

α -Hydride Abstraction *via* a Three-Step Pathway: Access to the Electron Rich Iron Methoxycarbene Complex $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(P,P'\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)(=\text{CHOMe})]^+\text{PF}_6^-$

Christophe Roger,^a Loïc Toupet,^b and Claude Lapinte^{a*}

^a Laboratoire de chimie des organométalliques, UA CNRS 415, Université de Rennes I, campus de Beaulieu, 35042 Rennes cedex, France

^b Laboratoire de Physique cristalline, UA CNRS 804, Université de Rennes I, campus de Beaulieu, 35042 Rennes cedex, France

The rare iron methoxycarbene $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(P,P'\text{-Ph}_2\text{PCH}_2\text{CH}_2)(=\text{CHOMe})]^+\text{PF}_6^-$ (**4**) is cleanly synthesised by a three-step α -hydride abstraction; the first paramagnetic iron(III) species, $\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(P,P'\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)(\text{CH}_2\text{OMe})]^+\text{PF}_6^-$ (**2**), is characterised by single crystal X-ray diffraction and the second intermediate, $\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(P,P'\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)(=\text{CHOMe})$ (**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 stoichiometric reactions.

It has been demonstrated that C–H bond activation from the transition metal alkyl $\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{Me})\text{CH}_2\text{R}$, 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 $\text{Fe}(\text{Cp}^*)(\text{CO})_2(\text{CH}_2\text{OH})(\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5)$ by $\text{Ph}_3\text{C}^+\text{PF}_6^-$.^{3,4} Further experiments suggest that available mechanistic data on other Ph_3C^+ /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 $\text{Fe}(\text{Cp}^*)(\eta^2\text{-dppe})\text{CH}_2\text{OMe}$ (**1**) ($\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$)† as the starting material.^{9–10} The cyclic voltammogram (CH_2Cl_2 , $\text{Bu}^n\text{N}^+\text{PF}_6^-$, 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 $\text{Fe}(\text{Cp}^*)(\eta^2\text{-dppe})\text{X}$.^{10c,d}

Red complex (**1**) reacts cleanly at 20 °C with $\text{Ph}_3\text{C}^+\text{PF}_6^-$ in methylene chloride affording the air stable iron(III) methoxymethyl cation $[\text{Fe}(\text{Cp}^*)(\eta^2\text{-dppe})(\text{CH}_2\text{OMe})]^+\text{PF}_6^-$ (**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 $-\text{CH}_2-$ and $\text{MeO}-$ 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_5Me_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 $\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)\text{CH}_2\text{R}$ series.¹¹

Since the redox potential of the reversible system (**1**) \rightleftharpoons (**2**) is 0.75 V more negative than that of $\text{Ph}_3\text{C}^+ \rightleftharpoons \text{Ph}_3\text{C}^\cdot$ (+ 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_3C^+ according to an E.T. mechanism, $\text{Ph}_3\text{C}^\cdot$ is unable to abstract H^\cdot 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 stoichiometric amount of

† Selected spectroscopic data for (**1**): $\text{Fe}(\text{Cp}^*)(\eta^2\text{-dppe})(\text{CH}_2\text{OMe})$ ¹H n.m.r. (C_6D_6 , Me_4Si) δ 7.68–7.11 (m, 20 H, Ph), 3.82 (t, 2H, CH_2OMe , $^3J_{\text{PH}}$ 4.3 Hz), 2.49 (s, 3H, OMe), 1.48 [m, 4H, $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$], 1.38 (s, 15H, C_5Me_5); ¹³C {¹H} n.m.r. (C_6D_6 , Me_4Si) δ 145–130 (m, Ph), 85.9 (s, C_5Me_5), 79.4 (t, CH_2OMe , $^2J_{\text{PC}}$ 25.3 Hz), 62.9 (OMe), 31.6 [t, $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$, J_{PC} 21 Hz], 10.2 (C_5Me_5); ³¹P {¹H} n.m.r. (C_6D_6 , H_3PO_4 85%) δ 112.2 p.p.m. ($\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$).

