Inorg. Chem. **2007**, *46*, 10400–10409

Inorganic Chemistry
Article

Lithium Aryloxo Magnesiates: an Examination of Ligand Size and Donor Effects

Maria Felisa Zuniga,[†] Johannes Kreutzer,[†,‡] Weijie Teng,[†] and Karin Ruhlandt-Senge*[,†]

Department of Chemistry, 1-014 Center for Science and Technology, Syracuse University,
Syracuse, New York 13244-4100, and Department of Chemistry, Technical University of Graz,
Stremayergasse 16, A-8010 Graz, Austria

Received July 17, 2007

The combination of equimolar amounts of LiOAr and Mg(OAr)_2 (OAr = aryloxide) in polar media afforded several lithium aryloxomagnesiates. Factors influencing the structural chemistry of the compounds, such as the degree of ligand bulk, type of Lewis base donors, and crystallization solvent, are examined. Structural characterization reveals a discrete, solvent-separated species, $[\text{Li(thf)}_4][\text{Mg(BHT)}_3]\cdot\text{THF}$ (**1**) (BHT = $2,6\text{-}t\text{Bu}_2\text{-4-MeC}_6\text{H}_2\text{O}$) and a family of molecular compounds with various Li/Mg stoichimetries, including a 1:1 Li/Mg ratio in $[\text{LiMg(Odpp)}_3(\text{thf})_2]\cdot0.5\text{PhMe}$ (**2**) (Odpp = $2,6\text{-Ph}_2\text{C}_6\text{H}_3\text{O}$) and $[\text{Li(Et}_2\text{O)Mg(Odpp)}_3]\cdot0.5\text{PhMe}$ (**3**), a 2:1 Li/Mg ratio as in $[\{\text{Li(thf)}_2\}_2\text{Mg(OMes)}_4]\cdot2\text{THF}$ (**4**) (OMes = $2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{O}$) and $[\{\text{Li(tmeda)}\}_2\text{Mg}(m\text{-Odtp})_4]\cdot0.5\text{Et}_2\text{O}$ (**5**) (m-Odtp = $3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3\text{O}$), and a novel 2:3 Li/Mg ratio in $[\{\text{Li(thf)}_2\}_2\text{Mg}_3(m\text{-Odtp})_8(\text{thf})_2]\cdot3\text{THF}$ (**6**). Two new homometallic magnesium bis(aryloxides), $\text{Mg(Odpp)}_2(\text{thf})_2$ (**7**) and $\text{Mg(Odpp)}_2(\text{Et}_2\text{O})_2$ (**8**), are also included for the sake of comparison. The solution behavior of the heterobimetallic compounds in arene and polar solvent is analyzed by ^{1}H NMR spectroscopy.

Introduction

While the coordination chemistry of magnesium organometallics has been well established, heterobimetallic compounds resulting from the combination of alkali and magnesium compounds, generally recognized as "ate" complexes, are now starting to be developed. The "ate" complexes attract attention due to their unique synthetic properties, such as in selective halogen–magnesium exchange using various lithium alkylmagnesiates[1] and deprotonation and metalation reactions using alkyl, as well as amide heterobimetallic derivatives.[2] Further, these compounds have been recognized as valuable polymerization initiators.[3] Previous work on the elucidation of the solid-state structures of the heterobimetallic complexes focused on solvated alkyl and aryl derivatives with various alkali metal/magnesium stoichiometries. Examples of compounds displaying a 1:1 ratio of alkali metal/magnesium include $[\text{Li(thf)Mg}(2,4,6\text{-tri-}^i\text{PrC}_6\text{H}_2)_3]$[4] and $[\{\text{Li(TMEDA)}\}_2\text{Mg}_2(\text{Ph})_6]$;[5] a 2:1 ratio is observed in $[\{\text{Li(TMEDA)}\}_2\text{Mg(Me)}_4]$.[6] More recently, Mulvey and co-workers have contributed a number of alkali amide magnesiates encompassing a range of molecular architectures including simple solvated or unsolvated compounds (e.g., $[\text{LiMg}\{\text{N(CH}_2\text{Ph)}_2\}_3(\text{pyr})]$[7] and $[\text{LiMg}\{\text{N(SiMe}_3)_2\}_3]$,[8] respectively), a compound with 2:1 Li/Mg ratio (e.g., $[\text{Li}_2\text{Mg}\{\text{N(CH}_2\text{Ph)}_2\}_4]$),[7] and heteroleptic magnesiates (e.g., $[\text{LiMg}\{\text{N(SiMe}_3)_2\}_2(\text{R})(\text{D})]$ (R = ^{s}Bu, D = pyr; R = ^{t}Bu)).[9] The group of heterobimetallic compounds is complemented through recent work focusing on complexes with multinuclear arrangements based on combinations of alkali and magnesium metals, known as "inverse crown ethers".[10]

---

* To whom correspondence should be addressed. E-mail: kruhland@syr.edu. Phone: 315-334-1306. Fax: 315-443-4070.

[†] Syracuse University.

[‡] Technical University of Graz.

(1) See for example: (a) Inoue, A.; Kitagawa, K.; Shinokubo, H.; Oshima, K. *J. Org. Chem.* **2001**, *66*, 4333. (b) Iida, T.; Wada, T.; Tomimoto, K.; Mase, T. *Tetrahedron Lett.* **2001**, *42*, 4841. (c) Krasovskiy, A.; Straub, B. F.; Knochel, P. *Angew. Chem., Int. Ed.* **2006**, *45*, 159.

(2) Mulvey, R. E.; Mongin, F.; Uchiyama, M.; Kondo, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 3802 and references therein.

(3) (a) Antkowiak, T. A.; Hall, J. E.; (Bridgestone Corporation, Japan). Application: EP, 1996, p 20. (b) Hsieh, H. L.; Wang, I. W. *Macromolecules* **1986**, *19*, 299. (c) Deffieux, A.; Shcheglova, L.; Barabanova, A.; Marechal, J. M.; Carlotti, S. *Macromol. Symp.* **2004**, *215*, 17.

(4) Waggoner, K. M.; Power, P. P. *Organometallics* **1992**, *11*, 3209.

(5) Thoennes, D.; Weiss, E. *Chem. Ber.* **1978**, *111*, 3726.

(6) Greiser, T.; Kopf, J.; Thoennes, D.; Weiss, E. *Chem. Ber.* **1981**, *114*, 209.

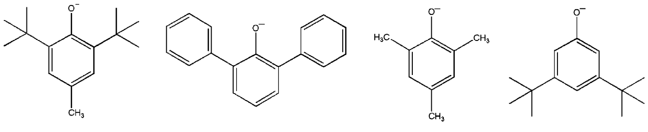
(7) Clegg, W.; Henderson, K. W.; Mulvey, R. E.; O'Neil, P. A. *J. Chem. Soc., Chem. Commun.* **1994**, 769.

(8) Kennedy, A. R.; Mulvey, R. E.; Rowlings, R. B. *J. Am. Chem. Soc.* **1998**, *120*, 7816.

(9) Andrikopoulos, P. C.; Armstrong, D. R.; Kennedy, A. R.; Mulvey, R. E.; O'Hara, C. T.; Rowlings, R. B.; Weatherstone, S. *Inorg. Chim. Acta* **2007**, *360*, 1370.

10.1021/ic701423r CCC: $37.00

Scheme 1. Aryloxo Ligands Exhibiting Different Degrees of Steric Bulk



(a) BHT (b) Odpp (c) OMes (d) *m*-Odtp

A group of heterobimetallic compounds that has received significantly less attention are alkoxide/aryloxide based; this dearth of information is in sharp contrast to an extensive family of homometallic magnesium alkoxides and aryloxides.[11] The few examples of heterobimetallic alkoxides/aryloxides are predominantly heteroleptic, including $[\{MMg[N(iPr)_2]_2OR\}_2]$ (M = Li, R = *n*Oct; M = Na, R = *n*Bu or *n*Oct)[12] and $[\{MMg(Bu)_2(t\text{-}OBu)(TMEDA)\}_2]$ (M = Na or K),[13] the only homoleptic species being $[\{Li(TMEDA)\}_2Mg(2\text{-}MeC_6H_4O)_4]$[14] and the multinuclear $[\{LiMg_4(2\text{-}MeC_6H_4O)_7O\}]$.[14]

Access to heterobimetallic complexes is generally hampered by a strong tendency to form the homometallic species. Such challenges may be correlated to those encountered in the preparation of heteroleptic magnesium compounds, as demonstrated in the work on magnesium amide thiolates wherein symmetrized products formed by ligand redistribution are frequently isolated.[15]

Aside from expanding the number of available alkali magnesiates involving oxygen-based ligands, our work is aimed toward the systematic examination of diverse factors influencing their formation and structures, which include ligand properties and size, and the nature of donors and solvent systems. The preparation of these s-block systems enhances our understanding on their unique coordination chemistry that can assist in exploring their potential synthetic utilities. Further, the heterobimetallic compounds provide important insights into the structural trends within the alkaline earth metals. We have previously reported a series of heterobimetallic M/Ba (M = Li, Na, K, Cs) aryloxo complexes that exhibited a clear correlation between intermetallic ratio and structural features.[16] In this report, various substituted phenoxides (BHT (butylated hydroxyl toluene) = 2,6-di-*t*-butyl-4-methyl, Odpp = 2,6-diphenyl, OMes = 2,4,6-trimethyl, *m*-Odtp = 3,5-di-*t*-butyl) with a range of steric bulkiness are utilized for the preparation of the target heterobimetallic compounds (Scheme 1). Aryloxides are an attractive choice for oxygen-based ligands due to their availability, solubility in organic solvents, and ease of derivatization. Coordinating solvents such as THF and TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) are introduced to examine their effects on solvation, stabilization, alkali/magnesium ratio, and ion-association of the complexes. In addition, the influence of the solvent system is also investigated to shed light on the solvent-dependence of the formation of the heterobimetallic complexes versus the homometallic analogues.

