Mono-substituted Derivatives of Tetracarbonyldi-π-cyclopentadienyldi-iron

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STUDIES on the substitution reactions of the dinuclear metal carbonyls $Mn_2(CO)_{10}$,[1] $Co_2(CO)_8$,[2] and $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$[3] with various tertiary phosphines in solution have shown that neutral or ionic bis-substituted complexes are readily formed at ambient or elevated temperatures. Mono-substituted derivatives of the above parent carbonyls have been isolated but their syntheses either employed indirect methods or were performed under controlled experimental conditions.[3–5]

We have now found that the reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ with the tertiary phosphines and phosphites L = PEt_3, $PPr^n{}_3$, $PBu^n{}_3$, PPh_2Et, PPh_3, $P(OMe)_3$, $P(OEt)_3$, $P(OPr^i)_3$, $P(OBu^n)_3$, and $P(OPh)_3$ in refluxing benzene affords neutral, TABLE

Compound	ν (CO) (cm.$^{-1}$) measured in a, C_6H_{12}; b, CH_2Cl_2. Relative intensities in parentheses		C_5H_5 Proton resonance τ ($CDCl_3$). Relative intensities in parentheses
(I); L = PPr^n_3	1934 (5·7), 1746 (10)	a	5·43 (1); 5·71 (1)
(I); L = PPh_3	1960 (4·5), 1936 (4·5), 1740 (10)	a	Not measured
(I); L = $P(OMe)_3$	1964 (7·7), 1944 (2·3), 1750 (10)	a	5·30 (1); 5·43 (1)
(I); L = $P(OPh)_3$	1971 (6·8, 1948 (4·2), 1760 (10)	a	5·21 (1); 5·90 (1)
(II); L = $P(OPh)_3$	1979	b	5·80
(III); L = $P(OPh)_3$	2074, 2034	b	5·99
(IV); L = $P(OPh)_3$	2017ms, 2007s, 1969s, 1952w, 1944w	a	5·03 (1); 5·70 (1), J_{PH} 1·3 c./sec.

diamagnetic products of formula, (as shown by the analytical data) (π-$C_5H_5)_2Fe_2(CO)_3L$ (I). The n.m.r. data are also consistent with mono-substitution. Bis-substitution could not be effected in spite of varying the experimental conditions, such as the ligand to parent carbonyl ratio or the reaction time.

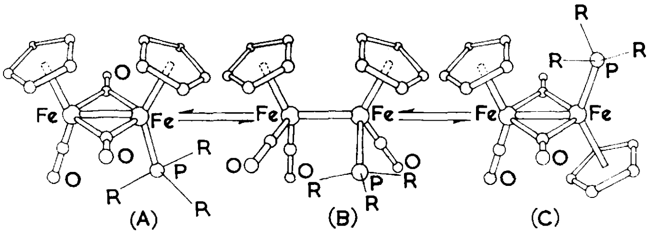

FIGURE. *Possible structures of* (π-$C_5H_5)_2Fe_2(CO)_3PR_3$ *in solution, showing the stereochemistry of the iron atoms only.*

The i.r. spectra of all mono-substituted derivatives synthesised exhibit bands corresponding to both bridging and terminal carbonyl-stretching modes. Whereas the compounds (I; L = PEt_3, PPr^n_3, PBu^n_3, and PPh_2Et) show only one peak in the terminal carbonyl region, the others [I; L = PPh_3, $P(OMe)_3$, $P(OEt)_3$, $P(OPr^i)_3$, $P(OBu^n)_3$, and $P(OPh)_3$] show two. This is attributed to the presence of more than one isomer of the latter compounds in solution. Three possible structures are as shown in the diagram. Isomer (B) would be expected to show three terminal carbonyl modes of comparable intensity while isomers (A) and (C) will exhibit one. From a comparison of the frequencies and relative intensities of the carbonyl stretching modes of the various derivatives it is concluded that the complexes (I; L = PEt_3, PPr^n_3, PBu^n_3, and PPh_2Et) exist as either the "*cis*" (A) or "*trans*" (C) isomer while [I; L = PPh_3, $P(OMe)_3$, $P(OEt)_3$, $P(OPr^i)_3$, $P(OBu^n)_3$, and $P(OPh)_3$] exist primarily as a mixture of the two bridged forms in solution. A similar equilibrium has recently been postulated for [(π-$C_5H_5)Fe(CO)_2]_2$ in solution.[6]

The reaction of [I; L = PEt_3, $P(OPr^i)_3$, or $P(OPh)_3$] with iodine afforded the expected products, (π-$C_5H_5)Fe(CO)_2I$ and (π-C_5H_5)Fe(CO)LI (II) in low yield only. The major product was the ionic derivative [(π-$C_5H_5)Fe(CO)_2L$]I (III), characterised as the tetraphenylborate. The iodination thus predominantly involves ultimate heterolytic-fission of the parent compound.

Stannous chloride was found to react readily with [I; L = $P(OPh)_3$] to yield as the major product (π-$C_5H_5)Fe(CO)_2Sn(Cl)_2Fe(CO)L$-($\pi$-$C_5H_5$) (IV) in which insertion of the reagent has occurred. The reaction is complex, however, and at least three other products including [(π-$C_5H_5)Fe(CO)_2]_2$ $SnCl_2$ (V) are formed. The compounds [I; L = PEt_3, $P(OPr^i)_3$] react similarly. I.r. spectroscopy showed, however, that for these derivatives the yield of (IV) was lower and that minor products different to those for [I; L = $P(OPh)_3$] were obtained. From i.r. evidence, it is found that [IV; L = $P(OPh)_3$] and (V) exist as a mixture of isomers in solution.

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