J. CHEM. SOC., CHEM. COMMUN., 1986

Synclinal and Anticlinal Isomers of the Iron Methoxycarbene Complex $[(\eta^5-C_5Me_5)Fe(CO)_2(=CHOMe)]^+$; Access to Functional Compounds

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The methoxymethyl complex $(\eta^{5}-C_5Me_5)Fe(CO)_2(CH_2OMe)$ (2) undergoes hydride abstraction with $Ph_3C^+PF_6^-$ at -80 °C and affords the secondary methoxycarbene complex $[(\eta^{5}-C_5Me_5)Fe(CO)_2(=CHOMe)]^+PF_6^-$ (1) as a mixture of two geometric isomers of which the *syn* form isomerizes upon warming; complex (1) adds PPh₃ yielding quantitatively $[(\eta^{5}-C_5Me_5)Fe(CO)_2(CHOMePPh_3)]^+PF_6^-$ (3), and converts Me_2PhSiH into $Me_2PhSiCH_2OMe$ (4), giving in the presence of the appropriate alkenes, the alkene complexes $[(\eta^{5}-C_5Me_5)Fe(CO)_2(CHO_2(CHOMePPh_3)]^+PF_6^-$ (5).

Secondary carbene-metal complexes, postulated as important intermediates in catalytic processes, are of considerable interest in organic synthesis. In extensive studies, Gladysz¹ demonstrated that chiral rhenium alkyl complexes undergo stereospecific α -hydride abstraction affording the synclinal or/and anticlinal alkylidene cations, depending on the substituent. Seeman and Davies² have reported conformational analysis for such asymmetric systems which rationalizes this feature. We now report the spectroscopic characterization of both the synclinal and anticlinal isomers of a new secondary methoxycarbene complex of the first-row transition metal in the C_5Me_5 series. We also describe its reactivity which illustrates the synthetic potential of this stabilized carbene complex, and access to alkene complexes.



Scheme 1

The thermally stable methoxycarbene complex $[(\eta^5-C_5Me_5)Fe(CO)_2(=CHOMe)]^+PF_6^-$ (1),[†] as for the C_5H_5 analogue,³ is synthesized from the methoxymethyl complex⁴ $(\eta^5-C_5Me_5)Fe(CO)_2(CH_2OMe)$ (2) by hydride abstraction with 1 equiv. of Ph₃C+PF₆⁻ at -80 °C in methylene chloride (100% yield of Ph₃CH by g.c.). Complex (1) (v_{CO} 2060-2010 cm⁻¹) is isolated as a yellow powder in quantitative crude yield after precipitation with pentane [reaction (1)].

$$(\eta^{5}\text{-}C_{5}\text{Me}_{5})\text{Fe}(\text{CO})_{2}(\text{CH}_{2}\text{OMe}) + \text{Ph}_{3}\text{C}^{+}\text{PF}_{6}^{-} \xrightarrow[-80\ ^{\circ}\text{C}]{-80\ ^{\circ}\text{C}}$$

$$[(\eta^{5}\text{-}C_{5}\text{Me}_{5})\text{Fe}(\text{CO})_{2}(=\text{CHOMe})]^{+}\text{PF}_{6}^{-} + \text{Ph}_{3}\text{CH} \quad (1)$$

$$(1)$$

^{+ 1}H and ¹³C n.m.r. data are for CD₂Cl₂ solutions unless noted otherwise. $[(η^5-C_5Me_5)Fe(CO)_2(=CHOMe)]^+PF_6^-$ (1): ¹H n.m.r. δ (-80 °C) 12.68 and 12.23 (br.s, =CH_{3yy} and br.s, =CH_{and}, total 1H), 4.70 (br.s, 3H, OMe), and 1.97 (s, 15H, C₅Me₅); δ (26 °C) 12.27 (s, 1H, =CH), 4.67 (s, 3H, OMe), and 1.94 (s, 15H, C₅Me₅); ¹³C n.m.r. δ 325.3 (=CH, d, ¹J_{C-H} 149.9 Hz), 209.6 (CO), 103.4 (C₅Me₅), 78.5 (OMe, q, ¹J_{C-H} 151.7 Hz), and 9.6 (C₅Me₅, q, ¹J_{C-H} 129.3 Hz); i.r., v_{CO}(CH₂Cl₂) 2060s and 2010s cm⁻¹.