We here present a series of lithium aryloxo magnesiates exhibiting different ion-association modes as detailed in the analysis of their solid-state structures—a solvent-separated ion species $[Li(thf)_4][Mg(BHT)_3]\cdot THF$ (**1**) and several solvated contact molecules with various Li/Mg stoichimetries such as 1:1 Li/Mg ratio in $[LiMg(Odpp)_3(thf)_2]\cdot 0.5PhMe$ (**2**) and $[Li(Et_2O)Mg(Odpp)_3]\cdot 0.5PhMe$ (**3**), 2:1 Li/Mg ratio in the THF solvate $[\{Li(thf)_2\}_2Mg(OMes)_4]\cdot 2THF$ (**4**) and the TMEDA solvate $[\{Li(tmeda)\}_2Mg(m\text{-}Odtp)_4]\cdot 0.5Et_2O$ (**5**), and the first example of 2:3 Li/Mg ratio demonstrated in $[\{Li(thf)_2\}_2Mg_3(m\text{-}Odtp)_8(thf)_2]\cdot 3THF$ (**6**). Our solid-state studies are supplemented by extensive solution studies in both arene and polar solvents.

Experimental Section

General Procedures. All reactions were carried out under inert gas conditions using standard Schlenk techniques or a Braun Labmaster 100 drybox. 2,6-Di-*t*-butyl-4-methylphenol and 2,4,6-tri-methylphenol were purified by sublimation before use. 2,6-Diphenylphenol and 3,5-di-*t*-butylphenol were purchased and used as received. Bu_2Mg as a 1.0 M solution in heptane and BuLi as a 2.0 M solution in cyclohexane were obtained commercially. All solvents were purified under standard procedures. ^1H NMR spectra were recorded by using a Bruker DPX 300 spectrometer. IR spectra (4000−650 cm^{-1}) were recorded as Nujol mulls between NaCl plates by using Nicolet IR200 spectrometer. The extreme moisture and oxygen sensitivity of the compounds did not give reliable elemental analyses, which is a recognized difficulty in alkaline earth metal chemistry.[17]

Crystallographic Studies. Suitable crystals for single-crystal X-ray diffraction were obtained for **1**−**8** as described below. Crystallographic analyses for all compounds were conducted as described previously.[18] Disorder was handled by introducing split positions. Respective occupancies were refined as follows. **1**, 60:40 for one of the THF molecules coordinated to lithium, 70:30 for THF solvate; **5**, 70:30 for TMEDA; **6**, 50:50 occupancy on the bridging aryloxides, 65:35 for THF molecule on Mg1. Some severely disordered solvents of crystallization were removed from the refinement using the “squeeze” function in the PLATON software package (one THF in **1**, 0.5 toluene in **2,** two THF in **4**, 0.5 Et_2O in **5**, and three THF in **6**).[19] Crystallographic data (excluding structure factors) for the structures reported herein have been deposited in the Cambridge Crystallographic Data Center (CCDC 652408−652413 and 653763−653764). These supplementary data can be obtained free of charge via www.ccdc.cam.ac.uk/data request/cif.

General Synthetic Procedure for 1−6. Two Schlenk tubes were charged with 2 and 4 mmol of the phenol, and each was dissolved

---

(10) Mulvey, R. E. *Organometallics* **2006**, *25*, 1060 and references therein.

(11) (a) Turova, N. Y. *The chemistry of metal alkoxides*; Kluwer Academic Publishers: Boston, 2002; p 568. (b) Bradley, D. C.; Mehotra, R. C.; Rothwell, I. P.; Singh, A. *Alkoxo and aryloxo derivatives of metals*, 2nd ed.; Academic Press; San Diego, 2001; p 704.

(12) Drewette, K. J.; Henderson, K. W.; Kennedy, A. R.; Mulvey, R. E.; O’Hara, C. T.; Rowlings, R. B. *Chem. Commun.* **2002**, 1176.

(13) Barnett, N. D. R.; Clegg, W.; Kennedy, A. R.; Mulvey, R. E.; Weatherstone, S. *Chem. Commun.* **2005**, 375.

(14) Henderson, K. W.; Mulvey, R. E.; Reinhard, F. B. M.; Clegg, W.; Horsburgh, L. *J. Am. Chem. Soc.* **1994**, *116*, 10777.

(15) Teng, W.; Englich, U.; Ruhlandt-Senge, K. *Inorg. Chem.* **2000**, *39*, 3875.

(16) Zuniga, M. F.; Deacon, G. B.; Ruhlandt-Senge, K. *Chem. Eur. J.* **2007**, *13*, 1921.

(17) Hays, M. L.; Hanusa, T. P.; Nile, T. A. *J. Organomet. Chem.* **1996**, *514*, 73 and references therein.

(18) Ruhlandt-Senge, K.; Englich, U. *Chem. Eur. J.* **2000**, *6*, 4063.

(19) Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, C43. (b) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool* **1998**.

in 20 mL solvent (THF for **1**, **2**, **4**, **5**, **6** and Et_2O for **3**) then cooled at 0 °C using an ice bath. LiOAr and $Mg(OAr)_2$ solutions were individually prepared in situ by adding *n*BuLi and Bu_2Mg to the THF or Et_2O phenolic solutions (2 and 4mmol, respectively). Both solutions were allowed to stir for 3 h at 0 °C. The clear colorless solutions were then combined and stirred and allowed to warm slowly to room temperature overnight. TMEDA (3 mL) was added to the mixture for **5**. In **1**, **4**, and **6**, the crystals were isolated from reaction solvent. In the case of **2**, **3**, and **5**, the reaction solvent was removed under vacuum and then replaced by toluene (40 mL) for **2** and **3** and Et_2O (20 mL) for **5**.

[Li(thf)$_4$][Mg(BHT)$_3$]·THF, 1. Solvent, THF; Solution 1, *n*BuLi (1.0 mL, 2 mmol), HBHT (0.44 g, 2 mmol); Solution 2, Bu_2Mg (2.0 mL, 2 mmol), HBHT (0.88 g, 4 mmol). Colorless crystals formed after cooling the mother liquor to −20 °C for 2 days. Yield: 0.42 (22%). Mp (sealed tube/N_2): 184−190 °C; ^{1}H NMR (300 MHz, 25 °C, C_6D_6): (THF solvate lost by exposure to vac) 2:1 ratio for aryloxide (BHT and BHT′); BHT: 1.59 (s, 18H, CH_3, *t*-Bu), 2.41 (s, 3H, *p*-CH_3),7.28 (s, 2H, *m*-aryl-H); BHT′: 1.72 (s, 9H, CH_3, *t*-Bu), 2.44 (s, 1.5H, *p*-CH_3), 7.34 (s, 1H, *m*-aryl-H), 1.18 (s, 4H, CH_2, THF), 3.51 (s, 4H, OCH_2, THF); ^{13}C (300 MHz, 25 °C, C_6D_6): only one set of resonances observed except for the *t*-Bu groups, 21.7 (*p*-CH_3), 25.4 (CH_2, THF), 31.9 and 32.7 (CH_3, *t*-Bu), 35.9 and 35.7 (C, *t*-Bu), 68.4 (OCH_2, THF), 121.5 (*m*-C), 126.0 (*p*-C), 137.8 (*o*-C), 160.9 (*ipso*-C); ^{1}H NMR (300 MHz, 25 °C, THF-d_8): 1.350 (s, 54H, CH_3, *t*-Bu), 2.15 (s, 9H, *p*-CH_3),6.65 (s, 6H, *m*-aryl-H), ^{13}C NMR (300 MHz, 25 °C, THF-d_8): 20.9 (*p*-CH_3), 31.9 (CH_3, *t*-Bu), 35.0 (C, *t*-Bu), 118.5 (*p*-C), 124.7 (*m*-C), 137.0 (*o*-C), 161.0 (*ipso*-C); IR (Nujol): $\nu^{-1} = 1751$(w), 1612(w), 1457(s), 1424(m), 1375(s), 1294(m), 1261(w), 1220(w), 1200(w), 1020(m), 914(w), 893(m), 848(m), 811(w), 783(w), 722(m).

[LiMg(Odpp)$_3$(thf)$_2$]·0.5PhMe, 2. Solvent, THF; recrystallization in toluene, Solution 1, *n*BuLi (1.0 mL, 2 mmol), HOdpp (0.50 g, 2 mmol); Solution 2, Bu_2Mg (2.0 mL, 2 mmol), HOdpp (1.0 g, 4 mmol). The volume of solution was reduced under vacuum and colorless crystals were obtained at 0 °C after 2 days. Yield: 0.15 g (15%). Mp (sealed tube/N_2): 158−164 °C; ^{1}H NMR (300 MHz, 25 °C, C_6D_6): 2.11 (s, 1.5H, CH_3−PhMe), 1.04 (s, 4H, CH_2, THF), 2.74 (s, 4H, OCH_2, THF), 6.82 (t, 3H; *p*-aryl-H), 6.89 (t, 6H; *p*-H(Ph)), 7.05 (t, 12H; *m*-H(Ph)), 7.15 (m, 2.5H, aryl-PhMe), 7.18 (d, 6H; *m*-aryl-H), 7.24 (d, 12H; *o*-H(Ph)); IR (Nujol): $\nu^{-1} = 1952$(w), 1882(w) 1812(w), 1666(w), 1602(m), 1492(w), 1456(s), 1409(m), 1380(m), 1304(w), 1281(w), 1252(w), 1240(w), 1229(w), 1176(w), 1082(w), 1065(m), 1024(m), 884(w), 855(m), 790(w), 744(s), 703(s), 627(w), 604(m).