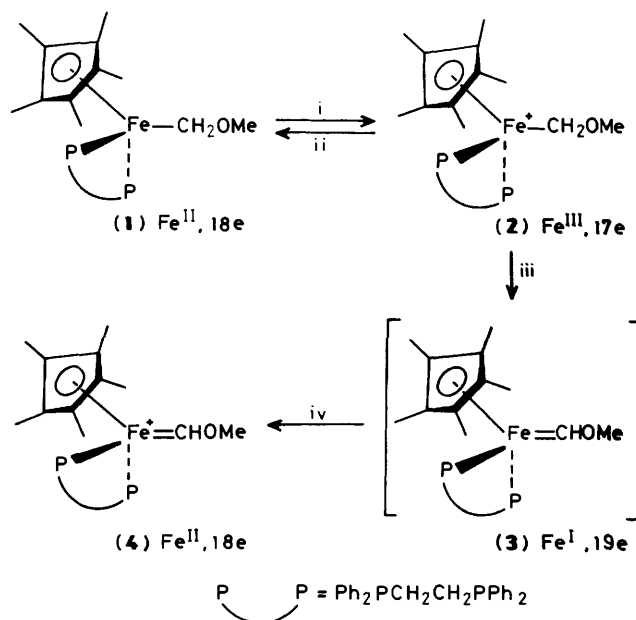
For (**2**): $[\text{Fe}(\text{Cp}^*)(\eta^2\text{-dppe})(\text{CH}_2\text{OMe})]^+\text{PF}_6^-$ Mössbauer doublet (77 K). Isomer shift vs. Fe = 0.35 mm s⁻¹, quadrupole splitting = 0.95 mm s⁻¹; e.s.r. (133 K) $g = 2.48, 2.03$.

For (**4**): $[\text{Fe}(\text{Cp}^*)(\eta^2\text{-dppe})(\text{CHOCH}_3)]^+\text{PF}_6^-$ ¹H n.m.r. (CD_2Cl_2 , Me_4Si) δ 12.31 (t, 1H, CHOMe , $^3J_{\text{PH}}$ 3 Hz), 7.58–7.11 (m, 20H, Ph), 3.23 (s, 3H, OMe), 1.41 (s, 15H, C_5Me_5), 1.35 (m, 4H, $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$); ¹³C n.m.r. (CD_2Cl_2 , Me_4Si) δ 306.2 (dt, CHOMe , $^1J_{\text{CH}}$ 142 Hz, $^2J_{\text{PC}}$ 57 Hz), 134–129 (m, Ph), 97.6 (s, C_5Me_5), 68.5 (q, OMe, $^1J_{\text{CH}}$ 145 Hz, 31.5 (tt, $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$, $^1J_{\text{CH}}$ 157 Hz, J_{PC} 21.5 Hz), 9.9 (C_5Me_5 , $^1J_{\text{CH}}$ 127 Hz); {¹H} (CD_2Cl_2 , H_3PO_4 85%) δ 106.4 ($\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$), -143.4 (PF_6^- , $^1J_{\text{PF}}$ 711 Hz).

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

‡ Crystal data for (**2**): $\text{C}_{38}\text{H}_{44}\text{F}_6\text{FeO}_3$, $M = 779.5$, monoclinic, $P2_1/n$, $a = 12.633(4)$, $b = 18.780(7)$, $c = 16.378(7)$ Å, $\beta = 102.17(3)$, $U = 3707.7(6)$ Å³, $D_c = 1.40$ g cm⁻³, $Z = 4$, $F(000) = 1812$, (Mo- K_α) = 0.71073 Å, $\mu(\text{Mo-}K_\alpha) = 5.9$ cm⁻¹, scan type $\omega/2\theta$ ($2\theta_{\text{max}} = 50^\circ$, $t_{\text{max}} = 60$ s), 3334 independent observed data [$I > 2\sigma(I)$] were collected at 296 K on an 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.

