Ditertiary Phosphine Derivatives of Tetracarbonyldi-π-cyclopentadienyldi-iron

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PREVIOUS studies on the substitution reactions of $[C_5H_5Fe(CO)_2]_2$ have shown that under extreme conditions triphenylphosphine,[1] 1,2-bis(diphenylphosphino)ethane (diphos), and 2,2,2″-terpyridyl (terpy)[2] replace the cyclopentadienyl group to yield the derivatives, $Fe(CO)_3(PPh_3)_2$, $Fe(CO)_3$-diphos, and $Fe(CO)_2$terpy, respectively. Furthermore the ligands $L_2 = Me_2S_2$,[3] Me_4P_2, Ph_4P_2, Me_4As_2[4] and $(CF_3)_4As_2$[5] react with $[C_5H_5Fe(CO)_2]_2$ under milder conditions to afford bridged products of the type $[C_5H_5Fe(CO)L]_2$, which contain terminal carbonyl groups only.

We have now found that the ditertiary phosphines $Ph_2P[CH_2]_nPPh_2$ (n = 1–3) react with tetracarbonyldi-π-cyclopentadienyldi-iron to yield novel derivatives $[C_5H_5Fe(CO)]_2Ph_2P[CH_2]_nPPh_2$ (I), in which the ligand, as well as the two carbonyl groups, bridges the iron atoms. These compounds are neutral, diamagnetic, and isomorphous. Infrared and n.m.r. data suggest that they have the structure as shown in the Figure; the bulkiness of the phenyl groups would force the cyclopentadienyl rings into the "*cis*" positions.

TABLE

	ν (CO) (cm.$^{-1}$) measured in ^{a} C_6H_{12}, ^{b} CH_2Cl_2	C_5H_5 proton resonance τ ($CDCl_3$)
$\{C_5H_5Fe(CO)_2\}_2$	2006ms, 1961s, 1793s^{a}	5·21
(I; $n = 1$)	1734vw, 1690(s)^{a}	5·73
(II; $n = 1$)	1826(ms), 1772(s,b)^{b}	very broad
$[\{C_5H_5Fe(CO)\}_2{\cdot}I{\cdot}Ph_2P{\cdot}CH_2{\cdot}PPh_2]BPh_4$ ..	1983^{b}	5·77
$[C_5H_5Fe(CO)_2Ph_2P{\cdot}C_2H_4{\cdot}PPh_2]I_3$	2055(s), 2013(s)^{b}	4·74
$\{C_5H_5Fe(CO)I\}_2Ph_2P{\cdot}C_2H_4{\cdot}PPh_2$	1948^{b}	5·66
$[C_5H_5Fe(CO)Ph_2P{\cdot}C_2H_4{\cdot}PPh_2][BF_4]$	1980^{b}	5·19

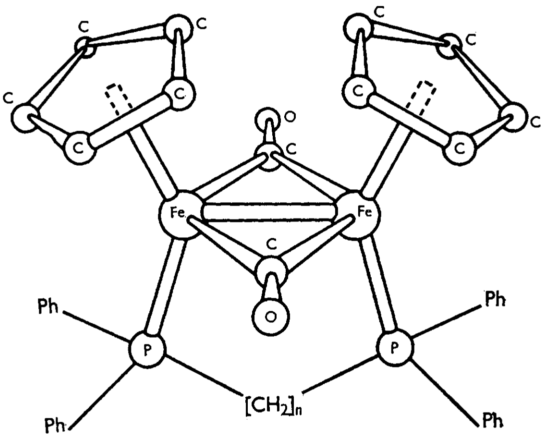

FIGURE. *Proposed structure for* $[C_5H_5Fe(CO)_2Ph_2P[CH_2]_nPPh_2$ (n = 1–3) *showing the stereochemistry of the iron atoms only.*

The Table shows that substitution of the terminal carbonyl groups in $[C_5H_5Fe(CO)_2]_2$ by the diphosphine ligands lowers the frequency of the bridging carbonyl stretching modes considerably. This effect may be attributed to the latter type carbonyls being able to participate in π-bonding. Similar effects are known for terminal and ketonic type carbonyl groups.^{6,7}

The reaction of $[C_5H_5Fe(CO)_2]_2$ with various monodentate tertiary phosphines and phosphites has yielded mono-substituted derivatives of formula $(C_5H_5)_2Fe_2(CO)_3L$ (L = ligand) in which one terminal carbonyl has been substituted. These derivatives exist as mixtures of isomers and will be the subject of a future publication.