 $\begin{array}{l} [(\eta^{5}\text{-}C_{5}Me_{5})\text{Fe}(\text{CO})_{2}(\text{CHOMePPh}_{3})]^{+}\text{PF}_{6}^{-} (3) \text{ at } -20\,^{\circ}\text{C: }^{1}\text{H} \\ \text{n.m.r. } \delta 7.74 & -7.65 (2 \times \text{m. } 15\text{H}, \, ^{+}\text{PPh}_{3}), 5.13 (\text{d. } 1\text{H}, \, ^{2}J_{\text{P-H}} ca. 1.5 \\ \text{Hz, CH}), 3.22 (\text{s. } 3\text{H}, \text{OMe}), \text{ and } 1.58 (\text{s. } 15\text{H}, \, C_{5}\text{Me}_{5}); \, ^{13}\text{C}\{^{1}\text{H}\} \\ \text{n.m.r. } \delta 218.2 (\text{CO}, \text{d. } ^{3}J_{\text{P-C}} \text{7} \text{Hz}), 215.4 (\text{CO}, \text{s}), 134.5 (\text{C}_{para} \text{Ph}), \\ 134.4 (\text{C}_{ortho} \text{Ph}), 130.3 (\text{C}_{meta} \text{Ph}, \text{d. } ^{3}J_{\text{P-C}} 11 \text{ Hz}), 121.6 (\text{C}_{ipso} \text{Ph}, \text{d.} , \\ ^{3}J_{\text{P-C}} 80 \text{ Hz}), 98.1 (C_{5}\text{Me}_{5}); \, ^{31}\text{P}^{-1}\text{H} \text{ n.m.r. } (\text{CD}_{2}\text{Cl}_{2}, \text{H}_{3}\text{PO}_{4}) \delta 27.1 \\ (^{+}\text{PPh}_{3}) \text{ and } -144.8 (\text{PF}_{6}^{-}, \text{septet}, \, ^{1}J_{\text{P-F}} 713 \text{ Hz}); \text{i.r.}, \, \text{v}_{\text{CO}} (\text{CH}_{2}\text{Cl}_{2}) \\ 2000\text{s and } 1960\text{s cm}^{-1}. \end{array}$

 $\begin{array}{l} Me_2PhSiCH_2OMe~(4):~^{1}H~n.m.r.~(C_6D_6,~Me_4Si~ext.)~\delta~7.55~(m,~2H,~Ph),~7.21~(m,~3H,~Ph),~3.17~(s,~3H,~OMe),~3.15~(s,~2H,~CH_2),~and~0.31~(s,~6H,~Me);~^{13}C\{^{1}H\}~n.m.r.~(C_6D_6,~Me_4Si~ext.)~137.9~(C_{ipso}~Ph),~134.2~(C_{onho}~Ph),~129.5~(C_{para}~Ph),~128.1~(C_{meta}~Ph),~66.6~(CH_2),~63.2~(OMe),~and~-4.3~(Me);~[M-~Me]^+~(C_9H_{13}OSi),~m/z~165.0749~(calc.~165.0735). \end{array}$

[$(\eta^{5}-C_{5}Me_{5})Fe(CO)_{2}(C_{2}H_{4})$]+PF₆⁻ (**5a**): ¹H n.m.r. δ 3.14 (s, 4H, C₂H₄) and 1.94 (s, 15H, C₅Me₅); ¹³C{¹H} n.m.r. δ 211.8 (CO), 102.6 (C₅Me₅), 59.5 (C₂H₄), and 9.5 (C₅Me₅); i.r., v_{CO} (CH₂Cl₂) 2050s and 2020s cm⁻¹. [$(\eta^{5}-C_{5}Me_{5})Fe(CO)_{2}(CH_{2}=CHPh)$]+PF₆⁻ (**5b**): ¹H n.m.r. δ 7.35–7.26 (2 × m, 5H, Ph), 4.89 (dd, 1H, ³J_{H-H} trans 14.6 Hz, ³J_{H-H} cis 8.8 Hz, CHPh), 3.97 (dd, 1H, ²J_{H-H} gem 1.8 Hz, Hz), 3.03 (dd, 1H, H_E), and 1.94 (s, 15H, C₅Me₅); ¹³C{¹H} n.m.r. δ 12.2 (Conthol 2), 136.0 (C_{ipso} Ph), 131.0 (Cpara Ph), 130.2 (Conthol Ph), 126.9 (C_{meta} Ph), 102.4 (C₅Me₅), 86.4 (CHPh), 52.4 (CH₂), and 9.6 (C₅Me₅); i.r., v_{CO} (CH₂Cl₂) 2060s and 2020s cm⁻¹.

Satisfactory elemental analyses of these yellow cations could not be obtained because of contamination by $[(\eta^5-C_5Me_5)Fe(CO)_3]^+PF_6^-$, the decomposition product of complex (1). Fractional crystallisation did not allow their separation in analytically pure form.



