Journal of Organometallic Chemistry, 475 (1994) 229-232

Aspects of the chemistry of the mixed ferrocene $[MeO(CH_2CH_2O)_3(CH_2)_3C_5Me_4]Fe(C_5H_5)$. Generation of the unusual α-ferrocenyl carbocation $\{[MeO(CH_2CH_2O)_3(CH_2)_3C_5Me_4]Fe(C_5H_4CH_2)\}^+$

Ulrich Siemeling and Gunnar Hüffmann

Fakultät für Chemie der Universität Bielefeld, Universitätsstraße 25, D-33615 Bielefeld (Germany)

(Received January 17, 1994)

Abstract

The mixed ferrocene $[MeO(CH_2CH_2O)_3(CH_2)_3C_5Me_4]Fe(C_5H_5)$ (**1**), accessible by reaction of C_5H_5Li with $[MeO(CH_2CH_2O)_3(CH_2)_3C_5Me_4]FeCl$, is formylated with $POCl_3$/DMF (DMF = *N,N*-dimethylformamide) to give the ferrocenyl aldehyde $[MeO(CH_2CH_2O)_3(CH_2)_3C_5Me_4]Fe(C_5H_4CHO)$ (**2**). Compound **2** is reduced with $LiAlH_4$ to yield the alcohol $[MeO(CH_2CH_2O)_3(CH_2)_3C_5Me_4]Fe(C_5H_4CH_2OH)$ (**3**), which is an excellent precursor for the unusual α-ferrocenyl carbocation $\{[MeO(CH_2CH_2O)_3(CH_2)_3C_5Me_4]Fe(C_5H_4CH_2)\}^+$ (A^+).

Key words: Iron; Ferrocene

1. Introduction

More than 80% of all organometallic compounds of the transition metals are cyclopentadienyl complexes with C_5H_5 and C_5Me_5 being the most prominent cyclopentadienyl systems used [1]. However, during the past few years functionalized cyclopentadienyl systems that do not just act as innocent spectator ligands have become very attractive.

Functionalization of the cyclopentadienyl moiety by a pendant oligoethylene glycol ether tentacle leads to the very interesting class of cyclopentadienyl ligands of general type R_4C_5–X–$(OCH_2CH_2)_nOMe$ (R = H, Me; X = spacer group); owing to their special coordination and solubility properties, these ligands show great promise for (i) the design of non-ionic water-soluble organometallics, (ii) the synthesis of redox-active podands and related supramolecular assemblies, and (iii) the development of catalysts based on the hemilabile-ligand principle [2].

In this context, the ligand $Me_4C_5(CH_2)_3$-$(OCH_2CH_2)_3OMe$ has proved to be particularly convenient from a synthetic point of view [2b,d]. One aspect of its hemilabile qualities is, for example, its ability reversibly to stabilize reactive metal-ligand fragments such as "K" and "FeCl" coordinated to its cyclopentadienyl unit. This is due to the influence of the tentacle, which can act as a (potentially tetradentate) intramolecular donor [2b,d,f].

It is interesting to assess the abilities of the tentacle to stabilize reactive situations which are quite different from a metal-ligand fragment coordinated to the cyclopentadienyl moiety of the ligand. A fascinating object for investigating this issue is the unusual α-ferrocenyl carbocation A^+, which we envisage to be much more stable than the parent cation $[C_5H_5FeC_5H_4CH_2]^+$ and also even more stable than higher methylated species such as $[(Me_4C_5H)Fe(C_5Me_4CH_2)]^+$ [3] or $[(Me_5C_5)Fe(C_5Me_4CH_2)]^+$ [4] (Fig. 1) [5].

The cation $[C_5H_5FeC_5H_4CH_2]^+$ is known to be thermally unstable in chlorocarbon solution above *ca.* −20°C. It can be stabilized, however, by addition of several equivalents of diethyl ether; one ether molecule is found to bind strongly to the cationic centre, whereas several others constitute a mobile solvent sphere [6].

Correspondence to: Dr. U. Siemeling.

