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Ether- and amine-substituted cyclopentadienes as ligands in organometallic compounds: examples for iron and barium

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Abstract

Cyclopentadienes with Lewis donor atoms in side chains of the type $C_5H_5CH_2CH_2R$ (R = OCH_3, OC_2H_5, $CH_2OC_2H_5$, $N(CH_3)_2$, $OCH_2CH_2OCH_3$) are described. After deprotonation, these compounds can be used as ligands in main group and transition element chemistry, as shown by the examples of bariocenes and ferrocenes. ^{13}C-NMR evidence for the Lewis base stabilization of $Ba(C_5H_4CH_2CH_2OCH_2CH_2OCH_3)_2$ is presented. The compounds [parent cyclopentadiene for R = $OCH_2CH_2OCH_3$; $Ba(C_5H_4CH_2CH_2OCH_2CH_2OCH_3)_2$; $Fe(C_5H_4CH_2CH_2R)_2$ for all R] are characterized by ^{1}H- and ^{13}C{^{1}H}-NMR, IR, MS and elemental analysis.

Keywords: Iron; Barium; Cyclopentadienes; Metallocenes; Ferrocenes; Intramolecular coordination

1. Introduction

The cyclopentadiene ligand is one of the most versatile ligands in organometallic chemistry [1]. The ligand can be altered to achieve steric hindrance and then used to stabilize unusual geometries or oxidation states [2]. The neutral cyclopentadiene ligand precursors also can be substituted to include other possible donor atoms in side chains. The syntheses of cyclopentadienes with donor sites in the side chain and the utilization of this type of ligand in the chemistry of main group elements and transition metals has been reported recently by us, and others [3–8]. There appear, however, to be few reports of species containing more than one Lewis base per pendant tail on the ring [8]. Such species have the potential to be greater than four coordinate upon metal center coordination. In particular, barium, with an ionic radius of 142 pm [9], demands a high coordination environment. Although examples of coordination numbers as low as four [10,11] can be found, more commonly encountered species are eight or ten coordinate [12].

2. Results and discussion

2.1. Syntheses of cyclopentadienes

The cyclopentadiene ligand occupies three coordination sites and has a charge of negative one, if bonded in an η^5 fashion. The introduction of side chains with Lewis donor sites keeps the charge at negative one, but it now is possible to include inter- or intramolecular coordination to a central metal atom. This can lead to stabilization of coordinatively unsaturated species, and also can influence further reaction.

The ether- or amine-substituted ligands are synthesized by the reaction of NaCp with the appropriate alkyl halide or tosylate in THF (Eq. (1)). After aqueous workup, the monosubstituted cyclopentadienes **2** are obtained as a mixture of two regioisomers **A** and **B**, Form 1 (see Experimental Section) [3,13]. The preparation of **2e** can be accomplished by using either the bromide **1e** or tosylate **1f**, both of which are obtainable from 2-(2-methoxy)ethoxyethanol. Reaction of one equivalent of NaCp with one equivalent of either **1e** or **1f** in THF at 25°C for 24 h affords the cyclopentadiene **2e**. The cyclopentadienes **2** are colorless liquids at ambient conditions. On prolonged storage at ambient

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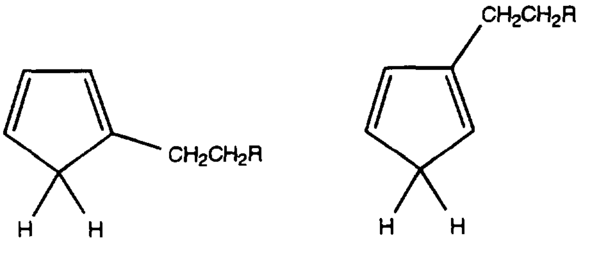


A **B**

Form 1.

temperature, however, they dimerize and, therefore, are stored at −30°C.

$$NaC_5H_5 + \underset{1}{XCH_2CH_2R} \rightarrow \underset{2}{C_5H_5CH_2CH_2R} + NaX \quad (1)$$

1a: X = Cl, R = OCH_3; **1b**: X = Cl, R = OC_2H_5; **1c**: X = Cl, R = $CH_2OC_2H_5$; **1d**: X = Cl, R = $N(CH_3)_2$; **1e**: X = Br, R = $OCH_2CH_2OCH_3$; **1f**: X = p-$CH_3C_6H_4SO_3$, R = $OCH_2CH_2OCH_3$.

