Journal of Organometallic Chemistry, 426 (1992) 279–285
Elsevier Sequoia S.A., Lausanne
JOM 22350

Cyclopentadienylmagnesium alkoxides derived from polyfunctional alcohols

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(Received August 16, 1991)

Abstract

Magnesocene (**1**) reacts with polyfunctional alcohols (**2a**, *N,N*-dimethylethanolamine; **2b**, 2-ethoxyethanol; **2c**, 2-(2-ethoxyethoxy)ethanol; **2d**, 2-{[(2-dimethylamino)ethyl]methylamino}ethanol) to yield polymeric cyclopentadienylmagnesium alkoxides (**3a–d**). Compounds **3a–d** dissolve in pyridine to yield solutions containing pyridine adducts (**4a–d**) of the corresponding monomers, which may be isolated in the cases of **4a,b**. These compounds all appear to contain formally 12-electron, pseudo-6-coordinate magnesium. Compound **1** reacts with 2,4-dimethyl-6-t-butylphenol (**5**) to form cyclopentadienyl (2,4-dimethyl-6-t-butylphenoxy)magnesium (**6**), in which the steric bulk of the phenoxide ligand stabilizes the monomeric, 8-electron configuration.

Introduction

Bis(η^5-cyclopentadienyl)magnesium (magnesocene) was first prepared in 1954 [1], and arguments about the nature of the metal-ring bonding have continued sporadically ever since. Various authors have used a battery of spectroscopic techniques to assign either an ionic or a covalent structure to the molecule. In addition there have been a number of theoretical studies, and it appears that the best current description of magnesocene includes at least partial covalent character in the metal-ring bonding [2]. In previous work we have shown that the degree of covalency appears to be increased by the introduction of trimethylsilyl substituents on the cyclopentadienyl ring [3].

Monocyclopentadienyl derivatives of magnesium have received rather less attention, despite the extensive use of cyclopentadienyl Grignard reagents as synthetic intermediates. The crystal and molecular structures of two derivatives of cyclopentadienylmagnesium bromide have been reported [3,4]. A number of cyclopentadienylmagnesium alkyls have also been studied [5,6].

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Cyclopentadienylmagnesium compounds are usually formally 12-electron species; this corresponds to approximate octahedral coordination, assuming that the cyclopentadienyl ring occupies three coordination sites. Cyclopentadienyl(ethoxy)magnesium thus adopts a tetrameric, cubane-like structure, in which each ethoxide ligand bridges between three magnesium atoms [7]. We were interested in preparing a monomeric base-free cyclopentadienylmagnesium alkoxide, in which the electronic and steric requirements of the magnesium atom are satisfied by intramolecular coordination of additional donor substituents on the alkoxide ligand. The results of our investigations are presented below.

Results and discussion

Magnesocene (**1**) reacts readily with proton donors *via* cleavage of one or both metal-ring bonds. In principle therefore, treatment of **1** with one molar equivalent of alcohol should lead directly to the cyclopentadienylmagnesium alkoxide. An analogous technique has been used successfully to prepare methylmagnesium alkoxides [8]. We have indeed found that a toluene solution of **1** reacts readily with a range of polyfunctional alcohols (eq. 1): *N,N*-dimethylethanolamine (**2a**); 2-methoxyethanol (**2b**); 2-(2-ethoxyethoxy)ethanol (**2c**); 2-{[(2-dimethylamino)-ethyl]methylamino}ethanol (**2d**).

$$(\eta\text{-}C_5H_5)_2Mg + ROH \xrightarrow[20°C]{\text{Toluene}} [(\eta\text{-}C_5H_5)MgOR]_x \qquad (1)$$

(**1**) (**3a–d**)

(**2a**, $R = -CH_2CH_2NMe_2$;
2b, $R = -CH_2CH_2OMe$;
2c, $R = -CH_2CH_2OCH_2CH_2OEt$;
2d, $R = -CH_2CH_2NMeCH_2CH_2NMe_2$)

