α-Hydride Abstraction *via* a Three-Step Pathway: Access to the Electron Rich Iron Methoxycarbene Complex [Fe(η5-C5Me5)(*P,P'*-Ph2PCH2CH2PPh2)(=CHOMe)]+PF6−

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The rare iron methoxycarbene [Fe(η5-C5Me5)(*P,P'*-Ph2PCH2CH2)(=CHOMe)]+ PF6− (**4**) is cleanly synthesised by a three-step α-hydride abstraction; the first paramagnetic iron(III) species, Fe(η5-C5Me5) (*P,P'*-Ph2PCH2CH2PPh2)-(CH2OMe)]+ PF6− (**2**), is characterised by single crystal *X*-ray diffraction and the second intermediate, Fe(η5-C5Me5)-(*P,P'*-Ph2PCH2CH2PPh2(=CHOMe) (**3**), by e.s.r. spectroscopy.

Electron transfer (ET) pathways are involved in the C–H bond activation of metal alkyl intermediates in a variety of catalytic reactions.[1] Thus, it is important to understand the mechanistic basis for hydride abstraction in well defined stoicheiometric reactions.

It has been demonstrated that C–H bond activation from the transition metal alkyl W(η5-C5H5)2(Me)CH2R, gives rise to hydride transfer to the trityl cation as hydride acceptor, by a two-step electron transfer, radical transfer mechanism.[2] We have used e.s.r. spectroscopy to detect radical cation inter-mediates in the abstraction of the α-H from the iron hydroxymethyl complex Fe(Cp*)(CO)2(CH2OH)(Cp* = η5-C5Me5) by Ph3C+PF6−.[3,4] Further experiments suggest that available mechanistic data on other Ph3C+/metal alkyl reactions are consistent with this pathway.[5—8] We report here the first example in which hydride transfer from a transition metal alkyl to hydride acceptors occurs *via* a three-step pathway *i.e.*, electron transfer, proton transfer, electron transfer.

We have used the new electron rich thermally stable

but air sensitive Fe(Cp*)(η^2-dppe)CH$_2$OMe (1) (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$)† as the starting material.[9—10] The cyclic voltammogram (CH$_2$Cl$_2$, Bu$^n_4$N$^+$PF$_6^-$, Pt, 20 °C) of (1) shows a reversible one-electron wave at E_a −0.45 V vs. Standard Calomel Electrode (S.C.E.), a value close to those already observed for Fe(Cp*)(η^2-dppe)X.[10c,d]

Red complex (1) reacts cleanly at 20 °C with Ph$_3$C$^+$PF$_6^-$ in methylene chloride affording the air stable iron(III) methoxy-methyl cation [Fe(Cp*)(η^2-dppe)(CH$_2$OMe)]$^+$PF$_6^-$ (2) in 92% yield (Scheme 1). Reversal of this reaction by treatment of (2) with 1 equiv. potassium and exposure to 20 kHz ultrasonic irradiation[10c] affords (1) specifically in 90% yield. The structure of (2) has been unambiguously established by a single crystal X-ray analysis (Figure 1).‡ The cyclopentadienyl is planar to within ±0.005 Å, and the methyl carbon atoms are above this plane $ca.$ 0.2 Å away from the iron atom. The Cp* centroid, the iron, and the oxygen atoms are nearly planar, together with the two carbon atoms of the –CH$_2$– and MeO– groups, this plane being normal to the plane of the C$_5$-ring. The methoxymethyl group is placed between the two phosphorous atoms, whereas the α-hydrogen atoms are located close to the C$_5$Me$_5$ ligand. Thus, those hydrogen and oxygen atoms are sterically protected against approach of bulky reagents by a cage formed by the phenyl of the dppe ligand and the permethylated cyclic ligand. These structural data are rather different from those observed for the Fe(C$_5$H$_5$)(CO)(PPh$_3$)CH$_2$R series.[11]

