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Synthesis and Structure of [*trans*-{1,2-Bis(κ^2-*O*,*O*-*N*-phenylcarbamoyl)cyclopentadienylbis(thf)}magnesium]·4thf

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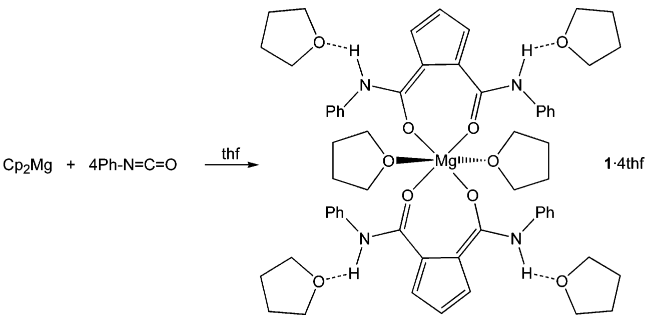
*Summary: The reaction of magnesocene, Cp$_2$Mg, with phenylisocyanate (1:4 equivalents) in thf solvent affords [trans-{1,2-bis(N-phenylcarbamoyl)cyclopentadienylbis(thf)}magnesium]·4thf (**1**·4thf), the structure of which has been determined by single-crystal X-ray diffraction. The structure of **1**·4thf provides evidence for a metal tethering effect in the 1,2-selective formation of other bis-carbamoyl ligands similar to that reported in this work.*

Introduction

The synthesis of functionalized metallocenes continues to be an active area of research due to the increasing use of such complexes in a range of important chemical and technological processes. In particular, attention has focused on the preparation of ferrocenes bearing functional groups on the cyclopentadienyl ligands. In many cases these functional groups may be introduced by Friedel−Crafts substitutions on one or both of the cyclopentadienyl ligands or, alternatively, from the nucleophilic addition of lithioferrocene to electrophiles.[1] Despite the relative ease with which many substituents may be introduced into metallocene ligand frameworks, the incorporation of certain important functional groups such as carbamoyl, [C(O)NH$_2$], and derivatives thereof, has proven to be somewhat more challenging. However, the discovery that sodium cyclopentadienide reacts with *tert*-butylisocyanate (^{t}BuNCO) (1:2 stoichiometry) has provided a very convenient and highly selective route to the bis(*tert*-butylcarbamoyl)cyclopentadienyl complex [Na{C$_5$H$_3$-1,2-(CONH^{t}Bu)$_2$}].[2] This sodium complex was characterized by infrared and NMR spectroscopic methods and was subsequently employed in transmetalation reactions with transition metal halides, leading to the complexes [M{η^5-C$_5$H$_3$-1,2-(CONH^{t}Bu)$_2$}$_2$] (M = Fe, Ru) and [Zr{κ^2-*O*,*O*-C$_5$H$_3$-1,2-(CONH^{t}Bu)$_2$}$_2$Cl$_2$], in which the precise coordination mode of the ligand depends on the hard/soft character of the transition metal.[3,4]

Results and Discussion

Scheme 1



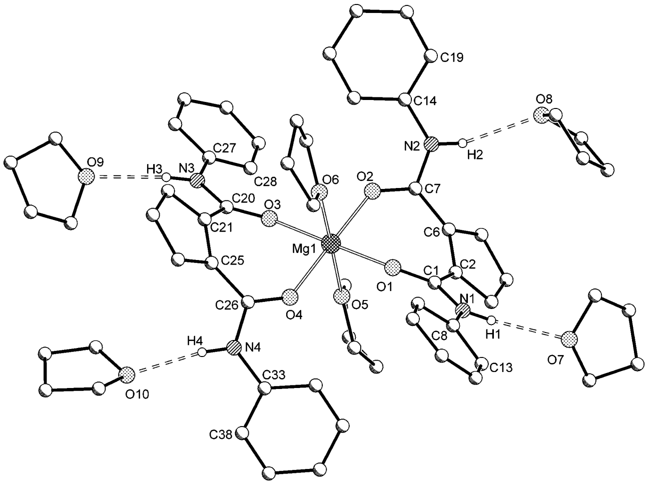


Figure 1. Molecular structure of **1**·4thf. Hydrogen atoms, except those engaged in H-bonding, are omitted.

