Notes

Synthesis and Characterization of a Dimagnesiated Aromatic Compound: Oligomeric Derivatives of 1,4-Bis(chloromagnesio)-2,5-di-*tert*-butylbenzene

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Summary: The synthesis of 1,4-bis(chloromagnesio)-2,5-di-tert-butylbenzene was conducted by treating 1,4-bis(chloromercurio)-2,5-di-tert-butylbenzene with methylmagnesium chloride. The dimagnesiated compound was characterized by hydrolysis, halogenation, and treatment with allyl bromide. NMR spectra suggest that 1,4-bis(chloromagnesio)-2,5-di-tert-butylbenzene exists as a mixture of oligomers.

Introduction

Grignard reagents have been intensively studied over the last century.[1] Despite the abundance of aromatic compounds bearing one magnesium substituent, there are very few examples of aromatic compounds containing two or more magnesium groups attached to the same ring.[2−5] Evidence for aromatic "poly-Grignard" derivatives has come from analysis of products obtained upon electrophile addition.[2,4] The crystal structure of tetrameric *o*-phenylenemagnesium has been reported, which exists with one terminal magnesium−carbon bond and one ortho carbon bridging between two magnesiums of the tetrameric unit.[3] Furthermore, several dimeric arylmagnesium compounds with bridging aryl groups have been structurally characterized.[6] However, structural information on aromatic "poly-Grignard" reagents of the type that might be generated and used in typical synthetic procedures has not been reported. We have recently described the syntheses of perlithiated,[7] permagnesiated,[8] and perzincated ruthenocenes,[9] which were prepared by reaction of the appropriate methylmetal with a permercurated ruthenocene. Given the facile preparation and novelty of the permetalated ruthenocenes, we sought to extend this chemistry to polymetalated benzene derivatives.[10] Herein we describe the synthesis and reactivity of 1,4-bis(chloromagnesio)-2,5-di-*tert*-butylbenzene. NMR spectra of this compound suggest that it exists as a mixture of oligomers obtained by shifting of the Schlenk equilibrium from the monomer.

Results and Discussion

The preparative chemistry is outlined in Scheme 1. The requisite dimercurated derivative **2** was prepared from 1,4-di-*tert*-butylbenzene (**1**) by fusion with mercuric trifluoroacetate (2.2 equiv) at 210 °C,[11] followed by treatment with sodium chloride in water/methanol. 1,4-Di-*tert*-butylbenzene could not be tri- or tetramercurated under the fusion conditions, even with excess mercuric trifluoroacetate and extended heating. Exclusive formation of the 1,4-dimercurated compound, as opposed to the 1,3-isomer, was evident from the NMR spectra.

Treatment of **2** with methylmagnesium chloride (4.5 equiv) in refluxing 1,2-dimethoxyethane (DME) for 18 h led to a white suspension containing 1,4-bis(chloromagnesio)-2,5-di-*tert*-butylbenzene (**3**). Hydrolysis at room temperature afforded **1** (80%), while quenching with D_2O resulted in **1**-d_2 (71%) with >95% deuterium incorporation in the 2- and 5-positions. Since the carbon−mercury bond is stable to hydrolysis under the reaction conditions, the hydrolysis experiments are consistent with the formulation of **3** as a dimagnesiated species. Treatment of **3** with bromine afforded 1,4-dibromo-2,5-di-*tert*-butylbenzene (**4**, 90%),[12] while addition of iodine gave 1,4-diiodo-2,5-di-*tert*-butylbenzene

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(1) For leading references, see: *Handbook of Grignard Reagents*; Silverman, G. S., Rakita, P. E., Eds.; Dekker: New York, 1996. Bickelhaupt, F. *J. Organomet. Chem.* **1994**, *475*, 1. Walborsky, H. M.; Topolski, M. *J. Am. Chem. Soc.* **1992**, *114*, 3455. Noyori, R.; Kitamura, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 49. Garst, J. F. *Acc. Chem. Res.* **1991**, *24*, 95. Walling, C. *Acc. Chem. Res.* **1991**, *24*, 255. Walborsky, H. M. *Acc. Chem. Res.* **1990**, *23*, 286. Erdik, E. *Tetrahedron* **1984**, *40*, 641. Lai, Y.-H. *Synthesis* **1981**, 585. Felkin, H.; Swierczewski, G. *Tetrahedron* **1975**, *31*, 2735.