0022-328X/94/$7.00
SSDI 0022-328X(94)24529-R

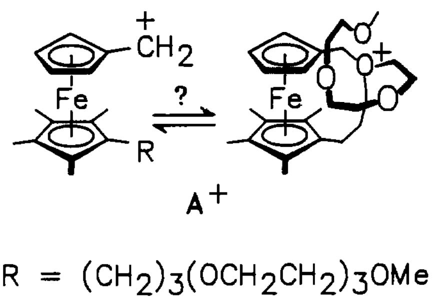


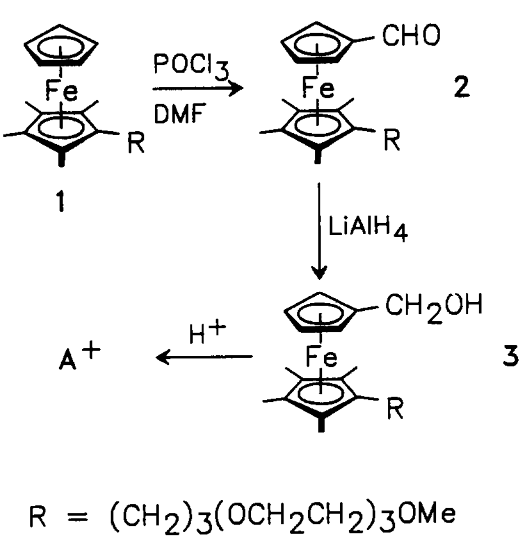
Fig. 1.

This situation could be mimicked by the ether oxygens of the tentacle in A^+, as indicated in Fig. 1.

2. Results and discussion

Scheme 1 shows our route to A^+; it is essentially analogous to a well-established synthetic path leading to $[C_5H_5FeC_5H_4CH_2]^+$ [7].

The mixed ferrocene $[MeO(CH_2CH_2O)_3(CH_2)_3C_5Me_4]Fe(C_5H_5)$ (**1**), which is accessible via reaction of C_5H_5Li with $[MeO(CH_2CH_2O)_3(CH_2)_3C_5Me_4]FeCl$ [2d], can be formylated in a Vilsmeier reaction with $POCl_3$/DMF (DMF = *N,N*-dimethylformamide) in dichloromethane to give the ferrocenyl aldehyde $[MeO(CH_2CH_2O)_3(CH_2)_3C_5Me_4]Fe(C_5H_4CHO)$ (**2**) as a dark red oil in 67% yield after chromatographic work-up. The aldehyde **2** can be reduced to the ferrocenyl alcohol **3** with $LiAlH_4$ in diethyl ether; **3** is obtained as a yellow oil in almost quantitative yield. As indicated by the standard reaction conditions and good product yields, the tentacle does not seem to interfere with the formylation and the reduction reaction.



Scheme 1.

NMR spectroscopic data for compounds **2** and **3** are essentially unexceptional. In the ^1H NMR spectrum of **2**, recorded in $CDCl_3$, the aldehyde proton gives rise to a resonance at 9.66 ppm, which is close to the values observed for the closely related species $(1,2\text{-}Me_2C_5H_3)Fe(C_5H_4CHO)$ (9.86 ppm) [8] and $(Me_4C_5H)Fe(Me_4C_5CHO)$ (10.03 ppm) [4] in the same solvent and is identical to the value observed for the tentacle-free analogue $(Me_5C_5)Fe(C_5H_4CHO)$ in CD_2Cl_2 [9]. For the ring protons of **2**, two triplets ($^3J = 1.8$ Hz) at 4.23 and 4.14 ppm, respectively, are observed. The trimethylene spacer group gives rise to signals at 3.36 ($Me_4C_5CH_2CH_2C\mathit{H}_2OR$), 2.35 ($Me_4C_5C\mathit{H}_2CH_2CH_2OR$) and 1.55 ppm ($Me_4C_5CH_2C\mathit{H}_2CH_2OR$), respectively [$R = (CH_2CH_2O)_3Me$]. The signals for the ring methyl groups are observed at 1.80 and 1.81 ppm. The $(OCH_2CH_2)_3$ part of the tentacle gives rise to multiplets centred at 3.54 and 3.63 ppm; the resonance of the OMe group is observed at 3.36 ppm. The alcohol **3** exhibits very similar chemical shift values for the tentacle part of the molecule. However, owing to its increased electron density as compared to **2**, the resonances for the ring protons are shifted more than 0.5 ppm upfield and are found to be concealed by the lowfield multiplet for the $(OCH_2CH_2)_3$ part of the tentacle centred at 3.63 ppm. The CH_2OH group gives rise to a doublet ($^3J = 6.7$ Hz; CH_2) at 4.27 and a triplet ($^3J = 6.7$ Hz; OH) at 1.38 ppm; upon metathesis with D_2O, the triplet vanishes and the doublet collapses to a singlet.