Although a mechanism to account for the formation of [Na{C$_5$H$_3$-1,2-(CONH^{t}Bu)$_2$}] has been proposed, structural authentication of this key intermediate has remained elusive. In this paper we report the synthesis and structure of the title compound (complex **1**·4thf), a close relative of [Na{C$_5$H$_3$-1,2-(CONH^{t}Bu)$_2$}], formed from the reaction of magnesocene, Cp$_2$Mg, and phenyl isocyanate according to Scheme 1.

Complex **1**·4thf is the first structurally authenticated main group metal complex of this ligand type. The molecular structure of **1**·4thf (Figure 1 and Table 1) consists of two mutually *trans*-[κ^2-*O*,*O*-1,2-bis(*N*-phenylcarbamoyl)cyclopentadienyl] ligands, two *trans* thf ligands, and four thf molecules hydrogen-bonded to the carbamoyl N−H groups.

The Mg−O bond distances to the bis-carbamoyl ligands are in the range 2.012(4)−2.045(4) Å (average 2.028 Å) and are shorter than the Mg(1)−O(5) and Mg(1)−O(6) distances to the thf ligands of 2.136(5) and 2.139(5) Å, respectively. Since the range of *cis*-[O−Mg−O] angles is quite broad at 84.8(2)−94.1(2)° (average

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Table 1. Selected Bond Distances and Angles for Complex 1·4thf

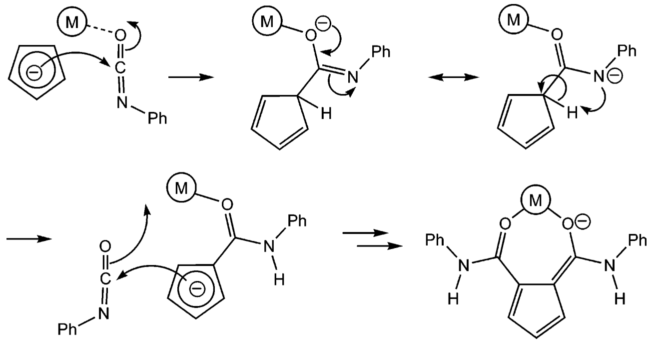
Mg(1)−O(1)	2.013(4)	C(2)−C(3)	1.431(8)	N(2)−H(2)	0.87(5)	C(25)−C(26)	1.438(8)
Mg(1)−O(2)	2.045(4)	C(2)−C(6)	1.439(8)	O(3)−C(20)	1.244(6)	C(27)−N(3)	1.357(7)
Mg(1)−O(3)	2.012(4)	C(3)−C(4)	1.396(8)	O(4)−C(26)	1.251(6)	C(26)−N(4)	1.361(7)
Mg(1)−O(4)	2.042(4)	C(4)−C(5)	1.400(8)	C(20)−C(21)	1.450(8)	N(3)−H(3)	0.99(6)
Mg(1)−O(5)	2.136(5)	C(5)−C(6)	1.404(8)	C(21)−C(22)	1.424(8)	N(4)−H(4)	0.87(5)
Mg(1)−O(6)	2.139(5)	C(6)−C(7)	1.434(8)	C(21)−C(25)	1.421(8)	O(7)−H(1)	2.13(6)
O(1)−C(1)	1.259(6)	C(1)−N(1)	1.357(7)	C(22)−C(23)	1.386(8)	O(8)−H(2)	2.18(5)
O(2)−C(7)	1.259(6)	C(7)−N(2)	1.361(7)	C(23)−C(24)	1.391(8)	O(9)−H(3)	2.15(6)
C(1)−C(2)	1.439(8)	N(1)−H(1)	0.99(6)	C(24)−C(25)	1.404(8)	O(9)−H(4)	2.28(4)

