2110 *Organometallics* 1987, *6*, 2110–2116

Main Group–Conjugated Organic Anion Chemistry. 1. Synthesis of Magnesium Anthracene, Silylated Anthracenes, or Fluoranthene Tetrahydrofuran and Tertiary Amine Complexes and of Magnesium Cyclooctatetraene: X-ray Structure of [MgL(TMEDA)]·[MgL(THF)$_2$] (L = 9,10-Bis(trimethylsilyl)anthracene)

Teresa Alonso, Stephen Harvey, Peter C. Junk, Colin L. Raston,* Brian W. Skelton, and Allan H. White

Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, 6009, Australia

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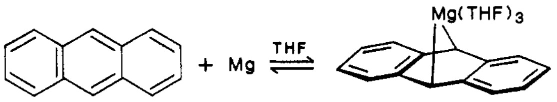
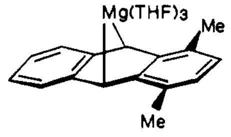
Mg(An)(THF)$_3$ (1, THF = tetrahydrofuran) decomposes in toluene or benzene to Mg(An)(THF)$_2$ (5) and then to elemental magnesium. Mg(An)(THF)(TMEDA) (6), prepared from its constituents or by treating 1 with TMEDA, and Mg(An)(PMDETA) (7) and Mg(An){(−)-sparteine} (8), prepared by treating 1 with the appropriate amine, are stable in these solvents (An = anthracene, TMEDA = N,N,N',N'-tetramethylethylenediamine, PMDETA = N,N,N',N'',N''-pentamethyldiethylenetriamine). Mg(AnSiMe$_3$)(TMEDA) ((9, AnSiMe$_3$ = 9-(trimethylsilyl)anthracene) and Mg{An(SiMe$_3$)$_2$}(TMEDA) (10, An(SiMe$_3$)$_2$ = 9,10-bis(trimethylsilyl)anthracene) form on adding excess TMEDA to Mg(AnSiMe$_3$)(THF)$_2$ (3) and Mg{An(SiMe$_3$)$_2$}(THF)$_2$ (4), either prepared by treating the substituted anthracenes with magnesium or 1 in THF; 9 and 10 react with THF yielding Mg(AnSiMe$_3$)(THF)(TMEDA) (11) and 4 in equilibrium with 10. Mg(Fl)$_2$(THF)$_6$ (12), prepared from magnesium and Fl (= fluoranthene) or Fl and 1 in THF, slowly decomposes in TMEDA to magnesium metal and fluoranthene. Mg(COT)(THF)$_{2.5}$ (13) has also been prepared from 1 and COT and via an anthracene-catalyzed reaction of magnesium and COT (= cyclooctatetraene). Recrystallization of 4 from a mixture of THF and TMEDA gave the 1:1 crystalline complex 4:10, as shown by an X-ray structure determination; the discrete molecules of 4 and 10 have each magnesium attached to the C-9 and C-10 anthracene carbon centers, Mg–C = 2.21$_8$ and 2.22$_3$ Å, respectively.

Introduction

Ramsden detailed in patents in 1967 and 1968 that elemental magnesium reacts with conjugated olefins[1] and fused aromatic compounds[2] in tetrahydrofuran (= THF) yielding organomagnesium complexes, e.g., Mg(An)(THF)$_3$ (1, An = anthracene), formally containing Mg^{2+} and hydrocarbyl dianions. Recently there has been a spate of research reports on complex 1 and some new substituted anthracene complexes, Mg(AnMe$_2$)(THF)$_2$ (2, AnMe$_2$ = 1,4-dimethylanthracene),[3] Mg(AnSiMe$_3$)(THF)$_3$ (3, AnSiMe$_3$ = 9-(trimethylsilyl)anthracene),[4] and Mg{An(SiMe$_3$)$_2$}(THF)$_2$ (4, An(SiMe$_3$)$_2$ = 9,10-bis(trimethylsilyl)anthracene).[4,5] These deal with the rate and reversibility of formation of 1 (eq 1),[6,7] the synthesis of 1 from sodium anthracene and magnesium bromide,[8] the nature of the metal to anthracene interactions (NMR studies on 1[6] and X-ray structure determinations on 2[3] and 4[4]), and the remarkable properties of 1. It reacts in a variety of ways including as a dinucleophile[9,10] and as a source of atomic magnesium,[9,11,12] e.g., formation of novel Grignard reagents, and anthracene, on treating 1 in THF with benzylic halides,[12] which we will develop in subsequent papers in this series.



(1)



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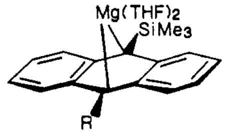

3, R = H
4, R = SiMe3

Other categories of reaction of 1 are the formation of adducts between 1 and dialkylaluminum hydrides in THF,[6] and that in the presence of anthracene and magnesium bromide[8] or chloride[3] in THF, 1 undergoes conproportionation to the radical anion of anthracene, the same species being formed in mixtures of magnesium, anthracene, and magnesium chloride in THF.[13] In the absence of magnesium halides, electron transfer from An^{2-} in 1 to free An occurs only at low temperature, ca. −30 °C.[3]

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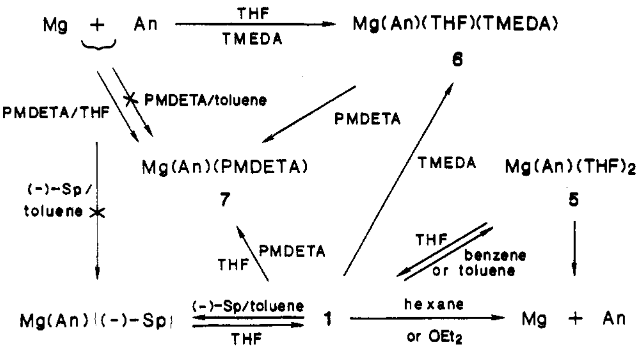
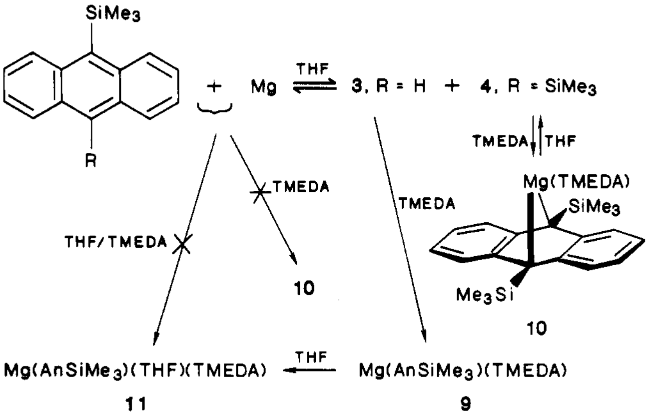
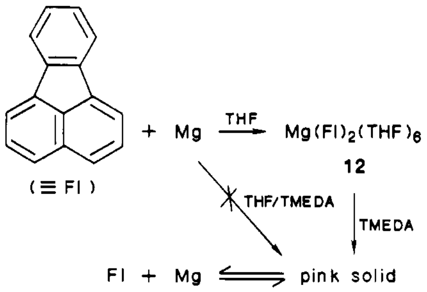
Scheme I



