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Preliminary communication

Synthesis and reactivity of a new class of half-sandwich arene-iron complex: structure of $[C_6H_3Me_3Fe(C_3H_5)(CO)]PF_6$

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Abstract

A new class of air-stable half-sandwich areneiron(II) complex is described, and a preliminary account given of the reactivity and structure of one of the complexes, $[(C_6H_3(CH_3)_3)Fe(C_3H_5)(CO)]PF_6$.

Half sandwich areneiron(II) complexes are extremely rare [1], which is surprising in view of the great deal of attention paid to the related compounds of chromium [2] and manganese [3], and the extensive chemistry of half-sandwich cyclopentadienyliron(II) complexes [4]. We report here the synthesis of a new type of air-stable half-sandwich areneiron(II) complex. A preliminary examination of the reactions of these new species has revealed that judicious selection of reagents determines whether or not the arene ligand is involved in the reaction.

Current arene-iron chemistry stems from the conventional Fischer–Hafner synthesis, in which sandwich complexes such as $[Fe(arene)_2]^{2+}$ are made [4], or from the specialist metal vapour technique which has recently been used to generate a number of highly reactive iron(0) compounds [5]. We have been examining the synthesis of areneiron(II) complexes [6,7], seeking new straightforward routes to these potentially important species.

The new arene complexes $[(arene)Fe(allyl)(CO)]PF_6$ (2) ** can be isolated from the reaction of $(allyl)FeBr(CO)_3$ (1) with arenes in the presence of a strong Lewis acid (Scheme 1). The reaction differs from the well-known reaction used to make $[(arene)Mn(CO)_3]^+$ complexes [8] because of the presence of the organic allyl group in the substrate complex. This has an important effect, and the isolation of these complexes requires careful selection of reaction conditions because the complexes lie on a reaction sequence that ultimately produces $[Fe(arene)_2]^{2+}$ (3) complexes [9].

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** See footnote p. C12.

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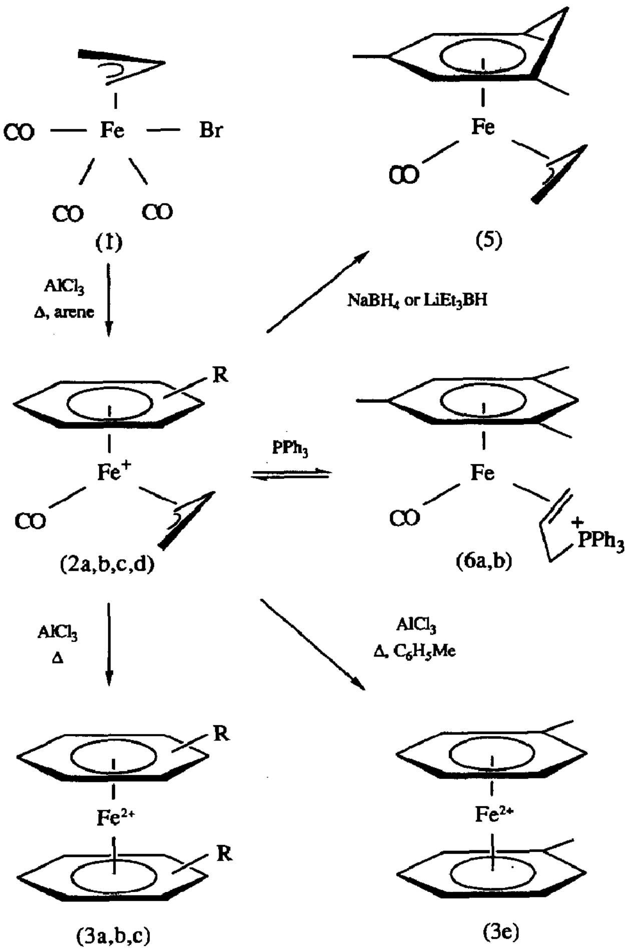

Scheme 1. The formation and reactions of $[(\text{arene})\text{Fe}(\text{allyl})(\text{CO})]^+$ complexes. Allyl = CH_2CHCH_2 and arene = benzene (a), mesitylene (b), or hexamethylbenzene (c); allyl = $CH_2CCH_3CH_2$ and arene = mesitylene (d).