However a 1:1 mole ratio of reactants does not lead to a single product. This is only achieved by using an excess of **1** such that the magnesocene:alcohol ratio is 2:1, which implies that a ligand redistribution equilibrium (analogous to the Schlenk equilibrium for Grignard reagents) is established. An excess of **1** is required to inhibit significant formation of the dialkoxymagnesium (eq. 2).

$$2(\eta\text{-}C_5H_5)MgOR \rightleftharpoons 1 + Mg(OR)_2 \qquad (2)$$

The cyclopentadienylmagnesium alkoxides (**3a–d**) are air- and moisture-sensitive off-white solids, involatile and insoluble in all but strongly coordinating solvents such as pyridine. They decompose without melting at 125–200°C and are evidently polymeric in nature. For those alkoxides containing a single additional donor function this is not unexpected, since the magnesium atom is unable to achieve its preferred 12-electron, 6-coordinate structure by intramolecular coordination alone. However, the fact that **3c** and **3d** also exist preferentially as polymers is something of a surprise: it implies that intermolecular coordination competes effectively with intramolecular coordination in this system.

Various structures may be envisaged for **3a–d**. The simplest involves the presence of linear chains as depicted in Fig. 1; it is probable however that cross-linking of the chains occurs *via* 4-coordinate oxygen atoms.

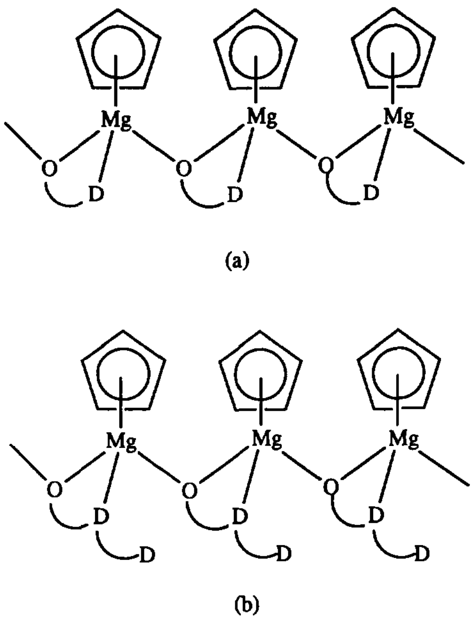


Fig. 1. Schematic simplified structures of (a) **3a,b** and (b) **3c,d**.

In an attempt to increase the solubility of the products we have carried out an analogous series of reactions using decamethylmagnesocene [9]. However, we were not successful in isolating pure compounds in this case.

Compounds **3a–d** dissolve readily in pyridine-d_5 and NMR spectra of their solutions have been recorded. The data are summarized in Tables 1 and 2.

We presume that these solutions contain monomeric species in which two pyridine molecules complete the coordination sphere of the magnesium atom.

$$\mathbf{3a\text{–}d} + \text{py (excess)} \longrightarrow \underset{(\mathbf{4a\text{–}d})}{(\eta\text{-}C_5H_5)Mg(py)_2OR} \qquad (3)$$

(py = pyridine)

This view is reinforced by the isolation of two such species (**4a,b**) by low-temperature crystallization. The presence of pyridine in these adducts is readily observed

Table 1

^{1}H NMR spectroscopic data for **3a–d** in C_5D_5N

3a	6.69 (s, 5H, C_5H_5), 3.78 (t, J = 4.8 Hz, 2H, $-OCH_2-$), 2.44 (t, J = 4.8 Hz, 2H, $-CH_2N-$), 2.20 (s, 6H, $-N(CH_3)_2$)
3b	6.71 (s, 5H, C_5H_5), 3.96 (t, J = 4.4 Hz, 2H, $-OCH_2-$), 3.52 (t, J = 4.4 Hz, 2H, $-CH_2O-$), 3.31 (s, 3H, $-OCH_3$)
3c	6.65 (s, 5H, C_5H_5), 4.01 (t, J = 5.1 Hz, 2H, $-OCH_2-$), 3.71 (s, 4H, $-OCH_2CH_2-$), 3.69 (t, J = 5.1 Hz, 2H, $-CH_2O-$), 3.64 (q, J = 7.1 Hz, 2H, $-CH_2CH_3$), 1.34 (t, J = 7.1 Hz, 3H, $-CH_3$)
3d	6.62 (s, 5H, C_5H_5), 4.1–2.1 (broad, 6H, $-CH_2-$), 3.07 (t, J = 5.2 Hz, 2H, $-CH_2-$), 2.55 (s, 3H, $-NCH_3$), 2.45 (s, 6H, $-N(CH_3)_2$)

