Synthesis and Characterization of a Stable Iron–Methylene Complex; Methylene Activation by Electron Transfer Catalysis (ETC)

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The first stable iron–methylene complex $[Fe(C_5Me_5)(dppe)(=CH_2)]^+BF_4^-$ ($\mathbf{2}^+$) (dppe = P,P'-$Ph_2PCH_2CH_2PPh_2$) has been isolated and fully characterized; the methylene ligand has been activated by electron transfer catalysis (ETC) to initiate a ligand exchange reaction with acetonitrile, or the cyclopropanation of styrene with a coulombic efficiency of 100.

Since Schrock's report[1] of the successful isolation of $(C_5H_5)_2TaCH_3(CH_2)$, a rich chemistry of metal–methylene complexes has evolved. Unsubstituted methylene complexes have been studied by several groups, but such stable compounds are still rare.[2] These species have been attributed a key role in a wide variety of catalytic processes such as alkene metathesis and Fischer–Tropsch syntheses or stoicheiometric reactions such as the cyclopropanation of alkenes.[3] The patterns of reactivity involve either electrophilic or nucleophilic properties of the carbene ligands, but their role in electron transfer (ET) reactions has not been established. However, there is great interest in transition metal derivatives because of their conceptual relationship to catalytically active metal surfaces and the related ET processes.[4] We report here (i) the synthesis, isolation, and full characterization of $[Fe(C_5Me_5)(dppe)(=CH_2)]^+BF_4^-$ ($\mathbf{2}^+$) (dppe = P,P'-$Ph_2PCH_2CH_2PPh_2$), which represents to date the only first row transition metal methylene complex to be thermally stable and isolable, and its redox chemistry, together with (ii) the cyclic voltammetry, and (iii) the electron transfer catalysis (ETC) of methylene ligand substitution and cyclopropane formation.

Treatment of $Fe(C_5Me_5)(dppe)(CH_2OMe)$ ($\mathbf{1}$)[5] with HBF_4-OEt_2 at −90 °C in anhydrous diethyl ether resulted in the formation of a light brown precipitate, identified after crystallization from CH_2Cl_2/OEt_2 as the iron methylene complex $[Fe(C_5Me_5)(dppe)(=CH_2)]^+BF_4^-$ ($\mathbf{2}^+$) (Scheme 1). Compound ($\mathbf{2}^+$), isolated in 95% yield, is a thermally- and air-stable solid which decomposes at 160 °C without melting. Slightly soluble in tetrahydrofuran (THF), it dissolves readily in acetonitrile and methylene chloride. Crystallization from the latter affords red–brown microcrystals containing solvent molecules, as shown by spectroscopic data and analysis.† The ^1H n.m.r. spectrum of ($\mathbf{2}^+$) (CD_2Cl_2, 20 °C) at 300 MHz exhibits a characteristic low field methylene proton signal, δ 14.86 (t, $^3J_{PH}$ 7 Hz), and the proton-coupled ^{13}C n.m.r. spectrum (CD_2Cl_2, 20 °C) confirms the proposed structure; the resonance due to the carbene carbon atom appears as a downfield triplet of triplets at δ 311.8 ($^1J_{CH}$ 150 Hz; $^2J_{CP}$ 24 Hz). Variable temperature ^1H n.m.r. experiments reveal typical metal–methylene behaviour for ($\mathbf{2}^+$): the low field triplet broadens below 10 °C, coalesces at −28 °C, and at −80 °C exhibits two resonances at δ 13.85 (t, H_b, J_{PH} 13 Hz) and 15.88 (t, H_a, J_{PH} 1 Hz) corresponding to the two magnetically nonequivalent methylene hydrogen atoms. This reversible behaviour corresponds to a free energy of activation, $\Delta G^‡$, for the iron–carbon bond rotation of 10.7 ± 0.2 kcal mol^{-1} (44.7 ± 0.8 kJ mol^{-1}).[6]

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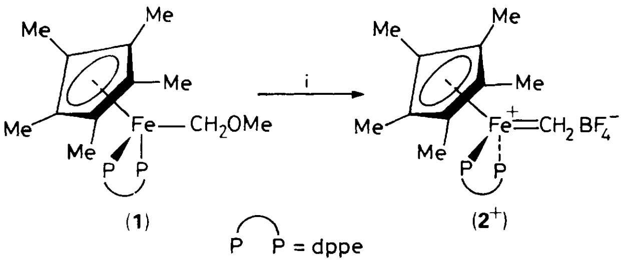
† *Selected spectroscopic data* for $[Fe(C_5Me_5)(dppe)(=CH_2)]^+BF_4^-$ ($\mathbf{2}^+$): satisfactory elemental analyses were obtained; ^1H n.m.r. (CD_2Cl_2, −80 °C) δ 1.15 (s, 15H, C_5Me_5), 2.10 (m, 4H, CH_2PPh_2), 7.30 (m, 20H, Ph), 13.85 (t, 1H, H_a, $^3J_{PH}$ 13 Hz), 15.58 (t, 1H, H_b, $^3J_{PH}$ 1 Hz); ^{13}C n.m.r. (CD_2Cl_2, 25 °C) δ 9.9 (q, C_5Me_5, $^1J_{CH}$ 126 Hz), 32.04 (tt, CH_2PPh_2, $^1J_{CH}$ 125 Hz, J_{PC} 21 Hz), 102.7 (s, C_5Me_5), 133.0 (m, Ph), 311.8 (tt, $Fe{=}CH_2$, $^1J_{CH}$ 150 Hz, $^2J_{PC}$ 24 Hz); ^{31}P n.m.r. (CD_2Cl_2, 25 °C) δ 93.3 p.p.m.