(2) For leading references, see: Wittig, G.; Bickelhaupt, F. *Chem. Ber.* **1958**, *91*, 883. Hart, F. A.; Mann, F. G. *J. Chem. Soc.* **1957**, 3939. Smith, C. F.; Moore, G. J.; Tamborski, C. *J. Organomet. Chem.* **1971**, *33*, C21. Tamborski, C.; Moore, G. J. *J. Organomet. Chem.* **1971**, *26*, 153. Haper, R. J., Jr.; Soloski, E. J.; Tamborski, C. *J. Org. Chem.* **1964**, *29*, 2385. Ghosh, T.; Hart, H. *J. Org. Chem.* **1988**, *53*, 3555. Harada, H.; Hart, H.; Du, C.-J. F. *J. Org. Chem.* **1985**, *50*, 5524.

(3) Tinga, M. A. G. M.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Horn, E.; Kooijman, H.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 2808.

(4) Eaton, P. E.; Lee, C.-H.; Xiong, Y. *J. Am. Chem. Soc.* **1989**, *111*, 8016.

(5) For a structural discussion of di-Grignard compounds, see: Bickelhaupt, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 990.

(6) (a) Thoennes, D.; Weiss, E. *Chem. Ber.* **1978**, *111*, 3726. (b) Markies, P. R.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; van der Sluis, P.; Spek, A. L. *J. Organomet. Chem.* **1990**, *393*, 315.

(7) Bretschneider-Hurley, A.; Winter, C. H. *J. Am. Chem. Soc.* **1994**, *116*, 6468.

(8) Seneviratne, K.; Bretschneider-Hurley, A.; Winter, C. H. *J. Am. Chem. Soc.* **1996**, *118*, 5506.

(9) Seneviratne, K.; Winter, C. H. *Organometallics* **1997**, *16*, 2498.

(10) Synthesis and properties of hexalithiobenzene: Baran, J. C., Jr.; Hendrickson, C.; Laude, D. A., Jr.; Lagow, R. J. *J. Org. Chem.* **1992**, *57*, 3759. Xie, Y.; Schaefer, H. F., III. *Chem. Phys. Lett.* **1991**, *179*, 563. Smith, B. J. *Chem. Phys. Lett.* **1993**, *207*, 403.

(11) These conditions are an adaptation of those used to prepare hexakis[(trifluoroacetoxy)mercurio]benzene: Deacon, G. B.; Farquharson, G. J. *Aust. J. Chem.* **1976**, *29*, 627; *J. Organomet. Chem.* **1974**, *67*, C1.

(12) Kofod, H.; Kumar, L.; Sutton, L. E. *J. Chem. Soc.* **1958**, 1790.

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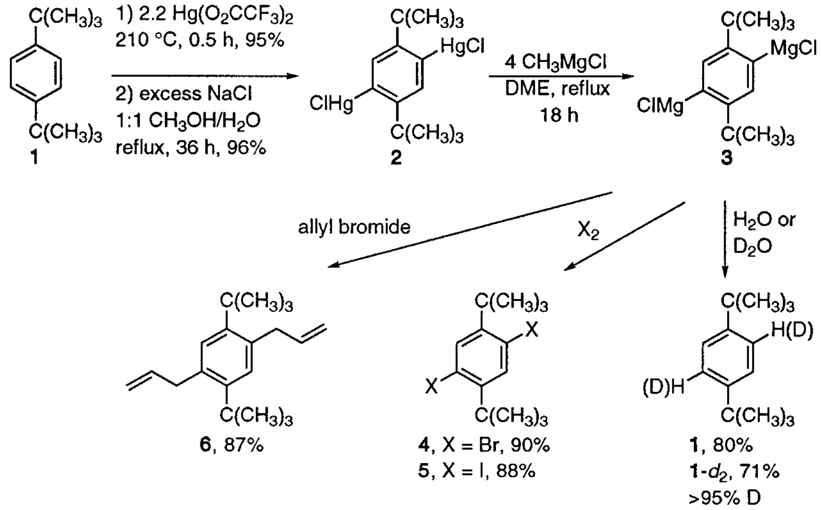
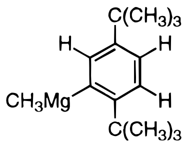
Scheme 1. Preparation and Reactions of 3



