

# Magnesium Adducts of Substituted Anthracenes – Preparation and Properties<sup>1)</sup>

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2-Methyl-, 1,4-dimethyl-, 9-methyl-, 9-ethyl-, 9,10-dimethyl-, and 9-phenylanthracene (**1a–f**) react with magnesium in THF at room temperature to afford the corresponding substituted magnesium anthracenes **2a–f**. 9,10-Diphenylanthracene (**1g**), however, reacts with magnesium under the same conditions to produce the deep-blue magnesium bis(9,10-diphenylanthracenide) · 6 THF (**4g**). Upon heating to 60°C in THF, **4g** reversibly dissociates to give magnesium 9,10-diphenylanthracene · 3 THF (**2g**) and **1g**, while prolonged heating at 60°C causes decomposition of **2g** to active magnesium (Mg<sup>0</sup>) and **1g**. In THF **2a–c**, **e**, and **f** exhibit temperature-dependent equilibria with **1a–c**, **e**, and **f** and magnesium. Compared with

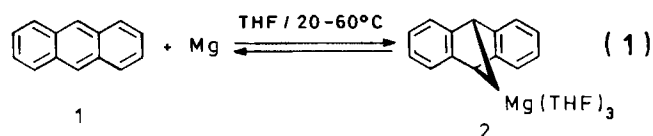
magnesium anthracene · 3 THF (**2**), these equilibria are strongly shifted toward substituted anthracenes and magnesium, and only at 0°C high conversions are achieved. The magnesium exchange between **2** and the substituted anthracenes **1a, b**, and **f** in THF has been experimentally verified. **2a, e**, and **f** react with organic halides in the same way as **2**, however, in the case of allyl, propargyl, and benzyl chloride the yields of Grignard compounds are lower than for **2**; with bromobenzene, the tendency for the radical transfer reaction is stronger than for **2**. Magnesium 9,10-dimethylanthracene (**2e**) reacts with ethyl acetate to give the bicyclic tertiary alcohol **9** by an intramolecular C–C coupling reaction.

While the reaction of magnesium with anthracene (**1**) in THF, affording orange, sparingly soluble magnesium anthracene · 3 THF (**2**), has been intensively investigated for some years now<sup>2)</sup>, relatively little is known about magnesium adducts of substituted anthracenes. Magnesium 1,4-dimethyl-<sup>3)</sup>, 9-(trimethylsilyl)-<sup>4)</sup>, 9,10-bis(trimethylsilyl)-<sup>4)</sup>, and 9-(benzyltrimethylsilyl)anthracene<sup>5)</sup> are the only substituted magnesium anthracenes described so far.

Our interest in the reaction of magnesium with substituted anthracenes has centered on the question if and how some unique properties of the parent compound **2** [temperature-<sup>6)</sup> and THF-dependent<sup>1)</sup> equilibrium (eq. 1), equilibrium with anthracene radical anions<sup>2,3)</sup>, **2** as a source of soluble zerovalent magnesium and a phase-transfer catalyst for magnesium<sup>2)</sup>] can be modified by introduction of substituents into the anthracene ring system. So, for instance, the question was raised if substituents can change the reactivity of magnesium anthracenes toward organic halides<sup>14)</sup>. A more practical aspect of the study has been the search for better soluble and crystallizable “magnesium anthracenes” than **2**, which eventually has led to the elucidation of the molecular structure of magnesium 1,4-dimethylanthracene · 3 THF (**2b**)<sup>3)</sup>. Recently, Raston et al. have succeeded in growing single crystals and determined the molecular structure of **2** by X-ray analysis<sup>7)</sup>.

In this paper we report on the preparation, spectroscopic characterization, and some chemical properties of seven al-

kyl- or phenyl-substituted magnesium anthracenes (**2a–g**) and of magnesium bis(9,10-diphenylanthracenide) · 6 THF (**4g**) and compare them with those of the parent compound **2**<sup>8,9)</sup>.



## Preparation, Spectroscopic Characterization and Equilibria of Substituted Magnesium Anthracenes

2-Methyl-, 1,4-dimethyl-, 9-methyl-, 9-ethyl-, 9,10-dimethyl-, and 9-phenylanthracene (**1a–f**) react with magnesium powder or chips in THF at room temperature in the same way as anthracene (**1**) to afford the corresponding substituted magnesium anthracenes **2a–f**. The sparingly soluble orange to reddish-brown microcrystalline compounds are isolated in 50–90% yield; the hydrolysis of **2a–f** produces Mg<sup>2+</sup> ions, the corresponding 9,10-dihydroanthracenes **3a–f**, and THF in the molar ratio of 1:1:3 (Table 1)<sup>8)</sup>. **2a** and **2b** are about four times as soluble as **2** in THF at room temperature, while the solubility of **2c, d, e**, and **f** is comparable to that of **2**<sup>6)</sup>.

