New Entry to Pentamethylcyclopentadienyl Iron Chemistry and the Methylene Complexes $[(\eta^5\text{-}C_5Me_5)Fe(CO)(L)(CH_2)]^+$ ($L = CO$ or PPh_3)†

Véronique Guerchais[a] **and Didier Astruc**[a,b]

[a] *Laboratoire de Chimie des Organométalliques, UA CNRS 415, Université de Rennes I, Campus de Beaulieu, 35042 Rennes Cedex, France*

[b] *Laboratoire de Chimie Moléculaire des Métaux de Transition, UA CNRS 35, Université de Bordeaux I, 351 Cours de la Libération, 33405 Talence Cedex, France*

$Na[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]$ (**1**), a precursor of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2(CH_2OMe)$ (**2**), is conveniently obtained by Na–Hg reduction of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ overnight (20 °C), complex (**2**) yielding $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(CH_2PPh_3)]BF_4$ (**3**) upon acid treatment in the presence of PPh_3 and converting styrene quantitatively into phenylcyclopropane upon reaction with $Me_3SiOSO_2CF_3$ giving $(\eta^5\text{-}C_5Me_5)Fe(CO)_2(OSO_2CF_3)$ (**4**); photolysis of (**2**) + PPh_3 produces $(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)(CH_2OMe)$ (**5**) which upon acid treatment affords the methylene complex $[(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)(CH_2)]^+$ (**6**).

Access to organometallic anions is important, mainly as a route to metal–carbon bond formation. Whereas $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ has been studied extensively,[1] the permethyl analogue has been little characterized and used.[2,3] The potassium salt[2,3] is known but characterization of the sodium salt has not been published.‡ We report here a convenient route to single *and* double iron–carbon bonds in the pentamethylcyclopentadienyl series starting simply by Na–Hg reduction of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$.§ The stabilizing effect of the permethylation should lead to easier handling of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2$ carbene complexes. Following Pettit's discovery of the transient species $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_2)]^+$,[4,5] a methylene transfer reagent, Brookhart[6] investigated the related complex $[(\eta^5\text{-}C_5H_5)Fe(Ph_2PCH_2CH_2PPh_2)(CH_2)]^+$ and has since reported efficient alkylidene transfer reagents.[7]

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† Part of the 3e cycle thesis of V.G. (University of Rennes, July 1984).

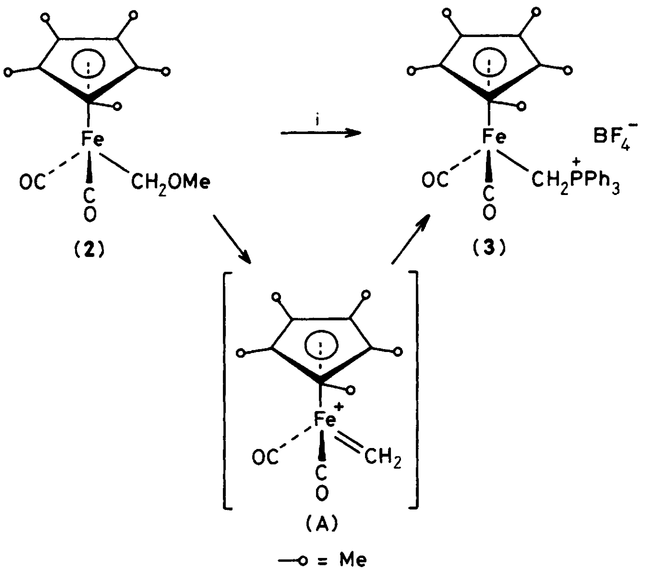
‡The sodium salt was briefly mentioned in a footnote, but characterization or details were not given: L. D. Hutchins, E. N. Duesler, and R. T. Paine, *Organometallics*, 1982, **1**, 1254 (ref. 13).

§It was first believed that Na–Hg does not reduce this dimer under ambient conditions and later that the reaction gives $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2Hg$.[3]

The present report is the first study of complexes with an iron–carbon double bond using C_5Me_5 as an ancillary ligand.