(**5**, 88%).[13] Addition of allyl bromide afforded 1,4-di-*tert*-butyl-2,5-diallylbenzene (**6**, 87%). Ketones and other carbonyl-containing compounds gave mixtures of many products upon reaction with **3**. Use of DME in the formation of **3** is critical. Other solvents (THF, Et_2O, HMPA, NEt_3, TMEDA) led to mixtures of (methylmercurio)benzene species, with <20% of **1** being isolated upon hydrolysis.

Given the excellent thermal stability of **3**, its isolation was carried out. Preparation of **3** as described above followed by evaporation of the solvent, washing of the resultant residue with hexane, and vacuum drying for 36 h at 80 °C afforded a white powder. This powder was sparingly soluble in dimethyl sulfoxide-d_6 and tetrahydrofuran-d_8 and was characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and CP/MAS ^{13}C NMR spectroscopy. In dimethyl sulfoxide-d_6, two products were observed in an 80:20 ratio. Free DME was also present. The ^1H and $^{13}C\{^1H\}$ NMR spectra are consistent with **7** as the major product, while we propose **8** to be the minor product on the basis of the similarity of its ^1H NMR spectrum to that of **7**. There was no evidence for deprotonation of dimethyl sulfoxide-d_6 by **3**, **7**, or **8** over 1 week at 23 °C. A ^1H NMR spectrum of the isolated solid in tetrahydrofuran-d_8 showed *tert*-butyl resonances for **7** and **8** in a 50:50 ratio and showed at least eight overlapping *tert*-butyl methyl resonances between δ 1.55 and 1.59 (ca. 40% of total methyl signal integration). The increased solubility of **8**, coupled with the new resonances, suggests that tetrahydrofuran-d_8 is better able to dissolve the components of the white powder than is dimethyl sulfoxide-d_6. A CP/MAS ^{13}C NMR spectrum of the isolated solid was recorded. The spectrum revealed more than one compound to be present, but showed resonances expected for a 1,4-dimagnesiated-2,5-di-*tert*-butylbenzene. At least three magnesiated carbon signals were observed between 160 and 174 ppm.[14] Both free and coordinated DME were also observed.



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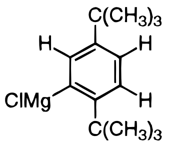

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The reactivity data outlined above, particularly the hydrolysis experiments, demonstrate that treatment of **2** with methylmagnesium chloride provides a dimagnesiated benzene in at least 71% yield (yield of **1**-d_2 obtained from treatment of **3** with D_2O). The spectroscopic data allow some insight into the structure adopted by **3**; the monomeric structure presented in Scheme 1 for simplicity cannot be the only dimagnesiated species present. The NMR spectra in dimethyl sulfoxide-d_6 showed only the monomagnesiated species **7** and **8**. We suggest that **7** and **8** are minor species that have the highest solubility among all of the products.[15] Bromination studies of **3** require that **7** and **8** constitute $\leq$10% of the compounds present. In tetrahydrofuran-d_8, the *tert*-butyl resonances between δ 1.55 and 1.59 in the ^1H NMR are too complicated for monomeric **3**. The low solubility of the compounds giving rise to the δ 1.55 and 1.59 resonances suggests that they are oligomers formed by shifting of the Schlenk equilibrium from monomeric **3**. Such an oligomeric mixture may be favored by the synthetic approach to **3**. Since magnesium chloride has a very low solubility in DME, the formation of oligomers may occur through irreversible elimination of magnesium chloride from **3**. We have previously shown that pentakis(chloromagnesio)pentamethylruthenocene exists as an oligomeric mixture, of which the monomer is a minor component at best.[8]

The results presented herein raise several important points. The regiospecific synthesis of **3** is significant, since existing routes to dimagnesiated aromatics require Lewis basic groups for ortho-magnesiation[4] or rely upon the inefficient reaction of a polyhalogenated benzene derivative with 2 equiv of magnesium metal (the second insertion is apparently slow due to the deactivating effect of the first chloromagnesio substituent).[2] While a few aliphatic di-Grignard reagents have been proposed to be polymeric on the basis of their low solubilities in

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(13) Bell, F. *J. Chem. Soc.* **1958**, 120.