Bu^tOK in tetrahydrofuran (THF) at -80 °C affording the new secondary methoxycarbene $[\text{Fe}(\text{Cp}^*)(\eta^2\text{-dppe})(=\text{CHOMe})]^+\text{PF}_6^-$ (**4**)† (45% yield) in addition to an equivalent amount of (**1**) and Bu^tOH . 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 $\text{Fe}(\text{Cp}^*)(\eta^2\text{-dppe})(=\text{CHOMe})$ (**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 stoichiometric amount of ferricinium as an oxidizing agent. Under these conditions, (**4**) is recovered with 92% yield (100% yield of Bu^tOH by g.c.).



Scheme 1. Reagents and conditions. i, 1 equiv. $\text{Ph}_3\text{C}^+\text{PF}_6^-$ {or 1 equiv. $[\text{Fe}(\text{C}_5\text{H}_5)_2]^+\text{PF}_6^-$ }, CH_2Cl_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^tOK , THF, 1 h, -80 °C; iv, 1 equiv. $[\text{Fe}(\text{C}_5\text{H}_5)_2]^+\text{PF}_6^-$ or (**2**), 0 °C.

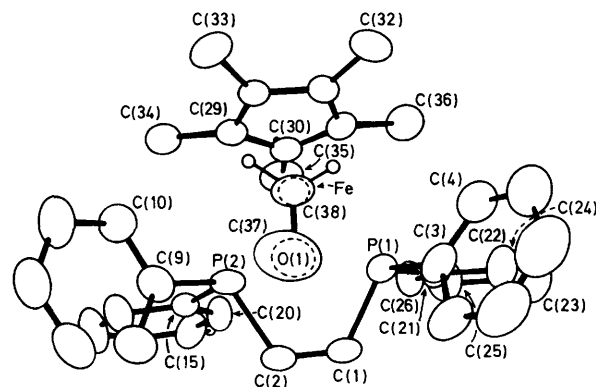


Figure 1. Molecular structure of $[\text{Fe}(\text{Cp}^*)(\eta^2\text{-dppe})(\text{CH}_2\text{OMe})]^+\text{PF}_6^-$ (**2**). Important bond lengths (Å), angles (°), and torsion angles (°): $\text{Fe}-\text{C}'$ 1.803(4), $\text{Fe}-\text{C}(38)$ 2.003(4), $\text{Fe}-\text{P}(1)$ 2.290(1), $\text{Fe}-\text{P}(2)$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

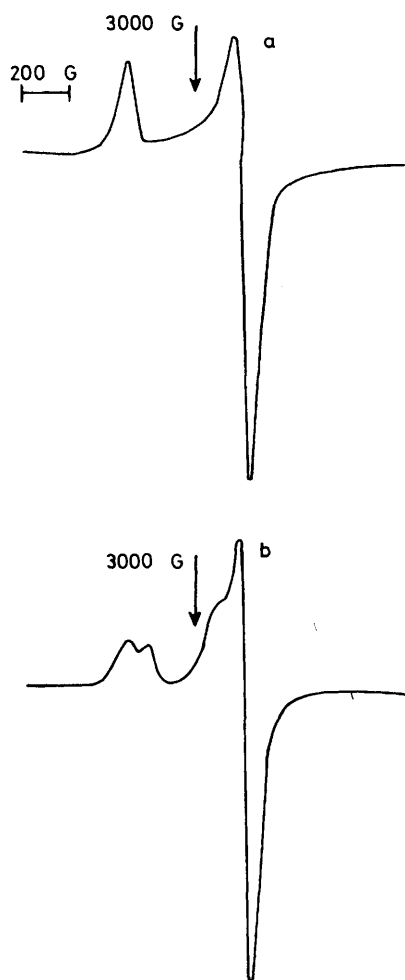


Figure 2. X-band (9.216 GHz) e.s.r. spectrum at 133 K in THF; (a) $[\text{Fe}(\text{Cp}^*)(\eta^2\text{-dppe})(\text{CH}_2\text{OMe})]^+\text{PF}_6^-$ (**2**) as pure sample ($g = 2.48, 2.03$); (b) (**2**) and 1 equiv. Bu^tOK immediately quenched at 77 K to allow the observation of (**2**) and (**3**) ($g = 2.40, 2.08$).