Scheme II



Scheme III

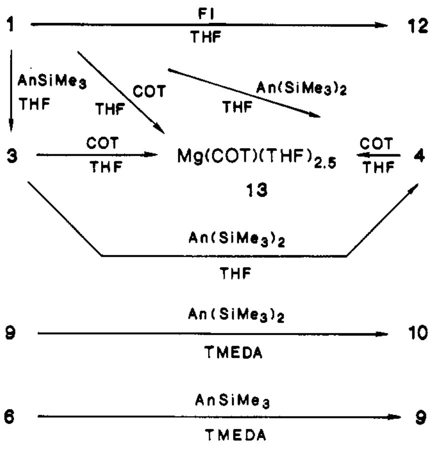


Herein we report (I) the decomposition of 1 to Mg(An)(THF)$_2$ (5), (II) the synthesis of derivatives of 1 (3–5), in which THF molecules have been displaced by tertiary amines, (III) an improved synthesis of 3 from magnesium and AnSiMe$_3$, (IV) a new method for preparing 3 and 4, namely, treatment of 1 with the corresponding silylated anthracene, (V) the synthesis of a fluoranthene (= Fl) magnesium complex based on a radical anion, and (VI) the X-ray structure determination of a 1:1 mixture of 4 and Mg{An(SiMe$_3$)$_2$}(TMEDA) (TMEDA = *N,N,N′,N′*-tetramethylethylendiamine). Also reported is a new synthesis of Mg(COT)(THF)$_{2.5}$ (COT = cyclooctatetraene) originally prepared by Lehmkuhl et al.[13] and a simple one-pot synthesis of An(SiMe$_3$)$_2$ previously prepared via multistep sequences.[4,14]

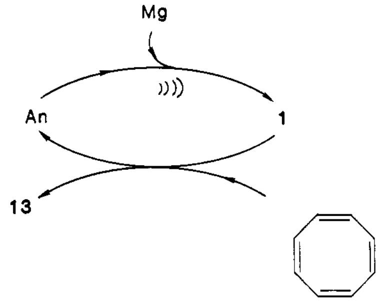
Results and Discussion

I. Syntheses. These are summarized in Schemes I–V and eq 2. Complex 1 was prepared by the literature method,[6] namely, stirring activated magnesium in THF at room temperature, except that 1,2-dibromoethane rather than bromoethane was used for activation of the metal.

Scheme IV



Scheme V



For a ca. twofold excess of anthracene all the metal powder is consumed over ca. 48 h yielding 1 as an orange solid. The mother liquor can be used for the synthesis of a new batch of 1 on addition of 1 equiv of magnesium and anthracene, and so on. We found that stirring the reaction mixture in a round-bottom flask gives coarser material that facilitates isolation of the complex. Moreover, while sonication can effect the reaction without the need for activation of the metal, the resulting very fine material presents isolation problems, and May and Baker magnesium powder was the most reliable magnesium available; others were generally much slower to react. Reactions involving magnesium activation using 1,2-dibromoethane dictate the presence of solvated magnesium bromide, and the mixtures are green due to the formation of the radical anion of anthracene (eq 2).[3,8] We found that unactivated

$$\mathrm{Mg} + 2\mathrm{anthracene} + \text{“}\mathrm{Mg(halide)_2}\text{”} \rightleftarrows \text{“}\mathrm{2Mg(An)(halide)(THF)}_n\text{”} \quad (2)$$

metal and THF devoid of magnesium halides yielded radical-free orange mixtures, although there was an induction period of several days; there is a claim that unactivated magnesium fails to react with An in THF.[6]

Complex 1 slowly decomposed in hexane or diethyl ether yielding a magnesium mirror after ca. 1 h. This is consistent with the inability to prepare a magnesium anthracene complex in diethyl ether[8] and that uncomplexed THF is required to stabilize 1 in these solvents in which, as in THF, they are only sparingly soluble.[6] In toluene or benzene, however, a yellow complex which analyzed as Mg(An)(THF)$_2$ (5) (Scheme I) (minutes) and then An and finely divided magnesium (minutes–hours) formed. Formation of 5 in aromatic solvents but not in hexane or diethyl ether may be due to a stabilizing solvent π-cloud–metal interaction after loss of one THF molecules. 5 can be regarded as a possible intermediate in the decomposition of 1 in solvents other than THF. Addition of THF to 5 rapidly gave complex 1.

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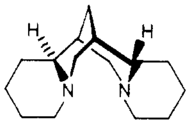
(14) (a) Harvey, R. G.; Cho, H. *J. Am. Chem. Soc.* **1974**, *96*, 2434. (b) Cho, H.; Harvey, R. G. *J. Org. Chem.* **1975**, *40*, 3097.

Addition of TMEDA to **1** or to a slurry of **1** in THF resulted in rapid formation of a yellow powder of Mg(An)(THF)(TMEDA) (**6**) (Scheme I). The same complex was also prepared directly from magnesium, An, THF, and TMEDA at room temperature. However, the reaction was much slower than the analogous reaction for the formation of **1**, ca. 7 days, cf. 48 h.[6] Also in contrast to the formation of **1** is that stoichiometric quantities of magnesium and anthracene, and also TMEDA suffice (cf. eq 1), indicating that **6** is of greater stability with respect to its constituents than **1**. This is consistent with **6** being indefinitely stable in hexane, diethyl ether, toluene, and benzene (cf. $\mathbf{1} \rightarrow \mathbf{5} \rightarrow$ Mg, Scheme I). We were unable to prepare a THF free complex from magnesium, An, and TMEDA. Evidently THF is required to effect the electron-transfer process. Nor were we able to prepare such a complex by treating **5** with TMEDA, complex **6** was always produced, albeit as a benzene solvate.

Addition of other tertiary amines to **1** in THF also resulted in THF displacement (Scheme I). PMDETA (= *N,N,N′,N″,N″*-pentamethyldiethylenetriamine) yielded Mg(An)(PMDETA) (**7**) (yellow powder), which was also prepared by this method on treating **6** with PMDETA in THF. (−)-Sparteine (= (−)-Sp) failed to react with **1** in THF whereas in toluene there was slow formation of Mg(An){(−)-Sp} (**8**) (yellow powder). This reaction may proceed via **5** (above) which is coordinatively unsaturated facilitating complexation of rather hindered (−)-Sp. Complex **7** could be prepared from its constituents, namely, An, Mg, and PMDETA in THF. No reaction was evident between An, Mg, and PMDETA or (−)-Sp in toluene. Complexes **6**–**8** are stable indefinitely in noncoordinating solvents, unlike **1** and **5**. Addition of THF to **8** resulted in (−)-Sp displacement and formation of **1** whereas **6** and **7** were unaffected. The higher stability of **6**–**8** is of interest in studying reactions of "magnesium anthracene" in solvents other than THF. Compound **8** is also of interest as a potential source of "optically active" magnesium. These aspects will be developed in subsequent papers in this series.