[Li(Et$_2$O)Mg(Odpp)$_3$]·0.5PhMe, 3. Solvent, Et_2O, recrystallization in toluene; Solution 1, *n*BuLi (1.0 mL, 2 mmol), HOdpp (0.5 g, 2 mmol); Solution 2, Bu_2Mg (2.0 mL, 2 mmol), HOdpp (1.0 g, 4 mmol). After reducing the volume of the clear colorless solution to 20 mL, crystalline materials were deposited. Yield: 0.71 g (40%). Mp (sealed tube/N_2): 158−164 °C; ^{1}H NMR (300 MHz, 25 °C, C_6D_6):0.352 (t, 6H, CH_3, Et_2O), 2.11 (s, 1.5H, CH_3−PhMe), 2.50 (q, 4H, OCH_2, Et_2O), 6.85 (t, 3H; *p*-aryl-H), 6.96 (t, 6H; *p*-H(Ph)), 7.15 (m, 2.5H, aryl-PhMe), 7.26 (d, 6H; *m*-aryl-H), 7.05 (t, 12H; *m*-H(Ph)), 7.40 (d, 12H; *o*-H(Ph)); IR (Nujol): $\nu^{-1} = 1969$(w), 1894(w), 1800(w), 1759(w), 1654(w), 1602(m), 1496(w), 1456(s), 1415(m), 1386(s), 1304(w), 1263(m), 1153(m), 1070(m), 1030(w), 1006(w), 925(w), 878(m), 849(m), 755(s), 703(s), 633(w), 610(m).

[{Li(thf)$_2$}$_2$Mg(OMes)$_4$]·2THF, 4. Solvent, THF; Solution 1, *n*BuLi (1.0 mL, 2 mmol), HOMes (0.27 g, 2 mmol); Solution 2, Bu_2Mg (2.0 mL, 2 mmol), HOMes (0.54 g, 4mmol). The volume of the mixture was reduced to 10 mL in vacuo and cooled at −20 °C, affording colorless crystals overnight. Yield: 0.38 g (44% based on LiOMes). Mp (sealed tube/N_2): 255 °C (dec); ^{1}H NMR (300 MHz, 25 °C, C_6D_6): (THF solvate lost by exposure to vac) 1:1:0.5 ratio for aryloxide (OMes, OMes′, OMes″), OMes/OMes′: 2.27 (s, 18H, *o*-CH_3/*p*-CH_3), 6.86 (s, 2H, *m*-aryl-H, OMes), 6.91 (s, 2H, *m*-aryl-H, OMes′), OMes″: 2.07 (s, 3H, *o*-CH_3), 2.21 (s, 1.5H, *p*-CH_3), 6.91 (s, 1H, *m*-aryl-H), 0.951 (m, 6H, CH_2, THF), 3.01 (m, 6H, OCH_2, THF); ^{13}C NMR (300 MHz, 25 °C, C_6D_6): only one set of resonances observed except for the *o*,*p*-CH_3 groups, 17.9 and 18.2 (*o*-CH_3), 20.9 and 21.5 (*p*-CH_3), 25.1 (CH_2, THF), 68.1 (OCH_2, THF), 124.9 (*p*-C), 126.2 (*m*-C), 129.4 (*o*-C), 158.4 (*ipso*-C); ^{1}H NMR (300 MHz, 25 °C, THF-d_8): 1.97 (s, 12H, *p*-CH_3), 2.07 (s, 24H, *o*-CH_3), 6.53 (s, 6H, *m*-aryl-H), ^{13}C NMR (300 MHz, 25 °C, THF-d_8): 16.3 (*p*-CH_3), 18.3 (*o*-CH_3), 120.8 (*p*-C), 124.6 (*m*-C), 126.6 (*o*-C), 157.4 (*ipso*, C); IR (Nujol): $\nu^{-1} = 2929$ (s), 2862 (s), 1730(w), 1602(w), 1450(s), 1374(s), 1310(m), 1258(m), 1147(w), 1048(w), 954(w), 919(w), 895(w), 843(m), 796(m), 744(m), 720(m), 668(w).

[{Li(tmeda)}$_2$Mg(*m*-Odtp)$_4$]·0.5Et$_2$O, 5. Solvent, THF, recrystallization in Et_2O; Solution 1, *n*BuLi (1.0 mL, 2 mmol), H(*m*-Odtp) (0.41 g, 2 mmol); Solution 2, Bu_2Mg (2.0 mL, 2 mmol), H(*m*-Odtp) (0.82 g, 4mmol). Colorless crystals formed after cooling the solution at 0 °C for a week. Yield: 0.97 g (89% based on Li(*m*-Odtp)). Mp (sealed tube/N_2): 205−210 °C; ^{1}H NMR (300 MHz, 25 °C, C_6D_6): (Et_2O solvate lost by exposure to vac) 1.43 (s, 72H, CH_3, *t*-Bu), 1.85 (s, 8H, NCH_2, TMEDA), 2.03 (s, 24H, CH_3, TMEDA), 6.91 (s, 12H, *o*, *p*-aryl-H); ^{13}C NMR (300 MHz, 25 °C, C_6D_6): 32.5 (CH_3, *t*-Bu), 35.0 (C, *t*-Bu), 46.0 (CH_3, TMEDA), 57.0 (NCH_2, TMEDA), 110.0 (*p*-C), 115.0 (*m*-C), 152.0 (*o*-C), 165.2 (*ipso*-C); ^{1}H NMR (300 MHz, 25 °C, THF-d_8): 1.18 (s, 72H, CH_3, *t*-Bu), 2.15 (s, 24H, CH_3, TMEDA), 2.30 (s, 8H, NCH_2, TMEDA), 6.56 (s, 12H, *o*,*p*-aryl-H); ^{13}C NMR (300 MHz, 25 °C, THF-d_8): 29.7 (CH_3, *t*-Bu), 32.7 (C, *t*-Bu), 43.8 (CH_3, TMEDA), 56.5 (NCH_2, TMEDA), 107.1 (*p*-C), 111.6 (*m*-C), 148.9 (*o*-C), 162.7 (*ipso*-C); IR (Nujol): $\nu^{-1} = 1596$(s), 1467(s), 1380(m), 1316(s), 1228(m), 1193(w), 1152(w), 1111(w), 1024(w), 977(m), 948(w), 878(w), 820(w), 785(w), 709(m), 610(m).

[{Li(thf)$_2$}$_2$Mg$_3$(*m*-Odtp)$_8$(thf)$_2$]·3THF, 6. Solvent, THF; Solution 1: *n*BuLi (1.0 mL, 2 mmol), H(*m*-Odtp) (0.41 g, 2 mmol); Solution 2, Bu_2Mg (2.0 mL, 2 mmol), H(*m*-Odtp) (0.82 g, 4mmol). The volume of the mixture was reduced to 20 mL in vacuo and cooled at 0 °C, affording colorless crystals after 3 days. Yield: 0.37 g (26% based on Mg(*m*-Odtp)$_2$). Mp (sealed tube/N_2): 280 °C (dec); ^{1}H NMR (300 MHz, 25 °C, C_6D_6): 1.57 (s, 4H, CH_2, THF), 1.57 (s, 18H, CH_3, *t*-Bu), 3.71 (s, 4H, OCH_2, THF), 7.37 (s, 3H, *o*, *p*-aryl-H); ^{13}C (C_6D_6) was not recorded due to the insolubility of **5** in the arene solvent; ^{1}H NMR (300 MHz, 25 °C, THF-d_8): (THF solvate lost by exposure to vac) 1.20 (s, 18H, CH_3, *t*-Bu), 6.49 (s, 2H, *o*-aryl-H), 6.62 (s, 1H, *p*-aryl-H); ^{13}C NMR (300 MHz, 25 °C, THF-d_8): 29.8 (CH_3, *t*-Bu), 33.2 (C, *t*-Bu), 108.0 (*p*-C), 110.8 (*m*-C), 149.1 (*o*-C), 160.9 (*ipso*-C); IR (Nujol): $\nu^{-1} = 1592$(s), 1457(s), 1384(m), 1363(m), 1318(m), 1249(m), 1200(w), 1122(m), 999(w), 975(m), 922(w), 897(w), 873(m), 848(m), 811(w), 705(m), 611(s).

Mg(Odpp)$_2$(thf)$_2$, 7. Bu_2Mg (2.0 mL, 2 mmol) was added dropwise to HOdpp (1.0 g, 4 mmol) dissolved in THF (30 mL). The solution was allowed to stir overnight at room temperature. The volume of the solution was reduced to 10 mL in vacuo and cooled at 0 °C, affording colorless crystals after 2 days. Yield: 0.55 g (42%). Mp (sealed tube/N_2): 156−160 °C; ^{1}H NMR (300 MHz, 25 °C, C_6D_6):0.89 (s, 8H, CH_2, THF), 2.65 (s, 8H, OCH_2, THF), 6.87 (t, 2H; *p*-aryl-H), 7.09 (t, 4H; *p*-H(Ph)), 7.21 (t, 8H; *m*-H(Ph)), 7.42 (d, 4H; *m*-aryl-H), 7.70 (d, 8H; *o*-H(Ph)); IR (Nujol): $\nu^{-1} =$

2956(s), 2845(s), 1940(w), 1882(w), 1829(w), 1759(w), 1724(w), 1671(w), 1578(m), 1543(m), 1456(s), 1374(s), 1298(m), 1240(w), 1176(m), 1082(m), 1065(m), 1018(s), 907(w), 866(s), 744(s), 691(s), 627(m), 586(m).