$Na^+[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]^-$
(1)

The anionic complex (**1**) is easily synthesized in quantitative crude yields by Na–Hg reduction of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ in tetrahydrofuran (THF) overnight at room temperature (the solution turns orange, as observed for the C_5H_5 series). This reaction is a more convenient route than the well known methods using an Na–K alloy[2] or a K mirror.[3] Complex (**1**), the precursor of (**2**)[3b] (75%), was isolated as a pyrophoric yellow powder (ν_{CO} 1870 and 1805 cm^{-1}). Photolysis of (**2**) in the presence of 1 equiv. of PPh_3 gave the new, air-sensitive, red complex (**5**).¶ The yield (50%) was optimized using i.r. monitoring in order to avoid decomposition of (**5**). The ^1H n.m.r. spectrum (C_6D_6) exhibits a multiplet (8 lines) at δ 3.87 assigned to the diastereotopic methylene fragment.



Scheme 1. *Reagents:* i, PPh_3, $HBF_4\text{–}OEt_2$, CH_2Cl_2, −90 °C.

$(\eta^5\text{-}C_5Me_5)Fe(CO)_2(OSO_2CF_3)$
(4)

$(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)(CH_2OMe)$
(5)

The methylene complex (A) may be generated from the ether precursor (**2**) by acid treatment or using $Me_3SiOSO_2CF_3$, as for the C_5H_5 analogue but attempts to record its ^1H n.m.r. spectrum failed as for the C_5H_5 compound.[8] However, this transient species was trapped with PPh_3, producing the new phosphonium salt (**3**)¶ (Scheme 1); this illustrates the electrophilic character of the methylene ligand. The methylene protons of (**3**) appear as a doublet at δ 1.60 ($^2J_{P\text{-}H}$ 14 Hz). The reactivity of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_2)]^-$ itself towards PPh_3 has not been reported.

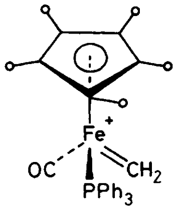
When this protonation ($HBF_4\text{–}OEt_2$) was carried out at −90 °C, and the mixture then allowed to warm to room temperature, neither ethylene nor $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(C_2H_4)]^+$ was detected, in contrast to the C_5H_5 analogue. Instead, CH_4 was formed, identified by mass spectroscopy, and the complexes $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(X)]^+$ (X = CO, OEt_2) and $(\eta\text{-}C_5Me_5)Fe(CO)_2Me$ were isolated. Given the presence of the methyl derivative, CH_4 must be produced by reductive elimination from the Fe^{IV} cationic methyl hydride $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(CH_3)(H)]^+$.

The methylene complex (A), as for the analogous C_5H_5 alkylidene cations,[7] reacted with styrene at −90 °C to form phenylcyclopropane in 100% yield (g.l.c.). In the presence of $Me_3SiOSO_2CF_3$, in CH_2Cl_2, the reaction of (**2**) with styrene afforded phenylcyclopropane and the new complex (**4**)¶ in 70% yield as red needles after crystallization from toluene–pentane. The ^{13}C absorption (CD_2Cl_2) for the CF_3 fragment in (**4**) appears as a quartet at δ 119.3.

Treatment of a CD_2Cl_2 solution of complex (**5**) at −90 °C with 1—2 equiv. of either CF_3CO_2H or $Me_3SiOSO_2CF_3$ in an n.m.r. tube gave the cationic methylene complex (**6**).¶

Its ^1H n.m.r. spectrum at −85 °C exhibits two low field broad signals at δ 16.67 and 15.10 for the non-equivalent methylene protons. The low-field ^{13}C resonance of the carbene carbon is located at δ 351.2 (doublet), an unambiguous characteristic of the methylene structure. Variable-temperature ^1H n.m.r. experiments showed coalescence of the methylene signals at −45 °C (80 MHz). A single broad signal at δ 15.95 was observed reversibly up to −10 °C. The free energy of activation ΔG^* for the Fe–C bond rotation calculated from these measurements is 44.35 kJ mol^{-1}. These results are consistent with the data published by Brookhart for the related compound $[(\eta^5\text{-}C_5H_5)Fe(Ph_2PCH_2CH_2PPh_2)(CH_2)]^+$.[6]

The electrophilic character of the methylene fragment decreases when backbonding of the metal increases upon permethylation of the C_5H_5 ring or upon substitution of CO by a phosphine ligand. The clean and convenient reaction sequence $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2 \rightarrow (\mathbf{1}) \rightarrow (\mathbf{2}) \rightarrow (\mathbf{3})$ makes (**2**)