2.2. Bariocenes

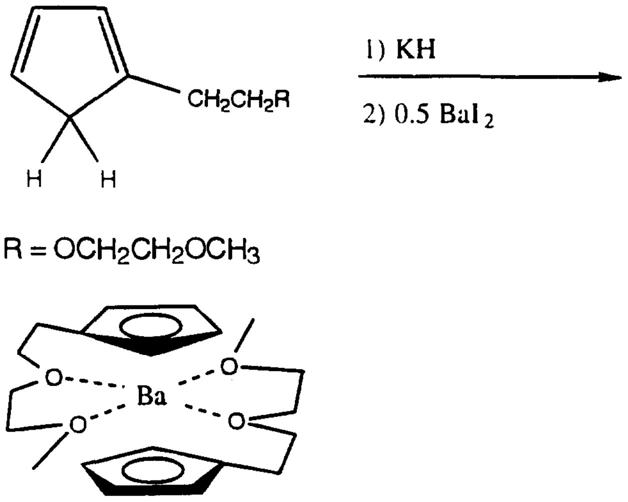
A previous report described the syntheses of *bis*(cyclopentadienyl)-barium compounds by oxidative addition [4]. Finely divided elemental barium, prepared by the reduction of BaI_2 with potassium metal (Eq. (2)), reacts with cyclopentadienes to give bariocenes and H_2 (Eq. (3)). The bariocenes **3** are light tan solids and can be used for the preparation of crystalline BaO [4]. Compounds **3a–d** are particularly insoluble in typical organic solvents. This resulted in poor solution ^{13}C-NMR data, and created an inability to definitively assign all spectral resonances. Likewise, solution cryoscopic molar mass determinations were not practical for these compounds. Mass spectral data suggest a monomeric vapor phase molecularity for these compounds.

Reaction of the cyclopentadiene **2e** with one equivalent of KH in THF leads to the formation of the potassium cyclopentadienide, which then is reacted with one-half of an equivalent of anhydrous BaI_2 in THF (Eq. (4)). After removal of the KI by filtration, the bariocene **3e** is the only product isolated. It is a brown viscous oil, slightly soluble in toluene, but more soluble in polar solvents such as THF. The yield for compound **3e** was observed to be enhanced by following the alternative pathway for its preparation, when compared to compounds **3a–d**. The net reaction is equivalent for each case, the primary reactants are BaI_2 and $C_5H_5CH_2CH_2R$, and the ultimate products are KI, H_2 and $Ba(C_5H_4CH_2CH_2R)_2$. The two pathways only differ in the order of salt elimination and redox reactions.

$$BaI_2 + 2\ K \rightarrow Ba + 2\ KI \quad (2)$$

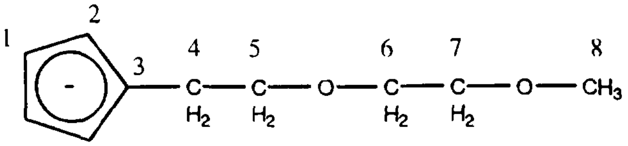
$$Ba + 2\ \underset{2}{C_5H_5CH_2CH_2R} \rightarrow \underset{3}{Ba(C_5H_4CH_2CH_2R)_2} + H_{2(g)} \quad (3)$$

3a: R = OCH_3; **3b**; R = OC_2H_5; **3c**: R = $CH_2OC_2H_5$; **3d**: R = $N(CH_3)_2$.