$Mg(Odpp)_2(Et_2O)_2$, 8. Bu_2Mg (2.0 mL, 2 mmol) was added dropwise to HOdpp (1.0 g, 4 mmol) dissolved in Et_2O (30 mL). The solution was allowed to stir at room temperature, and after 30 min, white crystalline product deposited at the bottom of the flask. Yield: 0.89 g (67%). Mp (sealed tube/N_2): 126−129 °C; ^1H NMR (300 MHz, 25 °C, C_6D_6):0.54 (s, 8H, OCH_2, Et_2O), 2.65 (s, 12H, CH_3, Et_2O), 6.84 (t, 2H; *p*-aryl-H), 7.10 (t, 4H; *p*-H(Ph)), 7.20 (t, 8H; *m*-H(Ph)), 7.36 (d, 4H; *m*-aryl-H), 7.65 (d, 8H; *o*-H(Ph)); IR (Nujol): $\nu^{-1} = 29266$(s), 2850(s), 1957(w), 1882(w), 1811(w), 1759(w), 1596(m), 1578(m), 1491(m), 1461(s), 1426(s), 1374(s), 1316(s), 1298(m), 1251(w), 1181(m), 1146(m), 1082(m), 1070(m), 1045(s), 1012(m), 901(w), 872(m), 802(w), 750(s), 709(s), 627(w), 610(w).

Results and Discussion

Syntheses. The lithium magnesiates were readily obtained from the reaction of equimolar amounts of in-situ-prepared LiOAr and $Mg(OAr)_2$ in THF (**1**, **2**, **4**, **5**, **6**) or Et_2O (**3**) solutions, prepared via the alkane elimination route (eqs 1 and 2). The two solutions were allowed to stir for 2−3 h to ensure completeness of the reaction then combined and stirred overnight (eq 3). In the case of **2**, **3**, and **5**, the compounds were isolated when the mother liquor was removed and subsequently replaced with toluene (for **2** and **3**) or Et_2O (for **5**). The strategy of combining the corresponding homometallic compounds to form the heterobimetallic product was previously employed in the synthesis of mixed Li/Mg amido,[8] alkyl,[6] and aryl complexes,[4,5] as well as heterobimetallic alkali compounds $[MM'\{N(SiMe_3)_2\}_2(thf)_3]$ ($M = Li$, $M' = Na$ or K; $M = Na$, $M' = K$).[20] In each of these cases the alkali or magnesium compounds were prepared and isolated before combining in the desired stoichiometric ratio. Conversely, the closely related magnesiate, $[\{Li(TMEDA)\}_2Mg(2\text{-}MeC_6H_4O)_4]$, was prepared by using a correct 2:1:4 stoichiometry of *n*BuLi, $(Bu)_2Mg$, and phenol followed by the addition of TMEDA.[14] A noteworthy observation in our work is that despite the consistent use of 1:1 reagent mixtures, 1:1 stoichiometry was only observed in **1**−**3**, while **4**−**6** display a 2:1 or 3:2 Li/Mg ratio, suggesting that ligands and donors play a significant role in the determination of the coordination chemistry of these compounds, complementing those reported for a series of heterobimetallic alkyl and amide derivatives.[4,21]

$$\mathrm{BuLi + HOAr \rightarrow LiOAr + BuH} \qquad (1)$$

$$\mathrm{MgBu_2 + 2HOAr \rightarrow Mg(OAr)_2 + 2BuH} \qquad (2)$$

$$\mathrm{LiOAr + Mg(OAr)_2 \xrightarrow{n\mathrm{donor}} [Li_{\mathit{x}}Mg_{\mathit{y}}(OAr)_{\mathit{x}+2\mathit{y}}(donor)_{\mathit{n}}]} \qquad (3)$$

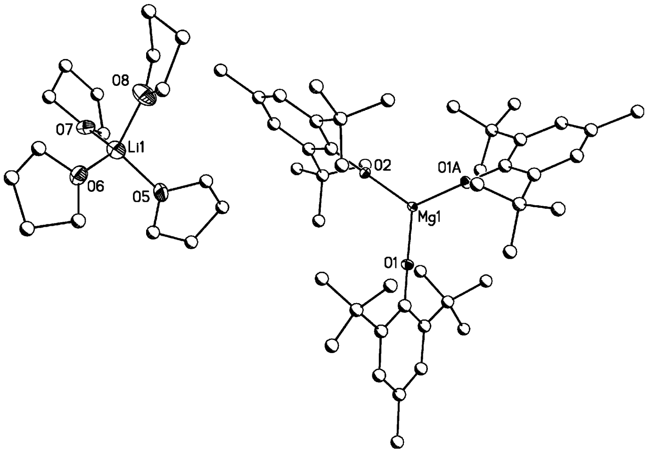


Figure 1. Structure of $[Li(thf)_4][Mg(BHT)_3]\cdot THF$, **1**. For clarity, the hydrogen atoms and THF solvate are not shown.

Compounds **1**, **4**, and **6** were obtained as colorless crystals that deposited from the mother liquor, while **2** and **3** and **5** were obtained after recrystallization from toluene or Et_2O, respectively. Crystals of **1** deposited from the THF solution at −20 °C with rather moderate yield due to highly soluble nature of the compound in THF at room temperature, necessitating the isolation of the product at low temperatures. Demonstrating the important influence of solvent on the formation of the heterobimetallic compounds, a similar route employing 2,6-diphenylphenol in THF led to the homometallic **7**, as confirmed by crystallographic analysis. Similarly, repeating the reaction in Et_2O afforded **8**. Heterobimetallic compounds **2** and **3** were obtained successfully upon removal of the THF or Et_2O solvent in vacuo, followed by the addition of toluene to dissolve the precipitate, affording the compounds at 0 °C after a few days.

Utilizing less sterically demanding ligands such as 2,4,6-trimethylphenol afforded the THF solvate **4** in modest yield. With the meta-substituted aryloxide ligand 3,5-di-*t*-butylphenol and in the presence of TMEDA, colorless crystals of **5** were formed after dissolving the crude product in Et_2O. Further, replicating the reaction using the same ligand in THF and in the absence of TMEDA allowed the isolation of **6** that crystallized readily from the solution. The formation of the target compounds is reproducible.

Structural Aspects. The molecular structures of **1**−**8**, including core structures of selected compounds, are shown in Figures 1−8, as obtained from their characterization using single-crystal X-ray diffraction. Pertinent bond distances and angles are summarized in Table 1, while relevant crystal data, data collection and structure refinement are detailed in Table 2. To the best of our knowledge, compound **1** represents the first structurally characterized heterobimetallic alkali−magnesium aryloxo species with unassociated three-coordi-

---

(20) Williard, P. G.; Nichols, M. A. *J. Am. Chem. Soc.* **1991**, *113*, 9671.

(21) Mulvey, R. E. *Chem. Commun.* **2001**, 1049 and references therein.

(22) For recent examples see: (a) Barley, H. R. L.; Clegg, W.; Dale, S. H.; Hevia, E.; Honeyman, G. W.; Kennedy, A. R.; Mulvey, R. E. *Angew. Chem., Int. Ed.* **2005**, *44*, 6018. (b) Nakata, N.; Izumi, R., Lee, V.; Sekiguchi, A. *J. Am. Chem. Soc.* **126**, 5058. (c) Hitchcock, P. B.; Lappert, M. F. Wei, X. H. *Dalton Trans.* **2006**, 1181. (d) Hilton, C. L.; King, B. T. *Organometallics* **2006**, *25*, 4058. (e) Bambirra, S.; Meetsma, A.; Hessen, B. *Organometallics* **2006**, *25*, 3454. (f) Alonso, P. J.; Arauzo, A. B.; Fornies, J.; Garcia-Monforte, M. A.; Martin, A.; Menjon, B.; Rillo, C.; Saiz-Garitaonandia, J. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 6707.

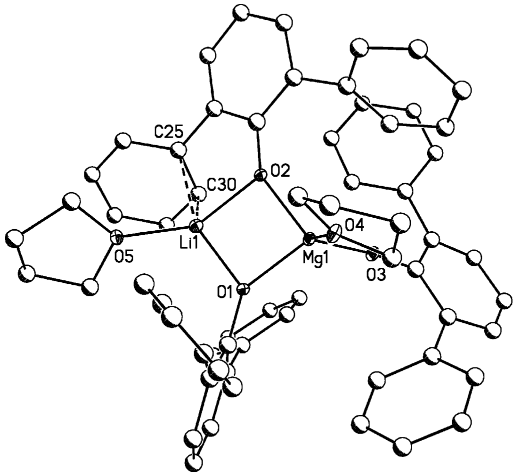


Figure 2. Structure of [LiMg(Odpp)$_3$(thf)$_2$], **2**. For clarity, the hydrogen atoms are not shown.