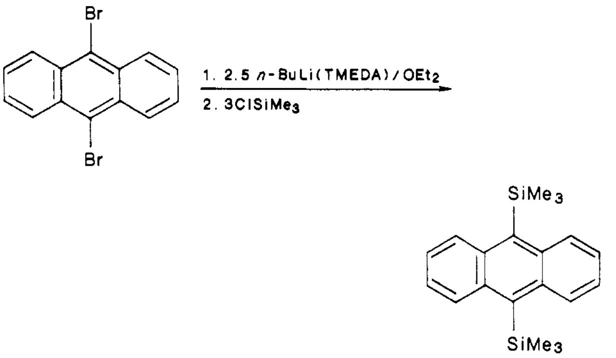


(−)-sparteine

Mg(AnSiMe$_3$)(THF)$_2$ (**3**) was prepared by a variation of the method of Lehmkuhl et al.,[4] viz., the use of excess AnSiMe$_3$ for consumption of all magnesium to overcome the problem of separating **3** from unreacted metal arising from an equilibrium like that established for **1** (eq 1). This also improved the yield from 36% to greater than 90%. Synthesis of the analogous bis(silylated) complex **4** is similar.[4] Reaction mixtures for the synthesis of **3** and **4** were deep green and gave broad featureless ESR singlets, $g = 2.0050$ and 2.0057, respectively, which are possibly radical anions of the substituted anthracenes.

Treating **3** or **4** with TMEDA gave the corresponding TMEDA-containing complexes **9** and **10**, and addition of THF to **9** yielded **11** (Scheme II), the monosilylated analogues of **6** (Scheme I). All of the silylated complexes are yellow. Complexes **3** and **11** are like **1**, **6**, and **7** in being sparingly soluble in THF; complex **4**,[4] however, has good solubility in THF from which it can be recrystallized. Complex **10**, which is in equilibrium with **4** in THF, is only slightly soluble in TMEDA, benzene, and toluene ruling out recrystallization as a means of purification. Complexes **9** and **10** could not be prepared from magnesium and the appropriate anthracene in TMEDA, and thus as for An it appears THF is essential to effect the assumed electron-transfer process. Even with a catalytic amount of THF in TMEDA no reaction was apparent between magnesium and AnSiMe$_3$ or An(nSiMe$_3$)$_2$ at ca. 20 °C.

AnSiMe$_3$ was readily prepared by the method of Cho and Harvey,[14] except that the dilithium reagent, derived from 9-(trimethylsilyl)-9,10-dihydroanthracene[14] and *n*-BuLi, was treated with mercuric(II) chloride rather than cadmium(II) chloride. The synthesis of An(SiMe$_3$)$_2$ was not as simple. The original method devised by Cho and Harvey was similar to their synthesis of AnSiMe$_3$. It involved treating dimetalated *trans*-9,10-bis(trimethylsilyl)-9,10-dihydroanthracene with cadmium(II) chloride. We found this method gave reliable yields after chromatography of ca. 35% but again with mercuric(II) chloride as the oxidant. Lehmkuhl et al. claim Cho and Harvey's method gives insufficient product which proved difficult to purify and developed a four-step sequence involving initially monolithiation of 9,10-dibromomanthracene, the overall yield being ca. 9–49%.[4] We found that An(SiMe$_3$)$_2$ can be isolated in ca. 53% via a one-pot reaction involving the dilithiation of 9,10-dibromoanthracene (eq 3).



(3)

The synthesis of the trans compound was according to published procedures[15] except that quenching the dianion of anthracene derived from reacting lithium and anthracene was at higher temperature. This enhanced the content of the trans compound in the reaction mixture. It is noteworthy that 9,10-bis(trimethylsilyl)-9,10-dihydroanthracenes are formed on treating **1** with ClSiMe$_3$,[9] and An(SiMe$_3$)$_2$ has been prepared by other methods.[16]

Complex **3** appears to be more stable with respect to decomposition to magnesium than **1** in, for example, benzene, the appearance of metal taking days which contrasts with minutes for **1**. The analogous complex with two trimethylsilyl groups, **4** is stable indefinitely in benzene and also in diethyl ether, toluene, and hexane. Thus the apparent inequality relating stability in solution (excluding THF) is $\mathbf{1} < \mathbf{3} < \mathbf{4}$. This correlates with the expected increase in electron affinity of anthracene on incorporating –SiMe$_3$ groups arising from the polarization influence of silicon.[17]

Fluoranthene (= Fl) reacted with magnesium in THF yielding a dark brown solid of composition Mg(Fl)$_2$(THF)$_6$ (**12**) based on a radical anion ($g = 2.0024$, broad featureless singlet) rather than a dianion as in complexes **1**–**11**. It is

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(18) Sobota, P.; Pluzinski, T.; Lis, T. *Z. Anorg. Allg. Chem.* **1986**, *533*, 215.

essentially insoluble in THF and is therefore likely to be ionic with discrete cations $[Mg(THF)_6]^{2+}$ and anions Fl^{-}. If this is so, it relates to the anthracene system that yields a similar radical anion containing species, viz., $[Mg_2Cl_3(THF)_6]^+[An]^-$, but only in the presence of magnesium halide.[3] The cation $[Mg(THF)_6]^{2+}$ has been authenticated elsewhere.[18]

For a stirred mixture of Fl and magnesium in THF the reaction was complete in ca. 48 h. However, the product was a very fine powder that posed isolation problems. A more manageable material was obtained by not stirring the reaction mixture for 4 days followed by sonication for ca. 2 h to react traces of magnesium. The related compound acenaphthylene failed to react with magnesium in THF; the dianion of acenaphthylene is implied as an intermediate in its reaction with Mg and $ClSiMe_3$ in hexamethylphosphoramide forming 1,2-bis(trimethylsilyl)acenaphthene.[19]

Treating **12** with TMEDA resulted in formation of a fine pink solid which slowly decomposed to crystalline magnesium over several hours (Scheme III). This is consistent with our inability to prepare the same solid from magnesium and Fl in a mixture of THF and TMEDA.

Metathetical exchange reactions involving a magnesium complex and substituted anthracene were found useful for the formation of **3** and **4** from **1**, **4** from **3**, **10** from **9**, and, **9** from **6** (Scheme IV). Complex **12** was also prepared by treating **1** with Fl, although here the conjugated compound acts as a one rather than a two-electron acceptor.

Cyclooctatetraene (= COT) rapidly reacted with **1**, **3**, and **4** yielding $Mg(COT)(THF)_{2.5}$ (**13**). The same complex has previously been prepared from magnesium and COT in THF, the reaction being catalyzed by $MgBr_2$.[13] We found this method to be very slow taking weeks for depletion of magnesium in the presence of excess COT. We believe the exchange reaction involving **1** is a more convenient synthesis of **13**, as is the sonicated reaction of magnesium with COT with a catalytic amount of anthracene in THF (Scheme V). Here the implied intermediate **1** undergoes metathetical exchange with COT, the reaction taking ca. 12 h.

II. Structural Commentary. Crystallization of complex **4** from a 1:25 ratio of TMEDA and THF yielded yellow prisms that were shown by a single-crystal X-ray structure determination to be comprised of discrete molecular units of **4** and the TMEDA analogue **10**, projections of which are shown in Figure 1, and THF molecules in the ratio 1:1:1.5. The magnesium atoms have distorted tetrahedral environments; in both molecules of **10** and **4** the metal centers bridge the C-9 and C-10 carbon atoms and are bound by two N centers of a TMEDA molecule, **10**, or oxygen atoms of two THF ligands, **4**. The distances of magnesium to C(2,7,9,14) carbons are all close to 2.6 Å.