3e (4)

Bariocene **3e** is depicted with the oxygen atoms coordinated to the central barium atom (Eq. (4)). In order to support this proposed structure, a series of ^{13}C-NMR experiments were conducted, and the results are summarized (Table 1). For a molecule having no coordination with the oxygen atoms, ferrocene **4e** was chosen (see below). The ^{13}C-NMR spectra of the free ligand **2e** and the ferrocene **4e** each possess signals for carbon atoms 6, 7, and 8 at almost the same resonance frequency Form 2. The signals for carbon atoms 4 and 5, however, are shifted due to the change from the cyclopentadiene **2e** to the aromatic cyclopentadienide **4e**. This supports the assumption that there is no coordination of the oxygen atoms evident in compound **4e**. Comparison between the ^{13}C-NMR spectra of **3e** and **4e**, each measured in C_6D_6 to eliminate solvent effects, show significant differences in the shifts for the carbon atoms 5, 6, 7, and 8. The carbon atoms 6 and 7 are far enough from the C_5 unit to be unaffected by



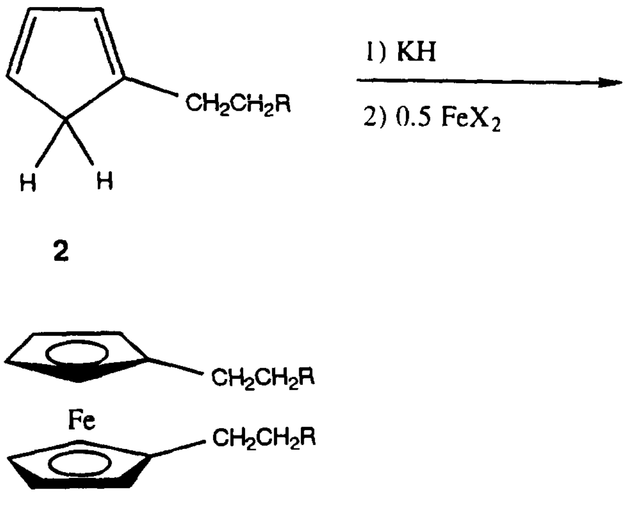
Form 2.

the different electron densities present in the rings of **3e** and **4e** (see below). The observed shift then suggests that residence of the oxygen atoms is in the coordination sphere of the barium center. This would orient the lone pairs of electrons on the two oxygen atoms in, toward the metal center, and give rise to the shifts, as observed for C(7) [3.3 ppm] and C(6) [1.8 ppm].

Cryoscopic molecular weight determination was not possible, owing to the poor solubility of **3e** in benzene. It is difficult, therefore, to determine if the coordination of the oxygen atoms takes place in an inter- or intramolecular fashion. Likewise, a high mass parent peak was not observed in the mass spectrum which could correspond to vapor phase oligomers.

2.3. Ferrocenes

The ferrocenes **4** can be synthesized by analogous procedures as those employed for the bariocenes described above. Thus, reaction of two equivalents of the potassium salt of the base-substituted cyclopentadiene and one equivalent of anhydrous $FeCl_2$ or $FeBr_2$ in THF (Eq. (5), only one regioisomer depicted) produces ferrocenes **4a**–**4d**, which are purified by high vacuum distillation. Compound **4e** was purified by filtration of a hexane solution through a layer of celite. All of the above-described ferrocenes are dark orange, air-stable liquids at ambient conditions and are soluble in nonpolar solvents such as hexane or toluene. The distillation of these compounds is accompanied by some decomposition. Therefore, elemental analyses (C, H) of these compounds are related somewhat to their distillation, and are susceptible to some error.



4 (5)

4a: X = Cl, R = OCH_3; **4b**: X = Cl, R = OC_2H_5; **4c**: X = Cl, R = $CH_2OC_2H_5$; **4d**: X = Cl, R = $N(CH_3)_2$; **4e**: X = Br, R = $OCH_2CH_2OCH_3$.