Scheme 1. *Reagents and conditions*: i, HBF_4–OEt_2 (1 equiv.), 3 h, −80 °C, 95% yield.

The stability of the methylene complex (**2**⁺) is in marked contrast with all its first and second row transition metal analogues, which disproportionate or decompose below room temperature.[2] This important increase in thermal stability is associated with an absence of electrophilic reactivity. Thus, the methylene compound (**2**⁺) neither reacts with alkenes (*i.e.*, ethene or styrene) to form cyclopropanes, nor affords adducts with nitrogen (pyridine) or phosphorus (trimethyl- or triphenyl-phosphine) nucleophiles as would be expected for an electrophilic methylene ligand. It is also reluctant to undergo acetonitrile ligand exchange below 30 °C and refluxing for 3 h in acetonitrile is needed for (**2**⁺) to be quantitatively transformed to $[Fe(C_5Me_5)(dppe)(MeCN)]^+ BF_4^-$ (**3**⁺).[7]

The cyclic voltammogram (CV) of (**2**⁺) (20 °C, CH_2Cl_2, 0.100 V/s) exhibits a cathodic peak potential associated with an anodic wave [$E°$ −0.170 V *vs.* standard calomel electrode (SCE)] [$E°$ for $(C_5H_5)_2Fe/(C_5H_5)_2Fe^+$ = 0.470 V *vs.* SCE] with a current peak ratio $i_p^a/i_p^c = 1$, as expected for a reversible Fe^{II}/Fe^{I} system (Figure 1a). However, the reduction of (**2**⁺) in CH_2Cl_2 with a stoicheiometric amount of a chemical reducing reagent (*i.e.* cobaltocene, $E°$ = −0.80 V *vs.* SCE) or (**1**) (E° = −0.58 V *vs.* SCE) affords after abstraction of a chlorine atom from the solvent, the chloro-organoiron $Fe(C_5Me_5)(dppe)Cl$ (**4**) in less than 1 min. The chloro complex (**4**), isolated in 85% yield, was identified by comparison with an authentic sample.[8] A similar reaction performed in the presence of 1 equivalent of phenylstyrene affords phenylcyclopropane (85% yield by g.c.). Moreover, a CH_2Cl_2 solution of derivative (**4**) reacts with 1 equivalent of MeCN affording instantly the known organometallic compound (**3**⁺), isolated in 90% yield (Scheme 2).

The CV of (**2**⁺) performed in CH_2Cl_2 with acetonitrile (5 equiv.) showed the lability of the methylene ligand in (**2**) (Figure 1b). The methylene substitution was carried out conveniently by inserting a set of platinum electrodes into the CH_2Cl_2 solution of (**2**⁺) and applying a negative potential (−0.6 V *vs.* SCE). Ligand exchange was complete within 2 min at 20 °C on a 1 mmol scale in the presence of acetonitrile (1 equiv.). The completion of the reaction was indicated by an abrupt diminution of the cathodic current and confirmed by CV (Figure 1c); compound (**3**⁺) was isolated in 90% yield. The electrocatalytic nature of the reaction was established from the measurement of the amount of current passed through the solution. A turnover number (coulombic efficiency) of 100 equivalents of (**3**⁺) per electron was observed. The wave corresponding to the cathodic substitution product oxidation (**3**/**3**⁺) was not detected, the complex (**3**) being a 19-electron, very labile radical which very quickly reduces (**2**⁺), to complete the cycle of the ETC process (equation 1).‡