In the first step, the Lewis acid abstracts the bromide, and if the reaction is stopped the known complex $[(\text{allyl})\text{Fe}(\text{CO})_4]^+$ (**4**) [10] can be isolated. The intermediate, however, is almost certainly $[(\text{allyl})\text{Fe}(\text{CO})_3]^+$, since the conversion into **4**

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* All the complexes **2a–2d** have been characterised spectroscopically and by C and H analysis. Typical spectroscopic data are as follows: for: $[(C_6H_3(CH_3)_3)Fe(C_3H_5)(CO)]PF_6$ (**2b**): $\nu(CO)$ 2022 cm^{-1} (CH_2Cl_2); ^1H NMR $(CD_3\ COCD_3)$: 6.37(s,3H,$C_6\mathit{H}_3(CH_3)_3$), 4.99(m,1H,C_3H_5), 3.53(d,2H,C_3H_5), 2.47(s,9H,$C_6H_3(CH_3)_3$), 1.68(d,2H,C_3H_5); $m/z = 245$ (M^+); ^{13}C NMR (ppm) 114 ($C_6H_3(CH_3)_3$), 94 ($C_6H_3(CH_3)_3$), 82 ($CH_2\mathit{C}HCH_2$), 48 ($\mathit{C}H_2CH\mathit{C}H_2$), 19 ($C_6H_3(CH_3)_3$).
For $(C_6H_4(CH_3)_3)Fe(C_3H_5)(CO)$ (**5b**); $\nu(CO)$ 1940 cm^{-1} (hexane); ^1H NMR (C_6D_6): 3.5(s,2H,($C_6\mathit{H}_4(CH_3)_3$), 3.46(m,1H,C_3H_5), 2.73(d,1H,$C_6\mathit{H}_4(CH_3)_3$), 1.93(d,1H,$C_6\mathit{H}_4(CH_3)_3$), 1.63(s,3H,$C_6H_4(C\mathit{H}_3)_3$), 1.60(d,2H,C_3H_5), 1.56(s,6H,$C_6H_4(C\mathit{H}_3)_3$), 0.42(d,2H,C_3H_5); $m/z = 246$ (M^+).
For $[(C_6H_3(CH_3)_3)Fe(CH_2CHCH_2PPh_2)(CO)]PF_6$ (**6b**): $\nu(CO)$ 1905 cm^{-1} (CH_2CL_2), ^1H NMR (CD_3COCD_3): 7.4(m,15H,$CH_2CHCH_2P\mathit{Ph}_3$), 5.08(s,3H,$C_6\mathit{H}_3(CH_3)_3$), 4.34(m,1H,$CH_2CHCH_2PPh_3$), 2.94(m,1H,$CH_2CHCH_2PPh_3$), 2.12(m,1H,$CH_2CHCH_2PPh_3$), 2.10(s,9H,$C_6H_3(C\mathit{H}_3)_3$), 1.66(d,1H,$CH_2CHCH_2PPh_3$), 1.36(d,1H,$CH_2CHCH_2PPh_3$); ^{31}P NMR (CD_3COCD_3) 56 ppm (m).

