Stirring was continued for 2 days at ambient temperature. The solidified alloy was liquefied by the addition of 32 g of K and the stirred suspension refluxed for 2 days. Then the reaction mixture was filtered through a glass frit by N_2 pressure, and the solids were extracted in a Soxhlet extractor with hexane/DME (1:1) for 50 h to yield 23.0 g of colorless **1b** (mp 340–350 °C). Recrystallization from hexane gave single crystals. Vacuum distillation of the higher boiling fractions from the filtrate in a four-bulb tube at 235 °C/0.002 mbar (air bath temperature) gave an additional 39 g of **1b**, thus leading to a total yield of 62 g (32%). The fraction collected around 200 °C/0.002 mbar (21 g) consists of a mixture of (*tert*-butylbenzene)·4BN(*i*-Pr)$_2$ and **1b**. Anal. Calcd for $C_{40}H_{84}B_5N_5$ (MW 689.20): C, 69.71; H, 12.29; B, 7.84; N, 10.16. Found: C, 69.65; H, 12.41; B, 7.69; N, 10.12. MS EI (70 eV), *m/z* (relative intensity): 689 (57) [M^+], 57 (100) [$C_4H_9^+$]. Selected NMR data (250 MHz, $CDCl_3$): $\delta(^1H)$ 5.79 (br, 1 H, H7), 1.81 (s, 2 H) + 2.36 (s, 2 H) (for H in 2, 3a, 5, and 8a). Signals of the isopropyl groups appear between 0.9 and 1.40 (60 H) and from 3.20 to 4.55 (10 H), while the *t*-Bu group gives a singlet at 1.05 (9 H). NMR $\delta(^{13}C)$ 165.2 (C6), 126.6 (br, C7), 40.1 (C34), 38.2 + 34.2 + 29.4 (br, C2, 3a, 5, 8a). NMR $\delta(^{11}B)$ 45.5 ($h_{1/2}$ = 600 Hz). The signals of the isopropyl groups are from δ 20 to 32 and 44 to 50, and the CH_3 of *t*-Bu is at 30.9.

A single-crystal X-ray structure analysis has been performed for **1b**.[6] Crystals of **1a** have been also studied by X-ray diffraction; however, the latter contain some disordered hexane near the center of symmetry and, accordingly, the formula mass is increased by one-half hexane per molecule. Furthermore, there is disorder of the isopropyl groups (the X-ray data for **1a** were collected at room temperature), so we will not discuss the structure of **1a** further. The results obtained for **1a** are deposited with the supplementary material and confirm that molecules **1a** and **1b** are of the same structural type.

Following the pattern of the products obtained so far from aromatic compounds and dehalogenation products of (dialkylamino)dihaloboranes,[2,3] the three-dimensional structures of $RC_6H_5{\cdot}5BNR'_2$ contain boron atoms only in sp^2 and carbon atoms in both sp^2 and sp^3 bonding situations. In the compounds of type **1** the ring of the aromatic hydrocarbon has been split into one C_1, one C_2, and one C_3 unit. As expected, the smallest angles of the skeleton are observed in the five-membered ring, the largest in the seven-membered ring, which also contains the remaining double bond. The C–C bond lengths increase upon higher substitution with boron atoms relative to normal C–C bond lengths between sp^3-hybridized carbon atoms. A complete assignment of the NMR spectra has not been possible due to the overlap of signals and the lack of coupling across the quadrupolar boron nuclei.

These results are not inconsistent with the presence of a free "borene" intermediate.

Acknowledgment. The financial support by the Volkswagen-Stiftung (A.M.), Fonds der Chemischen Industrie (A.M. and G.M.S.), and Leibniz program of the Deutsche Forschungsgemeinschaft (G.M.S.) is gratefully acknowledged.

Supplementary Material Available: For structures **1a** and **1b**, atomic coordinates and isothermal displacement parameters (Table I), bond lengths (Table II), bond angles (Table III), anisotropic displacement parameters (Table IV), hydrogen atom coordinates and isotropic displacement parameters (Table V), and a table of crystal and diffractometer data and structure solution and refinement (8 pages); listings of observed and calculated structure factors (33 pages). Ordering information is given on any current masthead page.