Within experimental error the "$Mg\{An(SiMe_3)_2\}$" geometry of both **4** and **10** are the same as that recently determined for pure **4**:[4] Mg–C = 2.23_3, **10**, 2.21_9 Å, **4**, cf. 2.22_3 Å, pure **4**; C–Mg–C = 78.9 (3)°, **10**, 78.1 (3)°, **4**, cf. 78.2 (3)°, pure **4**. The Mg–O distances of 2.01_4 Å in **4** are similar to those of 2.00_9 Å in pure **4**.[4] In the structure of **2**[3] the Mg–C distances are much longer than in **4**[4] and **10**, being 2.32 Å. The same compound is orange like the parent complex **1**. This is noteworthy as all other complexes of anthracene studied are yellow, and the difference in color may be related to different degrees of interaction of the metal with the hydrocarbyl groups. Moreover, **1** and **2** have the same ratio of metal to donor ligands (1:3) and it is thus reasonable to suspect that they have similar structures (see below) with rather long Mg–C distances. Yellow complex **6** is of greater stability than **1** (see above), presumably in consequence of the weaker donor property of TMEDA that allows stronger interaction between the metal and the hydrocarbyl group and thus less tendency for transfer of electrons from anthracene to magnesium. In addition, yellow **5**, derived from loss of THF from **1**, presumably has a greater metal–carbon interaction and thus shorter Mg–C bonds than those in **2**.

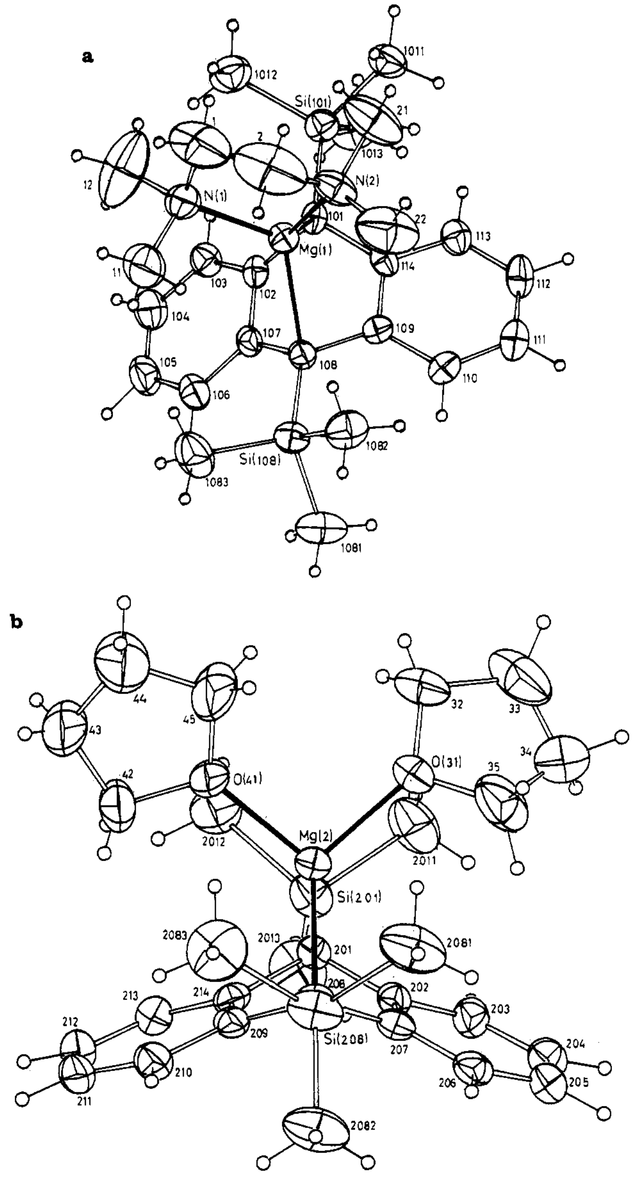

Figure 1. Projection of (a) $[Mg\{An(SiMe_3)_2\}(TMEDA)]$ and (b) $[Mg\{An(SiMe_3)_2\}(THF)_2]$ molecules showing 20% thermal ellipsoids for the non-hydrogen atoms (hydrogens have an arbitrary radii of 0.1 Å).

NMR data on **1** are consistent with polarized covalent bonding between the metal and the dianion.[6] By comparing the Mg–C distances in **2**, which are likely to be similar in **1** (see above), with those in **10** and **4**, it is reasonable to conclude that there is greater covalency in **10** and **4** than in **1** and **2**. The presence of only C-9 and C-10 to metal interactions in **2**,[3] **4**, and **10** contrasts with a π-interaction in $[Mg\{\eta^4\text{-}s\text{-}cis\text{-}PhC(H)C(H)C(H)C(H)Ph\}(THF)_3]$, Mg–C = 2.2_9 Å.[20] In the contact ion pair

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Table I. Non-Hydrogen Atom Coordinates

