Journal of Organometallic Chemistry, 329 (1987) C7–C10
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Labile benzene-iron complexes: crystal structure of *cis*- and *trans*-$FeHI(CO)_2(PPh_3)_2$

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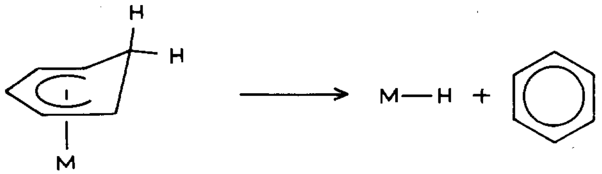
(Received April 21st, 1987)

Abstract

The lability of the benzene ligand in the new benzene-iron dimers, $[(\eta^6\text{-}C_6H_6)Fe(CO)_4FeR]BF_4$ ($R = \eta^5\text{-}C_6H_7$ (4) or $\eta^5\text{-}C_5H_5$ (5)), is demonstrated, and the use of benzene as a leaving group exploited in the reaction of $(\eta^5\text{-}C_6H_7)FeI(CO)_2$ with PPh_3 which gives the unexpected *trans* isomer, confirmed by an X-ray crystal structure, of $FeHI(CO)_2(PPh_3)_2$ (7) as the major product.

Our interest in benzene complexes [1] has been directed towards labile benzene ligands because the creation of multiple vacant coordination sites on a transition metal complex is valuable for both synthetic and catalytic applications. We report here the first members of a new class of benzene-iron dimer and show that the benzene ligand in these complexes is readily displaced. We then show how this lability may be exploited when starting with a related cyclohexadienyl complex. New unsaturated hydrido complexes are generated that can be trapped with PPh_3.



When $(C_6H_7)Fe(CO)_2I$ (1) [2] is treated with $Na[CpFe(CO)_2]$ (−78 °C, THF), two products may be isolated (Scheme 1), $(C_6H_7)_2Fe_2(CO)_4$ (2) [2] and $(C_6H_7)Fe(CO)_4FeCp$ (3). When either of these compounds is further treated with $[CPh_3]BF_4$ (0 °C, CH_2Cl_2) the green cationic benzene complexes $[(C_6H_6)Fe(CO)_4Fe(C_6H_7)]BF_4$ (4) and $[(C_6H_6)Fe(CO)_4FeCp]BF_4$ (5) may be isolated. Monitoring solutions of either of these complexes by ^1H NMR at room temperature reveals the rapid evolution of free benzene. The lability of the benzene ligands is comparable to that of the (arene)$Ni(C_6F_5)_2$ complexes [3] and arene exchange reactions are being investigated.