(14) Magnesiated carbon atoms in benzene derivatives typically resonate between 160 and 170 ppm: Screttas, C. G.; Micha-Screttas, M. *J. Organomet. Chem.* **1985**, *290*, 1. Allen, P. E. M.; Fisher, M. C. *Eur. Polym. J.* **1985**, *21*, 201. Jones, A. J.; Grant, D. M.; Russell, J. G.; Fraenkel, G. *J. Phys. Chem.* **1969**, *73*, 1624.

(15) NMR spectra of **2** place an upper limit of 2−3% for content of a monomercurated compound that would lead directly to **7** and **8**.

organic solvents,[5] the present study gives the first structural insight into an example of such a species. Moreover, care must be exercised when aromatic "poly-Grignard" reagents are generated in solution and used in synthetic procedures, since carbon−magnesium bonds of widely differing reactivity are likely to be present (e.g., ArMgCl, ArMgAr, $ArMgCH_3$) in the same molecule. Finally, many polymetalated benzene derivatives should be easily prepared from polymercurated precursors in analogy with the present study and the work of others.[3,10] Such molecules should be significant from a theoretical viewpoint and may have applications in synthesis. We are continuing to explore the properties of polymetalated aromatic compounds and will report our findings in due course.

Experimental Section

All reactions were carried out under an atmosphere of argon using either a Schlenk line with appropriate glassware or a glovebox. 1,2-Dimethoxyethane was distilled from sodium benzophenone ketyl prior to use. Tetrahydrofuran-d_8 and DMSO-d_6 were dried over sodium and activated 4-Å molecular sieves, respectively. Other solvents were used as received. 1,4-Di-*tert*-butylbenzene, mercuric trifluoroacetate, and other reagents were purchased from Aldrich Chemical Company. ^1H, $^{13}C\{^1H\}$, and ^{19}F NMR spectra were obtained at 500, 121, and 282 MHz, respectively, in the indicated solvents. Infrared spectra used potassium bromide, Nujol, or Fluorolube as the matrices as indicated. Mass spectra were obtained in the electron impact mode. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN, or Galbraith Laboratories, Knoxville, TN. Melting points were obtained on an Electrothermal Model 9200 melting point apparatus and are uncorrected.

1,4-Bis[(trifluoroacetoxy)mercurio]-2,5-di-*tert*-butylbenzene. A 250-mL round-bottomed flask, equipped with a condenser, was charged with mercuric trifluoroacetate (30.0 g, 70.0 mmol), which was heated with stirring until melted (180−190 °C), at which time crystalline **1** (6.08 g, 32.0 mmol) was added. The temperature was increased to 210 °C for 20 min, whereupon the melt solidified. The resulting white solid was collected on a medium-porosity glass frit and was washed with water (300 mL) and methanol (300 mL). Vacuum drying afforded 24.7 g (95%) of a white powder: dec range 300−310 °C; IR (KBr, cm^{-1}) 3100 (w), 2950 (s), 2878 (m), 1784 (m), 1679 (s), 1577 (w), 1472 (m), 1437 (m), 1416 (m), 1363 (m), 1312 (m), 1257 (m), 1188 (s), 1049 (s), 924 (w), 886 (m), 853 (m), 840 (s), 807 (s), 789 (m), 725 (s), 644 (w), 610 (w), 517 (m), 485 (w), 455 (m), 420 (w); ^1H NMR (acetone-d_6, δ) 7.91 (s, aromatic *H*), 1.53 (s, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (acetone-d_6, ppm) 160.85 (q, $J = 37$ Hz, *C*=O), 152.52 (s, $C{-}C(CH_3)_3$), 141.29 (s, *C*−Hg), 136.18 (s, aromatic *C*−H), 119.69 (q, $J = 273$ Hz, CF_3), 35.64 (s, $C(CH_3)_3$), 33.11 (s, $C(CH_3)_3$); ^{19}F (acetone-d_6, ppm) −74.3 (s).

