$[MeO(CH_2CH_2O)_3(CH_2)_3C_5Me_4]FeCl$: A Halfsandwich Iron(II) Chloride Complex of Remarkable Stability

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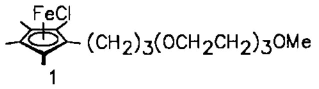
Reaction of iron(II) chloride with one equivalent of $[MeO(CH_2CH_2O)_3(CH_2)_3C_5Me_4]Li$ in THF yields the title halfsandwich complex **1**, which is stable in solution up to room temperature. Compound **1** reacts with C_5H_5Li and CO to give $[MeO(CH_2CH_2O)_3(CH_2)_3C_5Me_4]Fe(C_5H_5)$ (**2**) and $[MeO(CH_2CH_2O)_3(CH_2)_3C_5Me_4]Fe(CO)_2Cl$ (**3**), respectively, in high yields.



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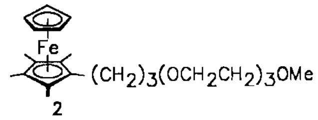

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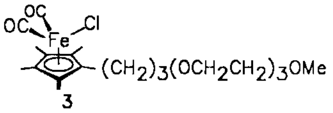

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Donor-functionalised spectator ligands such as phosphanes[1], nitrene ligands[2], and cyclopentadienyl systems[3] are currently attracting a lot of attention. Owing to their hemilabile coordination profile, the *reversible* stabilisation of reactive metal-ligand fragments can be achieved with these ligands.

We have recently described a series of cyclopentadienyl ligands of general type $MeO(CH_2CH_2O)_n{-}Z{-}C_5R_4$ (Z = spacer unit), which bear an oligoethylene glycol ether tentacle as donor functionality[4]. We have shown that these ligands are excellently suited for the reversible stabilisation of reactive complexes, either in the ligand periphery[5] or at a metal centre coordinate to the cyclopentadienyl moiety[6]. We now report on a unique example of such a stabilisation involving the highly reactive FeCl fragment.

Halfsandwich transition metal halide complexes $C_5R_5MX_n$ (X = Cl, Br) are versatile starting materials for the synthesis of a great variety of transition metal cyclopentadienyl compounds. They are well-known for most transition metals. However, for iron, no such compound has been described to date. Both $(C_5Me_5)FeBr$[7] and $[(Me_3Si)_3C_5H_2]FeBr$[8] are unstable in THF solution above ca. −80 °C even in the presence of the potentially chelating *O* donor dimethoxyethane (DME). In contrast, *N* or *P* donor-stabilised species such as $(C_5Me_5)Fe(PMe_3)_2Cl$ reported by Bercaw et al.[9] and $(C_5Me_5)FeCl(tmeda)$ (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) as well as $[(C_4H_8N)(CH_2)_2C_5Me_4]FeCl$ reported by Jonas et al.[10] are thermally stable crystalline compounds.

We succeeded in the preparation of the tentacle-bearing complex $[MeO(CH_2CH_2O)_3(CH_2)_3C_5Me_4]FeCl$ (**1**), which is thermally stable in THF solution up to room temperature for several days: When a mixture of equimolar amounts of iron(II) chloride and $[MeO(CH_2CH_2O)_3(CH_2)_3C_5Me_4]Li$ in THF cooled to −80 °C was allowed to warm slowly, a gradual colour change from grey to dark green was observed above ca. −60 °C, which was indicative of the formation of **1**. The resultant clear dark green solution could be stored under argon at room temperature for several days without any decomposition. However, it was not possible to isolate the compound. This is reminiscent of the behaviour of $(C_5Me_5)Fe(acac)(piperidine)$[9] (acac = acetylacetonato), which was originally believed to be $(C_5Me_5)Fe(acac)$[11].

We have characterised **1** by derivatisation. Reaction of **1** with one equivalent of C_5H_5Li at 0 °C gave the ferrocene **2** as an orange oil in 75% yield after flash chromatography. In a control experiment, equimolar amounts of $[MeO(CH_2CH_2O)_3(CH_2)_3C_5Me_4]Li$ and C_5H_5Li were dissolved in tetrahydrofuran and treated with a stoichiometric amount of iron(II) chloride at −80 °C. In this case, 68% of $(C_5H_5)_2Fe$ (based on C_5H_5Li) could be isolated. Treatment of **1** with carbon monoxide (excess) at −60 °C afforded **3** in a very swift reaction as a red oil in almost quantitative yield.

These results demonstrate that compound **1**, which is the first halfsandwich iron(II) halide complex stabilised exclusively by *O* donor groups, is remarkably stable *in the absence of substrates*. Its reactivity profile is governed by the very weakly coordinating ether oxygen atoms of the tentacle and mirrors the truely hemilabile character of the tentacle-functionalised cyclopentadienyl ligand towards the FeCl fragment. The relevance of the chelate effect for the coordination behaviour of this ligand was proved by a control experiment: When an equimolar mixture of $FeCl_2$ or $FeBr_2 \cdot DME$, C_5Me_5Li and tetraethylene glycol dimethyl ether in THF cooled to −80 °C was allowed to warm slowly, the formation of a dark green solution was observed above ca. −60 °C. The colour of this solution became lighter and more yellowish above ca. −20 °C. After storing the solution at room temperature for two days, it was cooled to 0 °C and treated with a solution of one equivalent of C_5H_5Li in THF. After standard workup, a light orange solid was obtained which consisted mainly of $(C_5H_5)_2Fe$ and $(C_5Me_5)_2Fe$ according to ^1H-NMR spectroscopy. In contrast to the analogous experiment yielding 75% of the unsymmetrical ferrocene **2**, only small amounts of the unsymmetrical product $(C_5H_5)Fe(C_5Me_5)$ were formed. We believe that the tentacle coordinates *intra*molecularly to the metal centre, since the solubility of **1** in THF is extremely high, which would be very unusual for oligomeric or polymeric species. An intramolecular coordination of the tentacle in related potassium

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cyclopentadienides was proved by molecular mass determinations and dynamic NMR spectroscopy[6,12].