---

[6] Crystal data for **1b**: $C_{40}H_{84}B_5N_5$, MW = 689.2, triclinic, space group $P\bar{1}$, a = 11.330 (2) Å, b = 11.902 (3) Å, c = 17.931 (4) Å, α = 87.43 (1)°, β = 86.94 (1)°, γ = 69.32 (2)°, V = 2258.1 Å^3, Z = 2, d_{calcd} = 1.014 g/cm^3, μ = 0.057 mm^{-1}, F_{000} = 768, λ(Mo $K\alpha$, graphite monochromator) = 0.7107 Å. The data were collected with use of $2\theta-\omega$ scans on a Stoe-Siemens AED diffractometer at 153 K: 5901 measured and unique reflections and 4637 observed reflections with $F \geq 3\sigma(F)$; $2\theta_{max}$ = 45°. The structure was determined by direct methods (SHELXS-86[7]). All non-hydrogen atoms were refined anisotropically. A riding model with idealized hydrogen geometry was employed for H-atom refinement, and the hydrogen thermal parameters were refined isotropically with those of atoms bonded to the same carbon atom constrained to be equivalent. Refinement of 467 parameters converged with R = 0.059, R_w = 0.060, $w^{-1} = \sigma^2(F) + 0.0006F^2$, and maximum/minimum rest electron density 0.30 e Å^{-3}/–0.24 e Å^{-3}.

[7] Sheldrick, G. M. *Acta Crystallogr.* 1990, *A46*, 467.

---

^{13}C CP/MAS NMR Spectroscopy of Magnesium–Anthracene and –Cyclooctatetraene Complexes: Graphite-Assisted Degradation of a Magnesium–Anthracene Complex

William M. Brooks, Colin L. Raston,* and Rodney E. Sue
Division of Science and Technology, Griffith University, Nathan, Brisbane, Queensland 4111, Australia

Frank J. Lincoln and Justin J. McGinnity
Department of Physical and Inorganic Chemistry, The University of Western Australia, Nedlands, Western Australia 6009, Australia

Received April 9, 1991

Summary: ^{13}C CP/MAS NMR spectroscopy shows that [Mg(anthracene)(THF)$_2$], derived from decomposition of [Mg(anthracene)(THF)$_3$], has Mg–C9,10 interactions and that Mg(cyclooctatetraene)(THF)$_{2.5}$ has an aromatic dianion: graphite accelerates the decomposition of [Mg(anthracene)(THF)$_3$], in toluene (via [Mg(anthracene)(THF)$_2$]) or diethyl ether, to its constituents, affording highly activated and finely divided magnesium (ca. 6 μm) rather than an intercalation compound.

The magnesium–anthracene complex [Mg(anthracene)(THF)$_3$] (**1**; THF = tetrahydrofuran) is an important source of magnesium either via reactions involving the complex directly or from activated magnesium arising from decomposition of **1** to its constituents.[1-6] The decompo-

---

[1] Alonso, T.; Harvey, S.; Junk, P. C.; Raston, C. L.; Skelton, B. W.; White, A. H. *Organometallics* 1987, *6*, 2110.

[2] Harvey, S.; Junk, P. C.; Raston, C. L.; Salem, G. *J. Org. Chem.* 1988, *53*, 3134.

