Journal Of Organometallic Chemistry, 296 (1985) C37—C39
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

MECHANISM OF THE FORMATION OF METHYLIRON COMPLEXES BY PROTONATION OF METHOXYMETHYLIRON COMPLEXES

STEPHEN G. DAVIES* and TIMOTHY R. MABERLY
The Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY (Great Britain)

(Received August 24th, 1985)

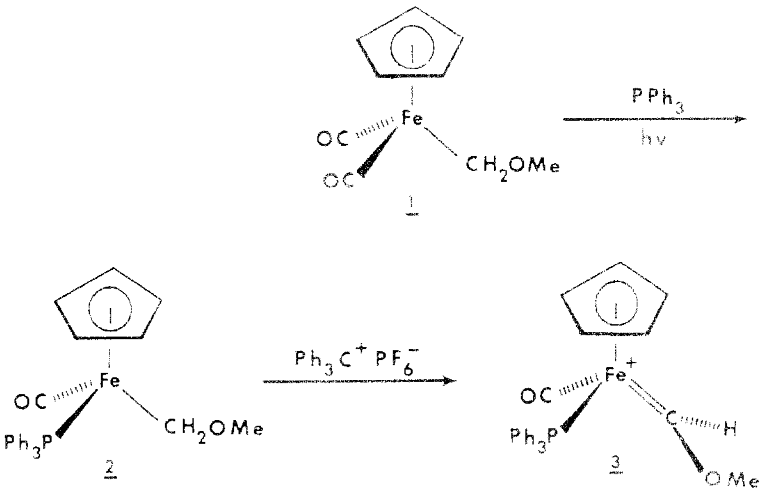
Summary

Addition of [(η^5-C_5H_5)Fe(CO)(PPh_3)CH_2OMe] to HBF_4 etherate generates [(η^5-C_5H_5)Fe(CO)(PPh_3)=CH_2]$^+$ BF_4^- which abstracts hydride from the starting complex to generate equimolar amounts of [(η^5-C_5H_5)Fe(CO)-(PPh_3)Me] and [(η^5-C_5H_5)Fe(CO)(PPh_3)=CH(OMe)]$^+$ BF_4^-.

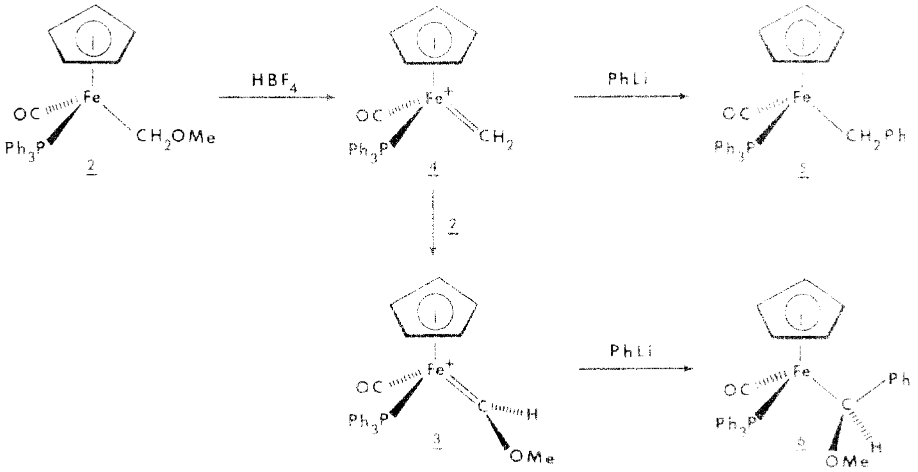
It has recently been reported that protonation of the methoxymethyl complex [(η^5-C_5Me_5)Fe$(CO)_2CH_2OMe$] generates the methyl complex [(η^5-C_5Me_5)Fe$(CO)_2$Me] [1]. This result confirms Pettit's earlier observations on [(η^5-C_5H_5)Fe$(CO)_2CH_2OMe$] [2] but in neither case has any mechanistic evidence been presented. We describe here some of our mechanistic studies on this type of reaction, which indicate a disproportionation mechanism between an initially formed methylene cationic complex and the starting methoxymethyl complex. It is a general reaction for methoxymethyl complexes to generate on acid treatment cationic methylene complexes which can act as methylene transfer agents [3] or disproportionate to form cationic η^2-ethene complexes [2,4].

The methoxymethyliron complex **2** is readily available by ligand exchange on the known [(η^5-C_5H_5)Fe$(CO)_2CH_2OMe$] (**1**) [5]. Hydride abstraction from **2** with trityl cation generates the methoxymethylene cationic complex **3** [6]. We have recently shown that nucleophilic addition to cation **3** is highly stereoselective [7], and were interested to determine whether nucleophilic additions to similar substituted methylene complexes lacking the methoxyl group were also stereoselective.