Anal. Calcd for $C_{18}H_{20}F_6Hg_2O_4$: C, 26.51; H, 2.41. Found: C, 26.38; H, 2.51.

1,4-Bis(chloromercurio)-2,5-di-*tert*-butylbenzene (2). A mixture of 1,4-bis[(trifluoroacetoxy)mercurio)]-2,5-di-*tert*-butylbenzene (24.7 g, 30.3 mmol), sodium chloride (8.85 g, 0.151 mol), water (200 mL), and methanol (200 mL) was refluxed for 2 days. The resulting white powder was collected on a medium-porosity glass frit and was washed with hexanes (300 mL), methanol (300 mL), and diethyl ether (300 mL). Vacuum drying afforded **2** as a white powder (19.3 g, 96%): dec range 300−330 °C; IR (KBr, cm^{-1}) 3090 (vw), 2952 (s), 2878 (s), 2792 (w), 2744 (w), 1472 (s), 1450 (m), 1392 (m), 1362 (s), 1312 (m), 1259 (m), 1241 (m), 1201 (w), 1175 (m), 1158 (w), 1053 (s), 1024 (w), 942 (vw), 929 (vw), 888 (m), 835 (w), 733 (vw), 669 (vw), 645 (vw), 627 (vw), 501 (w), 487 (m), 457 (m), 419 (vw); ^1H NMR ($CDCl_3$, δ) 7.32 (s, aromatic *H*), 1.32 (s, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 147.98 (s, $C{-}CH_3)_3$), 133.78 (s, *C*−Hg), 124.86 (s, aromatic *C*−H), 33.29 (s, $C(CH_3)_3$), 31.38 (s, $C(CH_3)_3$).

Anal. Calcd for $C_{14}H_{20}Cl_2Hg_2$: C, 26.46; H, 3.05. Found: C, 26.54; H, 3.18.

Treatment of 3 with Water. A 100-mL Schlenk flask was charged with **2** (0.500 g, 0.757 mmol) and 1,2-dimethoxyethane (35 mL). A 3.0 M solution of methylmagnesium chloride in tetrahydrofuran (1.1 mL, 3.4 mmol) was added to the resulting suspension. The solution was refluxed for 17 h to afford a white suspension. Water (0.30 mL, 17 mmol) was added to the solution at room temperature, and the solution was stirred for 1 h. The solvent was removed under reduced pressure, and the residue was extracted with hexane (50 mL). The hexane extract was passed through a 2-cm pad of silica gel on a coarse glass frit. Elution with hexane (50 mL), followed by removal of the solvent under reduced pressure, afforded a white crystalline solid of **1** (0.117 g, 81%): ^1H NMR ($CDCl_3$, δ) 7.34 (s, aromatic *H*), 1.34 (s, $CH_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 147.99 (s, $C{-}C(CH_3)_3$), 124.87 (s, aromatic *C*−H), 34.22 (s, $C(CH_3)_3$), 31.39 (s, $C(CH_3)_3$).

Treatment of 3 with Bromine. Compound **3** was generated as above from **2** (0.510 g, 0.772 mmol) and a 3.0 M solution of methylmagnesium chloride in tetrahydrofuran (1.2 mL, 3.5 mmol) in 1,2-dimethoxyethane (35 mL). Bromine (0.30 mL, 5.8 mmol) was added to the solution at room temperature, and the solution was stirred for 1 h. The solvent was removed under reduced pressure, and the residue was extracted with hexane (50 mL). The hexane extract was passed through a 2-cm pad of silica gel on a course glass frit. Elution with hexane (50 mL), followed by removal of solvent under reduced pressure and recrystallization from methylene chloride, afforded **4** (0.243 g, 90%): mp 100−101 °C; ^1H NMR ($CDCl_3$, δ) 7.58 (s, aromatic *H*), 1.47 (s, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 146.86 (s, $C{-}C(CH_3)_3$), 134.98 (s, aromatic *C*−H), 121.44 (s, *C*−Br), 36.00 (s, $C(CH_3)_3$), 29.42 (s, $C(CH_3)_3$); MS (20 eV) *m/e* 348 (M^+, 36), 333 ($M^+ - CH_3$, 100).