Table 2

^{13}C NMR spectroscopic data for **3a–d** in C_5D_5N

3a	105.56 (C_5H_5), 64.18 ($-OCH_2-$), 59.09 ($-CH_2N-$), 45.96 ($-N(CH_3)_2$)
3b	105.72 (C_5H_5), 77.27 ($-OCH_2-$), 62.03 ($-OCH_3$), 60.83 ($-CH_2O-$)
3c	105.44 (C_5H_5), 76.02 ($-OCH_2$), 70.85 ($-CH_2-$), 70.59 ($-CH_2-$), 67.01 ($-CH_2-$), 66.88 ($-CH_2-$), 62.45 ($-CH_3$)
3d	105.52 (C_5H_5), 62.21 ($-CH_2-$), 58.88 ($-CH_2-$), 58.48 ($-CH_2-$), 57.45 ($-CH_2-$), 47.55 ($-N(CH_3)_2$), 45.22 ($-NCH_3$)

Table 3

Infrared spectroscopic data for **3a–d** and **4a,b** [a]

3a	1260s, 1096s, 1013s, 945m, 896m, 799m, 763m, 635w, 620w, 521w, 464w, 451w, 441w
3b	1303w, 1259m, 1249m, 1196w, 1137m, 1091s, 1068s, 1050s, 1011s, 914m, 834m, 778s, 721s, 594m, 465m, 451m, 395m, 312w
3c	1301w, 1282w, 1259m, 1128s, 1085s, 1053s, 1020s, 918m, 844m, 789m, 745s, 597m, 551m, 479s, 398m, 327m
3d	1240m, 1117s, 992s, 929w, 897w, 803m, 740m, 584w, 490w, 395w, 364w, 301w
4a	1599w, 1575w, 1259m, 1216w, 1122s, 1096w, 1070w, 1037s, 1011s, 942w, 891w, 799m, 742m, 705m, 629w, 489w
4b	1601m, 1577w, 1300m, 1282m, 1259m, 1246m, 1215w, 1178m, 1127s, 1097s, 1085s, 1056s, 1020s, 1006s, 934s, 918s, 902m, 843m, 807m, 791m, 744s, 700m, 553m, 480s, 401m, 326s

[a] Selected absorption maxima (cm^{-1}): s = strong; m = medium; w = weak.

by comparison of their infrared spectra with those of their polymeric precursors (Table 3).

Bands at 1601, 1577, 1215, 1127, 744, 700 cm^{-1} are diagnostic for coordinated pyridine [10], as can be seen by examination of the spectra of **3b** and **4b** (Fig. 2).

Compounds **4a,b** are crystalline orange solids, sensitive to air and moisture, which are readily soluble in pyridine, but less so in non-coordinating solvents. They have sharp melting points, but appear not to sublime: attempted measurement of mass spectra, either by EI–CI or FAB techniques, resulted in only weak detection