Since the redox potential of the reversible system (1) $\rightleftharpoons$ (2) is 0.75 V more negative than that of Ph$_3$C$^+$ $\rightleftharpoons$ Ph$_3$C· (+ 0.3 V),[8] electron transfer from (1) to the trityl cation is thermodynamically favoured. In contrast with the H-atom abstraction previously observed for the W,[2] Re,[7] and Fe[3] alkyl series which are known to transfer H$^-$ to Ph$_3$C$^+$ according to an E.T. mechanism, Ph$_3$C· is unable to abstract H· from (2). This feature has recently been mentioned in a similar reaction[10d] and can be explained (according to the structural data) by steric hindrance for the approach of the bulky trityl radical.

Compound (2) reacts with a stoicheiometric amount of

Bu^{t}OK in tetrahydrofuran (THF) at −80 °C affording the new secondary methoxycarbene [Fe(Cp*)(η^2-dppe)(=CHOMe)]$^+$·PF$_6^-$ (4)† (45% yield) in addition to an equivalent amount of (1) and Bu^{t}OH. This is a two-step reaction (Scheme 1), the first step being the proton abstraction by the base giving rise to the unstable intermediate compound Fe(Cp*)(η^2-dppe)-(=CHOMe) (3) immediately followed by an electron transfer from (3) to (2) in the second step. The synthesis of the secondary heterocarbene (4) is greatly improved by using a stoicheiometric amount of ferricinium as an oxidizing agent. Under these conditions, (4) is recovered with 92% yield (100% yield of Bu^{t}OH by g.c.).
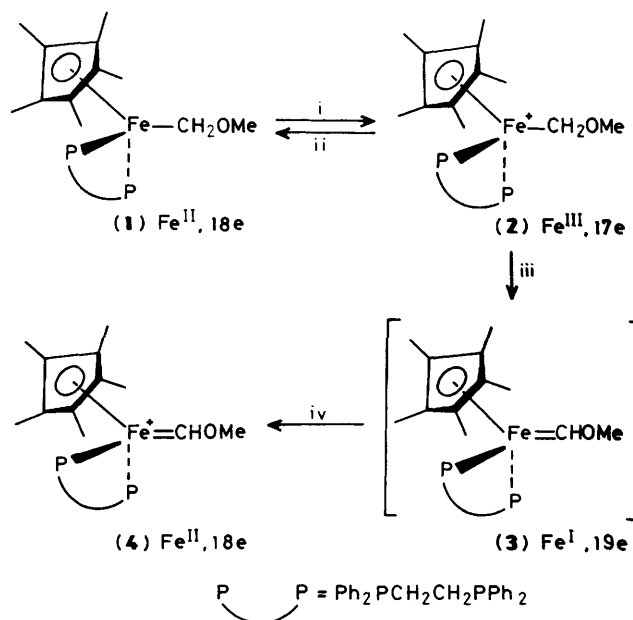
Scheme 1. *Reagents and conditions.* i, 1 equiv. Ph$_3$C$^+$PF$_6^-$ {or 1 equiv. [Fe(C$_5$H$_5$)$_2$]$^+$PF$_6^-$}, CH$_2$Cl$_2$, 30 min, 20 °C; ii, 1 equiv. K, expressed to 20 kHz ultrasonic irradiation,[10c] THF/toluene (20/80), 10 min, 20 °C; iii, 1 equiv. Bu^{t}OK, THF, 1 h, −80 °C; iv, 1 equiv. [Fe(C$_5$H$_5$)$_2$]$^+$PF$_6^-$ or (2), 0 °C.

