Reaction of Bis(cyclo-octa-1,5-diene)iron with Trimethyl Phosphite, Phosphorus Trifluoride, t-Butyl Isocyanide, Carbon Monoxide, and Bis-1,2-(diphenylphosphino)ethane; the Synthesis of [$Fe(N_2)(diphos)_2$]

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Summary Reaction of [$Fe(1,5\text{-}C_8H_{12})_2$] with $P(OMe)_3$ affords [$Fe(1,3\text{-}C_8H_{12})\{P(OMe)_3\}_3$], whereas, PF_3, CO, and Bu^tNC give [$Fe(1,5\text{-}C_8H_{12})L_3$] (L = PF_3, CO, or Bu^tNC); in contrast $Ph_2PCH_2CH_2PPh_2$ and dinitrogen give the Fe^0 dinitrogen complex [$Fe(N_2)(Ph_2PCH_2CH_2PPh_2)$].

The reaction of iron vapour with cyclo-octa-1,5-diene has been shown to give the thermally unstable and co-ordinately unsaturated complex bis(cyclo-octa-1,5-diene)iron.[1] Here we report the varied behaviour of the compound in its reactions with donor ligands.

The reaction of iron vapour with a solution of cyclo-octa-1,5-diene (10%) in methylcyclohexane, gave a reaction mixture containing $[Fe(1,5\text{-}C_8H_{12})_2]$, highly activated bulk iron, free $1,5\text{-}C_8H_{12}$, and by-products, and this solution was treated directly with the donor ligand at −78 °C. Alternatively the complex was first isolated at low temperatures as a crystalline material, and then treated with the ligand.

Reaction (−78 °C) with an excess of trimethyl phosphite afforded the yellow crystalline complex tris(trimethyl phosphite)(cyclo-octa-1,3-diene)iron[2] {^{13}C n.m.r. resonances[†] [room temp., $(CD_3)_2CO$, ^{1}H decoupled] at +26·7 (*C*H$_2$), 27·5 (*C*H$_2$, $^3J_{PC}$ 2·8 Hz), 50·4 (*C*H=CH, $^2J_{PC}$ 1·0 Hz), 51·6 (PO*C*H$_3$, $^3J_{PC}$ 2·2 Hz), and 86·0 (*C*H=CH) p.p.m., ^{31}P n.m.r. resonance (room temp.,) at 181·3 p.p.m. (downfield ext. H_3PO_4), and at −90 °C resonances at 178·9 (2P) and 187·9 (1P) p.p.m., $^2J_{PP}$ 39·0 Hz}. Both the ^{1}H and ^{13}C n.m.r. spectra showed the expected features for a cyclo-octa-1,3-diene complex. The dynamic behaviour is presumably related to that previously reported[3,4] for $[Fe(1,3\text{-}C_4H_6)(CO)_3]$ and $[Fe(C_8H_8)(CO)_3]$.

In contrast, a further study of the corresponding reaction with PF_3 in n-pentane (−78 °C) afforded the volatile, yellow, air-stable complex tris(phosphorus trifluoride)(cyclo-octa-1,5-diene)iron[‡] [^{13}C n.m.r. resonances (room temp., ^{1}H decoupled) at 32·6 (*C*H$_2$) and 76·9 (CH=CH) p.p.m.]. Analysis of the displaced cyclo-octadiene in this reaction showed it to be 95% of the 1,5-isomer. The same complex was also obtained by condensation of iron vapour with a mixture of cyclo-octa-1,5-diene and PF_3, and from the reaction of unrecrystallised $[Fe(1,5\text{-}C_8H_{12})_2]$ with PF_3 thus confirming the preliminary studies of this reaction.[1] Similar reactions with excess of t-butyl isocyanide yielded the orange, air-sensitive crystalline complex tris(t-butyl isocyanide)(cyclo-octa-1,5-diene)iron [^{13}C n.m.r. resonances (room temp. and −90 °C, ^{1}H decoupled) at 31·3, (*Me*$_3$CNC), 34·0 (CH$_2$), 55·4 (Me$_3$*C*NC), and 74·1 (*C*H=CH) p.p.m.]. Addition (−130 °C) of carbon monoxide to a solution of $[Fe(1,5\text{-}C_8H_{12})_2]$ in methylcyclohexane afforded a trace of $[Fe(CO)_5]$ and $[Fe(1,5\text{-}C_8H_{12})(CO)_3]$; there was no evidence for isomerisation of the cyclo-octadiene.

These observations suggest that the isomerisation of cyclo-octa-1,5-diene observed with trimethyl phosphite is the exception rather than the rule, and that the rate of isomerisation of iron(0) olefin complexes is very dependent on the nature of the other ligands attached to the iron.

Although attempts to displace either cyclo-octa-1,3-diene or -1,5-diene from these complexes with an excess of $P(OMe)_3$ or Bu^{t}NC were not successful, the reaction with bis-1,2-(diphenylphosphino)ethane (diphos) proved particularly interesting. Addition (−20 °C, argon atmosphere) of a solution (Et_2O) of diphos to $[Fe(1,5\text{-}C_8H_{12})_2]$ in methylcyclohexane gave a brown solution, decomposing above 0 °C to iron metal. However, if nitrogen was bubbled (0 °C) through the reaction mixture the five-co-ordinate iron(0) complex $[Fe(N_2)(diphos)_2]$ was formed, and could be isolated as a red crystalline complex [ν(Nujol) 2068 cm^{-1} (FeN$_2$)]. Treatment of a solution of the dinitrogen complex with carbon monoxide gave yellow crystals of $[Fe(CO)(diphos)_2]$ [ν(Nujol) 1810 cm^{-1} (CO)].

From the standpoint of synthesis our observations suggest that $[Fe(1,5\text{-}C_8H_{12})_2]$ provides an important entry to a number of new complexes, whose chemistry is currently being studied.

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[†] Tricarbonyl(cyclo-octa-1,3-diene)iron shows ^{13}C n.m.r. resonances (room temp.) at 25·2 p.p.m. (*C*H$_2$), 28·9 (*C*H$_2$), 63·2 (*C*=C), 91·8 (*C*=C), and 212·2 (*C*O).

[‡] No $Fe(PF_3)_5$ was formed in this reaction.

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