In contrast to anthracene and substituted anthracenes **1a–f**, 9,10-diphenylanthracene (**1g**) reacts with magnesium chips in THF at room temperature to yield the deep blue magnesium bis(9,10-diphenylanthracenide) · 6 THF (**4g**) (Table 1). The color and protolysis of **4g** affording a 1:1 mixture of **1g** and 9,10-dihydro-9,10-diphenylanthracene

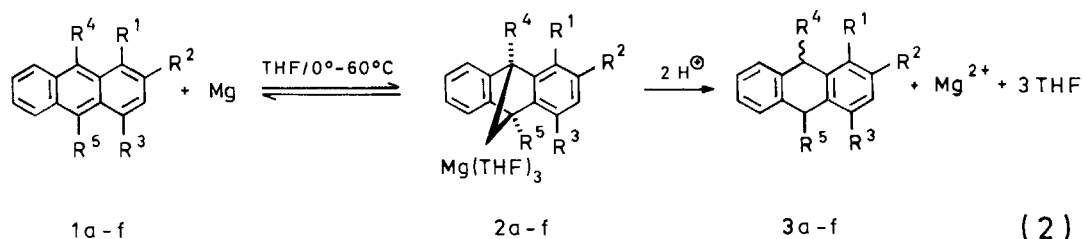
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Table 1. Data on the preparation and composition of substituted magnesium anthracenes **2a–f** and **4g**

Anthracene	[g] (mmol)	Mg [g] (mmol)	THF [ml]	Mg-anthracene	Yield[g] (%)	Empirical formula (MW)	C H Mg calcd. [%] found [%]	Mg : 3a–g : THF (molar ratio)
<b>1a</b>	1.01 (5.3)	1.48 (60.9)	70	<b>2a</b>	1.12 (48.9)	C <sub>15</sub> H <sub>12</sub> Mg·3THF (432.9)	74.91 8.38 5.62 74.91 8.13 5.67	1 : 1.16 : 3.06
<b>1b</b>	3.00 (14.5)	3.00 (123)	100	<b>2b</b>	5.03 (75.1)	C <sub>16</sub> H <sub>14</sub> Mg·3THF (446.9)	75.25 8.57 5.44 74.96 8.29 5.40	1 : 1.01 : 2.93
<b>1c</b>	2.80 (14.6)	3.10 (128)	100	<b>2c</b>	5.72 (90.5)	C <sub>15</sub> H <sub>12</sub> Mg·3THF (432.9)	74.91 8.38 5.62 74.98 8.22 5.56	1.12 : 1 : 3.02
<b>1d</b>	1.04 (5.0)	1.20 (49.4)	50	<b>2d</b>	1.95 (87.2)	C <sub>16</sub> H <sub>14</sub> Mg·3THF (446.9)	75.25 8.57 5.44 74.50 8.12 5.73	1 : 1.06 : 2.77
<b>1e</b>	1.12 (5.4)	0.12 <sup>a)</sup> (5.0)	30	<b>2e</b>	1.60 (71.6)	C <sub>16</sub> H <sub>14</sub> Mg·3THF (446.9)	75.25 8.57 5.44 75.12 8.06 5.53	1.11 : 1 : 2.97
<b>1f</b>	2.56 (10.1)	2.43 (100)	100	<b>2f</b>	4.16 (83.2)	C <sub>20</sub> H <sub>14</sub> Mg·3THF (495.0)	77.65 7.74 4.91 77.60 7.30 5.09	1 : 1.06 : 3.30
<b>1g</b>	3.22 (9.7)	3.40 (140)	100	<b>4g</b>	4.16 (76.8)	C <sub>52</sub> H <sub>36</sub> Mg·6THF (1117.8)	81.66 7.57 2.17 81.74 7.74 2.28	1.01 : 1.00(1.00) <sup>b)</sup> : 5.84

<sup>a)</sup> In this case active magnesium (Mg\*) resulting from dehydrogenation of MgH<sub>2</sub><sup>1)</sup> was used. – <sup>b)</sup> **1g**.