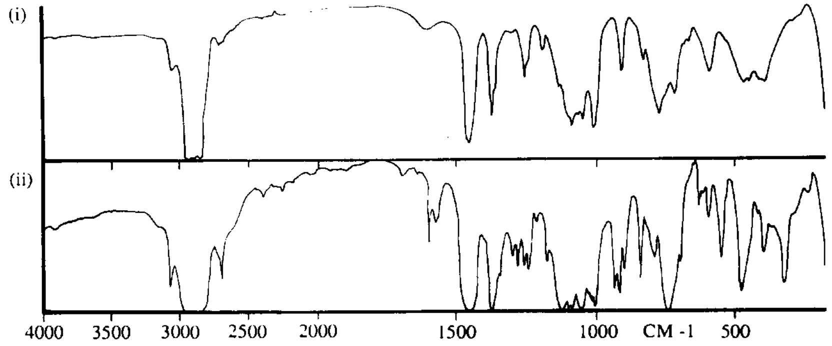
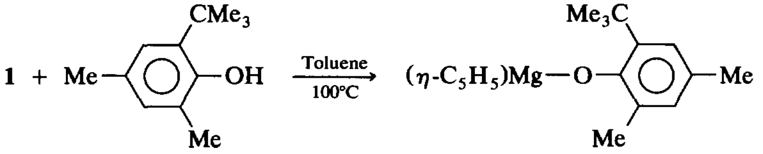


Fig. 2. Infrared spectra of (i) **3b** and (ii) **4b**, recorded as Nujol mulls between KBr disks.

of the molecular ions, together with fragments expected from the decomposition of the complexes. Although **3c,d** dissolve in pyridine to give orange-coloured solutions, it was not possible to isolate **4c,d** in a pure state.

The obvious preference for intermolecular interactions in this system suggests that an alternative approach is necessary in order to obtain monomeric species. Andersen *et al.* have utilized the steric bulk of the neopentyl ligand to prepare a monomeric base-free cyclopentadienylmagnesium alkyl [6]. We have therefore investigated the reaction of **1** with the bulky phenol 2,4-dimethyl-6-t-butylphenol (**5**). This reaction is slow, and only after extended heating at 100°C in toluene is the reaction complete.



(4)

(**5**) (**6**)

Cyclopentadienyl(2,4-dimethyl-6-t-butylphenoxy)magnesium (**6**) is a colourless crystalline solid, sensitive to air and moisture and soluble even in non-polar organic solvents. Its NMR and IR spectra are consistent with the proposed formulation. As with **4a,b**, it was not amenable to study by mass spectrometry. In the absence of structural data we assign a monomeric structure to **6** on the basis of steric inhibition of oligomerization. The related ligand 2,6-di-t-butyl-4-methylphenoxide has been used to stabilize monomeric tetrahedral aluminium compounds [11].

Conclusion

Cyclopentadienylmagnesium alkoxides derived from alcohols capable of further intramolecular coordination do not adopt simple monomeric structures. Rather, the presence of additional donor functions leads to the formation of intermolecular linkages and the production of polymers. Steric inhibition of oligomerization does however lead successfully to the synthesis of the first base-free monomeric cyclopentadienylmagnesium aryloxide.

Experimental

All operations were carried out under argon by use of standard Schlenk techniques in conjunction with a Miller–Howe system Sindex inert atmosphere glove box. Solvents were predried over molecular sieves, then distilled from molten alkali metal (Na, K or Na/K alloy as appropriate), and deoxygenated before use by boiling under reduced pressure and repeated saturation with inert gas. Infrared spectra were recorded on a Perkin–Elmer 983G spectrometer, as Nujol mulls between CsI or KBr discs. NMR spectra were recorded on a Nicolet AM300 spectrometer. Analyses were carried out in the microanalytical laboratory of this department. Melting points were measured on samples sealed in capillaries under argon with an electrothermal apparatus and are uncorrected. Compound **1** was prepared by direct reaction of cyclopentadiene with magnesium filings at 500–

Table 4

Analytical data for **3a–d**, **4a,b** and **6**

Compound	Colour	Melting point (°C)	Microanalysis (%) [a]		
			C	H	N
3a	Pale pink	dec. > 125	58.01 (60.87)	8.00 (8.51)	10.37 (7.89)
3b [b]	Off-white	dec. > 130	55.02 (58.42)	7.47 (7.35)	–
3c	Cream/pink	dec. > 150	59.78 (59.36)	7.87 (8.15)	–
3d	Off-white	dec. > 200	62.64 (61.43)	9.01 (9.45)	10.23 (11.94)
4a	Pale orange	90–92	69.50 (67.96)	7.87 (7.52)	12.41 (12.52)
4b	Orange	95–97	65.58 (66.98)	8.49 (6.89)	9.16 (8.68)
6	Colourless	235–238	76.04 (76.57)	8.27 (8.32)	–

[a] The microanalytical data relate to spectroscopically pure samples; discrepancies are presumably due to the extreme air- and moisture-sensitivity of the samples. [b] This product required washing with diethyl ether before a pure sample was obtained.

