	2.191(3) Å
Fe—C(Cp) average	2.097(7)	2.090(7)
Fe—C(carbonyl) average	1.768(7)	1.780(7)
C—O average	1.138(8)	1.134(7)
P—C average	1.878(8)	1.887(6)
P—O	—	1.478(5)
OC—Fe—CO	94.3(3)°	93.5(3)°
Fe—P—C average	107.4(5)	111.6(15)
Fe—P—O	—	121.6(2)
C—P—C	94.5(3)	96.4(3)
C—P—O average	—	106.4(4)

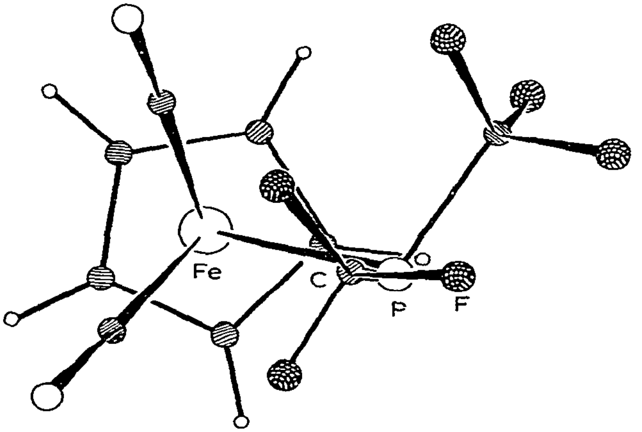

Fig. 1. Projection of $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{P}(\text{CF}_3)_2$ on to the least squares plane through the cyclopentadienyl ring.

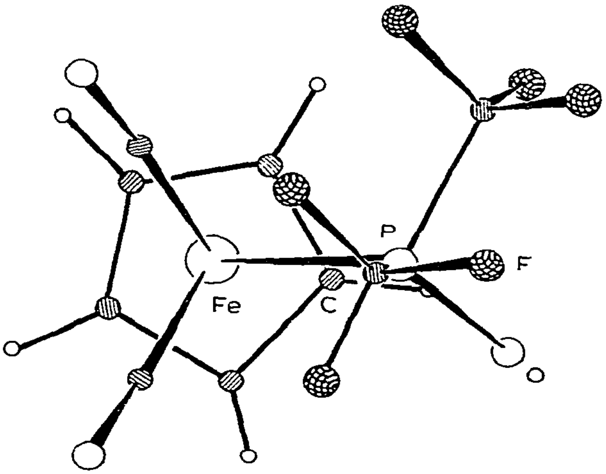

Fig. 2. Projection of $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{P}(\text{O})(\text{CF}_3)_2$ on to the least squares plane through the cyclopentadienyl ring.

by the results in Table 1 but the effect is small and within the limits of experimental error.

The frequency of ν(P=O) in $(CF_3)_2P(O)X$ compounds [2], where the atom attached to phosphorus in the Group X is C, N, O, or halogen, lies in the range 1282–1366 cm^{-1}, much higher than in $(\pi\text{-}C_5H_5)Fe(CO)_2P(O)(CF_3)_2$ where ν(P=O) is 1210 cm^{-1}. This implies that the extent of P—O π bonding is decreased in the metal complex, presumably through competition between O and Fe for the phosphorus *d* orbitals.

The almost identical C—O stretching frequencies in the complexes $(\pi\text{-}C_5H_5)\text{-}Fe(CO)_2P(E)(CF_3)_2$ (E = O, S, Se) suggest that the Fe—P bonding is very similar in all three complexes. The decreased electronegativity down the series may be compensated for by a decrease in the competitive E→P π bonding.

Crystallographic Data: (I), $(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$, $M = 346.0$. Monoclinic, $a = 8.602(7)$, $b = 11.924(9)$, $c = 12.859(9)$ Å, $\beta = 112.75(9)°$, $U = 1216.3$ Å^3, $Z = 4$, $D_c = 1.89$. Mo-K_α radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 14.7$ cm^{-1}. $F(000) = 680$. Space group $P2_1/c$ (C^5_{2h}, No. 14) by systematic absences. 1882 reflexions with $I > 3\sigma(I)$, four-circle diffractometer data, Fourier methods and least-squares refinement, R converged to 4.8% on completion of analysis.

(II), $(\pi\text{-}C_5H_5)Fe(CO)_2P(O)(CF_3)_2$, $M = 362.0$. Monoclinic, $a = 11.938(8)$, $b = 7.603(6)$, $c = 13.818(9)$ Å, $\beta = 100.97(8)°$, $U = 1231.3$ Å^3, $Z = 4$, $D_c = 1.95$. Mo-K_α radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 14.8$ cm^{-1}. $F(000) = 712$. Space group $P2_1/c$ (C^5_{2h}, No. 14) by systematic absences. 1777 reflexions with $I > 3\sigma(I)$, four-circle diffractometer data (graphite monochromator), Fourier methods and least-squares refinement, R converged to 4.5% on completion of analysis.

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