$C_5Me_4(CH_2)_3(OCH_2CH_2)_3OMe$: A Tentacle-bearing Cyclopentadienyl Ligand and its Use in Complex Chemistry

Ulrich Siemeling

Fakultät für Chemie, Universität Bielefeld, Universitätsstr., W-4800 Bielefeld 1, Germany

The reaction of 2,3,4,5-tetramethylcyclopent-2-enone with the Grignard reagent $MeO(CH_2CH_2O)_3(CH_2)_3MgCl$ **3** affords, after acidic workup, the novel cyclopentadiene $HC_5Me_4(CH_2)_3(OCH_2CH_2)_3OMe$ **4**, which allows the synthesis of cyclopentadienyl metal complexes that owing to the tentacle function show unusually high solubilities in solvents of all polarities; two such complexes are the ferrocene $[Fe\{C_5Me_4(CH_2)_3(OCH_2CH_2)_3OMe\}_2]$ **6** and the cobalt carbonyl $[Co(CO)_2\{C_5Me_4(CH_2)_3(OCH_2CH_2)_3OMe\}]$ **7**.

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 functionalised cyclopentadienyl systems that do not just act as innocent spectator ligands have become very attractive.

Recently, a series of ligands of general type $XSiMe_2(OCH_2CH_2)_nOMe$ ($X = C_5H_4$ or C_5Me_4, $n = 2$ or 3) was described.[2] The oligoethylene glycol ether substituent ('tentacle') on these ligands may have various interesting effects. Firstly, a relatively weak intramolecular coordination of the tentacle can reversibly stabilise reactive metal ligand fragments in a fashion similar to that of the well-known hemilabile phosphane ether ligands;[3] to date, mainly cyclopentadienyl ligands bearing strong donor substituents such as phosphane or amino units have been investigated,[4] and only very few examples of ether functionalised cyclopentadienes are known.[5] Secondly, the amphiphilic nature of the tentacle generally leads to an enhanced solubility of tentacle-bearing compounds in solvents of *all* polarities;[6] this effect may prove useful for the development of non-ionic water-soluble organometallics.[7] Thirdly, the tentacle can act as podand, and tentacle-bearing molecules often show supramolecular phenomena.[6]†

A disadvantage of cyclopentadienyl ligands of type $XSiMe_2(OCH_2CH_2)_nOMe$ is the high reactivity of the allylic C_5-ring–silicon bond in the respective cyclopentadienes $HXSiMe_2(OCH_2CH_2)_nOMe$. This bond can be cleaved by a variety of reagents [for example by Bu^{n}Li, TlOEt, and also by $Co_2(CO)_8$], which narrows the applicability of these ligands in complex chemistry.[9] It seemed therefore desirable to synthesise analogous cyclopentadienyl ligands with a more stable attachment of the tentacle to the cyclopentadienyl ring, for example using an oligomethylene spacer group instead of the $SiMe_2$ unit.

I report the first example of such a system, namely the cyclopentadiene $HC_5Me_4(CH_2)_3(OCH_2CH_2)_3OMe$ **4**. This compound can be prepared in good yield from easily available starting materials (Scheme 1).

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† Compounds of the type $[Fe\{C_5H_4O(CH_2CH_2O)_nMe\}_2]$ (n = 0–3), which were prepared by functionalisation of ferrocene, show excellent complexing abilities for metal cations such as Na^+, K^+ and Tl^+ (ref. 8).

The Grignard reagent **3** as well as its precursors **1** and **2** were prepared using procedures analogous to those described for $\mathrm{MeO(CH_2CH_2O)_2(CH_2)_3MgCl}$ and its respective precursors by Okano *et al.*[10] The product is a yellow, viscous liquid (b.p. *ca.* 160 °C/10^{-3} mbar), which is obtained as a roughly statistical 2 : 2 : 1 mixture of all three possible isomers.

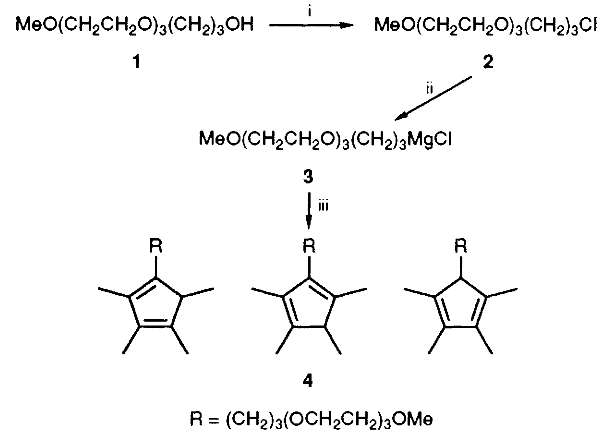
Like $\mathrm{C_5Me_5H}$, but unlike the cyclopentadienes of type $\mathrm{HXSiMe_2(OCH_2CH_2)}_n\mathrm{OMe}$, **4** may be cleanly deprotonated by reaction with 1 equiv. of $\mathrm{Bu^nLi}$ in tetrahydrofuran (THF) to yield the respective lithium cyclopentadienide **5a**. The analogous potassium compound **5b** can be prepared by reaction of **4** with 1 equiv. of potassium metal in hot toluene. Compounds **5a** and **5b** are quite soluble in THF and also in hot toluene; this is in sharp contrast to the extremely low solubility of the respective $\mathrm{C_5Me_5}$ analogues in these solvents and is indicative of an intramolecular coordination of the tentacle leading to essentially monomeric units in solution.