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† *Selected spectroscopic data* for (1): Fe(Cp*)(η^2-dppe)(CH$_2$OMe) ^{1}H n.m.r. (C$_6$D$_6$, Me$_4$Si) δ 7.68—7.11 (m, 20 H, Ph), 3.82 (t, 2H, CH_2OMe, $^3J_{PH}$ 4.3 Hz), 2.49 (s, 3H, OMe), 1.48 [m, 4H, Ph$_2$P-(CH_2)$_2$PPh$_2$], 1.38 (s, 15H, C$_5$Me$_5$); ^{13}C {^{1}H} n.m.r. (C$_6$D$_6$, Me$_4$Si) δ 145—130 (m, Ph), 85.9 (s, C$_5$Me$_5$), 79.4 (t, CH_2OMe, $^2J_{PC}$ 25.3 Hz), 62.9 (OMe), 31.6 [t, Ph$_2$P(CH_2)$_2$PPh$_2$, J_{PC} 21 Hz], 10.2 (C$_5$Me$_5$); ^{31}P{^{1}H} n.m.r. (C$_6$D$_6$, H$_3$PO$_4$ 85%) δ 112.2 p.p.m. (Ph$_2$P(CH_2)$_2$PPh$_2$).

For (2): [Fe(cp*)(η^2-dppe)(CH$_2$OMe)]$^+$PF$_6^-$ Mössbauer doublet (77 K). Isomer shift vs. Fe = 0.35 mm s^{-1}, quadrupole splitting = 0.95 mm s^{-1}; e.s.r. (133 K) g = 2.48, 2.03.

For (4): [Fe(Cp*)(η^2-dppe)(CHOCH$_3$)]$^+$PF$_6^-$ ^{1}H n.m.r. (CD$_2$Cl$_2$, Me$_4$Si) δ 12.31 (t, 1H, CHOMe, $^3J_{PH}$ 3 Hz), 7.58—7.11 (m, 20H, Ph), 3.23 (s, 3H, OMe), 1.41 (s, 15H, C$_5$Me$_5$), 1.35 (m, 4H, Ph$_2$P(CH_2)$_2$PPh$_2$); ^{13}C n.m.r. (CD$_2$Cl$_2$, Me$_4$Si) δ 306.2 (dt, CHOMe, $^1J_{CH}$ 142 Hz, $^2J_{PC}$ 57 Hz), 134—129 (m, Ph), 97.6 (s, C$_5$Me$_5$), 68.5 (q, OMe, $^1J_{CH}$ 145 Hz), 31.5 (tt, Ph$_2$P(CH_2)$_2$PPh$_2$, $^1J_{CH}$ 157 Hz, J_{PC} 21.5 Hz), 9.9 (C$_5$Me$_5$, $^1J_{CH}$ 127 Hz); {^{1}H} (CD$_2$Cl$_2$, H$_3$PO$_4$ 85%) δ 106.4 (Ph$_2$P(CH_2)$_2$PPh$_2$), −143.4(PF$_6$, $^1J_{PF}$ 711 Hz).

Satisfactory elemental analyses were obtained for (1), (2), and (4).

‡ *Crystal data* for (2): C$_{38}$H$_{44}$F$_6$FeOP$_3$, M = 779.5, monoclinic, $P2_1/n$, a = 12.633(4), b = 18.780(7), c = 16.378(7) Å, β = 102.17(3), U = 3707.7(6) Å^3, D_c = 1.40 g cm^{-3}, Z = 4, $F(000)$ = 1812, (Mo-K_α) = 0.71073 Å, μ(Mo-K_α) = 5.9 cm^{-1}, scan type $\omega/2\theta$ ($2\theta_{max}$ = 50°, t_{max} = 60 s), 3334 independent observed data [$I > 2\sigma(I)$] were collected at 296 K on a Enraf–Nonius diffractometer. The structure was solved by direct methods and Fourier techniques, and refined by full-matrix least squares to R = 0.043, R_w = 0.040. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Figure 1. Molecular structure of [Fe(Cp*)(η^2-dppe)(CH$_2$OMe)]$^+$PF$_6^-$ (2). Important bond lengths (Å), angles (°), and torsion angles (°): Fe–C(') 1.803(4), Fe–C(38) 2.003(4), Fe–P(1) 2.290(1), Fe–P(2) 2.256(1), C(38)–H(38A) 0.99(5), C(38)–H(38B) 0.86(4); P(1)–Fe–P(2) 85.23(5), H(38A)–C(38)–H(38B) 111(3). Fe–C(38)–O 115.9(3), C(31)–C(30)–C'–Fe 90.3(2), C'–Fe–C(38)–O 174.4(3) C'–Fe–C(38)–H(38B) 66(3), P(1)–Fe–C(38)–H(38B) 73(3), P(1)–Fe–C(38)–O 46.5(3), P(2)Fe–C(38)–O 38.6(3), P(2)–Fe–C(38)–H(38A) 86(2), H(38A)–C(38)–Fe–C' 50(3). C' = C$_5$ centroid.