Table 1
$^{13}C\{^1H\}$ data for compounds **2e**, **3e**, and **4e**

Compound (solvent)	4	5	6	7	8
2e ($CDCl_3$)	30.1/30.8	70.7/71.2	70.0	72.0	58.9
4e ($CDCl_3$)	29.6	71.9	70.0	72.2	58.9
4e (C_6D_6)	30.0	72.2	70.3	72.3	58.5
3e (C_6D_6)	29.9	71.3	68.5	75.6	58.3

Spectroscopic data for the iron compounds are compiled (experimental section). The ^1H and $^{13}C\{^1H\}$-NMR spectroscopic data for compound **2e** are very similar to those of the previously described cyclopentadienes **2a**–**2d**, and clearly indicate the presence of two isomers [3,13]. The presence of the cyclopentadienide anion in **3e** is shown by ^1H and $^{13}C\{^1H\}$-NMR. The signals for the C_5 ring atoms are observed 35–40 ppm downfield from the ring carbons in the ferrocene **4e** [14]. One reason for this phenomenon lies in the size difference: the Ba^{2+} ion is about twice as large as the Fe^{2+} ion (Ba^{2+}: 142 pm, Fe^{2+}: 78 pm [9]) and orbital overlap, therefore, is greater in the case of iron. A second reason is the difference in electronegativity between Fe and Ba (Ba: 1.0, Fe: 1.6 [9]). The proposed bent structure of the bariocene, in contrast to the presumed linear ferrocene, should bear a minor impact on this shift in the ^{13}C NMR [15]. The mass spectra of the ferrocenes **4** all show the parent peak and fragments resulting from the loss of one base-substituted Cp fragment.

3. Summary

The preparation of ether- and amine-substituted cyclopentadienes has been demonstrated. These compounds have been used successfully in the chemistry of transition metals and main group elements, as shown by the examples of ferrocenes and bariocenes. ^{13}C-NMR evidence for the Lewis base stabilization in monosubstituted, diether-containing bariocenes by coordination of the ether oxygen atoms to the barium center was presented. The substituted ferrocenes do not reveal comparable behavior, as indicated by ^{13}C-NMR.

4. Experimental details

4.1. General comments

All manipulations were carried out with the exclusion of air and moisture in an atmosphere of purified nitrogen, using standard Schlenk or glove box techniques. Solvents were dried using standard literature methods. NaCp was prepared by the reaction of NaH with freshly distilled cyclopentadiene. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. NMR spectra were obtained on a Varian Gemini 300, using residual ^1H in the ^2D solvent (^1H) and natural abundance ^{13}C in the solvent (^{13}C) as internal standards (^1H (300.1 MHz), $^{13}C\{^1H\}$ (75.5 MHz)). GC/MS experiments were carried out on a Hewlett Packard HP 5880/5990A system. IR spectra were obtained on a Perkin Elmer 983 spectrometer. Anhydrous BaI_2, $FeCl_2$ and $FeBr_2$ were purchased from a commercial vendor (Strem) and used as received, without additional purification.

4.2. Syntheses of the cyclopentadienes **2a–2d**

The detailed syntheses of compounds **2a–2d** are described elsewhere [3].

4.3. Synthesis of 2-(2-methoxyethoxy)ethylcyclopentadiene, 2e

4.3.1. Use of 2-(2-methoxyethoxy)bromoethane, $BrCH_2CH_2OCH_2CH_2OCH_3$

A sample of 13.3 g (72.7 mmol) of $BrCH_2CH_2OCH_2CH_2OCH_3$ (obtained by the reaction of the alcohol with PBr_3)[16] is added slowly to a solution of 6.4 g (72.6 mmol) of NaCp in THF at 0°C. After warming to 25°C, the reaction mixture is stirred for 16 h, during which time a colorless solid precipitates. The solid is removed by filtration and the solvent is removed using a rotary evaporator. The brown residue is distilled at 0.5 Torr and 57–58°C giving 5.9 g (48%) of a colorless liquid.