atom	[Mg{An(SiMe$_3$)$_2$}(TMEDA)] (*n* = 1)			[Mg{An(SiMe$_3$)$_2$}(THF)$_2$] (*n* = 2)		
	x	*y*	*z*	*x*	*y*	*z*
Mg	0.12136 (7)	−0.01085 (31)	0.04329 (9)	0.15139 (8)	0.16520 (30)	0.30728 (9)
			Ligand			
C(*n*01)	0.1107 (2)	−0.1189 (8)	−0.0204 (2)	0.1787 (2)	0.1144 (8)	0.2645 (3)
C(*n*02)	0.1482 (2)	−0.1483 (8)	−0.0037 (2)	0.1599 (2)	−0.0091 (8)	0.2532 (3)
C(*n*03)	0.1618 (2)	−0.2688 (9)	−0.0063 (3)	0.1760 (2)	−0.1279 (9)	0.2548 (3)
C(*n*04)	0.1968 (3)	−0.2940 (10)	0.0116 (3)	0.1578 (3)	−0.2430 (10)	0.2457 (3)
C(*n*05)	0.2200 (2)	−0.1985 (11)	0.0308 (4)	0.1227 (3)	−0.2424 (10)	0.2342 (3)
C(*n*06)	0.2082 (2)	−0.0750 (10)	0.0332 (3)	0.1056 (2)	−0.1272 (9)	0.2311 (3)
C(*n*07)	0.1727 (2)	−0.0474 (9)	0.0172 (2)	0.1235 (2)	−0.0098 (9)	0.2414 (2)
C(*n*08)	0.1586 (2)	0.0825 (8)	0.0205 (3)	0.1074 (2)	0.1172 (9)	0.2414 (3)
C(*n*09)	0.1279 (2)	0.1121 (8)	−0.0222 (3)	0.1212 (2)	0.2165 (8)	0.2200 (3)
C(*n*10)	0.1204 (2)	0.2340 (9)	−0.0435 (3)	0.1014 (2)	0.3142 (9)	0.1904 (3)
C(*n*11)	0.0906 (3)	0.2564 (10)	−0.0838 (3)	0.1158 (3)	0.4080 (9)	0.1737 (3)
C(*n*12)	0.0685 (3)	0.1572 (11)	−0.1050 (3)	0.1510 (3)	0.4034 (10)	0.1844 (3)
C(*n*13)	0.0749 (2)	0.0365 (10)	−0.0850 (3)	0.1712 (2)	0.3076 (9)	0.2119 (3)
C(*n*14)	0.1038 (2)	0.0096 (8)	−0.0440 (2)	0.1576 (2)	0.2137 (8)	0.2313 (3)
Si(*n*01)	0.07791 (7)	−0.24757 (29)	−0.04379 (9)	0.22627 (7)	0.12602 (33)	0.29099 (10)
C(*n*011)	0.0335 (2)	−0.1951 (12)	−0.0533 (3)	0.2468 (3)	0.0090 (14)	0.3388 (4)
C(*n*012)	0.0876 (3)	−0.3876 (11)	−0.0038 (4)	0.2403 (3)	0.2887 (13)	0.3184 (4)
C(*n*013)	0.0738 (3)	−0.3152 (12)	−0.0995 (4)	0.2488 (3)	0.1026 (14)	0.2530 (5)
Si(*n*08)	0.18796 (7)	0.21463 (30)	0.05260 (10)	0.06301 (7)	0.12904 (40)	0.23760 (10)
C(*n*081)	0.2127 (3)	0.2883 (12)	0.0227 (5)	0.0573 (3)	0.0256 (16)	0.2809 (4)
C(*n*082)	0.1647 (3)	0.3516 (11)	0.0651 (4)	0.0273 (3)	0.0884 (15)	0.1805 (4)
C(*n*083)	0.2220 (3)	0.1654 (13)	0.1090 (4)	0.0536 (4)	0.2935 (15)	0.2529 (5)
			Tetrahydrofuran[a]			
	solvent			ligand		
	x	*y*	*z*	*x*	*y*	*z*
O(51);O(31)	0.0323 (6)	0.7186 (28)	0.0744 (10)	0.1604 (2)	0.0638 (7)	0.3641 (2)
C(52);C(32)	0.0250 (8)	0.7257 (43)	0.1122 (14)	0.1866 (4)	0.0821 (15)	0.4070 (4)
C(53);C(33)	0.0147 (10)	0.5941 (51)	0.1146 (13)	0.1974 (4)	−0.0512 (17)	0.4251 (4)
C(54);C(34)	0.0235 (13)	0.5515 (33)	0.0753 (16)	0.1772 (5)	−0.1375 (15)	0.3916 (5)
C(55);C(35)	0.0018 (11)	0.6589 (82)	0.0544 (14)	0.1462 (4)	−0.0630 (15)	0.3626 (4)
O(61);O(41)	0.0155 (25)	0.6091 (81)	0.2881 (28)	0.1554 (2)	0.3430 (6)	0.3339 (2)
C(62);C(42)	0.0371 (34)	0.6022 (123)	0.2910 (26)	0.1530 (6)	0.4579 (12)	0.3080 (5)
C(63);C(43)	0.0335 (21)	0.6528 (69)	0.2427 (40)	0.1574 (9)	0.5629 (15)	0.3380 (6)
C(64);C(44)	−0.0037 (71)	0.7131 (81)	0.2254 (32)	0.1583 (7)	0.5134 (18)	0.3776 (6)
C(65);C(45)	−0.0112 (22)	0.6412 (66)	0.2642 (46)	0.1586 (6)	0.3740 (13)	0.3763 (5)
			TMEDA Ligand			
N(*n*)	0.1368 (2)	−0.0992 (9)	0.1077 (3)	0.0839 (2)	0.0874 (8)	0.0598 (3)
C(*n*1)	0.1695 (3)	−0.0395 (17)	0.1408 (4)	0.0496 (3)	0.0363 (17)	0.0329 (5)
C(*n*2)	0.1453 (6)	−0.2415 (17)	0.1123 (5)	0.0811 (4)	0.2249 (16)	0.0557 (7)
C(*n*)	0.1093 (4)	−0.0881 (24)	0.1204 (4)	0.0943 (4)	0.0540 (22)	0.1096 (5)

[a] THF (6) is disordered about a symmetry element and atoms accordingly have a site occupancy of 0.5.

structure of [Li$_2$(An)(TMEDA)$_2$] each metal center is η^6 to a ring of almost planar anthracene (see below).[21] Essentially ionic bonding here but covalent bonding in the magnesium anthracene complexes would account for differences in color, the lithium complex being purple and the magnesium complexes orange or yellow.

The angle subtended by the two N centers and Mg in **10**, 85.1 (4)°, is as expected less than those in **4**, 97.8 (3)° and 99.6 (2)°.[4] It compares with the 81.5 (3)° value in [MgMe$_2$(TMEDA)][22] in which the Mg–N distances are somewhat longer (2.257 (6) and 2.227 (6) Å, cf. 2.12_6 Å). The presence of only two donor groups in **4** and **10**, and in **3** and **9**, rather than three as in **1** and **2** is presumably steric in origin, although greater interaction between the metal and the silyl-substituted anthracenes at the C-9 and C-10 positions as a consequence of polarization and concentration of charge by silicon[17,23] would lead to lower solvation requirements of magnesium.

Table II. Magnesium Environments[a]

molecule	*l* = 1	*l* = 2
	Distances (Å)	
Mg(*l*)–C(*l*01)	2.222 (9)	2.215 (11)
Mg(*l*)–C(*l*08)	2.224 (10)	2.222 (7)
Mg(*l*)–L(1)	2.116 (9)	2.015 (7)
Mg(*l*)–L(2)	2.136 (10)	2.013 (7)
	Angles (deg)	
C(*l*01)–Mg(*l*)–C(*l*08)	78.9 (3)	78.1 (3)
C(*l*01)–Mg(*l*)–L(1)	123.8 (4)	120.2 (3)
C(*l*01)–Mg(*l*)–L(2)	126.1 (3)	121.0 (4)
C(*l*08)–Mg(*l*)–L(1)	123.2 (3)	121.5 (3)
C(*l*08)–Mg(*l*)–L(2)	125.5 (4)	120.1 (3)
L(1)–Mg(*l*)–L(2)	85.1 (4)	97.8 (3)

[a] For L(1,2) read N(1,2) for *l* = molecule 1 and O(3,4) for *l* = molecule 2.

Obviously with magnesium bridging C-9 and C-10 positions the –SiMe$_3$ groups have a cisoid arrangement. The substituted anthracene is folded along th C-9–C-10 vector, the dihedral angle between the two sections being 42.9°, **10**, 41.2°, **4**, cf. 45° in pure **4**,[4] 40.9° in **2**,[3] and 31.3° in [Mg(μ-An)(THF)$_3$(μ-H)AlEt$_2$].[5] In free An(SiMe$_3$)$_2$ there

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[21] Rhine, W. E.; Davis, J.; Stucky, G. *J. Am. Chem. Soc.* **1975**, *97*, 2079.