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°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

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 ligand¹⁴ 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.

We thank Profs. J. E. Guerschais (Brest) and F. Varret (Le Mans) for e.s.r. and Mössbauer facilities, Laboratoires Standa (Caen) for financial support to C. R., and Drs. J. R. Hamon, V. Guerschais, and S. Sinbandhit for helpful discussions.

Received, 22nd January 1988; Com. 8/00221E

References

- (a) J. W. Parshall, 'Homogeneous Catalysis,' Wiley, New York, 1980, p. 16, 39–41, 85–90, 172–173; (b) R. J. Kazlauskas and M. S. Wrighton, *J. Am. Chem. Soc.*, 1982, **104**, 6005; (c) H. W. Turner and R. R. Schrock, *ibid.*, 1982, **104**, 2331.
- (a) J. C. Hayes and N. J. Cooper, *J. Am. Chem. Soc.*, 1982, **104**, 5570; (b) P. Jernakoff and N. J. Cooper, *ibid.*, 1984, **106**, 3026.
- V. Guerschais and C. Lapinte, *J. Chem. Soc., Chem. Commun.*, 1986, 663.
- (a) V. Guerschais and C. Lapinte, *J. Chem. Soc., Chem. Commun.*, 1986, 894; (b) V. Guerschais, Thesis, Rennes 1987; (c) V. Guerschais, C. Lapinte, J. Y. Thépot, and L. Toupet, *Organometallics*, 1988, **7**, in the press.
- S. J. Hannon and T. G. Traylor, *J. Org. Chem.*, 1981, **46**, 3645.
- R. S. Bly, R. K. Bly, M. M. Hossain, G. B. Silverman, and E. Wallace, *Tetrahedron*, 1986, **42**, 1093.
- G. S. Bodner, J. A. Gladysz, M. F. Nielsen, and V. D. Parker, *J. Am. Chem. Soc.*, 1987, **109**, 1757.
- (a) D. Mandon, L. Toupet, and D. Astruc, *J. Am. Chem. Soc.*, 1986, **108**, 1320; (b) D. Mandon, Thesis, Rennes, 1985.
- C. Roger and C. Lapinte, manuscript in preparation. Other $\text{FeCp}^*(\eta^2\text{-dppe})\text{X}$ has been very recently reported.¹⁰
- (a) M. L. H. Green and L. L. Wong, *J. Chem. Soc., Dalton Trans.*, 1987, 411; (b) R. G. Bray, J. E. Bercaw, H. B. Gray, M. D. Hopkins, and R. A. Paciello, *Organometallics*, 1987, **6**, 922; (c) C. Roger, P. Marseille, C. Salus, J. R. Hamon, and C. Lapinte, *J. Organomet. Chem.*, 1987, **336**, C13; (d) J. Morrow, D. Catheline, M. H. Desbois, J. M. Manriquez, J. Ruiz, and D. Astruc, *Organometallics*, 1987, **6**, 2605.
- S. G. Davies, I. M. Dordor-Hedgecock, K. H. Sutton, and M. Whittaker, *J. Am. Chem. Soc.*, 1987, **109**, 5711.
- C. Lapinte, D. Catheline, and D. Astruc, *Organometallics*, 1984, **3**, 817.
- A. L. Lehninger, 'Biochimie,' Flammarion, Paris, 1973.
- N. G. Connelly, N. J. Forrow, B. P. Gracey, S. A. R. Knox, and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1985, 14.