O(1)−Mg(1)−O(2)	89.0(2)	O(2)−Mg(1)−O(6)	91.9(2)	O(1)−C(1)−C(2)	124.8(5)	O(3)−C(20)−N(3)	118.6(6)
O(1)−Mg(1)−O(3)	178.6(2)	O(3)−Mg(1)−O(4)	89.4(2)	O(1)−C(1)−N(1)	119.0(6)	O(3)−C(20)−C(21)	124.9(6)
O(1)−Mg(1)−O(4)	90.6(2)	O(3)−Mg(1)−O(5)	94.1(2)	C(2)−C(1)−N(1)	116.1(5)	C(21)−C(20)−N(3)	116.5(5)
O(1)−Mg(1)−O(5)	87.3(2)	O(3)−Mg(1)−O(6)	84.8(2)	Mg(1)−O(2)−C(7)	133.2(4)	Mg(1)−O(4)−C(26)	133.7(4)
O(1)−Mg(1)−O(6)	93.8(2)	O(4)−Mg(1)−O(5)	91.1(2)	O(2)−C(7)−C(6)	124.7(6)	O(4)−C(26)−C(25)	126.1(6)
O(2)−Mg(1)−O(3)	91.0(2)	O(4)−Mg(1)−O(6)	89.0(2)	O(2)−C(7)−N(2)	119.2(6)	O(4)−C(26)−N(4)	118.1(6)
O(2)−Mg(1)−O(4)	179.1(2)	O(5)−Mg(1)−O(6)	178.9(2)	C(6)−C(7)−N(2)	116.1(6)	C(25)−C(26)−N(4)	115.8(5)
O(2)−Mg(1)−O(5)	88.1(2)	Mg(1)−O(1)−C(1)	136.4(4)	Mg(1)−O(3)−C(20)	138.2(4)		

90.00°), the coordination geometry at Mg(1) is best described as distorted tetragonal. The structural features within the two bis-carbamoylfulvene units of the bidentate ligands are essentially identical, and so a detailed description of only one ligand is merited. Thus the C−C bond distances range from 1.396(8) [C(3)−C(4)] to 1.439(8) Å [C(2)−C(6)] (average 1.42 Å), and the O(1)−C(1) and O(2)−C(7) distances are equal at 1.259(6) Å, suggesting an appreciable degree of π-delocalization across the bidentate ligands. The lengths of the hydrogen bonds between the carbamoyl hydrogens and the oxygen atoms of the four additional thf molecules fall within the range 2.13(6)−2.28(4) Å. A search of the Cambridge Crystallographic Database reveals that H···O hydrogen bond distances have a broad range of 0.753−2.056 Å and therefore that the lengths of the hydrogen bonds in **1**·4thf are in fact the longest measured with oxygen as the acceptor.[5] Elemental analysis and ^{1}H NMR spectroscopy reveal that either placing **1**·4thf under vacuum and heating to 60 °C or refluxing in toluene, for 1 h in both cases, effects complete removal of the hydrogen-bonded thf ligands.

The only other structurally characterized examples of complexes containing κ^2-*O*,*O*-bis-carbamoyl ligands are Δ/Λ-[Zr{κ^2-*O*,*O*-C_5H_3-1,2-(CONH^{t}Bu)$_2$}$_2$Cl$_2$], [Zr{κ^2-*O*,*O*-C_5H_3-1,2-(CONH^{t}Bu)$_2$}Cl$_3$(thf)], and [CpZr{κ^2-*O*,*O*-C_5H_3-1,2-(CONH^{t}Bu)$_2$}Cl$_2$(thf)], which were formed by addition of the sodium salt of the bis-carbamoyl ligand to the appropriate Zr(IV) chloride precursor.[4] It has been suggested that selective formation of the 1,2-bis-carbamoyl ligand in this case is due to resonance stabilization. However, whereas this effect may play an important role in the formation of the ligand, the structure of **1**·4thf suggests that the s-block metal may also be partly responsible for the 1,2-selectivity through a tethering effect. That is, initial coordination of phenylisocyanate to the oxophilic magnesium is likely to occur (hard−hard interaction), thus tethering the organo component to magnesium (or sodium). Following initial isocyanate coordination the cyclopentadienide ligand is now in close proximity to the substrate and readily adds to the isocyanate carbon atom, and subsequent steps proceed according to Scheme 2, with the ensuing chelate ring enforcing a 1,2-relationship between the two carbamoyl substituents.