R = H if not noted otherwise

a : R<sup>2</sup> = CH<sub>3</sub>

b : R<sup>1</sup>, R<sup>3</sup> = CH<sub>3</sub>

c : R<sup>4</sup> = CH<sub>3</sub>

d : R<sup>4</sup> = C<sub>2</sub>H<sub>5</sub>

e : R<sup>4</sup>, R<sup>5</sup> = CH<sub>3</sub>

f : R<sup>4</sup> = C<sub>6</sub>H<sub>5</sub>

(**3g**) suggest the presence of a 9,10-diphenylanthracene radical anion<sup>10)</sup>, i.e. **4g** is a homolog of the blue magnesium bis(anthracene) · 6 THF, the latter being stable only at ≤ –25°C<sup>3)</sup>. Upon heating to 60°C in THF, **4g** reversibly dissociates to the brown magnesium 9,10-diphenylanthracene · 3 THF (**2g**) and free **1g**, while prolonged heating at 60°C in the absence of **1g** leads to the decomposition of **2g** to active magnesium (Mg\*)<sup>1)</sup> and **1g**<sup>3)</sup>. The system Mg/1g/THF thus displays between +20 and +60°C the same type of temperature-dependent equilibrium between the radical anion (in **4g**) and the “dianion” (in **2g**) as does the system Mg/1/THF between –25 and +20°C<sup>3)</sup>.

The compounds **2a–g** and **4g** have been characterized by their IR and Raman spectra (Tables 2 and 3), **2a, b**, and **e** by their <sup>13</sup>C-NMR spectra (Table 4), and **2a** and **b** also by <sup>1</sup>H-NMR spectra (Experimental). In addition the X-ray structure of **2b**<sup>3)</sup> has been determined.

Those IR and Raman bands of **2a–g**, which are hardly influenced by the substituents of anthracene, are found at similar positions as the corresponding bands of **2** (Tables 2 and 3). The spectra differ significantly from those of free anthracenes<sup>11)</sup>. Complexation of anthracenes with Mg is most clearly observed in the IR spectra by the 1600-cm<sup>–1</sup>

ring-stretching vibration, which is shifted to 1555–1570 cm<sup>–1</sup>, and by the CH out-of-plane vibration (isolated H in

Scheme 1

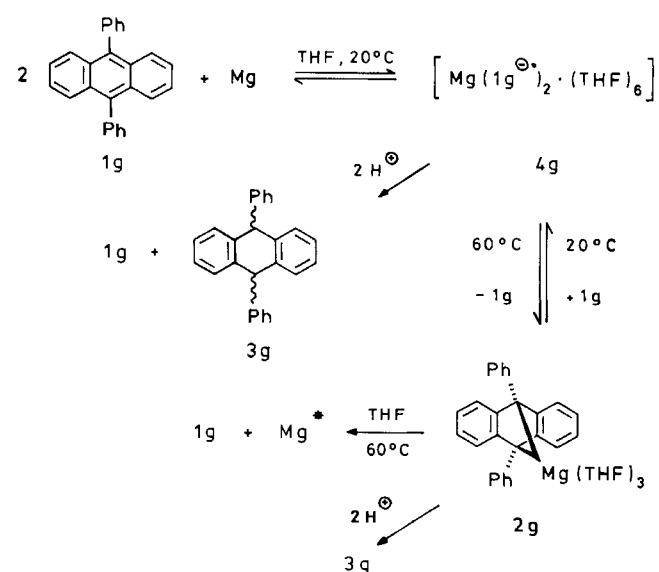


Table 2. Selected IR data of the compounds **2**, **2a–g**, and **4g** ( $\text{cm}^{-1}$ , nujol)

<b>2</b> <sup>11)</sup>	<b>2a</b>	<b>2b</b>	<b>2c</b>	<b>2d</b>	<b>2e</b>	<b>2f</b>	<b>2g</b>	<b>4g</b>
434 m	424 m	439 m	439 s	441 m	443 m	448 m	451 w	
		471 w	496 m			495 w		
	588 m	570 m	577 w	594 w	537 m	558 w	518 m	
		698 w			673 w	572 w	593 m	593 m
						588 s	615 w	609 w
						611 m	632 m	634 w
717 s	721 s	727 s	724 s	720 s	739 s	702 s	708 vs	705 s
756 m	754 m	762 m	754 w	733 m		723 s	746 vs	731 s
	793 m	787 m				739 s	755 s	755 s
817 s	815 s	805 s	790 s	796 s		753 s	773 w	
	852 m		831 w	856 m		795 s		
				875 m		849 m	1046 m	886 w
						1064 m		1011 s
							1068 m	1048 w
								1070 w
1104 w	1112 w		1115 m	1114 w	1127 m	1105 m		
		1140 vw		1143 w	1149 w	1142 m	1151 m	1157 m
							1172 w	
1174 w	1176 m	1172 vw	1172 m	1171 w	1177 w	1174 w		
1201 w	1200 w	1196 w	1200 w			~1200 s		
		1230 m	1229 s					
1250 vs	1250 vs	1246 vs	1251 vs	1238 vs	~1235 vs	~1240 vs	1218 vs	
				1267 s		1292 m	1251 w	
								1304 s
								1328 vs
					1337 m	1353 s		
1364 m	1363 m	1374 s	1358 m	1358 m	~1365 w			
	1404 w		1399 w					
			1425 s	1428 s	1428 s	1425 s		
1437 s	~1445 s	~1435 s	1442 s	1443 m		1440 s	1429 s	
						1488 s	1482 m	1491 m
					1545 w			1508 s
1570 m	1575 m	1558 m	1570 m	1566 m	1565 s	1565 s	1562 s	1562 m
						1592 m	1590 m	1591 s
1024 s	1025 vs	1024 vs	1024 vs	1030 vs	~1022 vs	1031 vs	1017 s	~1020 m
875 s	880 s	875 s	~870 s	~870 s	876 s	876 vs	863 s	~860 m