Addition of trifluoroacetic acid to a $CDCl_3$ solution of the alcohol **3** at room temperature leads to an immediate colour change of the solution from light yellow to orange. The ^1H NMR spectrum of this solution proves the clean formation of the cation A^+. It is noteworthy that A^+ is stable in solution at room temperature for several days as proved by NMR spectroscopy; this is in contrast to all other primary α-ferrocenyl carbocations known to date, including $[(Me_4C_5H)Fe(C_5Me_4CH_2)]^+$ [3] and $[(Me_5C_5)Fe(C_5Me_4CH_2)]^+$ [4]. The signals for the ring protons are observed as triplets ($^3J = 2.2$ Hz) at 5.66 and 4.19 ppm, respectively. The (formally cationic) CH_2 moiety gives rise to a singlet at 5.37 ppm, which is very close to the value of 5.27 ppm observed for $[(Me_4C_5H)Fe(C_5Me_4CH_2)]^+$ [3] and $[(Me_5C_5)Fe(C_5Me_4CH_2)]^+$ [4]. The trimethylene spacer group shows resonances at 3.71, 2.28 and 1.76 ppm for the $Me_4C_5CH_2CH_2C\mathit{H}_2OR$, $Me_4C_5C\mathit{H}_2CH_2CH_2OR$ and $Me_4C_5CH_2C\mathit{H}_2CH_2OR$ protons, respectively [$R = (CH_2CH_2O)_3Me$]. The methoxy resonance is observed at 3.53 ppm. The ring methyl groups give rise to two singlets at 1.88 and 1.87 ppm. The remaining broad signal at 3.85 ppm integrates for *ca.* 14 protons and is due to the 12

$(OCH_2CH_2)_3$ protons of the tentacle; the *ca.* 2 additional protons may stem from the water produced in the reaction and from ether-coordinated protons due to the excess of trifluoroacetic acid in the mixture.

The broadness of the signal at 3.85 ppm is consistent with a dynamic process which may be due to (i) proton hopping between ether oxygens and (ii) stabilization of the cationic centre of the molecule by the ether oxygens similar to that observed for $[(C_5H_5)Fe(C_5H_4CH_2)]^+$ in the presence of diethyl ether [6]. To exclude the possibility of protonation of ether oxygens by excess acid, it is necessary to add a stoichiometric amount of acid to the alcohol **3** when generating the cation. This is easily achieved by doing the experiment not on a ^1H NMR scale (using only a few mg of **3**) but on a ^{13}C NMR scale (using several hundred mg of **3**), in which case the desired amount of trifluoroacetic acid can be added quite accurately via a microsyringe. Additionally, this procedure provides the opportunity of directly studying the methylium carbon NMR resonance using dynamic NMR spectroscopy in order to investigate the putative dynamic carbocation-oxonium ion equilibrium shown in Fig. 1. However, data from variable-temperature ^{13}C NMR spectroscopy are inconclusive and will be discussed elsewhere, together with the results of further experiments that are currently under way.

In conclusion, the unusual α-ferrocenyl carbocation $\mathbf{A}^+$ has been synthesized. The high stability of this species indicates that stabilization involving the tentacle takes place. It is as yet unclear whether the proposed carbocation-oxonium ion equilibrium plays a substantial role in this stabilization.

3. Experimental details

Unless stated otherwise, all experiments were carried out with rigorous exclusion of air and moisture under an atmosphere of purified argon using standard Schlenk techniques. All solvents and reagents were appropriately dried and purified. Elemental analyses were performed by the microanalytical laboratory of the Universität Bielefeld. NMR spectra were obtained on a Bruker AM 300 spectrometer (300.133 MHz, ^1H, external TMS; 75.453 MHz, ^{13}C, external TMS); where necessary, assignments of ^{13}C resonances were made using *J*-modulated spectra.