The compounds (I; $n = 1$–3) are readily oxidised by various agents including halogens and pseudo-halogens, stannic chloride, and mercuric chloride. Treatment of a benzene solution of (I; $n = 1$–3) with an equimolar amount of iodine at room temperature does not afford the expected neutral iodo-complex, $[C_5H_5Fe(CO)I]_2Ph_2P[CH_2]_nPPh_2$, but an ionic compound (1 : 1 electrolyte in acetone) which precipitates from solution as the iodide. The analytical data for the tetraphenylboron derivative is consistent with the presence of the cation $\{[C_5H_5Fe(CO)]_2Ph_2P[CH_2]_nPPh_2\}^+$ ($n = 1$–3). As shown by the i.r. spectra in the C–O stretching region, the carbonyl groups in these ionic compounds are bridging. These bands are unusually broad, for example the half-band width for $\{[C_5H_5Fe(CO)]_2Ph_2P{\cdot}C_2H_4{\cdot}PPh_2]\}BPh_4$ (in CH_2Cl_2) is *ca.* 190 cm.$^{-1}$. Its magnetic moment corresponds to that for one unpaired electron. This suggests that iodine oxidation of (I; $n = 1$–3) occurs with loss of one electron, affording a product with an effective "one-electron metal–metal bond".

The complexes $\{[C_5H_5Fe(CO)]_2Ph_2P[CH_2]_nPPh_2\}BPh_4$ (II; $n = 1$–3) are very sensitive to oxidative or reductive attack, as expected for compounds with the above type of metal–metal bond. Hydrazine reduction of (II; $n = 2$) is extremely rapid, the parent compound (I; $n = 2$) being obtained in quantitative yield. Alcohol reduces similarly although the reaction proceeds much slower. Oxidation of (II; $n = 2$ or 3) with excess of iodine yields predominantly a product $\{C_5H_5Fe(CO)_2Ph_2P[CH_2]_nPPh_2\}BPh_4$ in which only one phosphorus atom of the diphosphine ligand is bonded to the iron. This represents an example of asymmetric cleavage, but does not occur for (II; $n = 1$). The iodine is inserted across the two iron atoms to afford an ionic compound $\{[C_5H_5Fe(CO)]_2{\cdot}I{\cdot}Ph_2PCH_2PPh_2\}BPh_4$ in which the carbonyl groups are now terminal but the iodine bridging. Similar type insertion reactions have been found for $[C_5H_5Fe(CO)_2]_2$.^{8}

The iodo-compound $[C_5H_5Fe(CO)I]_2Ph_2P[CH_2]_nPPh_2$ ($n = 1$–3) may be obtained by slowly adding an equimolar amount of iodine to a refluxing benzene solution of (I; $n = 1$–3), the ease of formation being reduced as n alters from 3 to 1. However, excess of iodine reacts with neutral (I; $n = 1$–3) in CH_2Cl_2 to yield the same product as the corresponding reaction between (II; $n = 1$–3) and iodine. This, together with the observation that $\{[C_5H_5Fe(CO)]_2$-$Ph_2P[CH_2]_nPPh_2\}I_3$ ($n = 1$–3) decomposes slowly in CH_2Cl_2 to yield as one of the products $[C_5H_5Fe(CO)I]_2Ph_2P[CH_2]_nPPh_2$, suggests that the paramagnetic complex [(I) (Anion)] is formed as an intermediate in the direct formation of $[\{C_5H_5Fe(CO)\}_2\cdot I\cdot Ph_2PCH_2PPh_2]$ [Anion], $[C_5H_5$-$Fe(CO)_2Ph_2P[CH_2]_nPPh_2]$ [Anion] ($n = 2$ or 3) or $[C_5H_5Fe(CO)I]_2Ph_2P[CH_2]_nPh_2$ ($n = 1$, 2 or 3) from the corresponding neutral (I).

Bromine behaves similarly to iodine in the above reactions except that the neutral bromo-derivative is more readily obtained at lower temperatures.

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