Table 3. Raman wave numbers of the compounds **2** and **2a–f** ( $\text{cm}^{-1}$ , solid compounds)

<b>2</b> <sup>11)</sup>	<b>2a</b>	<b>2b</b>	<b>2c</b>	<b>2d</b>	<b>2e</b>	<b>2f</b>
347 m		383 s	363 m	363 m	359 m	348 w
		443 m			465 m	420 w
507 s	508 s	493 vs	500 s			500 w
	520 s	575 m	560 vs	540 s	568 s	565 s
			583 w	565, 595 s		595 s
615 s	620 m	620 vs		630 m		633 m
		789 m				
816 m	823 m	810 s	805 w	800 w, 850 w		
1025 m	1033 w	1030 m	1028 w	1025 w	1020 w	1048 w
1204 m	1208 w	1205 m		1200 w		
		1223 m		1240 w		
1328 m	1340 m	1330 s	1338 w	1335 s	1338 w	1347 m
1534 w	1535 vw	1530 m	1540 vw	1525 w	1530 vw	1530 vw

the 9,10 position), which occurs in the region of  $800\text{ cm}^{-1}$  compared with nearly  $900\text{ cm}^{-1}$  in free anthracenes. A strong absorption near  $1250\text{ cm}^{-1}$  (**2a–g**) is another dominant indication of bound anthracenes, but it is remarkable that in **4g** this band is missing, and a strong absorption at  $1328\text{ cm}^{-1}$  appears instead.

The  $^{13}\text{C}$ -NMR spectra of **2a**, **2b** and **2e** (Table 4) show that the anthracene skeleton in these compounds has been preserved. The chemical shifts and the  $^1J_{\text{C,H}}$  coupling constants indicate that the strongest interaction with magnesium takes place at C-9 and C-10. For **2a** and **2b** the changes in the chemical shifts relative to the corresponding chemical shifts of magnesium anthracene (**2**)<sup>6)</sup> are consistent with predictions based on methyl-substituent effects. The C-9 and C-10 signals of **2b** are shifted by 3.6 ppm to higher field by the  $\gamma$ -methyl groups. In the case of **2e**, the introduction of the methyl groups into the C-9 and C-10 positions of the anthracene might be expected to produce a downfield shift of the  $^{13}\text{C}$ -resonance line of these atoms by about 8 ppm relative to the corresponding signal of **2** ( $\delta_{\text{C}} = 57.7$ )<sup>6)</sup>. However, an upfield shift of 3.3 ppm is observed, indicating that the methyl-substituent effect is more than compensated by a stronger Mg–C-9,C-10 bond in **2e** compared with **2**. On the basis of protolysis, similarity of IR, Raman, and  $^{13}\text{C}$ -NMR spectra and the molecular structures of **2**<sup>7)</sup> and **2b**<sup>3)</sup>, it can be concluded that the monomeric structure with the magnesium bound to C-9 and C-10 positions of the anthracene skeleton is also present in **2a** and **2c–g**.

The position and the temperature dependence of the equilibria eq. (2) have been investigated between 0 and  $+60^\circ\text{C}$ . For this purpose the compounds **1a–c** and **1e–g** are dis-

Table 4.  $^{13}\text{C}$ -NMR data for substituted magnesium anthracenes **2a**, **b**, and **e** and magnesium anthracene  $\cdot 3$  THF (**2**)<sup>a)</sup>

Com- pound		C-atoms														
		1	4	5	8	2	3	6	7	9	10	11	12	13	14	CH <sub>3</sub>
<b>2a</b>	$\delta_{\text{C}}$	115.4	113.7	113.8 <sup>b)</sup>	114.0 <sup>b)</sup>	125.9	118.3	117.8 <sup>c)</sup>	118.0 <sup>c)</sup>	56.7 <sup>d)</sup>	57.9 <sup>d)</sup>	146.3 <sup>e)</sup>	142.9	146.3 <sup>e)</sup>	145.9 <sup>e)</sup>	21.4
	$^1J_{\text{CH}}$	149	150 $\pm$ 3	150	150	-	151	154	154	137	136	-	-	-	-	125
<b>2b</b>	$\delta_{\text{C}}$		118.0		114.7		119.5		118.2		54.1		142.6		145.9	20.3
	$^1J_{\text{CH}}$		-		150 $\pm$ 2		151		154 $\pm$ 2		137		-		-	123
<b>2e</b>	$\delta_{\text{C}}$			111.7				118.1			54.4		146.4			16.6
	$^1J_{\text{CH}}$			150 $\pm$ 2				154		-	-		-		121	
<b>2</b> <sup>6)</sup>	$\delta_{\text{C}}$			114.1				118.1			57.7		145.9			
	$^1J_{\text{CH}}$			148.6				153.4			138.0		-			