3.1. Preparations

3.1.1. $[MeO(CH_2CH_2O)_3(CH_2)_3C_5Me_4]Fe(C_5H_4CHO)$ (2)

A solution of $[MeO(CH_2CH_2O)_3(CH_2)_3C_5Me_4]Fe(C_5H_5)$ (**1**) [2d] (2.78 g, 6.23 mmol) in dichloromethane (10 ml) is cooled to 0°C. $POCl_3$ (2.30 g, 15.0 mmol) and DMF (2.2 ml, *ca.* 28 mmol) are added. The mixture is stirred under reflux for 20 h. After cooling to room temperature, an ice-cold solution of potassium carbonate (5.0 g, *ca.* 36 mmol) in water (30 ml) is added. The mixture is vigorously stirred at room temperature for 1 h. The following work-up procedure may be performed in the air. The organic layer is separated. The aqueous phase is extracted with diethyl ether (2 × 20 ml). The combined organic phases are dried over magnesium sulfate, filtered and the filtrate reduced to *ca.* 10 ml *in vacuo*. The product is isolated from this solution by flash chromatography (silica gel, diethyl ether eluent, $R_f = 0.70$) as a deep-red oil. Yield 1.98 g (67%). Anal. Found: C, 63.30; H, 7.97. Calcd. for $C_{25}H_{38}FeO_5$ (474.15): C, 63.33; H 8.02%. ^1H NMR ($CDCl_3$): $\delta = 1.55$ (m; 2H, $Me_4C_5CH_2C\mathit{H}_2CH_2O$), 1.80 and 1.81 (2s; together 12H, $\mathit{Me}_4C_5CH_2CH_2CH_2O$), 2.35 (t, $^3J = 7.6$ Hz; 2H, $Me_4C_5C\mathit{H}_2CH_2CH_2O$), 3.35 (s; 3H, OMe), 3.36 (t, $^3J = 6.6$ Hz; 2H, $Me_4C_5CH_2CH_2C\mathit{H}_2O$), 3.51–3.55 and 3.60–3.65 [both m; together 12H, $(CH_2CH_2O)_3$], 4.14 and 4.23 (both t, $^3J = 1.8$ Hz; together 4H, $C_5\mathit{H}_4CHO$), 9.66 (s; 1H, CHO). ^{13}C NMR ($CDCl_3$): $\delta = 10.9$ ($\mathit{Me}_4C_5CH_2CH_2CH_2O$), 22.8 and 30.7 ($Me_4C_5\mathit{C}H_2\mathit{C}H_2CH_2O$), 59.0 (OMe), 70.1, 70.6 and 71.9 (all OCH_2), 71.7 and 77.3 (both ring CH); 80.1 (quart. *C*-CHO), 82.0 and 82.6 (both quart. *C*-Me), 86.0 [quart. $\mathit{C}\text{-}(CH_2)_3O$], 193.8 (CHO).

3.1.2. $[MeO(CH_2CH_2O)_3(CH_2)_3C_5Me_4]Fe(C_5H_4CH_2OH)$ (3)

A mixture of the aldehyde **2** (1.67 g, 3.52 mmol) and $LiAlH_4$ (150 mg, 3.95 mmol) in diethyl ether (40 ml) is stirred under reflux for 12 h. After cooling to 0°C, the mixture is hydrolyzed by dropwise addition of a saturated ammonium chloride solution (20 ml). The following work-up procedure may be performed in the air. The organic layer is separated. The aqueous phase is extracted with diethyl ether (3 × 20 ml). The combined organic phases are dried over magnesium sulfate. After filtration, volatiles are removed *in vacuo* leaving the product as a bright yellow oil. Yield 1.62 g (97%). Anal. Found: C, 63.07; H, 8.34. Calcd. for $C_{25}H_{40}FeO_5$ (476.16): C, 63.06; H 8.47%. ^1H NMR ($CDCl_3$): $\delta = 1.38$ (t, $^3J = 6.7$ Hz; 1H, OH), 1.56 (m; 2H, $Me_4C_5CH_2C\mathit{H}_2CH_2O$), 1.85 and 1.86 (2s; together 12H, $\mathit{Me}_4C_5CH_2CH_2CH_2O$), 2.40 (t, $^3J = 7.5$ Hz; 2H, $Me_4C_5C\mathit{H}_2CH_2CH_2O$), 3.35 (s; 3H, OMe), 3.38 (t, $^3J = 6.2$ Hz; 2H, $Me_4C_5CH_2CH_2C\mathit{H}_2O$), 3.51–3.56 and 3.61–3.69 [both m; together 16H, $(CH_2CH_2O)_3$ and $C_5\mathit{H}_4CH_2OH$], 4.27 (d, $^3J = 6.7$ Hz; 2H, $C\mathit{H}_2OH$). ^{13}C NMR ([$^2H_8$]-toluene: $\delta = 11.3$ ($\mathit{Me}_4C_5CH_2CH_2CH_2O$), 23.5 and 31.7 ($Me_4C_5\mathit{C}H_2\mathit{C}H_2CH_2O$), 58.6 (OMe), 60.5 ($CH_2OH$), 70.7, 70.9, 71.1 and 72.4 (all OCH_2), 72.5 (ring CH); 80.1 and 80.5 (both quart. *C*-Me), 84.5 and 87.1 (both quart. *C*-CH_2).