Both alkali metal derivatives can be used for the preparation of metal complexes. For example, reaction of **5a** or **5b** with iron(II) chloride in THF leads to the formation of the ferrocene **6**, which is obtained as a yellow oil in moderate yield after chromatographic purification of the crude product.

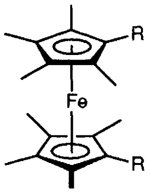
Like $\mathrm{C_5Me_5H}$, but unlike the cyclopentadienes of type $\mathrm{HXSiMe_2(OCH_2CH_2)}_n\mathrm{OMe}$, **4** cleanly reacts with octacarbonyl dicobalt in boiling dichloromethane in the presence of cyclohexa-1,3-diene. The cobalt complex **7** is obtained as a dark red oil in almost quantitative yield.‡

Both the ferrocene **6** and the cobalt complex **7** are very soluble in organic solvents of all polarities (*e.g.* hexane, toluene, diethyl ether, acetonitrile); they are also soluble in water–methanol.

In summary, a cyclopentadienyl ligand has been prepared which seems to combine the synthetic versatility of 'ordinary' cyclopentadienyl ligands like $\mathrm{C_5Me_5}$ with the characteristics of tentacle molecules. The results presented here augur well for the development of a rich complex chemistry of ligands of this type, especially with a view to aqueous organometallic chemistry.



Scheme 1 *Reagents and conditions*: i, $\mathrm{SOCl_2}$–pyridine, 14 h reflux in benzene; ii, Mg, THF, 20 °C, 3–4 h; iii, 2,3,4,5-tetramethylcyclopent-2-enone, THF, 0 °C, 14 h, acidic workup with hydrochloric acid (20%)



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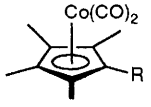

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$\mathrm{R = (CH_2)_3(OCH_2CH_2)_3OMe}$

I thank the Deutsche Forschungsgemeinschaft for financial support and Professor Dr P. Jutzi for his continued interest in this work.

Received, 18th June 1992; Com. 2/03219H

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‡ The Grignard reagent **3** and the alkali metal compounds **5a** and **5b** were characterised through derivatisation. All other new compounds gave satisfactory microanalytical and spectroscopic data. *NMR spectroscopic data* for **4, 6** and **7** (^{1}H NMR: 300.1 MHz, ext. $\mathrm{Me_4Si}$; ^{13}C NMR: 75.4 MHz, ext. $\mathrm{Me_4Si}$; ^{59}Co NMR: 70.9 MHz, ext. $\mathrm{K_3[Co(CN)_6]}$):

4 (three isomers): ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.92–1.28 (m), 0.97 (d, *J* 7.6 Hz, allylic Me), 0.98 (d, *J* 7.6 Hz, allylic Me), 1.50–1.82 (m), 2.10–2.62 (m) [the signals between δ 0.92 and 2.62 integrate for 17 H and represent $\mathit{H}\mathrm{C_5}\mathit{Me}_4\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2(OCH_2CH_2O)_3Me}$], 3.30–3.66 [m, 17 H, $\mathrm{HC_5Me_4CH_2CH_2C}\mathit{H}_2\mathrm{(OC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{O)_3Me}$]; ^{13}C NMR ($\mathrm{CDCl_3}$) δ 10.9, 11.5, 11.6, 13.9 and 14.1 ($\mathrm{HC_5}\mathit{Me}_4\mathrm{CH_2CH_2CH_2OR}$), 21.8, 22.4, 23.3, 23.9, 29.3 and 30.1 ($\mathrm{HC_5Me_4}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2OR}$), 49.2, 51.3 and 55.6 (allylic ring Cs), 58.9 (OMe), 70.0, 70.4, 70.5, 70.9 and 71.8 ($\mathrm{HC_5Me_4CH_2CH_2}\mathit{C}\mathrm{H_2(O}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2O)_3Me}$), 133.4, 133.9, 134.7, 134.9, 135.6, 137.7, 138.0, 138.1, 138.7 and 141.5 (vinylic ring Cs).