<sup>a)</sup>  $\delta_{\text{C}}$  ( $\pm 0.1$  ppm) with respect to TMS; 75.5 MHz;  $^1J_{\text{CH}}$  ( $\pm 1$  Hz unless otherwise stated); saturated solutions in [D<sub>8</sub>]THF, 40°C. — <sup>b,c,d,e)</sup> These assignments may be reversed.

solved in THF and treated with a large excess (20:1) of Mg powder at 60°C until the chemical equilibrium has been attained, as judged by gas chromatographic analysis of the **3a–c**, **e–g/1a–c**, **e–g** ratios of the samples taken from the suspension after protolysis. As can be seen in Figure 1, for the substituted anthracenes **1a–c**, **e–g** at 60°C the equilibria are attained after roughly 20–25 h and, compared to **2**<sup>6)</sup>, are strongly shifted toward the starting materials. In accordance with the decomposition of **2g** in THF at 60°C (see above), almost no reaction is observed between Mg and **1g** at this temperature. The temperature in each experiment is then lowered stepwise to 40, 25, and 0°C and maintained for 8 or 16 hours, and the conversion of the reaction is determined again. As shown in Table 5, upon lowering the temperature the equilibria are displaced toward the products, and at 0°C almost quantitative conversions are achieved in most cases. It should be pointed out that for sparingly soluble magnesium anthracenes (**2**, **2a–c**, **2e–g**) the decrease in conversion with increasing temperature (Table 5) should result from both the decrease of the

Table 5. Conversion (%) of substituted anthracenes **1a–c**, **e–g** into substituted magnesium anthracenes **2a–c**, **e–g** with magnesium in THF (eq. 2) as a function of temperature and time<sup>a)</sup>

Temp.	Reaction	<b>2</b>	<b>2b</b>	<b>2c</b>	<b>2e</b>	<b>2f</b>	<b>2g</b>
[°C]	time [h] <sup>b)</sup>						
60	0.5	9	12	17	4	12	-
60	1	14	13	19	4	13	0.5
60	2	16	15	30	6	13	0.6
60	7	19	17	45	6	12	1
60	23	23	20	51	5	11	0.7
40	4	54	58	-	-	80	-
40	8	60	61	96	28	83	6
40	20	-	-	96	32	-	5
25	8	76	-	98	97	-	88
25	16	-	95	99	98	98	88
0	8	85	99	100	99	99	96

<sup>a)</sup> Initial concentration of **1a–c**, **e–g**:  $c = 0.05$  mol/l; Mg/**1a–c**, **e–g** = 20:1. — <sup>b)</sup> Time elapsed from the moment of temperature change.

equilibrium constants and increase of their solubilities at higher temperatures.

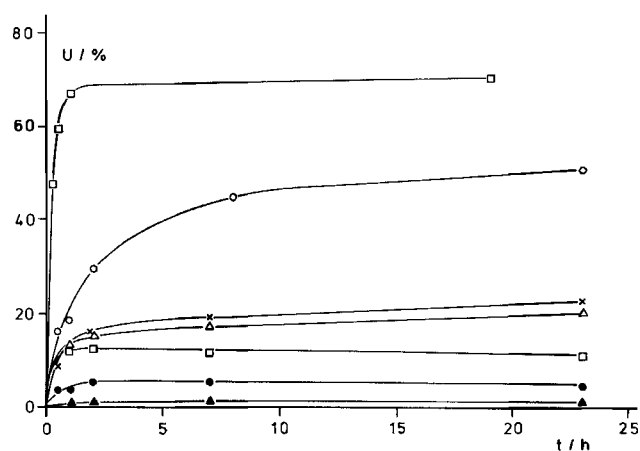
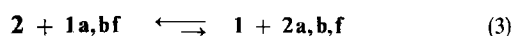


Figure 1. Conversion of anthracenes **1**, **1a–c**, **e–g** with Mg powder into magnesium anthracenes **2**, **2a–c**, **e–g** in THF at 60°C as a function of time (initial concentration of anthracenes 0.05 mol/l; Mg powder/**1**, **1a–c**, **e–g** = 20:1): —□—, **2**<sup>6)</sup>; —○—, **2c**; —×—, **2a**; —△—, **2b**; —■—, **2f**; —●—, **2e**; —▲—, **2g**

As a consequence of the equilibrium shift toward the starting materials at higher temperatures (Table 5), **2e** decomposes when heated to 60°C in a sufficient amount of THF producing **1e** and metallic active magnesium (Mg\*) (cf. ref.<sup>1)</sup>).