Scheme 2. Mechanism of Formation of a 1,2-Bis-carbamoylcyclopentadienyl Ligand Showing the Metal Tethering Effect Leading to 1,2-Selectivity



Conclusion

In summary, our report of the synthesis and structure of [*trans*-{1,2-bis(*N*-phenylcarbamoyl)cyclopentadienylbis(thf)}magnesium]·4thf from the reaction of magnesocene and phenylisocyanate suggests that polar metal cyclopentadienides may be of general use in the assembly of functionalized cyclopentadienyl ligands for metallocene complexes. The structural authentication of **1**·4thf also provides support for the previously postulated[2−4] mechanism of formation of 1,2-bis-carbamoyl ligands and also suggests that tethering by the s-block metal is partly responsible for the exclusive 1,2-selectivity in the reaction.

Experimental Section

General Procedures. Standard inert atmosphere techniques were used throughout. The thf solvent was predried over sodium wire and distilled from sodium/benzophenone. Phenylisocyanate was purchased from Aldrich and used as supplied.

A solution of Cp_2Mg (0.16 g, 1.0 mmol) in thf (20 mL) was cooled to 0 °C, and phenylisocyanate (0.48 g, 4.0 mmol) was added dropwise over 30 s. The initial yellow color of the reaction became dark red upon stirring for 20 h. The volume of the reaction mixture was then reduced to ca. 3 mL and the concentrated solution stored at −15 °C for several days. Red crystals of complex **1**·4thf (0.45 g, 61%) were obtained. Heating **1**·4thf to 60 °C in vacuo for 30 min affords complex **1**. Analytical and spectroscopic data for **1**: calcd for $C_{46}H_{46}N_4O_6Mg$, C 71.27, H 5.98, N 7.23; found, C 71.36, H 5.99, N 7.76; mp decomposes to a black solid above 220 °C; IR (Nujol mull, KBr plates)/cm^{-1} 3412.8 (N−H stretch), 3051.1 (sp^2 C−H

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stretch), 1723.0, 1709.7, 1625.5 (carbamoyl C−O stretch), 1590.0 (N−H bend), 1514.6, 1310.7, 1235.3 1066.8 (coordinated thf C−O stretch); ^{1}H NMR (400.13 MHz, C_6D_6) 7.70 (m, 8H, *o*-Ph) 7.25 (m, 8H, *m*-Ph), 6.96 (m, 4H, *p*-Ph), 6.63 (d, 1H, 3.59 Hz), 6.06 (d, 1H, 3.59 Hz), 5.63 (t, 1H, 3.59 Hz), 4.94 (br s, 4H, NH), 3.57 (m, 4H, thf), 1.73 (m, 4H, thf); ^{13}C NMR (400.13 MHz, C_6D_6) 169.1 (CONH), 134.7 (*ipso*-Ph), 131.1 (*p*-Ph), 127.9 (*o*-Ph), 127.0 (*m*-Ph), 115.8 (*ipso*-C_5H_3), 110.0, 106.3, 105.8 (CH of C_5H_3). Crystal data for **1**·4thf: formula, $C_{62}H_{78}MgN_4O_{10}$, fw 1063.59, T/K 180(2), λ/Å 0.71073, crystal system orthorhombic, space group $P2_12_12_1$, a/Å 8.0090(2), b/Å 22.4905(6), c/Å 31.5481(9), $\alpha = \beta = \gamma = 90.00°$ V/Å^3 5682.6(3), Z 4, density(calcd) g/cm^{-3} 1.243, μ/mm^{-1} 0.094, F(000) 2280, crystal size/mm 0.25 × 0.10 × 0.07, 2θ range/deg 3.62−25.00, reflections collected 13 253, indep reflections 8238 [R(int) = 0.0716], data/restraints/parameters 8214/0/694, goodness-of-fit on F^2 0.941, final R indices [$I > 2\sigma(I)$] $R_1 = 0.0778$, $wR_2 = 0.1191$, R indices (all data) $R_1 = 0.1750$, $wR_2 = 0.1408$, largest diff peak hole/e Å^3 0.203, −0.205.

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Supporting Information Available: Details of the structure determination of **1**·4thf are available free of charge via the Internet at http://pubs.acs.org.

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