0276-7333/91/2310-2098$02.50/0

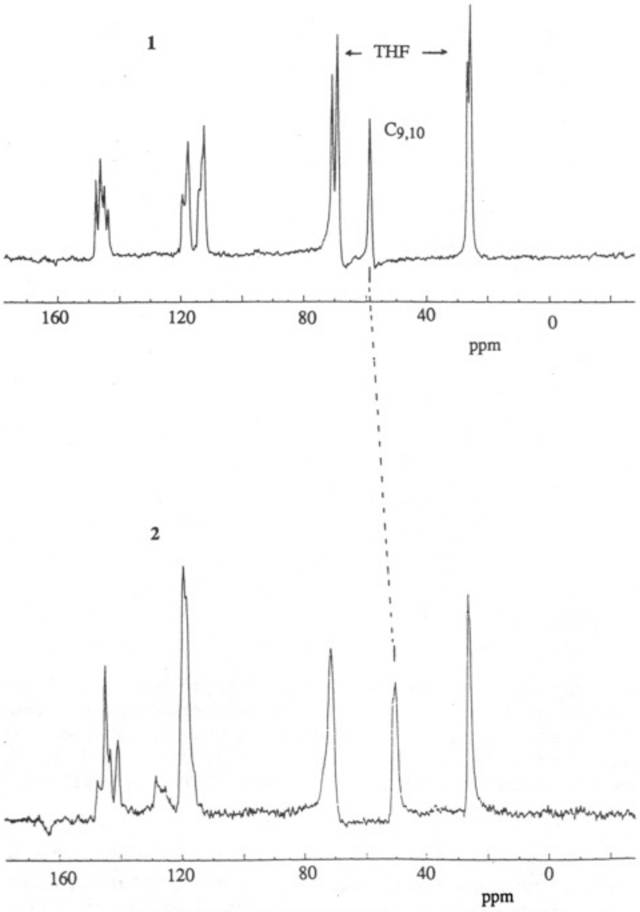
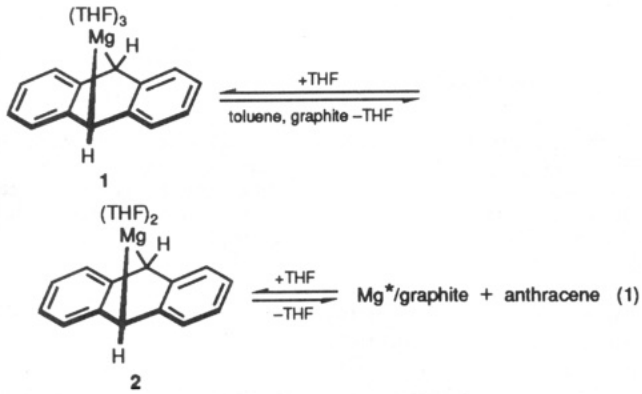


Figure 1. ^{13}C CP/MAS TOSS NMR spectra of $[Mg(anthracene)(THF)_3]$ (**1**) and $[Mg(anthracene)(THF)_2]$ (**2**).

sition occurs readily in hydrocarbons and donor solvents other than THF; in benzene or toluene it proceeds via a yellow intermediate believed to be $[Mg(anthracene)(THF)_2]$ (**2**).[1,4,5] Compound **1** acts as a source of magnesium when treated with COT (=cyclooctatetraene), yielding $Mg(COT)(THF)_{2.5}$ (**3**),[1] which in turn is a source of magnesium.[7]

Herein we report ^{13}C CP/MAS NMR spectroscopy of the highly air-sensitive complexes **1**–**3** and related compounds which suggest that (i) the magnesium centers are bound to the C9,10 positions of reduced anthracene, as established for the parent complex **1**,[8] $[Mg(1,4\text{-dimethylanthracene})(THF)_3]$,[9] and some silylated anthracene complexes[1,9] with use of X-ray diffraction data and (ii) the reduced COT in **3** is an aromatic species in the solid. We also report that graphite assists the decomposition of **1** in toluene, via **2** (eq 1) or in diethyl ether to finely divided magnesium with no evidence for the formation of a graphite–magnesium intercalation compound.

Figure 2. SEM photograph of a graphite flake formed by decomposition of $[Mg(anthracene)(THF)_3]$ in a graphite–diethyl ether slurry.