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Experimental

Air- and/or moisture-sensitive compounds were handled under purified argon by using standard Schlenk techniques. Solvents and reagents were appropriately dried and purified by using standard procedures. – NMR: Bruker AM 300 (300.133 MHz, ^1H, ext. TMS; 75.453 MHz, ^{13}C, ext. TMS). – CI-MS: VG Autospec (70 eV). – IR: Mattson Polaris FTIR (CsI windows). – Elemental analyses: Microanalytical laboratory, Universität Bielefeld.

In Situ Preparation of Chloro[1,2,3,4-tetramethyl-5-(4,7,10,13-tetraoxatetradecyl)cyclopentadienyl]iron(II) (**1**): A solution of *n*-BuLi in hexane (10.0 ml, 1.60 M, 16.0 mmol) is added dropwise with stirring to a solution of $MeO(CH_2CH_2O)_3(CH_2)_3C_5Me_4H$[4b] (5.22 g, 1.60 mmol) in THF (40 ml) cooled to 0°C. The resultant yellow solution of $[MeO(CH_2CH_2O)_3(CH_2)_3C_5Me_4]Li$ is added dropwise with stirring to a suspension of iron(II) chloride (2.03 g, 16.0 mmol) in THF (20 ml) cooled to −80°C. The mixture is allowed to warm to room temp. overnight. Above ca. −60°C the colour of the mixture changes gradually from grey to dark green. The resultant solution is used for the preparation of compounds **2** and **3**.

1,2,3,4-Tetramethyl-5-(4,7,10,13-tetraoxatetradecyl)ferrocene (**2**): A solution of *n*BuLi (10.0 ml, 1.60 M, 16.0 mmol) is added dropwise with stirring to a solution of cyclopentadiene (1.06 g, 16.0 mmol) in THF (30 ml) cooled to 0°C. The resultant solution of cyclopentadienyllithium is added dropwise with stirring at 0°C to a solution of **1** prepared in THF from 16.0 mmol of each $[MeO(CH_2CH_2O)_3(CH_2)_3C_5Me_4]Li$ and iron(II) chloride as described above. The resultant light brown solution is stirred overnight. Volatile components are removed in vacuo, and the residue is extracted with *n*-hexane (200 ml). The orange extract is filtered through Florisil and concentrated to ca. 25 ml. The product is isolated from this solution as an orange oil by flash chromatography (silica gel, *n*-hexane/diethyl ether gradient) and subsequent removal of the eluent. Yield 5.36 g (75%). – ^1H NMR ($CDCl_3$): δ = 1.57 (m, 2H, $C_5Me_4CH_2CH_2$) 1.88 and 1.89 (2s, 12H, C_5Me_4), 2.45 (t, J = 7.7 Hz, 2H, $C_5Me_4CH_2$), 3.35 (s, 3H, OMe), 3.38 (t, J = 6.6 Hz, 2H, CH_2OMe), 3.51–3.63 [m, 12H, $(OCH_2CH_2)_3$], 3.65 (s, 5H, C_5H_5). – $^{13}C\{^1H\}$ NMR($CDCl_3$): δ = 11.1 (C_5Me_4), 23.1 and 30.9 ($C_5Me_4CH_2CH_2$), 58.6 (OMe), 69.8, 70.2, 70.4, 70.5, 70.8 and 71.7 [$CH_2(OCH_2CH_2)_3$], 79.6, 80.0 and 83.9 (C_5Me_4). – MS, *m/z* (%): 446 (35) [M^+]. – $C_{24}H_{38}FeO_4$ (446.4): calcd. C 64.57, H 8.58; found C 64.91, H 8.84.

Dicarbonylchloro[1,2,3,4-tetramethyl-5-(4,7,10,13-tetraoxatetradecyl)cyclopentadienyl]iron(II) (**3**): A solution of **1** prepared in THF from 16.0 mmol of each $[MeO(CH_2CH_2O)_3(CH_2)_3C_5Me_4]Li$ and iron(II) chloride as described above is stirred under an atmosphere of carbon monoxide at −60°C for 1 h and is then allowed to warm to room temp. Volatile components are removed in vacuo, and the resultant dark red residue is extracted with *n*-hexane (200 ml). The red extract is filtered through Florisil and the solvent removed in vacuo leaving the product as a dark red oil. Yield 6.96 g (92%) – ^1H NMR (C_6D_6): δ = 1.34, 1.36 (2s, 12H, C_5Me_4), 1.80 (m, 2H, $C_5Me_4CH_2CH_2$), 2.06 (t, J = 7.7 Hz, 2H, $C_5Me_4CH_2$), 3.33 (s, 3H, OMe), 3.44 (t, J = 6.5 Hz, 2H, CH_2OMe), 3.51–3.63 [m, 12H, $(OCH_2CH_2)_3$]. – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 9.8 and 10.0 (C_5Me_4), 24.8 and 34.1 ($C_5Me_4CH_2CH_2$), 58.9 (OMe), 70.0, 70.7, 71.2, 71.4 and 72.1 [$CH_2(OCH_2CH_2)_3$], 96.4, 97.1 and 97.6 (C_5Me_4), 205.2 (CO). – MS, *m/z* (%): 472 (9) [M^+]. – IR (neat): $\tilde{\nu}$(CO) = 2030 cm^{-1} s, 1985 s. – $C_{21}H_{33}ClFeO_6$ (472.8): calcd. C 53.34, H 7.03; found C 54.11, H 7.36.

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