(6)

¶ Satisfactory elemental analyses were obtained for (**4**) and (**5**). Spectroscopic data: (**5**), ^1H n.m.r. (C_6D_6, Me_4Si) δ 7.75—7.05 (2 × m, 15H, PPh_3), 4.06—3.74 (ABq, 2H, CH_2), 3.05 (s, 3H, OMe), and 1.52 (s, 15H, C_5Me_5); ^{13}C n.m.r. (C_6D_6, Me_4Si) δ 223.9 (CO, d, $^2J_{P\text{-}C}$ 28.1 Hz), 137.1 (C_{ipso}Ph, d, $^1J_{P\text{-}C}$ 36.6 Hz), 134.7 (C_{ortho}Ph, d, $^2J_{P\text{-}C}$ 9.8 Hz), 129.1 (C_{para}Ph, d, $^4J_{P\text{-}C}$ 7.3 Hz), 127.9 (C_{meta}Ph, d, $^3J_{P\text{-}C}$ 9.8 Hz), 92.8 (C_5Me_5), 73.9 (CH_2, d, $^2J_{P\text{-}C}$ 20.7 Hz), 63.5 (OMe), and 9.6 ($C_5\mathit{Me}_5$); i.r. (pentane) 1900s (ν_{CO}) and 1060s ($\nu_{C\text{-}O}$) cm^{-1}. (**3**), ^1H n.m.r. (CD_3COCD_3, Me_4Si) δ 7.80 (m, 15H, PPh_3), 1.87 (s, 15H, C_5Me_5), and 1.60 (d, 2H, CH_2, $^2J_{P\text{-}H}$ 14 Hz); ^{13}C n.m.r. (CD_3CN, Me_4Si) δ 217.4 (CO, d, $^3J_{P\text{-}C}$ 2.9 Hz), 134.7 (C_{para}Ph, d, $^4J_{P\text{-}C}$ 2.9 Hz), 134.1 (C_{ortho}Ph, d, $^2J_{P\text{-}C}$ 10.3 Hz), 130.6 (C_{meta}Ph, d, $^3J_{P\text{-}C}$ 11.7 Hz), 125.5 (C_{ipso}Ph, d, $^1J_{P\text{-}C}$ 83.8 Hz), 98.6 (C_5Me_5), 9.4 ($C_5\mathit{Me}_5$), and −13.3 (CH_2, d, $^1J_{P\text{-}C}$ 36.8 Hz); ^{31}P n.m.r. (CD_3CN, H_3PO_4) δ 37.2 p.p.m.; i.r. (CH_2Cl_2) 2010 s (ν_{CO}), 1960s (ν_{CO}), and 1070 br. ($\nu_{B\text{—}F}$) cm^{-1}. (**4**), ^1H n.m.r. (CD_2Cl_2, Me_4Si) δ 1.73 (s, C_5Me_5); ^{13}C n.m.r. (CD_2Cl_2, Me_4Si) δ 212.6 (CO), 119.3 (q, CF_3), 98.2 (C_5Me_5), and 9.6 ($C_5\mathit{Me}_5$); *m/z* 340.0021; calc. for $M^+ - 2CO$ 340.0043; i.r. (CH_2Cl_2) 2060 s (ν_{CO}) and 2000 s (ν_{CO}) cm^{-1}. (**6**) ^1H n.m.r. (CD_2Cl_2, $CHCl_2$ int. ref. at δ 5.30) δ (−85 °C) 16.67 (br. s, 1H, CH_2), 15.10 (br., 1H, CH_2), 7.47 (m, 15H, PPh_3), 1.47 (s, 15H, C_5Me_5); coalescence at −45 °C; at −20 °C, δ 15.95 (br., 2H, CH_2); ^{13}C n.m.r. (−80 °C, CD_2Cl_2, Me_4Si ext. *vs.* CD_2Cl_2 at δ 54.5) δ 351.2 (CH_2, d, $^2J_{P\text{-}C}$ 23.6 Hz), 215.3 (CO, d, $^2J_{P\text{-}C}$ 31.5 Hz), 134.5—128.8 (PPh_3, m), 106.5 (C_5Me_5), and 9.5 ($C_5\mathit{Me}_5$).

an organometallic synthon for methylene transfers and the chemistry of this species is under investigation.

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