Details of NMR spectra[10] are given in Table I and Figure 1 for **1** and **2**; chemical shifts for **1** are in agreement with data obtained for the same compound in THF solution.[13] There are several peaks for each carbon in the solid state of **1** in accordance with the presence of two independent molecules in the asymmetric unit.[8] The major differences for the compounds occur in the resonances for the C9,10 positions, which correlate with the color of the complexes. The compound $[Mg(9\text{-methylanthracene})(THF)_3]$[6] (prepared from **1** and 9-methylanthracene) and **1** are both orange with C9,10 resonances at δ 58.5 ppm, whereas the corresponding signal is ca. δ 50 ppm in the yellow compounds, viz. **2** and $[Mg(anthracene)L_n]$ (L_n = THF–*N*,*N*,*N'*,*N'*-tetramethylethylenediamine,[1,4] *N*,*N*,*N'*,*N''*,*N''*-pentamethyldiethylenetriamine).[1,4] The shift upfield toward the shift for 9,10-dihydroanthracene (Table I) indicates these carbon atoms have greater sp^3 character, and therefore, there is a higher degree of covalency for the magnesium–carbon bonds. It also reflects the weaker donor strength of N-donors relative to O-donors, and in a comparison of data for **1** and **2** the partial loss of solvation is offset by increased metal–anion covalency. The solid-state ^{13}C spectrum of compound **3** shows only one resonance for cyclooctatetraene dianion at 91.5 ppm and resonances due to the THF coligands. Since fluxional behavior is unlikely in the solid, this rules out localized

---

(3) Bartmann, E.; Bogdanovic, B.; Janke, N.; Liao, S.; Schlichte, K.; Spliethoff, B.; Treber, J.; Westeppe, U.; Wilczok, U. *Chem. Ber.* **1990**, *123*, 1517. Bogdanovic, B.; Janke, N.; Kinzelmann, H. *Chem. Ber.* **1990**, *123*, 1507.

(4) Bogdanovic, B.; Janke, N.; Kinzelmann, H.-G.; Westeppe, U. *Chem. Ber.* **1988**, *121*, 33.

(5) Bogdanovic, B. *Acc. Chem. Res.* **1988**, *21*, 261.

(6) Bogdanovic, B.; Janke, N.; Kinzelmann, H.-G.; Seevogel, K.; Treber, J. *Chem. Ber.* **1990**, *123*, 1529.

(7) Hutchings, D. S.; Junk, P. C.; Patalinghug, W. C.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1989**, 973.

(8) Engelhardt, L. M.; Harvey, S.; Raston, C. L.; White, A. H. *J. Organomet. Chem.* **1988**, *341*, 39.

(9) Bogdanovic, B.; Janke, N.; Kruger, C.; Mynott, R.; Schlichte, K.; Westeppe, U. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 960. Lehmkuhl, H.; Skakoor, A.; Mehler, K.; Kruger, C.; Angermund, K.; Tsav, Y.-H. *Chem. Ber.* **1985**, *118*, 4239.

(10) Samples were packed in Kel-F inserts, made as described by Merwin et al. for a standard Bruker 7-mm double air bearing probe and a ZrO_2 rotor,[11] with use of a high purity nitrogen filled glovebox fitted with an aluminum–gallium–indium bubbler.[12]

(11) Merwin, L. H.; Sebald, A.; Espidel, J. E.; Harris, R. K. *J. Magn. Reson.* **1989**, *84*, 367.

(12) Shealy, J. R.; Woodall, J. M. *Appl. Phys. Lett.* **1982**, *41*, 88.

(13) Bogdanovic, B.; Liao, S.; Mynott, R.; Schlichte, K.; Westeppe, U. *Chem. Ber.* **1984**, *117*, 1378.

Table I. ^{13}C CP/MAS NMR Data (ppm) of Magnesium–Conjugated Anion Complexes and Relevant Organic Compounds[a]

compd[b]	An[c]	coligand	C9, 10	color
Mg(An)(THF)$_3$ (1)	147.5 117.2 112.0	70.5 66.9 25.8	58.5	orange
Mg(An)(THF)$_2$ (2)	144 119	71.6 26.3	50.5	yellow
Mg(An)(THF)(TMEDA)	145 117	57.3 (TMEDA) 46.0 (TMEDA) 72.0 (THF) 26.3 (THF)	48.0	yellow
Mg(An)(PMDETA)	147 118	58.2 57.3 46.3 44.9 41.1	49.5	yellow
Mg(9-Me-An)(THF)$_3$	146 119 117 112 16.2 (Me)	71.1 66.9 26.1	58.5	orange
dihydroanthracene	138 128		36.9	white
An	132.0, 129.1, 127.2, 124.6			
Mg(COT)(THF)$_{2.5}$ (3)	91.5 (COT)	69.7 (THF) 26.5 (THF)		