Anal. Calcd for $C_{14}H_{20}Br_2$: C, 48.30; H, 5.79. Found: C, 48.69; H, 6.00.

Treatment of 3 with Iodine. Compound **3** was generated as above from **2** (0.540 g, 0.763 mmol) and a 3.0 M solution of methylmagnesium chloride in tetrahydrofuran (1.0 mL, 3.0 mmol) in 1,2-dimethoxyethane (35 mL). Iodine (1.94 g, 7.64 mmol) was added to the solution at room temperature, and the solution was stirred for 1 h. The solvent was removed under reduced pressure, and the residue was extracted hexane (50 mL). The hexane extract was passed through a 2-cm pad of silica gel on a course glass frit. Elution with hexane (50 mL), followed by removal of the solvent under reduced pressure and recrystallization from methylene chloride, afforded **5** (0.297 g, 88%): mp 137 °C; ^1H NMR ($CDCl_3$, δ) 7.92 (s, aromatic *H*), 1.495 (s, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 149.48 (s, $C{-}C(CH_3)_3$), 142.22 (s, aromatic *C*−H), 95.52 (s, *C*-I), 35.80 (s, $C(CH_3)_3$), 29.59 (s, $C(CH_3)_3$); MS (20 eV) *m/e* 442 (M^+, 100), 427 ($M^+ - CH_3$, 83).

Anal. Calcd for $C_{14}H_{20}I_2$: C, 38.01; H, 4.56. Found: C, 38.11; H, 4.55.

Treatment of 3 with Allyl Bromide. Compound **3** was generated as above from **2** (0.508 g, 0.769 mmol) and a 3.0 M solution of methylmagnesium chloride in tetrahydrofuran (1.2 mL, 3.46 mmol) in 1,2-dimethoxyethane (35 mL). Allyl bromide (0.66 mL, 7.7 mmol) was added to the solution at room temperature, and the solution was stirred for 24 h. The solvent was removed under reduced pressure, and the residue was extracted with benzene (50 mL). The benzene extract was passed through a 2-cm pad of silica gel on a course glass frit. Elution with benzene (50 mL), followed by removal of the solvent under reduced pressure and recrystallization from pentanes, afforded **6** (0.181 g, 87%): mp 68 °C; ^1H NMR ($CDCl_3$, δ) 7.17 (s, aromatic *H*, 2 H), 5.99 (m, 1 H), 5.07 (dd, $J = 1.5, 3.0$ Hz, 1 H), 5.03 (dq, $J = 1.5, 9.9$ Hz, 1 H), 3.61 (dt, $J = 1.5, 6.0$ Hz, 2 H), 1.38 (s, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 144.61 (s, $C{-}\mathrm{C(CH_3)_3}$), 138.87 (s, $C\mathrm{H{=}CH_2}$), 135.09 (s, C−allyl), 130.02 (s, aromatic C−H), 115.34 (s, $\mathrm{CH{=}}C\mathrm{H_2}$), 38.50 (s, $C\mathrm{H_2}$), 35.16 (s, $C\mathrm{(CH_3)_3}$), 31.59 (s, $\mathrm{C(}C\mathrm{H_3)_3}$).

Anal. Calcd for $C_{20}H_{30}$: C, 88.82; H, 11.18. Found: C, 88.72; H, 11.29.