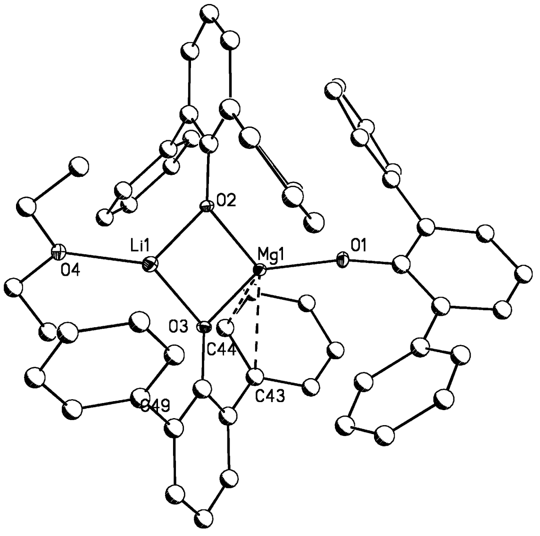


Figure 3. Structure of [Li(Et$_2$O)Mg(Odpp)$_3$]·0.5PhMe, **3**. For clarity, the hydrogen atoms and toluene solvate are not shown.

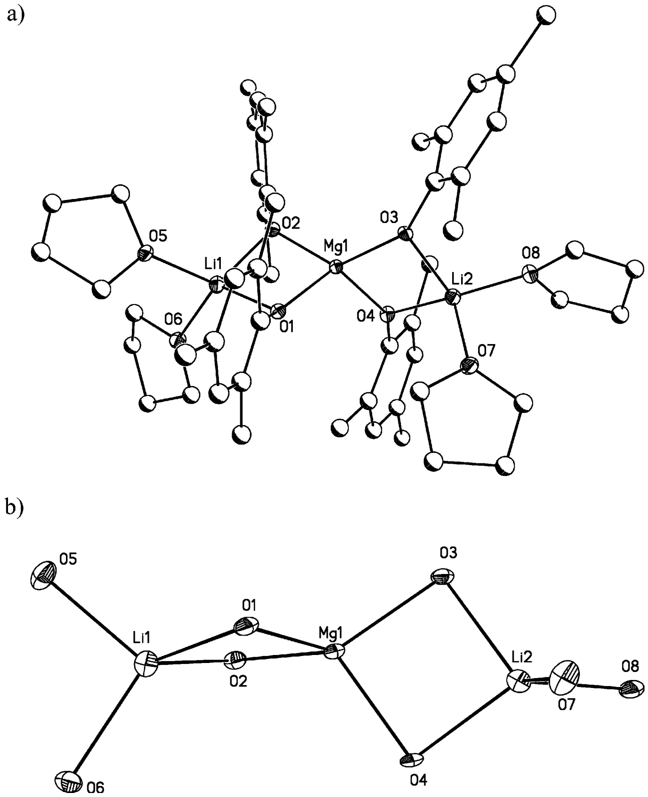


Figure 4. (a) [{Li(thf)$_2$}$_2$Mg(OMes)$_4$], **4**. For clarity, the hydrogen atoms are not shown. (b) Core structure of **4**.

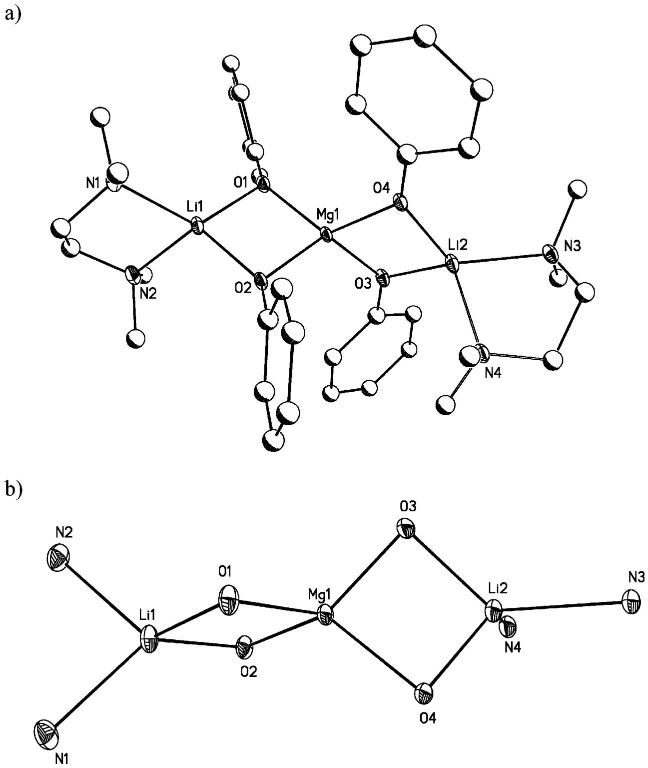


Figure 5. (a) Structure of [{Li(tmeda)}$_2$Mg(*m*-Odtp)$_4$], **5**. For clarity, the hydrogen atoms and *t*-butyl groups are not shown. (b) Core structure of **5**.

nate magnesium as the anion. The countercation consists of a lithium cation stabilized by four THF molecules arranged in a distorted tetrahedral fashion. The [Li(thf)$_4$]$^+$ cation is common and has been reported as a counteraction in numerous solvent-separated species.[22] The asymmetric unit of the molecule is composed of two-half crystallographically independent anionic moieties (Mg on inversion centers) and a tetracoordinate lithium center. Cation and anion are well separated with the closest proximity (Li1−Mg1) of 9.46 Å.

In both anions, magnesium adopts a trigonal planar geometry, with the O−Mg−O angles nearly equal to ideal values, in a narrow range of 119.13(5)−121.7(1)°. The aryloxide ligands on magnesium assume a propellerlike arrangement, with the aryl rings tilted from the MO$_3$ plane to reduce steric repulsion (for Mg(1), 63°, 63°, 62°; for Mg(2), 65°, 65°, 63°). The *t*-butyl groups on the ortho positions of the ligand provide the necessary steric saturation to allow the formation of a three-coordinate anion. The M(OAr)$_3^-$ motif shares the same trigonal planar geometry as in the alkyl derivative MgNp$_3^-$ (Np = neopentyl), which was obtained after the addition of cryptand to MgNp$_2$.[23] Similarly, a heterobimetallic amido-based magnesiate complex [Na-

---

[23] Squiller, E. P.; Whittle, R. R.; Richey, H. G.; Jr. *J. Am. Chem. Soc.* **1985**, *107*, 432.

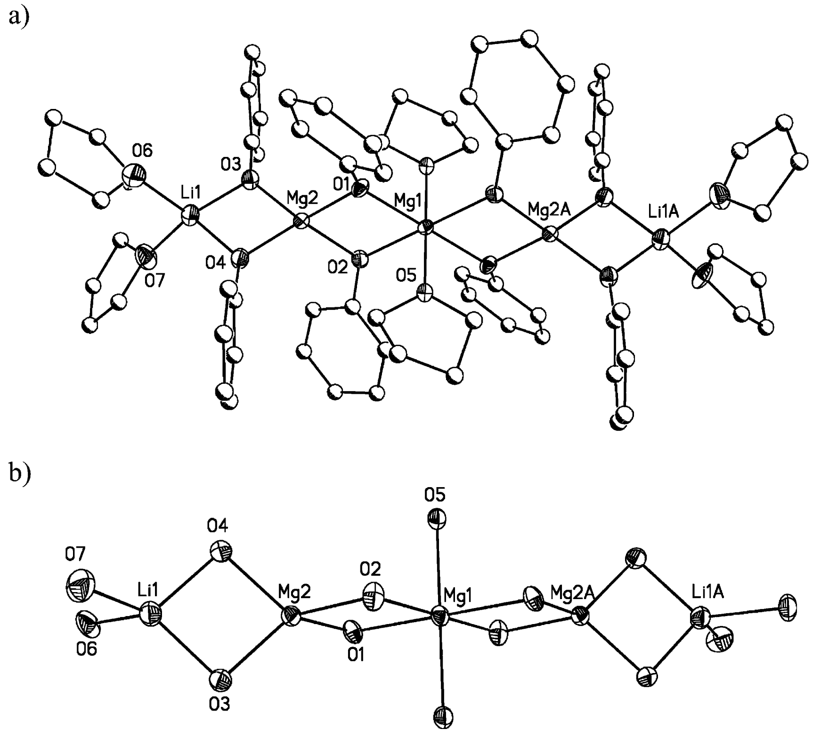


Figure 6. (a) Structure of $[\{Li(thf)_2\}_2Mg_3(m\text{-}Odtp)_8(thf)_2]$, **6**. For clarity, the hydrogen atoms and *t*-butyl groups are not shown. (b) Core structure of **6**.

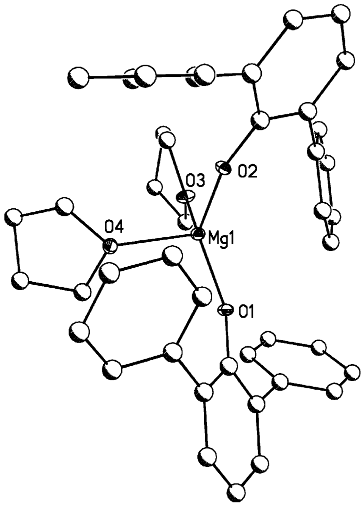


Figure 7. Structure of $Mg(Odpp)_2(thf)_2$, **7**. For clarity, the hydrogen atoms are not shown.

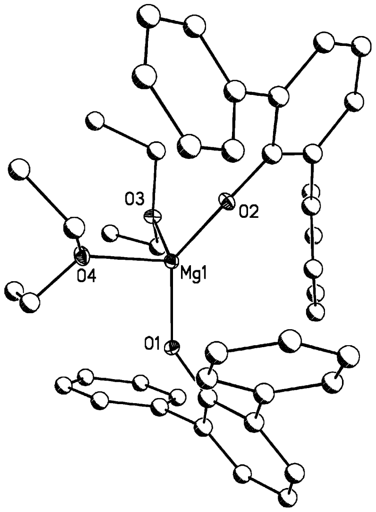


Figure 8. Structure of $Mg(Odpp)_2(Et_2O)_2$, **8**. For clarity, the hydrogen atoms are not shown.