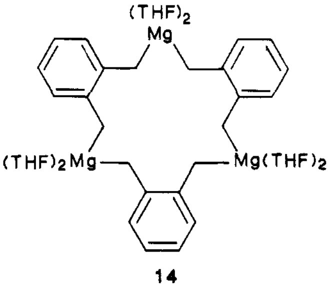
[22] Greiser, T.; Kopf, J.; Thoennes, D.; Weiss, E. *J. Organomet. Chem.* **1980**, *191*, 1.

[23] Schleyer, P. v. R.; Kos, A. J.; Wilhelm, D.; Clark, T.; Boche, G.; Decher, G.; Etzrodt, H.; Dietrich, H.; Mahdi, W. *J. Chem. Soc., Chem. Commun.* 1984, 1495.

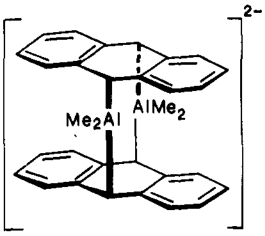
is folding due to the steric demands of the –$SiMe_3$ groups, but it is less severe at 14°.[4] Loss of aromatic character on reduction to a dianion is evident by elongation of the C-9 and C-10 to adjacent carbon atoms, 1.5_1[4] and 1.5_0 Å in **4**, 1.4_7 Å in **10**, and 1.4_7 Å in **2**,[3] cf. 1.4_2 Å in $An(SiMe_3)_2$.[4]

The C-9,10–Si distances in **4** (1.8_4,[4] 1.84_3 Å) and **10** (1.83_3 Å) are much shorter than the corresponding distances in free $An(SiMe_3)_2$ (1.8_8 Å)[4] and the Si–CH_3 distances (1.8_7 Å). This is typical of Si–C bonds where the carbon bears some charge[24] in consequence of the positive charge on silicon.[17,23]

Like other research groups[3,8] we have attempted to prepare suitable crystals of **1** for a structure determination in order to establish its degree of aggregation and also to try and relate structure to its unusual properties. While we were successful in collecting X-ray data on crystals formed over 2 months from an unstirred solution of anthracene, THF, and magnesium, we were unable to overcome the phase problem. Crystal data obtained are as follows: monoclinic, probable space group $C2/c$, a = 8.039 (5) Å, b = 37.48 (2) Å, c = 15.941 (6) Å, β = 101.95 (4)°, U = 4700 (4) Å^3, cf. Freeman and Hutchinson who recorded data in a triclinic cell of volume 4668 Å^3.[8] Although there are now three structure determinations on magnesium(2+) anthracene(2−) complexes showing monomeric species with the metal centers bridging the C-9 and C-10 positions, oligomeric structures are conceivable. In this context its worth noting the trinuclear structure of the related complex $[\{Mg(CH_2C_6H_4CH_2\text{-}o)\}(THF)_2]_3$ (**14**)[25] and the structure of $[(AlMe_2)_2(An)_2]^{2-}$ (**15**).[26]



14



15

Experimental Section

All the magnesium complexes are extremely air-sensitive and for their manipulation standard Schlenk techniques featured with dry and oxygen-free argon. Solvents were dried over and distilled from Na/K alloy (THF), Na (benzene, toluene, TMEDA, and OEt_2), or CaH_2 (hexane). $AnSiMe_3$,[14] *trans*-9,10-bis(trimethylsilyl)-9,10-dihydroanthracene,[15] **1**,[2] and **4**[4] were prepared by using literature methods, albeit modified (see text). PMDETA, (−)-sparteine sulfate, and magnesium were obtained respectively from Eastman Kodak, Aldrich, and May and Baker, (−)-sparteine being prepared by treating the sulfate with solid NaOH and then distilling in vacuo.

Characterization of the magnesium complexes was via microanalysis (Canadian Microanalytical Service) and ICPAES analysis (magnesium) and ^1H NMR data on their carbon tetrachloride decomposition products which yielded the ratio of anthracene to magnesium coligands. ^1H NMR spectra were recorded on a Hitachi Perkin-Elmer R-24B spectrometer at 60 MHz.

Synthesis of Mg(An)(THF)$_2$ (5). Benzene (40 cm^3) was added to **1** (10 g, 23.8 mmol) and the reaction mixture stirred for 30 min. During this time a slow color change, orange to yellow, was evident yielding a yellow solid. This was filtered, washed with benzene (2 × 20 cm^3), and dried in vacuo as the title complex: yield 8.1 g, 94.9%; mp 135 °C dec. Anal. Calcd for $C_{22}H_{26}O_2Mg$: C, 76.2; H, 7.55; Mg, 7.00. Found: C, 76.0; H, 7.25; Mg, 6.70.

Synthesis of Mg(An)(THF)(TMEDA) (6). Method I. To a stirred slurry of **1** (1.15 g, 2.75 mmol) in THF (20 cm^3) was added TMEDA (10 cm^3). The orange slurry immediately turned yellow yielding the title complex which was collected, washed with THF (3 × 20 cm^3), and dried in vacuo: yield 1.00 g, 94%; mp 120 °C dec. Anal. Calcd for $C_{24}H_{34}N_2OMg$: C, 73.8; H, 8.75; N, 7.15, Mg, 6.20. Found: C, 73.3; H, 8.60; N, 6.25; Mg, 6.90. The brown mother liquor gave a strong broad featureless ESR singlet, g = 2.0031. **Method II.** To a stirred suspension of magnesium powder (0.2 g, 8.2 mmol) in THF (10 cm^3) was added 1,2-dibromoethane (3 drops). The THF was removed after the evolution of ethylene had ceased and replaced with fresh THF (60 cm^3). Anthracene (3.0 g, 16.9 mmol) was then added until the solution turned green, whereupon TMEDA (5 cm^3, 33.3 mmol) was added. On stirring overnight a yellow precipitate of the title compound formed, and after 1 week all the magnesium had been consumed. The yellow powder was collected, washed with THF (3 × 20 cm^3), and then dried in vacuo; yield 2.93 g, 91%.

Synthesis of Mg(An)(PMDETA) (7). Method I. To a stirred mixture of **1** (2.48 g, 5.9 mmol) in THF (20 cm^3) was added PMDETA (5.08 cm^3, 4.1 g, 23.6 mmol). The orange slurry immediately reacted, yielding a bright yellow slurry, suspended in a green solution. The title complex was collected, washed with THF (3 × 20 cm^3), and then dried in vacuo: yield 1.87 g, 84%; mp 206–210 °C dec. Anal. Calcd for $C_{23}H_{33}N_3Mg$: C, 73.50; H, 8.85; N, 11.2; Mg, 6.45. Found: C, 71.8; H, 8.60; N, 10.3; Mg, 6.65. The green solution gave a strong broad featureless ESR singlet, g = 2.0036.

Method II. To a stirred mixture of **6** (0.57 g, 1.46 mmol) in THF (20 cm^3) was added PMDETA (0.33 cm^3, 0.28 g, 1.60 mmol). The solution rapidly turned deep green with a yellow precipitate of the title complex. This was collected, washed with THF (3 × 20 cm^3), and then dried in vacuo; yield 0.47 g, 86%.