3.1.3. Generation of $\{[MeO(CH_2CH_2O)_3(CH_2)_3C_5Me_4]Fe(C_5H_4CH_2)\}^+$ *(*A^+*)*

In a 5 mm NMR tube, trifluoroacetic acid (*ca.* 0.3 ml) is added to a solution of the alcohol **3** (*ca.* 10 mg) in $CDCl_3$ (*ca.* 0.5 ml). An instant colour change from light yellow to light brown is observed. Yield quantitative (according to ^1H NMR spectroscopic data). ^1H NMR ($CDCl_3$): $\delta = 1.76$ (m; 2H, $Me_4C_5CH_2CH_2CH_2O$), 1.87 and 1.88 (both s; together 12H, $Me_4C_5CH_2CH_2CH_2O$), 3.53 (OMe), 3.71 ($Me_4C_5CH_2CH_2CH_2O$), 3.85 [br s; *ca.* 14H, $(CH_2CH_2O)_3$ and possibly water and ether-coordinated protons (*vide supra*)], 4.19 and 5.66 (both t, $^3J = 2.2$ Hz; together 4H, $C_5H_4CH_2$), 5.37 (s; 2H, $C_5H_4CH_2$).

Acknowledgments

This work was financed by the Deutsche Forschungsgemeinschaft. U.S. wishes to thank Prof. Dr. P. Jutzi for his continued support and his interest in this work.

References

1 C. Janiak and H. Schumann, *Adv. Organomet. Chem., 33* (1991) 291.

2 (a) U. Siemeling, *J. Organomet. Chem., 429* (1992) C14; (b) U. Siemeling, *J. Chem. Soc., Chem. Commun.,* (1992) 1335; (c) U. Siemeling, B. Neumann and H.-G. Stammler, *Chem. Ber., 126* (1993) 1311; (d) U. Siemeling, presented at the 2nd International Conference Inorganic Chemistry, Stuttgart (Germany), 1993; (e) U. Siemeling, in N. Auner and J. Weis (eds.), *Organosilicon Chemistry,* VCH, Weinheim, 1994, p. 193; (f) U. Siemeling, presented at the Annual SON Meeting Coordination Chemistry and Homogeneous Catalysis, Lunteren (Netherlands), 1994.

3 (a) A.Z. Kreindlin, S.S. Fadeeva and M.I. Rybinskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.,* (1984) 403; (b) E.I. Fedin, A.L. Blumenfeld, P.V. Petrovskii, A.Z. Kreindlin, S.S. Fadeeva and M.I. Rybinskaya, *J. Organomet. Chem., 292* (1985) 257.

4 C. Zou and M.S. Wrighton, *J. Am. Chem. Soc., 112* (1990) 7578.

5 For reviews concerning ferrocenyl carbocations, see (a) W.E. Watts, *J. Organomet. Chem. Libr., 7* (1979) 399; (b) P.Vogel, *Carbocation Chemistry,* Elsevier, Amsterdam, 1985, Chapter 9; (c) A.A. Koridze, *Usp. Khim., 55* (1986) 277.

6 A. Ceccon, G. Giacometti, A. Venzo, D. Paolucci and D. Benozzi, *J. Organomet. Chem., 185* (1980) 231.

7 M. Hisatome and K. Yamakawa, *Tetrahedron, 27* (1971) 2101.

8 P. Krajnik, K. Schlögl and M. Widhalm, *Monatsh. Chem., 121* (1990) 413.

9 J.C. Calabrese, L.-T. Cheng, J.C. Green, S.R. Marder and W. Tam, *J. Am. Chem. Soc., 113* (1991) 7227.