$(PMDTA)_2][Mg(TMP)_3]$ (TMP = 2,2,6,6-tetramethylpiperidide) also displays a trigonal planar anion.[24] The anion in **1** is also isostructural and isoelectronic to the aluminum aryloxide $Al(OAr)_3$ (OAr = 2,6-*t*-Bu_2-4-MeC_6H_2O).[25] A three-coordinate magnesium center was also proposed in the recent $Mg(OAr)_3^-$ moiety (OAr = 2,6-*t*-$Bu_2C_6H_3O$), obtained as an asymmetric cleavage product from the dimeric $[Mg_2(\mu\text{-}OAr)_2(OAr)_2]$.[26] Characterized by solution studies and verified by theoretical work, experimental structural data remain elusive due to poor crystal quality.

Comparing the magnesiate ion in **1** with calculated structure of $Mg(OAr)_3^-$, the Mg−O distances in **1** fall within a small range and their average distances (Mg(1), 1.845(2) Å; Mg(2), 1.841(2) Å) are slightly shorter (ca. 0.03 Å) than the values found in the calculated structure,[26] while the Mg−O−C(Ar) angles in both cases are nearly linear (in **1**, av 178.4°; in the calculated structure, av 179.8°).[26] The linearity in the Mg−O−C(Ar) angles can be attributed to the steric effects brought about by the ortho substitution on the aryloxide. In comparison to the neutral magnesium aryloxides, the Mg−O(Ar) bond lengths in **1** are slightly shorter than the distances in the monomeric four-coordinated complexes $[Mg(OAr)_2(thf)_2]$ (av 1.864(1) Å) and $[Mg(OAr)_2(TMEDA)]$ (av 1.8803(8) Å) (OAr = 2,6-*t*-$Bu_2C_6H_3O$).[26] Compound **1** compares well with the closely related solvent-

---

[24] Graham, D. V.; Hevia, E.; Kennedy, A. R.; Mulvey, R. E.; O'Hara, C. T.; Talmard, C. *Chem. Commun.* **2006**, 417.

[25] Healy, V. M.; Barron, A. R., *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 921.

[26] Henderson, K. W.; Honeyman, G. W.; Kennedy, A. R.; Mulvey, R. E.; Parkinson, J. A.; Sherrington, D. C. *Dalton Trans.* **2003**, 1365.

Table 1. Crystallographic Data for Compounds **1**−**8**

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
formula	$C_{65}H_{109}LiMgO_8$	$C_{65.5}H_{59}LiMgO_5$	$C_{61.5}H_{53}LiMgO_4$	$C_{60}H_{92}$ Li_2MgO_{10}	$C_{70}H_{121}Li_2MgN_4O_{4.5}$	$C_{148}H_{240}Li_2Mg_3O_{17}$	$C_{44}H_{42}MgO_4$	$C_{44}H_{46}MgO_4$
fw	1049.77	957.31	886.31	1011.32	1128.84	2377.90	659.09	663.12
a (Å)	24.568(2)	10.675(2)	23.800(4)	12.058(1)	15.828(1)	15.387(2)	12.356(2)	10.825 (2)
b (Å)	16.419(1)	11.585(2)	10.032 (2)	16.759(2)	30.687(3)	16.720(3)	17.251(2)	11.562(2)
c (Å)	18.620(2)	22.593(4)	40.387(6)	16.976(2)	16.805(2)	18.272(3)	16.184(2)	16.074(3)
α (deg)	90	88.966(4)	90	113.962(2)	90	64.029(3)	90	74.475(3)
β (deg)	105.964(2)	83.303(4)	90.340(4)	97.261(2)	116.851(2)	72.115(3)	99.076(3)	83.284(3)
γ (deg)	90	68.629(3)	90	109.527(2)	90	68.707(3)	90	69.992(3)
V (Å^3)	7221.5(10)	2583.2(7)	9642(3)	2814.3(5)	7282.4(1)	3875.6(11)	3406.5(8)	1820.6(5)
Z	4	2	4	2	4	1	4	2
space group	*C*2	*P*−1	*C*2/*c*	*P*−1	*P*2(1)/*c*	*P*−1	*P*2(1)/n	*P*−1
d_{calc} (g/cm^3)	0.966	1.172	1.224	1.023	0.996	0.926	1.285	1.210
linear abs coeff (mm^{-1})	0.069	0.083	0.086	0.076	0.068	0.068	0.097	0.091
T (K)	100(2)	93(2)	96(2)	100(2)	98(2)	90(2)	95(2)	92(2)
2*θ* range (deg)	3.58−56.68	3.16−56.72	3.42−56.74	3.78−50.00	3.80−50.00	3.00−50.00	3.48−56.70	3.86 − 56.68
no. of indep. reflns	17761	12807	12066	9901	12820	13652	8484	8998
no. of params	755	622	614	580	740	973	442	442
R1, wR2 (all data)	0.0693, 0.1672	0.0944, 1387	0.0932, 0.1310	0.0851, 0.1753	0.0762, 0.1658	0.1112, 0.2352	0.0955, 0.1484	0.0657, 0.1235
R1, wR2 (>2*σ*)	0.0558, 0.1572	0.0577, 1272	0.0600, 0.1186	0.0627, 0.1636	0.0589, 0.1554	0.0751, 0.2163	0.0544, 0.1275	0.0500, 0.1152

separated potassium aryloxo zincate, $[K(thf)_6][Zn(OAr)_3]$ (OAr = 2,6-^{t}Bu$_2$C$_6$H$_3$O).[27] This finding is not surprising considering the almost similar ionic radii of magnesium and zinc (Mg (CN4) = 0.71 Å; Zn (CN4) = 0.74 Å),[28] which also accounts for the slightly longer Zn−O distances (av 1.867(2) Å) than those in magnesiate in **1**. As a consequence of the slightly elongated M−O distances, the O−Zn−O angles occur in a wider range (118.1(9)−133.0(10)°) than the values in **1**.

In contrast to the charge-separated structural motif in **1**, use of the less bulky ortho-substituted ligand, 2,6-diphenylphenol (HOdpp), afforded contact ion pairs shown in the molecular structures of **2** (Figure 2) and **3** (Figure 3). In both compounds, two aryloxides bridge the metal centers with the third ligand located at the terminus of magnesium. The coordination requirement at lithium is being saturated by a THF molecule in **2** or a diethyl ether molecule in **3**. Considering the larger steric demand of Et$_2$O as compared to THF, it appears intuitive that Et$_2$O completes the coordination sphere on lithium in **3**, providing the three-coordinate metal center. The smaller THF approaches the magnesium center in **2** to increase the coordination to four, while the larger Et$_2$O cannot coordinate due to steric overcrowding. The THF coordination on magnesium in **2** contrasts the $M(OR)_3^-$ motif in **1**, enabling the coordination of THF due to open space provided by the bridging function of the two aryloxides with a narrow O_{br}−Mg−O_{br} (br = bridging) angle of 89.04(6)°, while the other two O_{br}−Mg−O_{ter} (ter = terminal) angles are close to expected values for a trigonal geometry (119.45(6)° and 121.32(6)°). The magnesium center in **3** deviates, as well as from trigonal planar geometry, with a O_{br}−Mg−O_{br} angle of 85.63(6)°, and a wide range of O_{br}−Mg−O_{ter} angles (118.60(6)° and 131.19(6)°). The coordination of THF to the magnesium center in **2** is unusual, as the lithium center is expected to be the preferred site of nucleophilic attack than magnesium due to the former's more electropositive environment. The structure of **2** suggests that an open coordination environment on magnesium can also be a viable Lewis acidic site, thus providing important insights into the reactivity of the metal sites in "ate" complexes. Moreover, in the absence of a fitting donor, the vacancy in the coordination sphere of magnesium in the case of **3** also allows close contacts with the ligand as elucidated later in the discussion.

In **2** and **3**, the four-membered LiO$_2$Mg rings are planar, having the sum of endocyclic angles equal to 360°. The lithium centers exhibit a significant deviation from a trigonal environment (in **2** angles at Li, 90.2(1)°, 113.8(2)°, 144.6(2)°; in **3** angles at Li, 87.1(1)°, 122.9(2)°, 134.8(2)°); the narrow O−Li−O angles involve two oxygen atoms that bridge lithium and magnesium. To decrease steric repulsion, the terminal aryloxide on magnesium and donor on lithium in both compounds are in a transoid arrangement with respect to the LiO$_2$Mg plane. In addition, the bridging aryloxide rings tilt relative to the LiO$_2$Mg plane (tilt angles in **2**, 84.5° and

---

(27) Darensbourg, D. J.; Niezgoda, S. A.; Draper, J. D.; Reibenspies, J. H. *Inorg. Chem.* **1999**, *38*, 1356.

(28) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751.