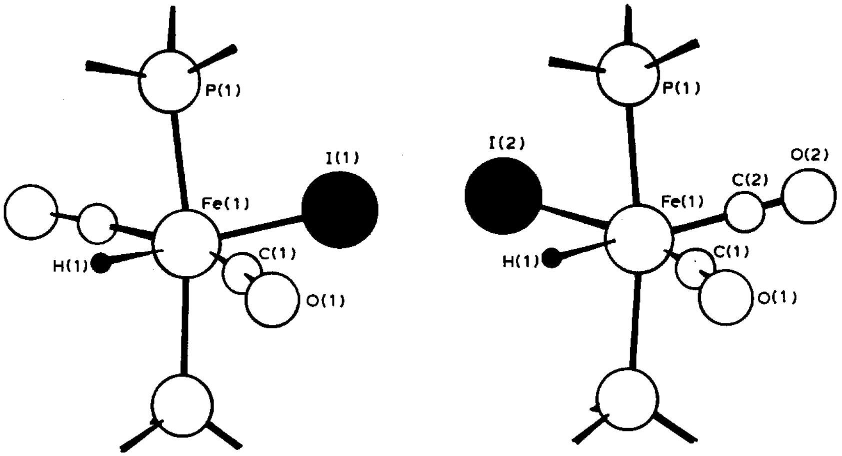


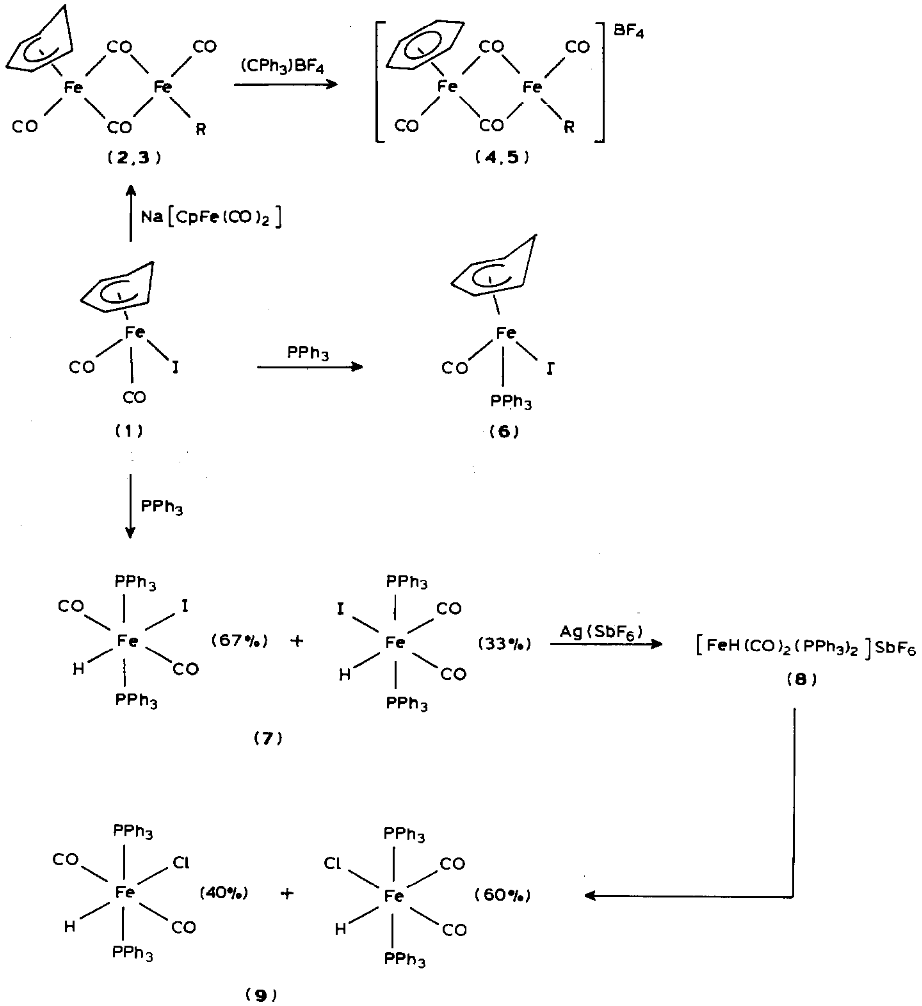
Fig. 1. The inner coordination spheres of *cis*- and *trans*-$FeHI(CO)_2(PPh_3)_2$. Distances and angles include: Fe–P 2.252(1), Fe–I(1) 2.580(1), Fe–I(2) 2.635(7), Fe–H 1.37(11), Fe–C(1) 1.696(8), C(1)–O(1) 1.165(14), Fe–C(2) 1.74(1), C(2)–O(2) 1.12(1) Å. I(1)–Fe–P 94.41 (4), I(1)–Fe–C(1) 100.5(3), H–Fe–P 85.59(4), H–Fe–C(1) 79.5 (3)°.

The labillity may be exploited (Scheme 1). When **1** is treated with PPh_3 (40 °C, THF) a single product may be isolated in high yield, $(C_6H_7)FeI(CO)(PPh_3)$ (**6**). This complex is directly analogous to the product obtained with $P(OPh)_3$ [4]. However, slightly more vigorous conditions (60 °C, benzene) give rise to benzene loss [5] and $FeHI(CO)_2(PPh_3)_2$ (**7**) is formed. Spectroscopic analysis did not indicate the expected *cis*-product [6] and therefore the product was characterised by X-ray crystallography * (Fig. 1).