Compound **2e**: analysis: found: C, 71.08; H, 9.38. $C_{10}H_{16}O_2$ (168.24) calc.: C, 71.39; H, 9.59%. colorless liquid, bp.: 57–58°C/0.5 Torr. IR (neat, NaCl plates, cm^{-1}) 3052 m, 2868 vs, b, 1596 w, 1446 s, 1358 s, 1279 m, 1240 s, 1196 s, 1104 vs. ^1H-NMR ($CDCl_3$) 2 isomers: δ 2.7 (m, 2 H, CH_2-$^cC_5$), 2.9 (d, $J = 8.4$ Hz, 2 H, CH_2), 3.4 (s, 3 H, CH_3), 3.5–3.8 (m, 6 H, CH_2O), 6.1–6.5 (m, 3 H, CH ($^cC_5$)). $^{13}C\{^1H\}$-NMR ($CDCl_3$): (2 isomers) δ 30.1, 30.8 (CH_2), 41.2, 43.6 (CH_2 of $^cC_5$), 58.9 (CH_3), 70.0 (CH_2), 70.7, 71.2 (CH_2), 72.0 (CH_2), 127.5, 127.7 (CH), 131.2, 132.6 (CH), 133.8, 134.9 (CH), 143.8, 146.2 (C^i). MS [*m/e* (rel. int. %)]: 168 (1) M^+, 123 (4) M^+-C_2H_5O, 92 (100) $C_7H_8^+$, 77 (48) $C_6H_5^+$, 59 (85) $C_3H_7^+$.

4.3.2. Use of 2-(2-methoxyethoxy)ethyltoluenesulfonate, $CH_3C_6H_5SO_3CH_2CH_2OCH_2CH_2OCH_3$

A sample of 20.75 g (75.6 mmol) of p-$CH_3C_6H_5SO_3CH_2CH_2OCH_2CH_2OCH_3$ (prepared from the alcohol and p-$CH_3C_6H_5SO_3Cl$)[17] is added to a solution of 6.6 g of NaCp in 200 ml of THF. A white–yellow suspension is formed and the reaction mixture is stirred for 16 h at 25°C and refluxed for an additional 2 h. After the addition of 300 ml of diethyl ether, the organic phase is washed with water, dried and evaporated. The residue then is distilled at 0.5 Torr and 57–58°C, yielding 6.8 g (54%) of **2e**.

The spectroscopic and analytical data are listed under Section 4.3.1.

4.4. Preparation of 3e

A solution of the potassium salt of the substituted cyclopentadiene is prepared from 0.58 g (14.5 mmol) of KH and 2.44 g (14.5 mmol) of compound **2e** in 60 ml of THF. This clear, colorless solution is added to a solution of 2.83 g (7.24 mmol) of anhydrous BaI_2 in 100 mL of THF and stirred at ambient temperature for 20 h. During this time, the reaction mixture turns brown and a colorless solid precipitates. The volatiles are removed at 5×10^{-2} Torr, the residue dissolved in 100 ml of toluene and filtered through a layer of celite. After removal of the toluene, 2.3 g (67%) of a brown viscous oil is obtained.

Compound **3e**: analysis: found: C, 51.27; H, 7.18. $C_{20}H_{30}BaO_4$ (471.78) calc.: C, 50.92; H, 6.41%. brown liquid. IR (neat, NaCl plates, cm^{-1}): 3050 m, 2909 vs, 2868 vs, 1446 m, 1350 m, 1193 m, 1117 vs, 1075 vs, 1040 s. ^1H-NMR (C_6D_6): δ 2.63 (t, $J = 7.5$ Hz, 4 H, $^cC_5$–CH_2), 3.40 (s, 6 H, CH_3), 3.5–3.7 (m, 12 H, CH_2–O), 6.08 (s, 4 H, $^cC_5H_4$), 6.26 (s, 4 H, $^cC_5H_4$). $^{13}C\{^1H\}$-NMR δ (C_6D_6): 29.9 ($^cC_5$–C), 58.3 (CH_3), 68.5 (CH_2), 71.3 (CH_2), 75.6 (CH_2), 107.2 (CH), 108.0 (CH), 121.5 (C^i).