[a] Spectra were recorded on a Bruker CXP-300 spectrometer using TOSS techniques with the sample spinning at approximately 3800 Hz. Proton 90° pulse times were less than 5 μs, and contact times were set to 5 ms. Recycle times of 5 s were used for the magnesium complexes, while the long T_1 (not measured) of 9,10-dihydroanthracene and anthracene required recycle delays of 200 and 500 s, respectively. Chemical shifts were referenced to the methine resonance of adamantane at 38.23 ppm. [b] An = anthracene; 9-Me-An = 9-methylanthracene; TMEDA = *N,N,N′,N′*-tetramethylethylenediamine; PMDETA = *N,N,N′,N″,N″*-pentamethylethylenetriamine. [c] Aromatic signals were generally broad multiplets.

Mg–C interactions and is consistent with an aromatic dianion either as in an ionic solid or as part of a contact ion pair. The low Mg:THF ratio is support for the latter.

Compound 1 (ca. 1 g) was slowly added (ca. 100-mg portions) to graphite (0.22 g, 20–60 mesh; Alfa Products) in toluene (ca. 50 mL). In the early stages of addition a yellow solid, 2, mixed with graphite formed over several seconds; then, over several minutes a gray mixture formed. (In the absence of graphite the formation of the intermediate alone takes ca. 30 min.) Further additions reacted more slowly, possibly because of the buildup of THF concentration stabilizing 1 (eq 1), taking ca. 3 h for the final portion to decompose. In diethyl ether no intermediate yellow solid was detected and degradation was complete after 75 min. Products were collected, washed with solvent, heated in vacuo (ca. 200 °C) to remove traces of anthracene, and analyzed with use of X-ray powder diffractometry, analytical transmission electron microscopy (TEM), and scanning electron microscopy (SEM).[14] The products were comprised of graphite flakes with magnesium particles dispersed on the surface with small flakes of graphite (Figure 2), the average size of the magnesium particles being 6 μm, which compares with 15 μm for activated magnesium derived from $MgCl_2$ and potassium metal in THF.[15] There was no evidence for the formation of intercalation compounds; the only such magnesium-containing compound is $C_{16}Mg(KI)_2$, on the basis of weak X-ray reflections,[16] although intercalation compounds of the heavier group 2 elements are well-known.[17] The magnesium–graphite mixture is not pyrophoric yet is a highly activated form of magnesium; in the presence of anthracene and THF all the magnesium is converted to compound 1 over ca. 20 min. This contrasts with ca. 48 h with use of commercially available magnesium.[1,4,5]

No decomposition of 1 was evident in a THF–graphite slurry, despite the fact that graphite has the highest electron affinity of all polycondensed hydrocarbons.[18] The presence of metal particles on the graphite surface suggests degradation involves electron transfer from anthracene(*n*–) to the graphite surface, which then acts as a reducing agent. In contrast, group 1 conjugated aromatic anion species are effective in yielding intercalation compounds.[18] Reaction between the radical anion of anthracene derived from 1 and magnesium chloride in THF[9a] resulted in formation of magnesium particles over 1 week, again with no intercalation, as was the case on condensing magnesium vapor in a hexane–graphite slurry. Compound 3 was stable in THF–graphite, but in toluene–graphite it also degraded to its constituents.

Acknowledgment. We thank the Australian Research Council for support of this work.

---

(14) X-ray powder diffraction patterns were recorded on a Rigaku Miniflex diffractometer in an airtight cell with a 0.5-mm Mylar window. Analytical transmission electron microscopy and scanning electron microscopy were performed on Philips 430 TEM and 505 SEM instruments, fitted with EDAX 9900 EDS analysis systems.

(15) Rieke, R. D. *Acc. Chem. Res.* **1977**, *10*, 301.

(16) Ungurenasu, C.; Palie, M. *Synth. React. Inorg. Met.-Org. Chem.* **1977**, *7*, 581.

(17) Guerard, D.; Chaabouni, M.; La Grange, P.; El Makrini, M.; Herold, A. *Carbon* **1980**, *18*, 257.

(18) Setton, R.; Beguin, F.; Hamwi, A.; Touzain, P. *Mater. Sci. Eng.* **1979**, *40*, 167.