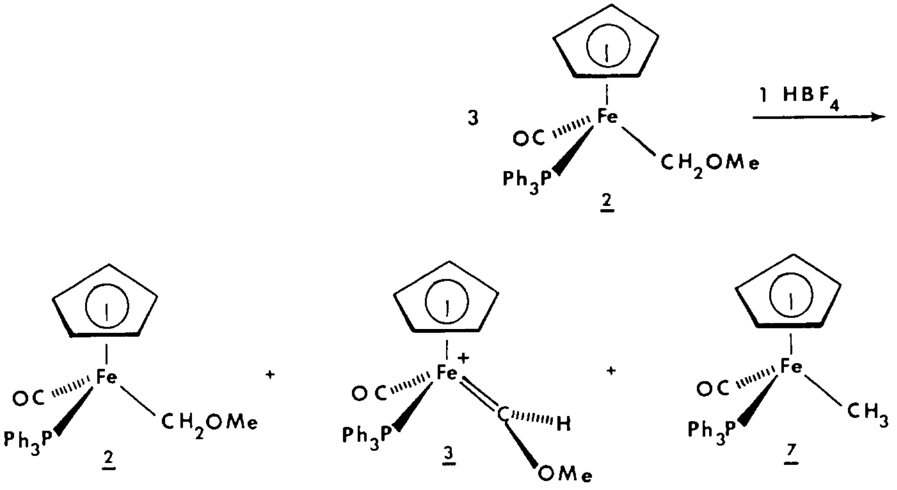
Addition of acid to complex **2** at −78°C followed by excess phenyllithium gave two isolable products in low yield; the expected benzyliron complex **5** presumably formed by addition of PhLi to the methyleneiron cation **4**, and unexpectedly the α-methoxybenzyl complex **6** as a single diastereoisomer.



The formation of 6 is consistent with addition of PhLi to the methoxymethylene complex 3 [7]. Indeed the same diastereoisomer 6 is formed when PhLi is added to an authentic sample of 3. These results indicate that the initially formed methyleneiron cation 4 is an excellent hydride abstractor capable of removing hydride from 2 with concomitant formation of the methyliron complex [(η^5-C_5H_5)Fe(CO)(PPh_3)Me] (7). The methyliron complex 7 would not be expected to survive the reaction conditions (excess acid) but would, as has been seen in related cases, be protonated and lose CH_4.



In order to verify this proposed mechanism, 3 equivalents of 2 were added slowly to 1 equivalent of HBF_4 etherate in tetrahydrofuran at −78°C. Work up gave quantitatively a 1/1/1 mixture of unreacted 2, methoxymethyleneiron cation 3 and the methyliron 7. These compounds were unambiguously identified by comparison of the ^1H NMR spectra and IR carbonyl stretching frequencies with those of authentic samples*.



The inverse addition of 2 to the acid allows the first equivalent of 2 to remove all of the acid with formation of 4, which subsequently reacts with the second equivalent of 2 to give 3 and 7. Under these conditions 7 is not generated in the presence of acid and is stable and isolable. This experiment clearly shows that the methylene cation 4 is capable of abstracting hydride from the methoxymethyl complex 2 to generate the more stable methoxymethylene cationic complex 3. Such a mechanism has been postulated previously to explain the mass spectrometric behaviour of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2OMe]$ [8].

Acknowledgements. We thank the SERC for a studentship (to TRM).

References

1 V. Guerchais and D. Astruc, Chem. Comm., (1985) 835.
2 P.W. Jolly and R. Pettit, J. Am. Chem. Soc., 88 (1966) 5044.
3 M. Brookhart, J.R. Tucker, T.C. Flood and J. Jensen, J. Am. Chem. Soc., 102 (1980) 1203.
4 M.L.H. Green, M. Ishaq and R.N. Whiteley, J. Chem. Soc. A., (1967) 1508; M. Brookhart, and G.O. Nelson, 99 (1977) 6099; J.H. Merrifield, G.Y. Lin, W.A. Kiel and J.A. Gladysz, ibid., 105 (1983) 5811.
5 T.C. Flood, F.J. DiSanti, and D.L. Miles, Inorg. Chem., 15 (1976) 1910.
6 A.R. Cutler, J. Am. Chem. Soc., 101 (1979) 604.
7 G.J. Baird, S.G. Davies, and T.R. Maberly, Organometallic, 3 (1984) 1764.
8 A.E. Stevens and J.L. Beauchamp, J. Am. Chem. Soc., 100 (1978) 2584.

---

*300 MHz ^1H NMR (CD_2Cl_2): 2, δ 7.4 (15H, m, aryl H), 4.37 (5H, d, J(PH) 1.1 Hz, C_5H_5), 4.1 (2H, m, CH_2), 2.95 (3H, s, OCH_3); 3, 13.24 (1H, s, C*H*OMe), 7.6—7.3 (15H, m, aryl H), 5.05 (5H, d, J(PH) 1.1 Hz, C_5H_5), 3.95 (3H, s, OCH_3); 7, 7.4 (15H, m, aryl H), 4.26 (5H, d, J(PH) 0.7 Hz, C_5H_5), —0.22 (3H, d, J(PH) 6.5 Hz, CH_3). IR (CH_2Cl_2): 2, 1905 cm^{-1} (CO); 3, 1995 cm^{-1} (CO); 7, 1905 cm^{-1} (CO).