Table 2. Selected Bond Distances and (Å) and Angles (deg)[a]

compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Mg−O(Ar)	1.848(1) (Mg1) 1.840(2) (Mg1) 1.839(1) (Mg2) 1.845(2) (Mg2)	1.944(1)[b] 1.936(1)[b] 1.853(1)[c]	1.834(1)[b] 1.916(1)[b] 1.932(1)[c]	1.947(2) 1.937(2) 1.920(2) 1.937(2)	1.925(1) 1.936(1) 1.928(1) 1.956(1)	2.080(2) (Mg1) 2.084(2) (Mg1) 1.959(2) (Mg2) 1.949(2) (Mg2) 1.926(2) (Mg2) 1.926(2) (Mg2)	1.876(1) 1.877(1)	1.869 (1) 1.880(1)
Mg−D[d]		1.994(2)				2.143(2)	2.030(2) 2.031(2)	2.046(1) 2.039(1)
Li−O(Ar)		1.894(3) 1.947(3)	1.923(3) 1.874(3)	1.942(4) 1.950(4) 1.933(4) 1.929(4)	1.936(1) 1.921(4) 1.933(4) 1.922(2)	1.908(5) 1.890(5)		
Li−D[d]	1.943(6) 1.937(5) 1.948(6) 1.966(5)	1.902(3)	1.935(3)	1.916(5) 1.995(4) 1.915(4) 1.954(4)	2.141(4) 2.095(4) 2.170(4) 2.140(4)	1.97(1) 1.999(5)		
O−Mg−O	120.08(5) (Mg1) 119.8(5) (Mg1) 119.13(5) (Mg2) 121.7(1) (Mg2)	89.04(6) 119.45(6) 121.32(6) 108.23(6)	85.63(6) 118.60(6) 131.19(6)	90.26(7) 115.81(8) 115.79(8) 131.98(8) 116.44(8) 89.42(7)	88.65(6) 124.45(7) 124.54(7) 119.58(7) 115.50(6) 87.40(6)	77.12(7) (Mg1) 102.88(7) (Mg1) 180.0(7) (Mg1) 83.25(8) (Mg2) 123.39(8) (Mg2) 121.69(9) (Mg2) 124.41(9) (Mg2) 121.65(9) (Mg2) 87.13(8) (Mg2)	90.73(7) 101.03(6) 102.61(6) 109.84(6) 112.97(6) 132.14(7)	99.73(5) 101.68(5) 103.98(5) 104.02(5) 105.45(5) 137.15(5)
Q$_{br}$−Li−O$_{br}$			87.1(1)	90.0(2) 89.3(2)	88.7(1) 88.2(2)	88.7(2)		
D−Li−D	111.5(3) 106.9(3) 112.3(3) 118.9(3) 103.9(3) 103.0(2)			112.0(2) 98.0(2) 103.1(2)	86.7(1) 85.3(1)	122.6(5) 101.7(7)		
Q$_{br}$−Li−D[d]			122.9(2) 134.8(2)	121.5(2) 118.7(2) 118.3(2) 111.7(2) 115.3(2) 110.6(2) 126.6(2) 112.0(2)	126.7(2) 120.9(2) 124.5(2) 112.1(2) 131.8(2) 109.5(2) 125.8(2) 117.9(2)	116.0(2) 114.9(5) 113.4(3)		
Mg−O$_{br}$−Li			93.1(1) 94.2(1)	88.7(1) 88.8(1) 89.25(1) 88.9(1)	91.2(1) 91.40(1) 91.3(1) 90.8(1)	92.3(2) 91.8(2)		
Mg−O$_{br}$−Mg						99.69(8) 99.92(8)		

[a] br = bridging. [b] Bridging aryloxide. [c] Terminal aryloxide. [d] D = THF (**1**, **2**, **4**, **6, 7**), Et_2O (**3, 8**), TMEDA (**5**).

25.3°; in **3**, 101.2° and 29.2°). The terminal Mg−O bond distances, 1.834(1) Å in **2** and 1.853(1) Å in **3**, are comparable to the terminal distances in $[Mg_2(\mu\text{-}OAr)_2(OAr)_2]$ (OAr = 2,6-*t*-$Bu_2C_6H_3O$) (1.823(3)−1.819(3) Å).[29] As expected, the bridging Mg−O bond lengths in **2** and **3** are considerably longer than the terminal one, with distances in **2** (1.944 (1) and 1.936(1) Å) greater than in **3** (1.916(1) and 1.932(1) Å) as rationalized by the higher coordination number in the former. Despite the higher formal coordination number in **2** and **3**, their bridging Mg−O bonds are shorter than the corresponding bond lengths in the aforementioned bisaryloxide complex (1.951(3)−1.971(3) Å),[29] while Li−O(aryloxo) bonds and Li−O(donor) bond lengths are comparable to the dimeric $[\{Li(Et_2O)(BHT)\}_2]$ (1.85(1) and 1.87(1), and 1.96(1) Å, respectively).[30]

Remarkable features of **2** and **3** are the metal−arene interactions between the metals and a pendant phenyl ring located on one of the bridging aryloxides. In **2**, the transoid arrangement of THF and terminal aryloxide presented a void in the coordination sphere of lithium, allowing encapsulation by a phenyl ring in an η^2 binding mode (Li−C distances: 2.628(4) and 2.615(4) Å). Similar stabilization of the alkali metal through secondary interactions has been previously seen in other heterobimetallic magnesiates.[8,31,32] Conversely, the lithium center in **3** lacks metal-π−phenyl interactions, rather displaying coordination to diethyl ether with a [M(donor)MgR_3] motif previously observed in several heterobimetallic amido[7,31,33] and aryl systems.[4] The significance of metal-π−phenyl interactions in the stabilization of these

---

(29) Calabrese, J.; Cushing, M. A., Jr.; Ittel, S. D. *Inorg. Chem.* **1988**, *27*, 867.

(30) Cetinkaya, B.; Gumrukcu, I.; Lappert, M. F.; Atwood, J. L.; Shakir, R. *J. Am. Chem. Soc.* **1980**, *102*, 2086.

(31) Hevia, E.; Kenley, F. R.; Kennedy, A. R.; Mulvey, R. E.; Rowlings, R. B. *Eur. J. Inorg. Chem.* **2003**, 3347.

(32) Forbes, G. C.; Kennedy, A. R.; Mulvey, R. E.; Roberts, B. A.; Rowlings, R. B. *Organometallics* **2002**, *21*, 5115.

(33) Forbes, G. C.; Kennedy, A. R.; Mulvey, R. E.; Rodger, P. J. A.; Rowlings, R. B. *J. Chem. Soc. Dalton Trans.* **2001**, 1477.

compounds is illustrated once more in **3** where the magnesium center exhibits Mg−C contacts (2.520(2) and 2.818(2) Å) in an η^2 fashion in lieu of THF coordination in **2**. Nicely demonstrated in the structures of **2** and **3**, competition between solvation/donation and metal−ligand secondary interactions is a nontrivial concept, influenced by the size and nature of ligand and donor. Metal-π−phenyl interactions provided by the Odpp ligand have been shown to be effective for the stabilization of homometallic[34] and heterobimetallic alkali/alkaline earth metal compounds.[16] It comes as no surprise that the lighter alkaline earth congener magnesium is effectively stabilized as well.

Further decreasing ligand bulk, 2,4,6-trimethylphenol (HOMes) and the meta-substituted 3,5-di-*t*-butylphenol (*m*-HOdtp), afforded the THF solvate **4** and TMEDA solvate **5** (Figures 4 and 5, Table 1). Compounds **4** and **5** share the same Li_2MgR_4 core as the aryloxomagnesiate [Li(TMEDA)$_2$Mg(2-MeOC$_6$H$_4$)$_4$],[14] which may be rationalized by the comparable ligand sizes. This structural motif is also known for several previously reported magnesiates using amide, alkyl, and enolate ligands,[21,35] as well as in the mixed Li/Ba,[16] Li/Sr,[36] and Li/Ca[36] complexes ([Li$_2$M(Odpp)$_4$], where M = Ba, Sr, Ca). In **4** and **5**, the magnesium atom is coordinated to four aryloxide ligands arranged in a severely distorted tetrahedral fashion, with two aryloxide ligands doubly bridging to a lithium atom. This arrangement provides two edge-sharing four-membered LiO_2Mg rings. The fused LiO_2Mg rings in **4** and **5** are orthogonal to each other with twist angles of 92° and 93°, respectively. The four aryloxides coordinated to the magnesium centers are arranged in a severely distorted tetrahedral fashion (O−Mg−O angles in **4**, 89.42(7)−131.98(8)°; in **5**, 87.40(6)−124.54(7)°), with the narrow angles involving the oxygen atoms bridging magnesium and one of the lithium centers. In **4**, each of the lithium centers is also coordinated to two THF donors, affording a distorted tetrahedral coordination. The O−Li−O angles involving the THF molecules (98.0(2)° and 103.1(2)°) and Li−O distances (1.915(4)−1.995(4) Å) are comparable to literature values.[37] The coordination at Li in **5** is filled by a TMEDA donor, with N−Li−N bite angles of 85.3(1)° and 86.7(1)° and Li−N distances in the range of 2.095(4)−2.170(4) Å. These values agree well to those found in related TMEDA solvated lithium derivatives.[6,14] Further, the three metal centers in **4** and **5** are arranged in a slightly nonlinear fashion apparently to minimize steric strain (Li1−Mg−Li2 angles in **4**, 157.1(1)°; in **5**, 165.58(2)°). The geometrical features in the core structure of **4** and **5** are comparable to those in the closely related complex [Li(TMEDA)$_2$Mg(2-MeC$_6$H$_4$O)$_4$][14] as demonstrated by the nearly square shape of the LiO_2Mg rings, with close to 90° endocyclic angles. In addition, the bridging M−O distances in **4** (Mg−O, av 1.935(2) Å; Li−O, 1.939(4) Å) and **5** (Mg−O, av 1.936(1) Å; Li−O, 1.929(4) Å) are also similar to the values in the previously reported compound (Mg−O, av 1.928(2) Å; Li−O, av 1.933(5) Å).