The structure reveals that a 67/33 mixture of the *trans* and *cis* isomers cocrystallise. This is the same mixture of isomers that is generated during the reaction when the reaction is monitored by ^1H NMR. Attempts to alter the ratio of isomers, or separate the two isomers have so far been unsuccessful. When **7** is treated with $AgSbF_6$ (1 equiv. in CH_2Cl_2) a highly reactive complex $[FeH(CO)_2(PPh_3)_2]SbF_6$ (**8**) may be isolated, in which the SbF_6 may be weakly associated with the metal. Significantly, **8** exists as a single isomer on the basis of IR and NMR data.

Treatment of **8** with Et_4NI regenerates **7** as the same 67/33 mixture of isomers. Other isomeric mixtures can also be generated by adding other ligands to **8**. Thus,

* *Crystal data*: $C_{38}H_{31}FeIO_2P_2$, $M = 764.13$, monoclinic, space group $C2/c$ (No. 15), a 23.360(11), b 9.783(5), c 22.257(11) Å, β 138.55(2)°, U 3367.0 Å^3, D_c 1.506 g cm^{-3} for $Z = 4$. The intensity data were collected on a Hilger and Watts Y290 diffractometer within the limits $1 < \theta < 25°$. μ(Mo-K_α) 15.15 cm^{-1}, no absorption correction was applied. The structure was solved by Patterson and Fourier methods on the basis of 2388 significant ($I > 3\sigma(I)$) reflections. Refinement by full-matrix least squares led to current values of the conventional R and R_w factors of 0.057 and 0.068 respectively. Phenyl hydrogens were placed from geometric considerations and included in the calculations without refinement. The hydride was located in a difference Fourier and included in the refinement isotropically. There was found to be a mixture of *trans*- and *cis*-$FeHI(CO)_2(PPh_3)_2$ in the crystal. The occupation factors refined to 0.674(3) for the *trans* isomer. The molecules are positioned on a 2-fold axis through the I, Fe, H atoms for the *trans* isomer, and the O(2), C(2), Fe, H atoms for the *cis* isomer. Lists of atomic coordinates and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.



Scheme 1

when treated with Et_4NCl, a 40/60 mixture of *trans/cis*-$FeHCl(CO)_2(PPh_3)_2$ (**9**) forms, and with MeCN a 60/40 mixture of *trans/cis*-$[FeH(NCMe)(CO)_2(PPh_3)_2]$-$SbF_6$ (**10**) is formed.

While much ruthenium and osmium chemistry is based on bis(triphenylphosphine) complexes, the comparable chemistry of iron has hardly been developed. In part this is due to the lack of the appropriate substrate complexes. Since **7** can be made in quantity from the readily available $[(C_6H_7)Fe(CO)_3]PF_6$ (7) [7], it should be an appropriate substrate.

We are currently investigating further reactions of **8** and the reaction that generates the unsaturated iron hydride complex.

