Stepwise Co-ordination of 1,2-Bis(diphenylphosphino)ethane to $[(\pi\text{-}C_5H_5)Fe(CO)_2(OCMe_2)]^+$: Isolation and Reactions of the Unidentate Intermediate

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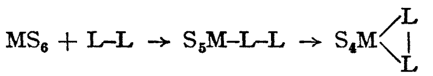
Summary Depending on relative concentrations, $[(\pi\text{-}C_5H_5)Fe(CO)_2(OCMe_2)]^+$ reacts with $Ph_2PCH_2{\cdot}CH_2PPh_2$ to give either the 1 : 1 $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2{\cdot}CH_2PPh_2)]^+$ or 2 : 1 bridged $[(\pi\ C_5H_5)Fe(CO)_2(Ph_2PCH_2{\cdot}CH_2PPh_2)Fe(CO)_2(\pi\text{-}C_5H_5)]^{2+}$ complexes.

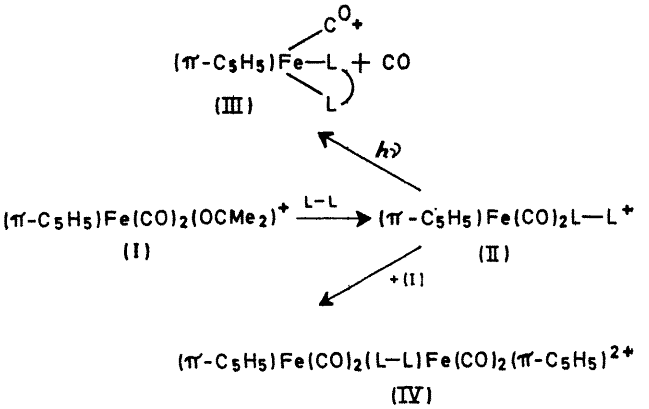
SUBSTITUTION reactions between octahedral metal complexes $[MS_6]$ and chelating bidentate ligands L–L occur by a two-step process



$$MS_6 + L\text{–}L \rightarrow S_5M\text{–}L\text{–}L \rightarrow S_4M\begin{matrix}L\\|\\L\end{matrix}$$

in which the first step is nearly always rate determining.[1] As a consequence the 1 : 1 intermediate S_5M–L–L or the bridged complex S_5M–L–L–MS_5, formed by further reaction of S_5M–L–L with M, cannot be isolated by direct reaction with L–L. In $[(\pi\text{-}C_5H_5)Fe(CO)_2(OCMe_2)]^+$ (I) only the co-ordinated acetone molecule is labile under mild conditions.[2] We find that reactions of (I) with $Ph_2PCH_2{\cdot}CH_2PPh_2$ (diphos = L–L) can be summarized as shown in the Scheme. The intermediate (II) can be isolated because of the unusual lability properties of (I). It can react further to give the bridged and chelated complexes.

Compound (II) is prepared under N_2 by the slow addition of an acetone solution of (I) to a stirred benzene solution containing a 5—10 molar excess of diphos. The reaction is complete within 1 h and (II) can then be isolated as its perchlorate salt, $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2{\cdot}CH_2PPh_2)](ClO_4)$. The salt undergoes no further reaction in refluxing dichloromethane for up to 4 h, but is rapidly converted into the chelated complex $[(\pi\text{-}C_5H_5)Fe(CO)(Ph_2PCH_2{\cdot}CH_2PPh_2)]^+$ when a dichloromethane solution is exposed to a sun lamp.



SCHEME

By reversing the order of addition and adding benzene solutions of either diphos, dithiahexane, or pyrazine to two-fold and greater excesses of (I) in acetone, the bridged complexes $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2{\cdot}CH_2PPh_2)Fe(CO)_2(\pi\text{-}C_5H_5)](ClO_4)_2$, $[(\pi\text{-}C_5H_5)Fe(CO)_2(MeSCH_2{\cdot}CH_2SMe)Fe(CO)_2(\pi\text{-}C_5H_5)](ClO_4)_2$, or $[(\pi\text{-}C_5H_5)Fe(CO)_2(NC_4H_4N)Fe(CO)_2(\pi\text{-}C_5H_5)](ClO_4)_2$ have been isolated. All of the complexes reported here have been characterized by elemental analyses and i.r. and n.m.r. spectra. Carbonyl stretching frequencies and n.m.r. data are given in the Table.

Acknowledgements are made to U.N.C. Materials Research Centre (through a contract with the Advanced Research Projects Agency), and to the National Science Foundation through a grant and a Science Development Award to the Department.

(*Received, December* 14*th* 1970; *Com.* 2162.)

TABLE

Compound	$\nu_{CO}(cm^{-1})$	$\pi\text{-}C_5H_5$ proton resonances	C_6H_5 proton resonances
$[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2{\cdot}CH_2PPh_2)](ClO_4)$	2057, 2014[a]	4·50[b]	2·50, 2·71[b]
$[(\pi\text{-}C_5H_5)Fe(CO)(Ph_2PCH_2{\cdot}CH_2PPh_2)](ClO_4)$	1980[a]	4·90[b]	2·45[b]
$[(\pi\text{-}C_5H_5)Fe(CO_2(Ph_2PCH_2{\cdot}CH_2PPh_2)Fe(CO_2(\pi\text{-}C_5H_5)](ClO_4)_2$ ..	2050, 1998[c]	4·88[d]	2·56[d]
$[(\pi\text{-}C_5H_5)Fe(CO)_2(MeSCH_2{\cdot}CH_2SMe)Fe(CO)_2(\pi\text{-}C_5H_5)(ClO_4)_2$ ..	2071, 2033[c]	4·52[d]	—
$[(\pi\text{-}C_5H_5)Fe(CO)_2(NC_4H_4N)Fe(CO)_2(\pi\text{-}C_5H_5)](ClO_4)_2$	2067, 2031[c]	4·11[d]	—

[a] In dichloromethane solution. [b] In $(CD_3)_2CO$, relative to $(CH_3)_2CO$ at τ 7·93. [c] In Nujol mulls. [d] In CD_3CN relative to CH_3CN at τ 8·00.

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[2] E. C. Johnson, T. J. Meyer, and N. Winterton, *Chem. Comm.*, 1970, 934; *Inorg. Chem.*, in the press.