In connection with the equilibria between magnesium, anthracenes, and magnesium anthracenes in THF [eqs. (1) and (2)] the experimental observation of the magnesium transfer from magnesium anthracene (**2**) to substituted anthracenes **1a**, **1b**, and **1f** [eq. (3)] is of interest<sup>9,12)</sup>. To demonstrate these exchange processes equimolar mixtures of **2** with each particularly substituted anthracene **1a**, **1b**, and **1f** have been stirred in THF at room temperature for 3 d. Protolysis and GC analysis of the resulting mixtures indicate the conversion of **2** to **2a**, **2b**, and **2f** to the extent of 10, 10 and 15%, respectively.



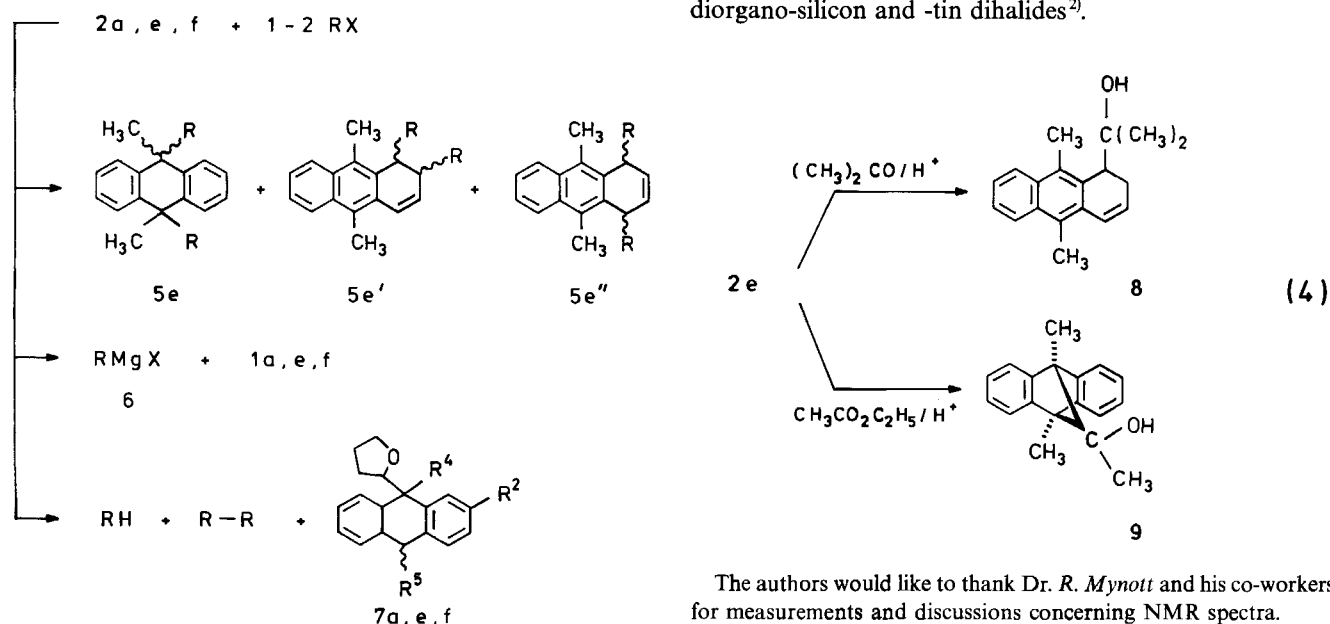
### Reactions of Substituted Magnesium Anthracenes with Organic Halides, Acetone, and Ethyl Acetate

In order to compare the reactivity of substituted magnesium anthracenes toward electrophiles with that of the parent compound **2**, the reactions of substituted magnesium anthracenes with selected organic halides, acetone, and ethyl acetate have been studied<sup>13</sup>.

Magnesium 9,10-dimethylanthracene (**2e**) reacts with ethyl or isopropyl bromide in THF in the same manner as **2**<sup>14</sup> yielding a mixture of **5e–5e''** (Table 6, entries 1, 2) but no Grignard compounds.

While **2** affords the corresponding Grignard compounds in high yields with allyl, propargyl, and benzyl chloride in THF<sup>14</sup>, their yields decrease sharply when the substituted magnesium anthracenes such as **2a,e**, and **f** are used instead of **2** (Table 6, entries 3–6); coupling products, rather than Grignard compounds, are formed with allyl and benzyl chloride, and in the case of propargyl chloride propyne and allene are produced.