Scheme 2. $\delta_{\rm CO}$ 218.2 (d, ${}^3\!J_{\rm C-P}$ 7 Hz) and 215.4 (s).

Monitoring the reaction by ¹H n.m.r. spectroscopy[‡] shows that the secondary methoxycarbene complex (1) is formed at -80 °C as a mixture of two geometric isomers. The ¹H n.m.r. spectrum (CD_2Cl_2) exhibits two low-field singlets in the ratio 90:10 at δ 12.68 and 12.23 assigned to the carbene proton of the synclinal and anticlinal forms. At -60 °C, the signal at δ 12.68 irreversibly decreases while the other increases and the isomerization is complete at -50 °C. On the basis of steric considerations, only the thermodynamically stable anticlinal isomer is then observed ($\delta_{\rm H}$: 12.27, $\delta_{\rm OMe}$: 4.67) (Scheme 1). This feature was not reported for the related complex in the C_5H_5 series.³ The proton-coupled ¹³C n.m.r. spectrum (CD₂Cl₂) of anti-(1) recorded at room temperature confirms the proposed structure:6 the resonance due to the carbene carbon atom appears characteristically downfield at δ 325.3 (d, ${}^{1}J_{C-H}$ 149.9 Hz) and the quartet attributed to the methoxy group is located at δ 78.5 (q, ${}^{1}J_{C-H}$ 151.7 Hz).

Complex (1) is also available from the reaction of the ether precursor (2) with 0.5 equiv. of Me₃SiOSO₂CF₃ or HBF₄– OEt₂. The transient methylene complex⁴ [(η^5 -C₅Me₅)Fe-(CO)₂(=CH₂)]⁺ thus generated abstracts a hydride from the starting material (2), giving (1) and the methyl derivative (η^5 -C₅Me₅)Fe(CO)₂Me, a behaviour already observed for cationic methylene metal complexes.⁷ As in the former reaction, the two isomers of (1) are formed at -80 °C in the same ratio.

The electrophilic cation (1) adds the weakly basic phosphine PPh₃ yielding quantitatively the new α -methoxyphosphonium salt $[(\eta^5-C_5Me_5)Fe(CO)_2(CHOMePPh_3)]^+PF_6^{-1}(3), \dagger$ as indicated by the spectroscopic data. The asymmetric α -C atom and the methoxy group appear as doublets, at, respectively δ 74.8 ($^{2}J_{C-P}$ 28 Hz) and 62.5 ($^{3}J_{C-P}$ 8 Hz) in the $^{13}C\{^{1}H\}$ n.m.r. spectrum (CD₂Cl₂) of (3) at -20 °C. Moreover, this spectrum exhibits a doublet at δ 218.2 ($^{3}J_{C-P}$ 7 Hz) and a singlet at δ 215.4, attributed to the non-equivalent carbonyl ligands. The particular pattern of CO signals can be explained by the structural features illustrated by the Newman projection established from the Karplus equation (Scheme 2). The preferential conformation probably arises from the steric bulk of the methoxy group.§ Attempts to isolate (3) failed; however the stable methylene phosphonium salt⁴

[‡] The observation of these ¹H n.m.r. spectra rules out a hydride abstraction *via* an electron transfer pathway, in contrast to the results obtained for the isostructural hydroxymethyl complex⁵ (η^{5} -C₅Me₅)Fe(CO)₂(CH₂OH).

[§] In the case of the previously reported methylene phosphonium adduct,⁴ the signal due to the equivalent carbonyl ligands appears as a doublet at δ 216.3 (${}^{3}J_{C-P}$ 2.9 Hz) from which the coupling constant is weaker.



Scheme 3. a; R = Hb; R = Ph

 $[(\eta^{5}-C_{5}Me_{5})Fe(CO)_{2}(CH_{2}PPh_{3})]^{+}PF_{6}^{-}$ (6), $[(\eta^{5}-C_{5}Me_{5})-Fe(CO)_{3}]^{+}PF_{6}^{-}$ (7), and MeOH are recovered.

$$[(\eta^{5}-C_{5}Me_{5})Fe(CO)_{2}(CH_{2}PPh_{3})]^{+}PF_{6}$$
(6)

$$[(\eta^{5}-C_{5}Me_{5})Fe(CO)_{3}]^{+}PF_{6}^{-}$$
(7)