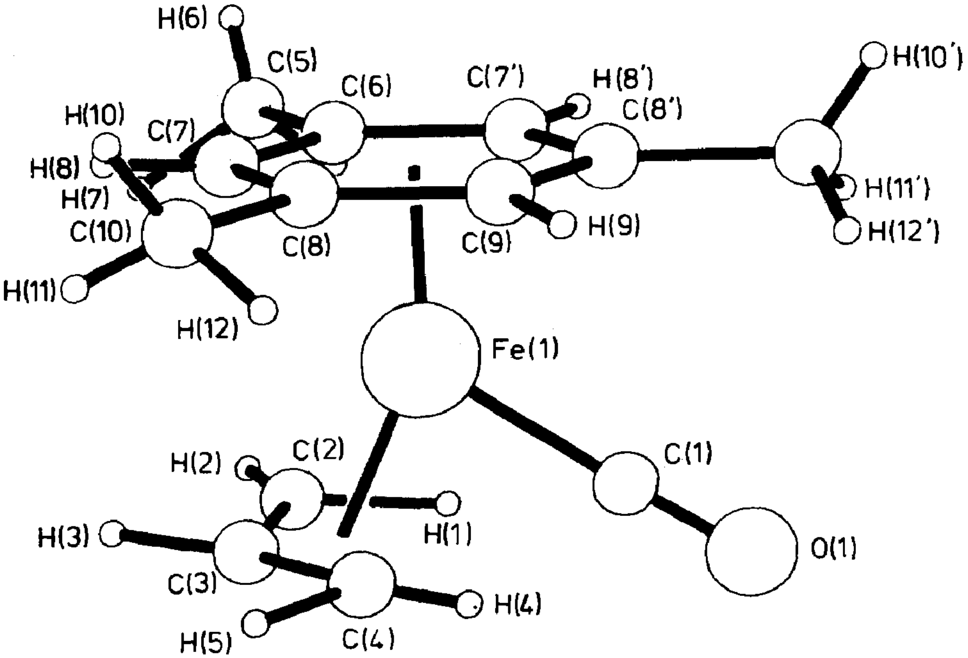

Fig. 1. The structure of [(mesitylene)Fe(allyl)(CO)]PF_6. Distances and angles include: Fe(1)–C(1) 1.87(1), Fe(1)–C(2) 2.09(1), Fe(1)–C(3) 2.00(1), Fe(1)–C(4) 2.05(2), Fe(1)–C(6) 2.137(7), Fe(1)–C(7) 2.120(5), Fe(1)–C(8) 2.140(5), Fe(1)–C(9) 2.104(7), C(1)–O(1) 1.11(2), C(2)–C(3) 1.45(3), (3)–C(4), 1.44(2), C(6)–C(7) 1.400(6), C(7)–C(8) 1.411(7), C(8)–C(9) 1.394(6) Å, C(1)–Fe(1)–C(3) 97.3(7), C(1)–Fe(1)–C(7) 165.7(7), C(3)–Fe(1)–C(7) 96.5(5), Fe(1)–C(1)–O(1) 173(1), C(2)–C(3)–C(4) 130(1)°.

during work-up has been reported [11]. As the temperature is raised to about 90 °C loss occurs, and the arene half-sandwich complexes are formed, and can be isolated in yields of up to 60%. Further heating of the reaction mixture leads to rapid formation of [Fe(arene)$_2$]$^{2+}$.

If the half-sandwich complexes are dissolved in a different arene in the presence of $AlCl_3$ and the solutions heated, replacement of the initial arene takes place and the symmetrical bisarene complexes are produced (**3c**).

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* *Crystal data*. $C_{13}H_{17}F_6FeOP$, $M = 390.07$, space group *Pnam*, *a* 14.254(3), *b* 1.461(2), *c* 10.013(3) Å, *U* 1635.77 Å^3, D_c 1.58 g cm^{-1} for $Z = 4$, $F(000) = 792$. The intensity data were collected on a Hilger and Watts Y290 diffractometer within the limits $1 < \theta < 25°$. μ(Mo-K_α) 9.04 cm^{-1}, no absorption correction was considered necessary. The structure was solved by Patterson and Fourier methods on the basis of 1266 significant [$I > 3\sigma(I)$] reflections. Refinement by full matrix least-squares led to final R and R_w values of 5.82 and 7.68, respectively, where the weighting scheme was based on a Chebyshev polynomial. Both the iron and phosphorus atoms lie on the crystallographic mirror plane together with 3 carbon atoms of the mesitylene and 2 fluorine atoms. The approximately equally space filling allyl and carbonyl groups are disordered equally across this mirror plane. Attempts to refine the structure in the alternative space group $Pna2_1$, without mirror symmetry and disorder were unsuccessful. Atoms C(1) and C(4) are very close in the averaged disordered cell, and so these atoms were refined with only isotropic vibrations and with some constraints on their positions. The remaining atoms were refined anisotropically. The mesitylene hydrogen atoms were located in a difference Fourier and refined isotropically. Allyl hydrogens were placed in calculated positions. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

The complex **2b** is the first half-sandwich areneiron(II) complex to be structurally characterised, Fig. 1 *. The overall geometry of the complex is like those of $[CpCo(allyl)(H_2O)]^+$ [12] and $(C_6H_6)Ru(allyl)I$ [13]. In all cases the allyl group adopts a similar conformation, and the spectra indicate that a single conformation is present in solution.

The new complexes are highly reactive; thus undergoing arene-exchange reactions and are attacked by a large range of nucleophiles, and are also electrochemically and photochemically active.

One of the major interests in complexes such as **2** lies in reactions involving nucleophilic addition. Simple rules for the addition of nucleophiles in such cases have been formulated [14]. These indicate that for the kinetic products of charge-controlled reactions addition should occur *exo* to the metal at the arene ligand. Reactions of **2b** indicate that the complex is susceptible to attack only by strong nucleophiles, and that this attack is not always charge controlled. Thus, while the addition of hydride occurs at the arene ligand, bulkier phosphine nucleophiles add to the allyl ligand. Hydride sources such as $NaBH_4$ and $LiEt_3BH$ give identical products such as **5**, which are neutral, sublimable, and highly air-sensitive.

In contrast when **2b** is treated with PPh_3 an equilibrium is established, and a large excess of the phosphine is required to generate significant amounts of the adduct **6b**. The equilibrium lies further towards the adduct when the benzene complex **2a** is used as substrate. When a more basic phosphine such as $P\text{-}n\text{-}Bu_3$ is used, no equilibrium can be detected, only the addition product. In each case the ^1H NMR spectrum reveals that addition occurs to a terminal rather than to the central carbon.

We are currently examining the other types of reaction of these complexes.

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