Attempts to prepare a THF solvate using *m*-HOdtp, which afforded the TMEDA solvate **5**, yielded **6** as depicted in Figure 6. Instead of the 2:1 Li/Mg ratio as seen in **5**, compound **6** displays an unprecedented 2:3 Li/Mg stoichiometry. The asymmetric unit of **6** contains only one-half of the molecule, wherein an inversion center on the central magnesium atom generates the second THF molecule on the axial position, one of the three magnesium atoms, second lithium atom, and four of the eight aryloxide ligands. The core framework of **6** (Figure 6b) is comprised of four fused four-membered rings, with two aryloxide ligands doubly bridging magnesium metals or magnesium and lithium metals. The fused Mg_2O_2 rings are on the same plane (tilt angle of 180°), while each of the LiO_2Mg rings lies orthogonally relative to this plane (tilt angles of 90°). This arrangement renders two types of coordination environments for the magnesium centers in **6**. The central magnesium has a pseudo-octahedral geometry wherein it is coordinated to THF molecules that occupy the open coordination sites on the trans or axial positions and four aryloxide ligands located at the equatorial positions, with O−Mg(1)−O angles in the range of 77.12(7)−102.88(7)°, the narrow angles involve aryloxides that doubly bridge two magnesium atoms (synopsis illustration). On the other hand, the two other magnesium centers are tetra-coordinated to four aryloxides arranged in a distorted tetrahedral fashion, linking magnesium centers or magnesium and lithium metals. Two THF molecules complete the coordination sphere of the lithium centers with O−Li−O angles of 101.7(5)°. In contrast to **4** and **5**, the metal centers are almost linear with Li(1)−Mg(2)−Mg(1) angle of 178.12(9)°. As rationalized by the higher coordination number in the central magnesium, the Mg(1)−O(Ar) distances are generally longer (av 2.082(2) Å) than those in the tetra-coordinated Mg(2) and Mg(3) (av 1.940(2) Å). The oligomeric arrangement in **6** can be ascribed to the flexibility of the phenoxide units to rotate out of the plane to avoid steric crowding, permitting the participation of more than one magnesium center in the architecture of the compound. This rationale was used to describe the tetranuclear arrangement in [{Li(TMEDA)}$_2$Mg$_2$Ph$_6$], in contrast to the more common dinuclear or trinuclear framework.[21]

The common structural motif in compounds **2**−**6** is the doubly bridging aryloxide moiety pattern also seen in heterobimetallic compounds involving combinations of lithium with heavier alkaline earth metals calcium, strontium, and barium bearing the HOdpp ligand.[16,36] Interestingly, the triply bridging moiety, as observed for the heavier alkali metals, is absent for lithium, likely a consequence of the small size of the metals. As such, lithium is unable to support a face-sharing motif. Predictions of metal ratios remain very challenging, supported by the occurrence of different metal ratios (1:1, 2:1, 2:3) despite a consistent stoichiometric ratio of 1:1.

As illustrated in Figures 7 and 8, the homometallic compounds **7** and **8** contain tetra-coordinated magnesium

---

(34) Deacon, G. B.; Forsyth, C. M.; Junk, P. C. *J. Organomet. Chem.* **2000**, *607*, 112.

(35) Hevia, E.; Henderson, K. W.; Kennedy, A. R.; Mulvey, R. E. *Organometallics* **2006**, *25*, 1778.

(36) Zuniga, M. F.; Deacon, G. B.; Ruhlandt-Senge, K. In preparation.

(37) Ruhlandt-Senge, K.; Englich, U.; Senge, M. O.; Chadwick, S. *Inorg. Chem.* **1996**, *35*, 5820.

centers, with the two $Odpp^-$ moieties and two donor molecules arranged in a severely distorted tetrahedral fashion. The O−Mg−O angles range from 90.73(7)° to 132.14(7)° in **7** and 99.73(5)° to 137.15(5)° in **8**; the wide angles involve the two aryloxide ligands. Consistent with the difference in donor size are the O(donor)−Mg−O(donor) angles, where the one in **7** (90.73(7)°, donor = THF) is narrower than in **8** (101.68(5)°, donor = Et_2O). The Mg−O(thf) and Mg−O(Et_2O)bond lengths in both compounds (av 2.03(2) and 2.05(1) Å, respectively) are slightly shorter than those in the six-coordinate magnesium in **6**, while the Mg−O(Ar) distances (av 1.877(1) Å in **7** and av 1.875(1) Å in **8**) are slightly longer than the ones in **1**, as expected for the lower coordination number of $Mg(OAr)_3^-$ in the latter.

Solution Studies. The behavior of compounds **1**−**6** in benzene-d_6 and THF-d_8 solutions was examined by NMR spectroscopy. Both ^1H and ^{13}C NMR spectra were recorded, but only results from the ^1H NMR will be discussed due to the generally more apparent differences in the spectra among the compounds. Relevant data are listed in the Experimental Section. The ^1H NMR spectrum of **1** in the arene solvent shows two sets of signals for the aryloxide ligand with a 2:1 ratio based on the integration in addition to signals for two metal-coordinated THF donors. The chemical shifts corresponding to the aromatic and aliphatic protons in the two sets of peaks differ by ∼0.10 ppm. This discrepancy to the crystallographic data, where the lithium cation is coordinated to four THF donors, indicates loss of the donor upon removal of mother liquor. The coordination at lithium may be filled by coordination with the aromatic solvent. Alternatively, one can consider the formation of contact molecules, e.g., $[Li(thf)_2Mg(\mu\text{-BHT})_2(BHT)]$, that has two bridging ligands and one terminal ligand coordinated to magnesium, analogous to the structural motif observed in **2** and **3**. In THF-d_8, wherein **1** is more soluble, only one set of aryloxide signals was observed, presumably affording the separated ion species. Notably, the same results were seen in the related zincate complex $[K(thf)_6][Zn(OAr)_3]$.[27]

Only one set of Odpp peaks is observed for **2** and **3** in benzene-d_6 despite having two ligand environments, bridging and terminal, as displayed in the solid-state structure of the compound. This can be explained by the rapid exchange between the aryloxides in the NMR time scale as frequently observed for dimeric compounds, such as $[Ca(\mu\text{-Odpp})_2(Odpp)_2]$.[34] In contrast to **1**, compounds **2** and **3** retain the metal/donor stoichiometry, suggesting that their structures are maintained in arene solution. A different solution behavior was seen in the THF-d_8 solutions of **2** and **3**, where overlapping and indistinguishable phenoxide peaks were evident, likely signifying ligand redistribution in the polar solvent. These findings are consistent with observations during the syntheses of **2** and **3,** wherein the homometallic compounds **7** and **8** were isolated in the polar THF or Et_2O solution, respectively, while use of toluene allowed the isolation of the heterobimetallic compound.

The ^1H NMR spectra in benzene-d_6 of the THF-solvates **4** and **6** show loss of the donor as in **1** based on the integrations of the aryloxide and donor peaks. There is an ∼25% donor loss in **4** and 50% in **6**. Three sets of signals, two of which coincide, for the aromatic and methyl protons are observed for **4**. The integration of the peaks gives a 1:1: 0.5 ratio for each type of aryloxide peaks, with the signals for the *o*- and *p*-CH_3 protons overlapping for two of the aryloxides. In contrast, the spectrum of **6** is simple and contains only one set of phenoxide signals, although this result may not be conclusive due to the low solubility of the compound in the arene solvent. In the polar medium, **4** and **6** are highly soluble and display only one set of aromatic peaks. This observation is consistent with the solid-state structure of **4** where only one type of aryloxides is expected. The methyl protons are also distinct, with the *p*-CH_3 slightly upfield (by ∼0.1 ppm) compared to the ones for the *o*-CH_3. In **6**, which has two phenoxide environments, those that connect two magnesium atoms and those that bridge magnesium and lithium atoms, the single set of peaks may indicate a fast exchange process.

The spectra of **5** in both benzene-d_6 and THF-d_8 reveal one set of peaks for the aryloxide and TMEDA in a 2:1 ratio, which suggests that the solid-state structure is retained in both polar and nonpolar media. Previous works describe how the relative positions of the chemical shifts of the two sets of protons in TMEDA (NCH_2 and CH_3) in benzene-d_6 can verify the coordination of the amine to the metal center.[35,38] Uncoordinated TMEDA in the arene solvent would have CH_3 at a relatively upfield chemical shift, while coordination to the metal will result in the reversal of the positions of the peaks. In the case of **5**, the CH_3 signal is more downfield (2.05 ppm) than that of NCH_2 (1.85 ppm), indicating that the TMEDA solvates the metal center.

Conclusions

The structural features within this group of compounds correlate with ligand bulk, with the use of a sterically demanding phenol such as HBHT affording an unassociated species while less bulky phenoxides afford molecular compounds. Predictions of metal ratios, however, remain very difficult. Other structure-determining factors such as Lewis base donors and the choice of solvent system provide insights on the importance of solvation to achieve coordination saturation and strategies on the isolation of the target compounds. Further, the ability of the ligand to participate in metal−π-arene interactions play an important role in the stabilization of the metal centers, a structural feature that opens exciting possibilities in alkaline earth chemistry.

Acknowledgment. We gratefully acknowledge support from the National Science Foundation (CHE-0505863) and the IRES grant (OISE-0456119) for support of J.K. Purchase of the X-ray diffraction equipment was made possible with grants from the National Science Foundation (CHE-9527858 and CHE-0234912), Syracuse University, and the W. M. Keck Foundation.

IC701423R

---

[38] Andrews, P. C.; Barnett, N. D. R.; Mulvey, R. E.; Clegg, W.; O'Neil, P. A.; Barr, D.; Cowton, L.; Dawson, A. J.; Wakefield, B. J. *J. Organomet. Chem.* **1996**, *518*, 85.