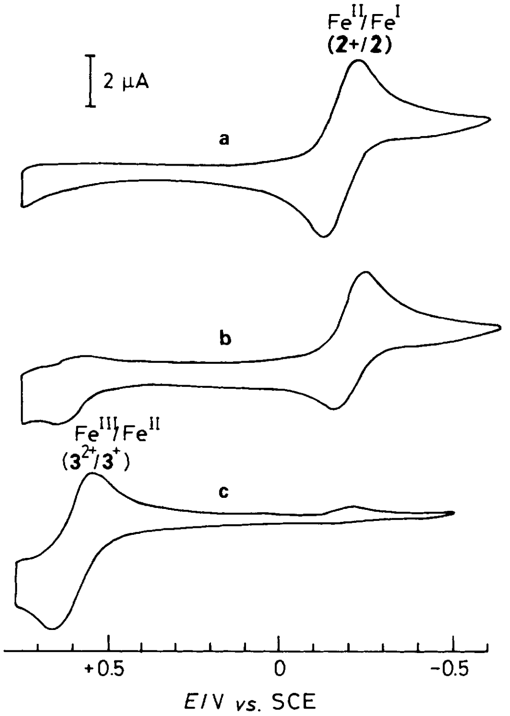
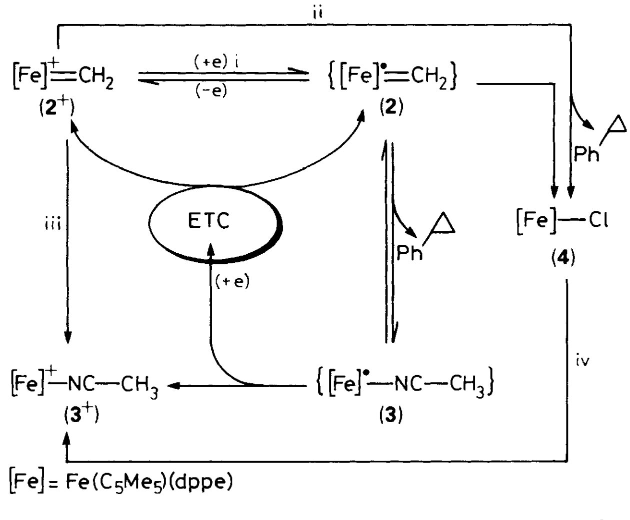


Figure 1. Cyclic voltammogram of (**2**⁺) in dichloromethane containing 0.1 M $Bu^n{}_4NPF_6$, at platinum electrode *vs.* SCE, scan rate 0.200 V/s. (a), Pure (**2**⁺); (b), (**2**⁺) and 5 equiv. of MeCN; (c), (**2**⁺) reduced with 0.01 Faraday/mol in the presence of 1 equiv. of MeCN or (**2**⁺) reduced over powdered iron in MeCN; an authentic sample of (**3**⁺)[7] exhibits a cyclic voltammogram identical to (c).



Scheme 2. *Reagents and conditions*: i, 0.01 Faraday/mol, CH_2Cl_2, 0.1 M $Bu^n{}_4NPF_6$, MeCN (1 equiv.), styrene (1 equiv.), 20 °C, 10 min; ii, 1 equiv. of (**1**) or cobaltocene, styrene (1 equiv.), CH_2Cl_2, 20 °C, 1 min; iii, MeCN, 3 h, 82 °C; iv, 1 equiv. of MeCN, CH_2Cl_2, 20 °C, 1 min.

The methylene fragment being a poor electron releasing ligand, the reaction product (**3**⁺) is a more electron rich complex than the starting compound (**2**⁺). This means that the cross electron transfer propagation step (equation 1) is an exergonic favoured process.

$$(\mathbf{3}) + (\mathbf{2}^+) \rightarrow (\mathbf{3}^+) + (\mathbf{2}) \qquad (1)$$

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‡ Methylene exchange could be performed in the presence of PMe_3 or CO ligands and the corresponding cations are identified by CV *vs.* the authentic samples prepared as in the literature.[7]

The electrocatalytically induced cyclopropanation reaction of styrene was performed at 20 °C with MeCN (1 equiv.) in less than 1 min by using 10 milliequivalents of current (coulombic efficiency = 100). A redox reagent [*i.e.* cobaltocene or (**1**)] can also be used as initiator. The quantity of the redox reagent needed to obtain the optimum yield was determined by varying the amount of cobaltocene or (**1**) and the coulombic efficiency was found to be 5. In both cases the phenylcyclopropane is quantitatively formed (100% yield by g.c.).

Finally, the stable iron–methylene compound (**2**$^+$) undergoes ETC ligand substitution in less than 1 min at 20 °C, whereas the thermal reaction required 3 h at 82 °C. A second important result comes from the reductive stimulation of the cyclopropanation of styrene. An ET path for the methylene transfer reaction in heterogeneous catalysis (*i.e.* Fischer–Tropsch process) may be significant in so far as ET through a metal surface should be facile. As an illustration of this important concept, we succeeded in carrying out the methylene ligand displacement by acetonitrile (50 °C, 100% yield) in 10 min by using freshly reduced powdered iron with a 10—50 μm particle diameter as a catalyst.

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6 The spectroscopic data of (**2**$^+$) are similar to observations of Brookhart's group for the analogous complex in the C_5H_5 series: the electron donor ability of the methyl substituents of the C_5Me_5 ring induces an upfield shift of the H_a proton (1.77 p.p.m.) and the carbene carbon atom (5.7 p.p.m.), and a weak increase rotation barrier about the Fe–C bond.[2b]

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9 C. Roger, L. Toupet, and C. Lapinte, work in progress.