A Binuclear Dihydride of Iron, $H_2Fe_2(CO)_6[P(CF_3)_2]_2$

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Summary The reaction of $Fe(CO)_5$ or $Fe_3(CO)_{12}$ with $(CF_3)_2PH$ gives $H_2Fe_2(CO)_6[P(CF_3)_2]_2$, which exists as a mixture of *cis*- and *trans*-isomers in solution.

THERE are only two reports of the reaction between binary iron carbonyls and a secondary phosphine. $Fe(CO)_5$ and $Fe_2(CO)_9$ react with PPh_2H[1] to give $Fe(CO)_4PPh_2H$ and $Fe(CO)_3(PPh_2H)_2$, respectively, whereas $Fe_2(CO)_6[P(C_6F_5)_2]_2$, a complex with two bridging phosphino-groups, has been isolated by heating $Fe_3(CO)_{12}$ under reflux with $P(C_6F_5)_2H$ in toluene.[2]

When $P(CF_3)_2H$ was heated with a slight excess of $Fe(CO)_5$ (100°, 8 hr.) in a sealed tube in the absence of solvent, a solid was precipitated. Careful fractional sublimation at 50° gave red crystals[3] of $Fe_2(CO)_6[P(CF_3)_2]_2$ (I) (3% yield) and pale lemon crystals of $H_2Fe_2(CO)_6[P(CF_3)_2]_2$ (II) (15% yield), a remarkably stable dihydride of a previously unreported type. Under more forcing conditions (140°, 30 hr.) the yield of (I) was increased at the expense of the dihydride. The use of $Fe_3(CO)_{12}$ in place of $Fe(CO)_5$ gave similar results.

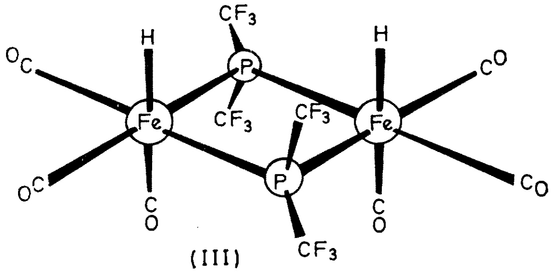
The mass spectrum of $H_2Fe_2(CO)_6[P(CF_3)_2]_2$ exhibited the parent ion (calculated *m/e* 619·7839; found, 619·7857 for ^{56}Fe isotope) and a fragmentation pattern similar to that of other compounds[4] containing $P(CF_3)_2$ bridging ligands. In hexane solution, strong i.r. bands were observed in the terminal carbonyl region at 2095 and 2054 cm.$^{-1}$ and in the C–F stretching region at 1175, 1149, and 1135 cm.$^{-1}$; the spectrum was unchanged in carbon tetrachloride solution but on heating a slow reaction ensued, probably giving Cl_2-$Fe_2(CO)_6[P(CF_3)_2]_2$.[5]

For n.m.r. studies the new compound was dissolved in

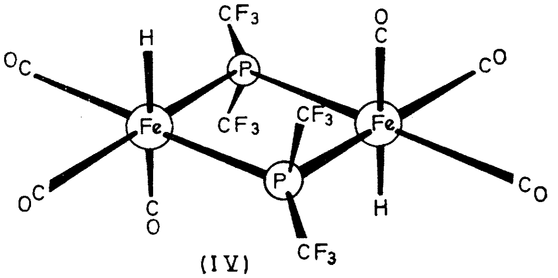
$Fe(CO)_5$ in which it was freely soluble and from which it could be recovered unchanged. The ^1H n.m.r. spectrum showed two triplets, total relative intensity 5 : 9, at τ15·60 (J_{HP} 41·8 Hz) and τ15·82 (J_{HP} 44·7 Hz), suggesting that the isomers (III) and (IV), each of which would give a triplet because of coupling to the equivalent phosphorus atoms, were present in solution. This was confirmed by the ^{19}F n.m.r. spectrum; the more abundant *trans*-isomer (IV), in which the fluorine nuclei in one phosphino-group are chemically equivalent to, but magnetically inequivalent to, those fluorine nuclei in the other phosphino-group, showed the expected $X_6AA'X_6'$ ($X = {}^{19}F$; $A = {}^{31}P$) spectrum[6] centred at $-105·8$ p.p.m. from C_6F_6 with $^2J_{FP}$ 55·0 Hz, $^4J_{FP}$ *ca.* 1·0 Hz, and $|^2J_{PP}|$ 175 Hz. The fluorine nuclei in (III) which are *cis* to hydrogen are chemically distinct from those *trans* to hydrogen and an $X_3M_3AA'M_3'X_3'$ pattern (X and M $= {}^{19}F$, $A = {}^{31}P$) is predicted and observed with chemical shifts at $-104·4$ and $-106·6$ p.p.m. from C_6F_6. The coupling constant between the two sets of fluorine atoms is $^4J_{FF}$ 8·5 Hz. Thus the n.m.r. spectrum gives evidence that the dihydride exists in two of the four isomers found by Grobe[5] for $Cl_2Fe_2(CO)_6[P(CF_3)_2]_2$.

The ^{57}Fe Mössbauer spectrum recorded at 77°K was consistent with the above structural assignments, only a sharp quadrupole doublet being observed with half-widths 0·27 and 0·28 mm./sec. There was no differentiation between the isomers (III) and (IV); this is to be expected as there are no structural differences between the isomers in the atoms directly attached to the resonating nucleus. The chemical isomer shift relative to sodium nitroprusside and the quadrupole splitting were 0·17 ± 0·01 and 0·92 ± 0·01 mm./sec., respectively.

The compound appears to be stable in air indefinitely in the solid state. It is also unaffected by oxygen in hydrocarbon or chlorinated solvents at room temperature, although it is decomposed by acetone, ether, or acetonitrile.



(III)



(IV)

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