Method III. To a stirred suspension of magnesium powder (0.1 g, 4.1 mmol) in THF (5 cm^3) was added 1,2-dibromoethane (4 drops). The THF was removed after the evolution of ethylene had ceased and replaced with fresh THF (60 cm^3). Anthracene (1.1 g, 6.18 mmol) was than added, and when the green color of the anthracene radical persisted, PMDETA (1.04 cm^3, 0.87 g, 5 mmol) was added. Almost immediately a yellow precipitate started to form. After 7 days no magnesium remained. The yellow precipitate of the title complex was isolated from the green solution as above; yield 1.51 g, 96.6%.

Synthesis of Mg(An){(−)-Sp} (8). To a stirred mixture of **1** (1.0 g, 2.88 mmol) in toluene (30 cm^3) was added (−)-sparteine (0.66 cm^3, 0.67 g, 2.88 mmol). A yellow slurry of the title complex in a lime green solution formed immediately. The product was collected, washed with toluene (3 × 20 cm^3), and then dried in vacuo: yield 0.98 g, 94.6%; mp 188 °C dec. Anal. Calcd for $C_{29}H_{36}N_2Mg$: C, 79.7; H, 8.30; N, 6.50; Mg, 5.55. Found: C, 77.1; H, 8.15; N, 5.80; Mg, 5.90. Ratio of An:(−)-Sp = 1.0:1.0 (^1H NMR of CCl_4 decomposition mixture).

Synthesis of Mg(AnSiMe$_3$)(THF)$_2$ (3). Method I. To a stirred suspension of magnesium powder (0.54 g, 22 mmol) in THF (5 cm^3) was added 1,2-dibromoethane (3 drops). The THF was removed after the evolution of ethylene had ceased and replaced with fresh THF (300 cm^3). 9-(Trimethylsilyl)anthracene (10 g, 40 mmol) was then added and the reaction mixture stirred at room temperature. The solution initially turned dark green, and after several hours a yellow precipitate formed. After ca. 72 h all of the magnesium had been consumed. The yellow solid was filtered, washed with THF (2 × 50 cm^3), and dried in vacuo as the title complex; yield 29.2 g, 92.1%.

Method II. To a stirred slurry of **1** (0.75 g, 1.99 mmol) in THF (10 cm^3) was added 9-(trimethylsilyl)anthracene (0.50 g, 1.8 mmol). A bright yellow microcrystalline solid of the title complex formed immediately. This was filtered, washed with THF (2 × 10 cm^3), and dried in vacuo; yield 0.70 g, 93%.

Synthesis of Mg(AnSiMe$_3$)(TMEDA) (9). Method I. TMEDA (20 cm^3) was added to **3** (3.18 g, 75.9 mmol) and the reaction mixture stirred for 30 min. The yellow solid was filtered, washed with TMEDA (2 × 5 cm^3), and dried in vacuo yielding the title complex: yield 2.62 g, 88%; mp 180 °C dec. Anal. Calcd for $C_{23}H_{34}N_2MgSi$: C, 70.7; H, 8.75; N, 7.20; Mg, 6.25. Found: C, 68.80; H, 8.40; N, 6.55; Mg, 5.89. Ratio of TMEDA:$AnSiMe_3$

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[25] Lappert, M. F.; Martin, T. R.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 1959.

[26] Brauer, D. J.; Stucky, G. D. *J. Organomet. Chem.* **1972**, *37*, 217.

= 1.0:1.08 (^{1}H NMR of CCl_4 decomposition mixture).

Method II. To a stirred slurry of **6** (0.56 g, 1.47 mmol) in TMEDA (10 cm^3) was added 9-(trimethylsilyl)anthracene (0.37 g, 1.47 mmol), and the mixture was stirred for 24 hours. [Note: little reaction had occurred after 1 h.] The yellow solid was filtered, washed with TMEDA (2 × 5 cm^3), and dried in vacuo yielding the title complex, yield 0.43 g, 76.7.

Synthesis of Mg(AnSiMe$_3$)(TMEDA)(THF) (11). THF (25 cm^3) was added to **9** (3.2 g, 82 mmol) and the reaction mixture stirred for 30 min. The yellow solid was filtered, washed with THF (2 × 20 cm^3), and dried in vacuo yielding the title complex: yield 3.3 g, 86.9%; mp 200 °C dec. Anal. Calcd for $C_{27}H_{42}N_2MgOSi$: C, 70.0; H, 9.15; N, 6.05; Mg, 5.25. Found: C, 69.7; H, 8.15; N, 5.95; Mg, 5.15.

Synthesis of 9,10-Bis(trimethylsilyl)anthracene. Method I. Modified Method of Cho and Harvey.[14] To a stirred solution of *trans*-9,10-bis(trimethylsilyl)-9,10-dihydroanthracene (5 g, 15.3 mmol) in cyclohexane (100 cm^3) and TMEDA (38.6 g, 333 mmol) was added a hexane solution of *n*-BuLi (24 cm^3, 1.6 M, 40 mmol) over a period of 10 min. The resulting red solution containing suspended orange solid was refluxed for 2 h, the characteristic purple color of the $An(SiMe_3)_2{}^{2-}$ appearing after ca. 45 min. The reaction mixture was allowed to cool for 5 min and the color discharged by the addition of $HgCl_2$ (8.4 g, 31 mmol). [Note: great care should be taken during this step as the reaction is extremely violent.] After the solution was stirred for 1 h at room temperature, water (100 cm^3) was slowly added and the mixture stirred for a further 30 min, whereupon the mixture was filtered through Celite to remove precipitated mercury and the resulting brown solution washed with water (5 × 100 cm^3) and dried over anhydrous $MgSO_4$ and the volatiles were removed in vacuo yielding 4.0 g of a dark brown oil. This was subject to flash Büchner chromatography on silica (50 g) using petroleum ether (500 cm^3) as the eluent. The volatiles were removed in vacuo yielding 4.6 g of an orange oil, shown by ^{1}H NMR to be a mixture of 9,10-bis(trimethylsilyl)anthracene and 9-(trimethylsilyl)anthracene, ca. 1:1. Flash chromatography of the mixture on neutral alumina (250 g) eluted with hexane gave, after rechromatography of mixed fractions, 9,10-bis(trimethylsilyl)anthracene (yield 1.74 g, 35%) and 9-(trimethylsilyl)anthracene (yield 1.8 g, 46.9%). The former was recrystallized from hexane as greenish yellow needles, mp 113–113.5 °C (lit. mp 112–113 °C[14]).

Method II. To a slurry of 9,10-dibromoanthracene (20 g, 5.95 mmol) in diethyl ether (500 cm^3) and TMEDA (17.3 g, 14.9 mmol), cooled to 0 °C, was added a hexane solution of *n*-BuLi (93.1 cm, 1.6 M, 14.9 mmol) over a period of 5 min. The deep red solution was then stirred at room temperature for 10 min during which the orange "dilithium reagent" precipitated from solution. Trimethylchlorosilane (13.6 g, 17.9 mmol) was added and the mixture stirred for 3 h. Volatiles were removed in vacuo, and the residual orange residue was taken up in petroleum ether (200 cm^3), washed with water (5 × 100 cm^3), and then dried over anhydrous $MgSO_4$. Volatiles were removed in vacuo yielding 23.6 g of a dark orange oil which was subjected to flash Büchner chromatography on silica (100 g) using petroleum ether (1000 cm^3) as the eluent. Removal of the solvent in vacuo yielded 22.1 g of a pale yellow oil shown by ^{1}H NMR and GC/MS to be a mixture of 9,10-bis(trimethylsilyl)anthracene and 9-bromo-10-(trimethylsilyl)anthracene in the ratio of 4:1. Crystallization from hexane at −80 °C gave the title compound as a pale yellow solid: yield 9.8 g, 53%; mp 113–114 °C.