Characterising data for complexes 3–10

3: ν(CO) 1980, 1770 cm^{-1} (nujol mull), ^1H NMR (C_6D_6) δ (ppm) 4.42 [t, 2H,

C_6H_7], 4.23 [m, 1H, C_6H_7], 4.15 [5, 5H, C_5H_5], 3.54 [t, 2H, C_6H_7], 2.20 [m, 1H, C_6H_7], 1.52 [d, 1H, C_6H_7], m/z 368 (M^+).
4: ν(CO) 2030, 1820 cm^{-1} (nujol mull), ^1H NMR (acetone-d_6) δ (ppm) 6.94 [s, 6H, C_6H_6], 6.40 (t, 1H, C_6H_7), 5.70 [t, 2H, C_6H_7], 4.41 [t, 2H, C_6H_7], 3.08 [dt, 1H, C_6H_7], 2.15 [d, 1H, C_6H_7].
5: ν(CO) 2010, 1820 cm^{-1} (nujol mull), ^1H NMR (acetone-d_6) δ (ppm) 6.93 [s, 6H, C_6H_6], 5.66 [s, 5H, C_5H_5].
6: ν(CO) 1950 cm^{-1} (CH_2Cl_2 solution), ^1H NMR ($CDCl_3$) δ (ppm) 7.5 [m, 15H, C_6H_5], 7.56 (t, 1H, C_6H_7], 5.38 [t, 1H, C_6H_7], 4.40 [dd, 1H, C_6H_7], 3.16 [t, 1H, C_6H_7], 2.57 [dt, 1H, C_6H_7], 1.54 (dd, 1H, C_6H_7], 1.03 [t, 1H, C_6H_7]; ^{13}C NMR (acetone-d_6) δ (ppm) 227.22 [d^2, J(PC) 20 Hz, CO], 135–128 [m, C_6H_5], 106.48, 95.41, 88.87, 48.47, 37.04, 22.64 [s, C_6H_7]; ^{31}P NMR ($CDCl_3$) δ (ppm) 62.41 [s].
7: *trans*-Isomer, ν(CO) 1945 cm^{-1} (CH_2Cl_2), ^1H NMR ($CDCl_3$) δ 8.6–7.2 [m, 15, C_6H_5], -17.23 [t, ^2J(PH) 40 Hz, FeH]; ^{13}C NMR ($CDCl_3$) δ (ppm) 211.71 [t, ^2J(PC) 25 Hz, CO]; ^{31}P NMR ($CDCl_3$) δ (ppm) 60.28 [d, ^2J(PH) 40 Hz, FeH], m/z 763 (M^+). *cis*-Isomer, ν(CO) 2015, 1960 cm^{-1}. ^1H NMR ($CDCl_3$) δ (ppm) 8.6–7.2 [m, 15, C_6H_5], -5.41 [t, ^2J(PH) 49 Hz, FeH]; ^{13}C NMR ($CDCl_3$) δ (ppm) 216.34 [t, ^2J(PC) 22 Hz, CO], 208.66 [t, ^2J(PC) 15 Hz, CO]; ^{31}P NMR ($CDCl_3$) δ (ppm) 60.27 [d, ^2J(PH) 49 Hz, FeH].
8: ν(CO) (CH_2Cl_2) 1973, 2038 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm) 7.2–7.5 [m, 15H, C_6H_5]; -3.27 (t, ^2J(PH) 49 Hz], m/z 637, ($M^+ - SbF_6$).
9: *trans*-Isomer ν(CO) (CH_2Cl_2) 1940 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm) 7.2–7.7 [m, 15H, C_6H_5]; -21.12 [t, ^2J(PH) 34 Hz, FeH]. *cis*-Isomer ν(CO) (CH_2Cl_2) 1960, 2014 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm) 7.2–7.7 [m, 15H, C_6H_5], -4.07 [t, ^2J(PH) 51 Hz, FeH].
10: *trans*-Isomer ν(CO) (CH_2Cl_2) 1969 cm^{-1}; ^1H NMR ($CDCl_3$), δ (ppm) 7.2–7.5 [m, C_6H_5, 15H], -17.96 [t, ^2J(PH) 32 Hz, FeH]; ^{31}P NMR ($CDCl_3$) δ (ppm) 62.6 (d, ^2J(PH), 32 Hz, FeH], m/z 678,637 (loss of MeCN). *cis*-Isomer ν(CO) (CH_2Cl_2) 2032, 1969 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm) 7.2–7.5 [m, C_6H_5, 15H], -5.49 [t, ^2J(PH) 43 Hz]; ^{31}P NMR ($CDCl_3$) δ 64.93 [d, ^2J(PH) 43 H_2 43 Hz], m/z 678,637.

We thank the SERC for a research studentship (SP).

References

1 M.P. Gomez-Sal, B.F.G. Johnson, J. Lewis, P.R. Raithby and A.H. Wright, J. Chem. Soc., Chem. Commun., (1985) 1682.
2 M.A. Hashmi, J.D. Munro, P.L. Pauson and J.M. Williamson, J. Chem. Soc. A, (1967) 240.
3 M.W. Eyring and L.J. Radonovich, Organometallics, 4 (1985) 1841.
4 D.A. Brown and S.K. Chawla, Inorg. Chem. Acta, 24 (1977) 71.
5 R.H. Crabtree and C.P. Parnell, Organometallics, 4 (1985) 519.
6 T.A. Albright, J.K. Burdett and M.-H. Wangbo, Orbital Interactions in Chemistry, John Wiley and Sons, 1985.
7 A.J. Birch and M.A. Heas, J. Chem. Soc. C, (1971) 2465.