4.5. Syntheses of the ferrocenes 4a–4d

For the preparation of the potassium cyclopentadienide, 0.12 mole (4.8 g) of KH is suspended in 50 ml of THF and 0.12 mole of the substituted cyclopentadiene is added (**2a**: 14.9 g, **2b**: 16.6 g, **2c**: 18.3 g, **2d**: 17.9 g). The mixture is heated for 1 h and the solution of the potassium salt is transferred into an addition funnel and added to a suspension of 7.61 g (0.06 mole) of $FeCl_2$ in 50 ml of THF. The reaction mixture is heated for 2 h at 60°C. After filtration of the precipitate and removal of the solvent, the product is purified by high-vacuum distillation.

Compound **4a**: yield 14.7 g (81%). analysis: found: C, 65.16; H, 7.82. $C_{16}H_{22}FeO_2$ (302.19) calc.: C, 63.60; H, 7.34%. orange–brown liquid, bp: 100°C/10^{-2} Torr. ^1H-NMR ($CDCl_3$): δ 2.54 (t, $J = 7.1$ Hz, 4 H, $^cC_5$-CH_2), 3.30 (s, 6 H, CH_3), 3.43 (t, $J = 7.1$ Hz, 4 H, CH_2–O), 4.00 (s, 8 H, $^cC_5H_4$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 29.4 ($^cC_5$–C), 58.2 (CH_3), 67.9 (CH), 68.8 (CH), 73.3 (C–O), 85.1 ($^cC_5$-C^i). MS [*m/e* (rel. int. %)]: 302 (100) M^+, 179 (24) M^+-C_5H_4R, 147 (26) M^+-C_5H_4R-CH_3O, 124 (26) $C_5H_4R^+$.

Compound **4b**: yield 16.8 g (85%). analysis: found: C, 67.49; H, 8.71. $C_{18}H_{26}O_2$ (330.24) calc.: C, 65.47; H, 7.94%. orange-brown liquid, bp: 118°C/5 × 10^{-3} Torr. ^{1}H-NMR (C_6D_6): δ 1.09 (t, $J = 6.9$ Hz, 6 H, CH_3), 2.55 (t, $J = 6.9$ Hz, 4 H, $^cC_5$–CH_2), 3.26 (q, 4 H, CH_2–CH_3), 3.40 (t, 4 H, CH_2–O), 3.90 (s, 4 H, CH) 3.94 (s, 4 H, CH). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 14.8 (CH_3), 29.5 ($^cC_5$–C), 65.9 (CH_2CH_3), 67.7 (CH), 68.8 (CH), 71.3 (C–O), 85.0 ($^cC_5$–C^i). MS [*m/e* (re. int. %)]: 330 (100) M^+, 242 (23) M^+–$C_2H_4OC_2H_5$–CH_3, 193 (22) M^+–C_5H_4R, 147 (17) M^+–C_5H_4R–OC_2H_5.

Compound **4c**: yield 18.1 g (84%). analysis: found: C, 64.28; H, 7.56. $C_{20}H_{30}FeO_2$ (358.29) calc.: C, 67.05; H, 8.44%. orange-brown liquid, bp: 120°C/5 × 10^{-3} Torr. ^{1}H-NMR ($CDCl_3$): δ 1.17 (t, $J = 6.6$ Hz, 6 H, CH_3), 1.73 (tt, $J = 7.4$ Hz, $J = 7.4$ Hz, 4 H, $C_5CH_2CH_2$), 2.33 (t, $J = 7.4$ Hz, 4 H, *c*-C_5-CH_2), 3.37 (t, $J = 7.4$ Hz, 4 H, CH_2–O), 3.43 (q, $J = 6.6$ Hz, 4 H, CH_2–CH_3), 3.96 (s, 8 H, $^cC_5H_4$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 14.8 (CH_3), 25.6 ($^cC_5$–C), 30.8 ($^cC_5$–C–C), 65.8 (C–CH_3), 67.6 (CH_2–O), 68.4 (CH), 69.9 (CH), 88.5 ($^cC_5$–C^i). MS [*m/e* (rel. int. %)]: 358 (100) M^+, 206 (52) M^+–C_5H_4R, 160 (63) M^+–C_5H_4R–OC_2H_5, 134 (98) M^+–C_5H_4R–$C_2H_4OC_2H_5$ 120 (32) M^+–C_5H_4R–$C_3H_6OC_2H_5$.