Synthesis of Mg{An(SiMe$_3$)$_2$}(THF)$_2$ (4). Method I. To a stirred slurry of **1** (0.52 g, 1.24 mmol) in THF (10 cm^3) was added 9,10-bis(trimethylsilyl)anthracene (0.40 g, 1.24 mmol). A yellow solid in a green solution immediately formed. Concentration in vacuo to ca. 3 cm^3 at ca. 65 °C yielded on slow cooling a yellow solid. This was filtered, washed with THF (5 cm^3), and dried in vacuo yielding the title complex, yield 0.25 g, 57%.

Method II. The same procedure was used as described in method I with **3** used in place of **1**; yield 63%.

Synthesis of Mg{An(SiMe$_3$)$_2$}(TMEDA) (10). TMEDA (10 cm^3) was added to **4** (1.02 g, 2.08 mmol) and the reaction mixture stirred for 30 min. The yellow/green solid was filtered, washed with TMEDA (2 × 5 cm^3), and dried in vacuo yielding the title complex: yield 0.89 g, 92.5%; mp 155 °C dec. Anal. Calcd for $C_{26}H_{42}N_2MgSi_2$: C, 67.4; N, 9.15; N, 6.05; Mg, 5.25. Found: C, 66.6; H, 8.90; N, 5.95; Mg, 5.55.

Synthesis of Mg(Fl)$_2$(THF)$_6$ (12). Method I. To magnesium powder (0.2 g, 8.2 mmol) activated with 1,2-dibromoethane (see above) in THF (30 cm^3) was added fluoranthene (4.0 g, 18 mmol). After several hours a brown solid started to form, and after ca. 72 h only a trace of magnesium remained, which was removed by sonication for 3 h. The dark brown solid of the title complex was filtered, washed with THF (3 × 20 cm^3), and dried in vacuo at room temperature; yield 6.4 g, 90%; mp 122 °C dec. Anal. Calcd for $C_{56}H_{68}O_6Mg$: C, 78.1; H, 7.95; Mg, 2.80. Found: C, 77.4; H, 7.65; Mg, 2.90.

Method II. To a stirred slurry of **1** (0.50 g, 1.2 mmol) in THF (30 cm^3) was added fluoranthene (0.48 g, 2.4 mmol). A dark brown precipitate of the title compound formed immediately which was collected, washed with fresh THF (3 × 30 cm^3), and then dried in vacuo; yield 0.98 g, 95%.

Synthesis of Mg(COT)(THF)$_{2.5}$ (13). To a stirred suspension of magnesium powder (0.2 g, 8.23 mmol) in THF (5 cm^3) was added 1,2-dibromoethane (4 drops). The THF was removed when the evolution of ethylene had ceased and replaced with fresh THF (30 cm^3). Anthracene (0.1 g, 0.56 mmol) was added and the flask placed in a sonic bath for ca. 12 h. Cyclooctatetraene (1.02 cm^3, 0.936 g, 9 mmol) was then added whereupon a white precipitate began to form after ca. 25 min and after 12 h all the magnesium had been consumed. The title compound was collected, washed with THF (3 × 20 cm^3), and then dried in vacuo; yield 2.28 g, 89%. Ratio COT:THF = 1.0:2.49 (^{1}H NMR of $CDCl_3$ decomposition mixture).

Structure Determination. A unique data set was measured to $2\theta_{max} = 45°$ by using a Syntex P2$_1$ four-circle diffractometer in conventional $2\theta/\theta$ scan mode. A total 8454 independent reflections were obtained, 4186 with $I > 3\sigma(I)$ being considered "observed" and used in the basically 9 × 9 block-diagonal least-squares refinement. Anisotropic thermal parameters were refined for the non-hydrogen atoms; hydrogen atoms (x, y, z, U_{iso}) were included at estimated values. Residuals on $|F|$, R and R', at convergence were 0.083 and 0.078 (statistical weights), respectively. Neutral complex scattering factors were used;[27] the computation used the XTAL-83 program system[28] implemented on a Perkin-Elmer 3240 computer by S. R. Hall.

Crystal Data. $[Mg\{An(SiMe_3)_2\}(TMEDA)][Mg\{An(SiMe_3)_2\}(THF)_2](THF)_{1.5}$: $C_{54}H_{84}Mg_2N_2O_2Si_4(THF)_{1.5} = C_{60}H_{96}Mg_2N_2O_{3.5}Si_4$; M_r 1062.4; monoclinic; $C2/c$, $a = 42.39\ (2)$ Å, $b = 10.369\ (3)$ Å, $c = 32.42\ (3)$ Å, $\beta = 114.85\ (3)°$, $U = 12934$ Å^3, $D_{calcd}\ (Z = 8) = 1.09\ g{\cdot}cm^{-3}$, $F(000) = 4628$; monochromatic Mo Kα radiation ($\lambda = 0.7106_9$ Å); $\mu_{Mo} = 1.5\ cm^{-1}$ (no absorption correction; capillary mounted specimen); $T = 295$ K.

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Registry No. **1**, 86901-19-1; **3**, 100908-25-6; **4**, 100908-24-5; **4·10**·1.5THF, 109927-18-6; **5**, 109906-70-9; **6**, 109906-72-1; **7**, 109889-35-2; **8**, 109906-74-3; **9**, 109906-76-5; **10**, 109906-78-7; **11**, 109906-80-1; **12**, 109889-36-3; **13**, 39292-45-0; An, 120-12-7; PMDETA, 3030-47-5; Fl, 206-44-0; COT, 629-20-9; $HgCl_2$, 7487-94-7; (−)-sparteine, 90-39-1; 9-(trimethylsilyl)anthracene, 56272-35-6; *trans*-9,10-bis(trimethylsilyl)-9,10-dihydroanthracene, 56272-37-8; 9,10-bis(trimethylsilyl)anthracene, 56272-36-7; 9,10-dibromoanthracene, 523-27-3; trimethylchlorosilane, 75-77-4.

Supplementary Material Available: Tables containing non-hydrogen atom anisotropic thermal parameters, hydrogen atom parameters, least-squares planes, and ligand geometries (13 pages); a listing of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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[27] Ibers, J. A., Hamilton, W. C., Eds. *International Tables for X-ray Crystallography*; Kynoch; Birmingham, England 1974; Vol. 4.

[28] Stewart, J. M.; Hall, S. R., Eds. *The XTAL System of Crystallographic Programs: User's Manual*; Technical Report TR-901, 1983; Computer Science Center, University of Maryland, College Park, MD.