Scheme 2



As in the case of **2**<sup>14</sup> the reactions of **2a,e**, and **f** with bromobenzene in THF involve a competition between the formation of Grignard compounds and the H-transfer reaction of the phenyl radical with the solvent, producing benzene and the tetrahydrofuran-yl-substituted dihydroanthracene derivatives **7a,e,f** (Scheme 2). The tendency toward the radical H-transfer reaction in the case of **2a,e**, and **f**, however, is stronger than in the case of **2**<sup>14</sup>, the maximum being observed for **2f** (Table 6, entries 7–9). The use of substituted magnesium anthracenes investigated thus offers no advantage over **2** for the preparation of Grignard compounds.

In the reaction of **2e** with acetone, the tertiary alcohol **8** has been obtained and identified by <sup>1</sup>H-NMR spectroscopy. Apparently because of steric hindrance and in contrast to **2**<sup>2,8</sup>, the attack of the electrophilic acetone takes mainly place at C-1 and not C-9 of **2e**<sup>13</sup>. The reaction of **2e** with ethyl acetate also differs from that of the parent compound **2**<sup>2,8</sup>, since the bicyclic tertiary alcohol **9** is obtained as the only reaction product (84% yield). In the reaction of **2** with ethyl acetate, no intramolecular C–C coupling products have been observed, however, **2** reacts intramolecularly with diorgano-silicon and -tin dihalides<sup>2</sup>.

The authors would like to thank Dr. R. Mynott and his co-workers for measurements and discussions concerning NMR spectra.

Table 6. Reactions of substituted magnesium anthracenes **2a,e,f** with organic halides (RX) in THF at room temperature

Entry	Substituted Mg anthracene [g (mmol)]	RX	Molar ratio RX/2a,e,f	THF [ml]	React. time [h]	Conversion [%]				reaction products				
						5	5'	5''	RMgX	1a,e,f [%]	RH	R-R	other	
1	<b>2e</b> 1.65 (3.7)	EtBr	2.3	60	12	97	33	40	12	–	1	–	–	–
2	<b>2e</b> 4.24 (10.4)	i-PrBr	2.4	100	2	98	28	18	13	–	2	–	–	–
3	<b>2a</b> 2.39 (5.5)	H <sub>2</sub> C=CHCH <sub>2</sub> Cl	1.0	80	27	–	–	–	–	58	–	4	21	–
4	<b>2f</b> 2.25 (4.6)	H <sub>2</sub> C=CHCH <sub>2</sub> Cl	1.0	80	27	–	–	–	–	51	85	7	18	–
5	<b>2e</b> 2.32 (5.7)	HC≡CCH <sub>2</sub> Cl	1.0	50	2	–	–	–	–	48	75	26	1	–
6	<b>2e</b> 2.02 (5.0)	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	1.0	80	3	98	–	–	–	18	77	7	51	–
7	<b>2a</b> 2.23 (5.2)	C <sub>6</sub> H <sub>5</sub> Br	1.0	80	48	–	–	–	–	26	–	49	–	23 (7a)
8	<b>2e</b> 2.20 (5.4)	C <sub>6</sub> H <sub>5</sub> Br	1.0	80	2	95	–	–	–	18	–	62	–	–
9	<b>2f</b> 2.47 (5.0)	C <sub>6</sub> H <sub>5</sub> Br	1.0	100	48	–	–	–	–	4	–	75	–	–

## Experimental

Raman spectra of the solid compounds **2a–f**: rotating sample cell, Coderg-LRT 800 instrument (excitation: krypton line 647.1 nm). — For other instruments used, see previous communication<sup>1)</sup>.

**2a–f and 4g from 1a–g and Mg**: The respective anthracene **1a–g** and Mg chips were suspended in THF, and 0.01 ml of EtBr was added. The suspensions were stirred at room temp. for 4 d, the precipitated orange to brown colored solids were separated from the excess of Mg chips by means of a syphon, filtered, washed three times with a few ml of THF, and dried in vacuo (0.1 mbar). The data on the preparation and composition of the compounds **2a–f** and **4g** are listed in Table 1. The filtrates from the preparation of **2a–f** were used to roughly determine the solubilities of the compounds in THF at room temperature by complexometric titration (0.1 M) of Mg<sup>2+</sup> after hydrolysis.

**Hydrolysis of the Compounds 2a–f and 4g**: An analytically weighed amount (0.1–0.2 g) of the particular compound was suspended in ether and hydrolyzed by the addition of H<sub>2</sub>O and diluted HCl. The organic layer was separated, the aqueous layer extracted with ether, and the combined extracts were dried with Na<sub>2</sub>SO<sub>4</sub>. After addition of 5–10 ml of a standard solution containing weighed amounts (6–7 mg/ml) of *n*-octanol and *n*-hexadecane in toluene, the solutions were analyzed by gas chromatography.