Treatment of the cation (1) with 1 equiv. of Me₂PhSiH leads to Me₂PhSiCH₂OMe⁸ (4)† in 40% yield (g.c.) which was isolated as a colourless liquid by preparative t.l.c. and identified by ¹H and ¹³C n.m.r. and mass spectroscopy. The formation of (4) results from the insertion of the methoxycarbene fragment into the Si-H bond of the silane,9 and is expected to liberate a co-ordination site on the iron moiety. Indeed, when the reaction is performed in the presence of an alkene (ethylene or styrene), besides (4), the new stable alkene complexes $[(\eta^5-C_5Me_5)Fe(CO)_2(CH_2=CHR)]^+PF_6^ (5a; R = H)^{\dagger}$ or $(5b; R = Ph)^{\dagger}$ are isolated, together with (7) as a by-product [spectroscopic ratio (5): (7) 80: 20; 80% crude yield] (Scheme 3). Characteristic upfield shifts¹⁰ are observed for the ¹H and ¹³C resonances of the alkene ligands of (5) compared with the free alkene. E.g., in the case of the ethylene complex (5a), the $CH_2=CH_2$ singlet resonance is shifted upfield to δ 3.14.

The stable heterocarbene complex (1), with its highly electrophilic properties, should be a useful reagent in organic and organometallic synthesis.

We are grateful to Drs. J.-R. Hamon, S. Sinbandhit, and J.-Y. Thépot for helpful discussions; B.A.S.F. is acknowledged for a gift of pentacarbonyl iron.

Received, 23rd January 1986; Com. 107

References

- W. A. Kiel, G.-Y. Lin, A. G. Constable, F. B. McCormick, C. E. Strouse, O. Eisenstein, and J. A. Gladysz, J. Am. Chem. Soc., 1982, 104, 4865; W. A. Kiel, G.-Y. Lin, G. S. Bodner, and J. A. Gladysz, *ibid.*, 1983, 105, 4958; W. E. Buhro, A. Wong, J. H. Merrifield, G.-Y. Lin, A. C. Constable, and J. A. Gladysz, Organometallics, 1983, 2, 1852; W. A. Kiel, W. E. Buhro, and J. A. Gladysz, *ibid.*, 1984, 3, 879.
- 2 J. I. Seeman and S. G. Davies, J. Chem. Soc., Chem. Commun., 1984, 1019; J. Am. Chem. Soc., 1985, 107, 6522.
- 3 A. R. Culter, J. Am. Chem. Soc., 1979, 101, 604
- 4 V. Guerchais and D. Astruc, J. Chem. Soc., Chem. Commun., 1985, 835.
- 5 V. Guerchais and C. Lapinte, J. Chem. Soc., Chem. Commun., in press.
- 6 The equivalence of the CO ligands indicates that the plane of the carbene ligand adopts a vertical orientation. See: A. M. Crespi and D. F. Shriver, *Organometallics*, 1985, 4, 1830.
- 7 S. E. Kegley, M. Brookhart, and G. R. Husk, Organometallics, 1982, 1, 760; W. Tam, G.-Y. Lin, W.-K. Wong, W. A. Kiel, W. K. Wong, and J. A. Gladysz, J. Am. Chem. Soc., 1982, 104, 141; J. Markham, W. Tolman, K. Menard, and A. Cutler, J. Organomet. Chem., 1985, 294, 45; S. G. Davies and T. R. Maberly, *ibid.*, 1985, 296, C37.
- 8 C. Eaborn and J. C. Jeffrey, J. Chem. Soc., 1957, 137.
- 9 J. A. Connor and P. D. Rose, J. Organomet. Chem., 1970, 24, C45; E. O. Fischer and K. H. Dötz, *ibid.*, 1972, 36, C4; J. A. Connor, P. D. Rose, and R. M. Turner, *ibid.*, 1973, 55, 111; J. A. Connor, J. P. Day, and R. M. Turner, J. Chem. Soc., Dalton Trans., 1975, 108.
- For alkene complexes in the (η⁵-C₅H₅)Fe series: J. W. Faller and B. V. Johnson, J. Organomet. Chem., 1975, **88**, 101; A. Cutler, D. Ehntholt, W. P. Giering, P. Lennon, S. Raghu, A. Rosan, M. Rosenblum, J. Tancrede, and D. Wells, J. Am. Chem. Soc., 1976, **98**, 3495; D. L. Reger and C. J. Coleman, J. Organomet. Chem., 1977, **131**, 153; D. L. Reger, C. J. Coleman, and P. J. McElligott, *ibid.*, 1979, **171**, 73; D. L. Reger and C. J. Coleman, *Inorg.* Chem., 1979, **18**, 3155; D. E. Laycock and M. C. Baird, Inorg. Chem. Acta, 1980, **42**, 263.