6: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.55 (br s, 24 H, $\mathrm{C_5}\mathit{Me}_4\mathrm{CH_2CH_2CH_2OR}$), 1.65 (br s, 4 H, $\mathrm{C_5Me_4C}\mathit{H}_2\mathrm{CH_2CH_2OR}$), 2.06 (br s, 4 H, $\mathrm{C_5Me_4CH_2C}\mathit{H}_2\mathrm{CH_2OR}$), 3.36 (s, 6 H, OMe), 3.37–3.67 [m, 28 H, $\mathrm{C_5Me_4CH_2CH_2C}\mathit{H}_2\mathrm{(OC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{O)_3Me}$]; ^{13}C NMR ($\mathrm{CDCl_3}$) δ 9.4 ($\mathrm{C_5}\mathit{Me}_4$), 21.4 ($\mathrm{C_5Me_4}\mathit{C}\mathrm{H_2CH_2CH_2OR}$), 30.5 ($\mathrm{C_5Me_4CH_2}\mathit{C}\mathrm{H_2CH_2}$-OR), 59.0 (OMe), 69.9, 70.5, 70.6, 70.9 and 71.9 [$\mathrm{C_5Me_4CH_2CH_2}$-$\mathit{C}\mathrm{H_2(O}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2O)_3Me}$], 78.3, 78.9 and 82.4 ($\mathit{C}_5\mathrm{Me_4}$).

7: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.64–1.69 (m, 2 H, $\mathrm{C_5Me_4CH_2C}\mathit{H}_2\mathrm{CH_2OR}$), 1.85 and 1.89 (s, 12 H, $\mathrm{C_5}\mathit{Me}_4\mathrm{CH_2CH_2CH_2OR}$), 2.35 (t, *J* 7.8 Hz, 2 H, $\mathrm{C_5Me_4C}\mathit{H}_2\mathrm{CH_2CH_2OR}$), 3.36 (s, 6 H, OMe), 3.45 (t, *J* 6.5 Hz, 2 H, $\mathrm{C_5Me_4CH_2CH_2C}\mathit{H}_2\mathrm{OR}$), 3.52–3.66 [m, 12 H, $\mathrm{C_5Me_4CH_2CH_2CH_2}$-$\mathrm{(OC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{O)_3Me}$]; ^{13}C NMR ($\mathrm{C_6D_6}$) δ 10.4 ($\mathrm{C_5}\mathit{Me}_4$), 22.0 and 32.2 ($\mathrm{C_5Me_4}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2OR}$), 58.6 (OMe), 70.4, 70.7, 70.9, 71.1 and 72.4 [$\mathrm{C_5Me_4CH_2CH_2}\mathit{C}\mathrm{H_2(O}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2O)_3Me}$], 96.6, 97.0 and 101.8 ($\mathit{C}_5\mathrm{Me_4}$), 208.4 (br, CO); ^{59}Co NMR ($\mathrm{C_6D_6}$) δ − 2470 ($\nu_{1/2}$ 10 000 Hz).

References

1 C. Janiak and H. Schumann, *Adv. Organomet. Chem.*, 1991, **33**, 291.
2 U. Siemeling, *J. Organomet. Chem.*, 1992, **429**, C14.
3 For a recent review, see A. Bader and E. Lindner, *Coord. Chem. Rev.*, 1991, **108**, 27.
4 See, for example C. Charrier and F. Mathey, *Tetrahedron Lett.*, 1978, **27**, 2407; C. Charrier and F. Mathey, *J. Organomet. Chem.*, 1979, **170**, C41; D. M. Bensley, Jr. and E. A. Mintz, *J. Organomet. Chem.*, 1988, **353**, 93; D. M. Bensley, Jr., E. A. Mintz and S. J. Sussangkarn, *J. Org. Chem.*, 1988, **53**, 4417; J. Szymoniak, J. Besançon, A. Dormond and C. Moïse, *J. Org. Chem.*, 1990, **55**, 1429 and references cited therein; T.-F. Wang, T.-Y. Lee, J.-W. Chou and C.-W. Ong, *J. Organomet. Chem.*, 1992, **423**, 31; P. Jutzi and J. Dahlhaus, unpublished results.
5 Q. Huang, Y. Qian, W. Xu, M. Shao and Y. Tang, *Wuji Huaxue*, 1985, **1**, 166 (*Chem. Abstr.*, 1986, **105**, 172640m); Q. Huang and Y. Qian, *Synthesis*, 1987, 910; D. Deng, C. Qian, G. Wu and P. Zengh, *J. Chem. Soc., Chem. Commun.*, 1990, 881; Q. Huang, Y. Qian, G. Li and Y. Tang, *Transition Met. Chem.*, 1990, **15**, 483; R. Fandos, A. Meetsma and J. H. Teuben, *Organometallics*, 1991, **10**, 59.
6 F. Vögtle, *Supramolekulare Chemie*, Teubner, Stuttgart, 1989 and references cited therein.
7 The subject has been recently reviewed; see M. Barton and J. D. Atwood, *J. Coord. Chem.*, 1991, **24**, 43.
8 S. Akabori, M. Ohtomi, M. Sato and S. Ebine, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 1455.
9 U. Siemeling, unpublished results.
10 T. Okano, K. Morimoto, H. Konishi and J. Kiji, *Nippon Kagaku Kaishi*, 1985, 486.