Isolation of 3. Compound **3** was generated as above from **2** (0.500 g, 0.757 mmol) and a 3.0 M solution of methylmagnesium chloride in tetrahydrofuran (1.1 mL, 3.40 mmol) in 1,2-dimethoxyethane (35 mL). The solvent was removed under reduced pressure to afford a white solid. The solid was washed three times with hexane (30 mL). Vacuum drying for 36 h in a drying pistol heated by refluxing ethanol gave a white powder (0.951 g): dec range >310 °C; IR (Fluorolube, $\mathrm{cm^{-1}}$) 3032 (w), 3020 (w), 3002 (w), 2946 (s), 2873 (m), 2851 (m), 2835 (m), 1487 (w), 1464 (s), 1418 (w), 1386 (w), 1370 (m), 1361 (m), 1356 (m); IR (Nujol, $\mathrm{cm^{-1}}$) 1276 (w), 1252 (w), 1238 (w), 1115 (m), 1103 (m), 1057 (s), 1023 (m), 1017 (m), 880 (m), 868 (m), 836 (w); ^{13}C CP/MAS NMR spectrum 174.04 (s, C−Mg), 165.43 (s, C−Mg), 160.18 (s, C−Mg), 154.67 (s, $C{-}\mathrm{C(CH_3)_3}$), 152.95 (s, $C{-}\mathrm{C(CH_3)_3}$), 135.75 (s, aromatic C−H), 127.14 (s, aromatic C−H), 124.50 (s, benzene C−H), 71.20 (s, free $\mathrm{CH_3O}C\mathrm{H_2}C\mathrm{H_2OCH_3}$), 70.37 (s, coordinated $\mathrm{CH_3O}C\mathrm{H_2}C\mathrm{H_2OCH_3}$), 61.66 (s, coordinated $C\mathrm{H_3OCH_2CH_2O}C\mathrm{H_3}$), 59.10 (s, free $C\mathrm{H_3OCH_2CH_2O}C\mathrm{H_3}$), 36.77 (s, $C\mathrm{(CH_3)_3}$), 35.82 (s, $C\mathrm{(CH_3)_3}$), 33.88 (broad s, $\mathrm{C(}C\mathrm{H_3)_3}$). Microanal. Found: C, 33.10, 33.46; H, 6.70, 6.75; Cl, 20.20, 20.09; Hg, 5.96, 5.91.

NMR Data for 7: ^{1}H NMR (DMSO-d_6, 23 °C, δ) 7.46 (d, J = 2.5 Hz, $\mathrm{C_2{-}}H$), 7.36 (d, J = 8.5 Hz, $\mathrm{C_5{-}}H$), 7.06 (dd, J = 2.5, 8.5 Hz, $\mathrm{C_4{-}}H$), 1.41 (s, $\mathrm{C(C}H_3\mathrm{)_3}$), 1.25 (s, $\mathrm{C(C}H_3\mathrm{)_3}$), 0.45 (s, $\mathrm{MgC}H_3$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (DMSO-d_6, 23 °C, ppm) 174.72 (s, C_1), 153.96 (s, C_3 or C_6), 146.09 (s, C_3 or C_6), 134.42 (s, C_2), 125.02 (C_4 or C_5), 123.17 (C_4 or C_5), 35.50 (s, $C\mathrm{(CH_3)_3}$), 34.15 (s, $C\mathrm{(CH_3)_3}$), 33.25 (s, $\mathrm{C(}C\mathrm{H_3)_3}$), 31.31 (s, $\mathrm{C(}C\mathrm{H_3)_3}$), 13.14 (s, $\mathrm{Mg}C\mathrm{H_3}$).

NMR Data for 8: ^{1}H NMR (DMSO-d_6, 23 °C, δ) 7.48 (s, J = 2.5 Hz, $\mathrm{C_2{-}}H$), 7.44 (d, J = 8.5 Hz, $\mathrm{C_5{-}}H$), 7.15 (dd, J = 2.5, 8.5 Hz, $\mathrm{C_4{-}}H$), 1.49 (s, $\mathrm{C(C}H_3\mathrm{)_3}$), 1.27 (s, $\mathrm{C(C}H_3\mathrm{)_3}$); there was insufficient signal to noise to measure the $^{13}\mathrm{C}\{^1\mathrm{H}\}$ spectrum. The ^{1}H NMR data are equally consistent with **8** being bis(2,5-di-*tert*-butylphenyl)magnesium.

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Supporting Information Available: NMR spectra of the dimagnesiated white solid (8 pages). Ordering information is given on any current masthead page.

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