Compound **4d**: yield: 14.8 g (75%). analysis: found: C, 68.03; H, 8.53. $C_{18}H_{28}FeN_2$ (328.30) calc.: C, 65.85; H, 8.60%. orange-brown liquid, bp: 103°C/5 × 10^{-3} Torr. ^{1}H-NMR ($CDCl_3$): δ 2.17 (s, 12 H, CH_3), 2.34 (m, 4 H, CH_2), 2.38 (m, 4 H, CH_2–N), 3.91 (s, 8 H, $^cC_5H_4$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 27.4 ($^cC_5$–C), 45.1 (CH_3), 60.9 (CH_2–N), 67.6 (CH), 68.4 (CH), 86.5 ($^cC_5$–C^i). MS [*m/e* (rel. int. %)]: 328 (25) M^+, 283 (2) M^+–$N(CH_3)_2$, 270 (4) M^+–$CH_2N(CH_3)_2$, 190 (6) M^+–C_5H_4R, 147 (1) M^+–C_5H_4R–$N(CH_3)_2$, 134 (2) $C_5H_4R^+$. high-resolution MS (*m/e*): calc. 328.1595, found 328.1594.

*4.6. Synthesis of compound **4e***

A solution of the potassium salt of the substituted cyclopentadiene is prepared by adding 3.3 g (19.6 mmol) of compound **2e** to a suspension of 0.8 g (19.9 mmol) of KH in 50 ml of THF. The solution then is transferred into an addition funnel and added dropwise to a suspension of 2.1 g (19.8 mmol) of $FeBr_2$ in 50 ml of THF. The reaction mixture is stirred for 20 h at ambient temperature and all volatiles are removed at 5 × 10^{-2} Torr. The residue was extracted twice with 50 ml each of hexanes and the combined hexane extracts are filtered through a layer of celite. After removal of the hexanes at 5 × 10^{-2} Torr, 5.5 g (71%; based on **2e** added) of an orange oil are obtained.

Compound **4e**: analysis: found: C, 60.95; H, 8.22. $C_{20}H_{30}FeO_4$ (390.30) calc.: C, 61.55; H, 7.75%. orange liquid. IR (neat, NaCl plates, cm^{-1}): 3085 w, 2919 vs, 2870 vs, 1468 m, 1454 m, 1356 m, 1245 vs, 1198 s, 1117 vs, 1040 s, 1025 s. ^{1}H-NMR ($CDCl_3$): δ 2.63 (t, $J = 7.5$ Hz, 4 H, $^cC_5$–CH_2), 3.40 (s, 6 H, CH_3), 3.5–3.7 (m, 12 H, CH_2–O), 4.01 (d, $J = 1.8$ Hz, 4 H, $^cC_5H_4$), 4.02 (d, $J = 1.8$ Hz, 4 H, $^cC_5H_4$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 29.6 ($^cC_5$–C), 58.9 (CH_3), 68.0 (CH), 69.0 (CH), 70.0 (C–O), 71.9 (C–O), 72.2 (C–O), 85.3 ($^cC_5$–C^i) (peak assignment by DEPT). MS [*m/e* (rel. int. %)]: 390 (55) M^+, 223 (100) M^+–C_5H_4R.

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