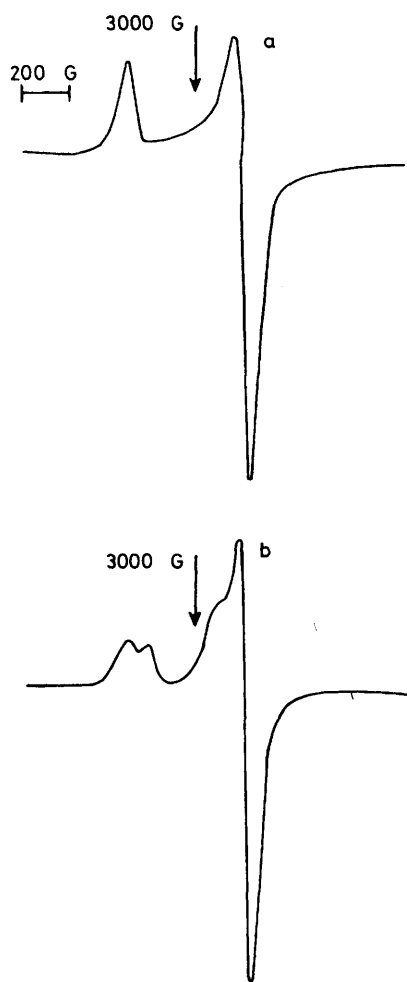**Figure 2.** X-band (9.216 GHz) e.s.r. spectrum at 133 K in THF; (a) $[Fe(Cp^*)(\eta^2\text{-dppe})(CH_2OMe)]^+PF_6^-$ (2) as pure sample ($g = 2.48$, 2.03); (b) (2) and 1 equiv. Bu^tOK immediately quenched at 77 K to allow the observation of (2) and (3) ($g = 2.40$, 2.08).

consistent with previous observation for monomeric iron(III) and iron (I).[3,12]

Hydride abstraction through a two one-electron transfer, deprotonation mechanism is well known in biological reactions and especially those involving dinucleotide co-factors.[13] Knox has used a similar route for activation of a μ-alkylidene ligand[14] in binuclear complexes. We have shown that an iron secondary heterocarbene complex may be rapidly and cleanly synthesized *via* a three-step hydride abstraction pathway. This new mode of C–H bond activation of metal alkyls, *i.e.*, E.T., proton transfer, and E.T., promises to provide a means of directing the regiochemistry of α-, and β-hydride abstraction.

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The paramagnetic intermediate (3), a formally iron(I) 19-electron species, has been characterized by e.s.r. spectroscopy (Figure 2). An e.s.r. sample is obtained by adding Bu^tOK to a THF solution of (2) at $-100\,^{\circ}C$ in an e.s.r. 2 mm quartz tube before quenching the reaction at 77 K. The e.s.r. spectrum of the reaction medium, at 133 K, displays two signals close to $g = 2$ corresponding to the paramagnetic methoxymethyl compound (2) and two other signals of almost the same intensities attributed to (3). These values are

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