600°C, as described by Barber [12]. The alcohols **2a–d** and **5** were purified as follows.

2a: Fractionally distilled (134–137°C) from KOH.

2b: Passed through a column of activated alumina; allowed to stand over $MgSO_4$; fractionally distilled (124–126°C) from Na.

2c: Fractionally distilled (192–198°C) from KOH.

2d: Fractionally distilled (205–210°C) from KOH.

5: Fractionally distilled (118–120°C, 10 mmHg) from a 4A molecular sieve.

Cyclopentadienylmagnesium alkoxides, 3a–d, and the pyridine adducts, 4a,b

The procedure employed in the preparation of **3a–d** is described below for the case of **3a**. Yields (based on the alcohols) were essentially quantitative.

To a solution of **1** (1.53 g, 9.71 mmol) in toluene (50 ml) was added dropwise with stirring, a toluene solution of **2a** (0.5 ml, 4.97 mmol). There was an immediate precipitate. The cloudy white solution was stirred at 20°C for 4 h. A pale pink solid was isolated by filtration, washed twice with toluene, and dried *in vacuo*.

Spectroscopic data for **3a–d** are summarized in Tables 1, 2 and 3. Analytical data are given in Table 4.

Compounds **3a,b** dissolved readily in pyridine to give clear orange solutions from which **4a,b** could be crystallized at −30°C. Spectroscopic and analytical data for **4a,b** are given in Tables 3 and 4.

Cyclopentadienyl(2,4-dimethyl-6-t-butylphenoxy)magnesium (6)

To a solution of **1** (1.00 g, 6.47 mmol) in toluene (50 ml) was added a toluene solution of **5** (1.15 g, 6.47 mmol). The mixture was heated at 100°C for 100 h. The solvent was then removed *in vacuo* to yield an oily off-white solid, which was crystallized from pentane at −30°C. The colourless crystals were isolated by

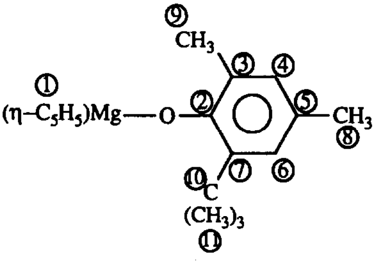


Fig. 3. Carbon numbering scheme for **6**.

decantation, washed with a little cold pentane, and dried *in vacuo*. Analytical data for **6** are given in Table 4. Spectroscopic data are as follows. ^1H NMR (C_6D_6): δ 7.10 (s, 1H, Ar-H), 6.87 (s, 1H, Ar-H), 6.05 (s, 5H, C_5H_5), 2.26 (s, 3H, Ar-CH_3), 2.19 (s, 3H, Ar-CH_3), 1.33 (s, 9H, -$C(CH_3)_3$) ppm. ^{13}C NMR (C_6D_6) (assignments in brackets refer to the numbering scheme in Fig. 3 and are based in part on calculated substituent effects for aromatic carbon atoms [13]): δ 151.57 (C2), 136.07 (C7), 128.90 (C4), 127.77 (C5), 125.91 (C3), 125.40 (C6), 105.15 (C1), 33.87 (C10), 30.78 (C11), 19.74 (C8), 17.44 (C9) ppm. IR (selected bands): 1313m, 1263s, 1221s, 1136s, 1103s, 1013s, 893w, 850m, 801s, 777s, 753w, 713w, 650w, 617w, 596w, 566w, 522m, 499m, 380m cm^{-1}.

Acknowledgement

O.N.D.M. acknowledges the support of D.E.N.I. in the provision of a postgraduate studentship.

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