For the measurements of <sup>13</sup>C- (Table 4) and <sup>1</sup>H-NMR spectra, 30–50 mg of a particular compound was stirred in 5 ml of [D<sub>8</sub>]THF for 12 h. The precipitate was allowed to settle and the clear yellow supernatant liquid transferred into the NMR tube using a pipette.

<sup>1</sup>H NMR of **2a** (400 MHz; [D<sub>8</sub>]THF; 25 °C): δ = 6.00 (m; 6,7-H), 5.94 (m; 5,8-H), 5.85 (s; 3,4-H), 5.82 (s; 1-H), 3.45 (s; 9-H), 3.49 (s; 10-H), 1.92 (s; CH<sub>3</sub>). — <sup>1</sup>H NMR of **2b** (200 MHz; [D<sub>8</sub>]THF; 25 °C): δ = 5.97 (s; 5,6,7,8-H), 5.82 (s; 2,3-H), 1.90 (s; CH<sub>3</sub>); the signals of 9,10-H are obscured by the solvent.

**2g from 4g**: 2.00 g (1.8 mmol) of **4g** was suspended in 40 ml of THF and the suspension stirred at 60 °C for 4 h, whereby the originally blue suspension took on a brown color. The suspension was filtered at 60 °C, and the brown precipitate washed with 10 ml of warm THF and dried in vacuo (0.1 mbar). Yield: 0.67 g (65%).

C<sub>26</sub>H<sub>18</sub>Mg · 3 THF (571.1) Calcd. C 79.92 H 7.41 Mg 4.26  
Found C 78.46 H 6.83 Mg 4.99

The hydrolysis of 114.4 mg of **2g**, according to the procedure described above, produced 41.8 mg of THF, 66.9 mg of **3g**, and 0.8 mg of **1g**.

Mg : **3g** : THF = 1.17 : 1.00 : 2.88

The brown filtrate from the preparation of **2g** was allowed to cool down slowly to room temperature, whereby the color of the solution changed from brown to blue, and the deep-blue crystals of **4g** precipitated from the solution. Filtration, washing with THF, and drying in vacuo afforded 0.23 g (12%) of **4g**.

**Thermal Decomposition of 2g in THF**: 0.81 g (1.4 mmol) of **2g** was stirred in 100 ml of THF at 60 °C for 10 h resulting in the formation of a grey suspension of Mg\*. A 1.0-ml sample was taken from the suspension, filtered off, and the precipitate washed with 1 ml of THF. After the addition of 1.0 ml of a standard solution (6 mg of *n*-C<sub>28</sub>H<sub>58</sub>/ml toluene) the resulting solution was analyzed by gas chromatography. Found: 0.33 g of **1g** and 0.093 g of **3g**.

**Determination of the Equilibria of Eq. (2) in the Temperature Range Between 0 and +60 °C**<sup>6)</sup>: In each experiment a double-walled cylindrical 150-ml flask, equipped with a thermocouple and a mag-

netic stirrer, was charged with 2.43 g (0.10 mol) of Mg powder (50 mesh), 75.0 ml of THF, and 0.06 ml of EtBr, and the mixtures were stirred at room temperature for 20 h. The mixtures were then heated and kept at 60 °C by means of a thermostat provided with a circulatory system. With continuous stirring (1100 rpm) 5.0 mmol of each compound **1a–c**, **e–g** dissolved each in 25.0 ml of THF (Mg/**1a–c**, **e–g** = 20:1; initial concentration: *c* = 0.05 mol/l) was at once added to the stirred suspensions, whereby the reaction started immediately, recognizable by the green color of the solution. At defined intervals (Table 5 and Figure 1) 2.0-ml aliquots were taken from the stirred suspension with a pipette and the samples injected into 2.0 ml of a standard solution [toluene/CH<sub>3</sub>OH = 50:1 (vol/vol)] which contained an analytically weighed amount of *n*-hexadecane (ca. 10 g/l) as a reference. The Mg(OMe)<sub>2</sub> formed was left to precipitate and the clear solution analyzed by gas chromatography. With continuous stirring, the mixtures were then successively cooled to 40, 25, and 0 °C and kept at each of these temperatures for 8 or 16 h and analyzed again. The conversion of substituted anthracenes **1a–c**, **e–g** into the corresponding substituted magnesium anthracenes **2a–c**, **e–g** [eq. (2)] was calculated from the chromatographically determined percentages of **3a–c**, **e–g** and **1a–c**, **e–g** in the protolyzed samples according to

$$\text{conversion (\%)} = \frac{3a-c, e-g \text{ \%}}{3a-c, e-g \text{ \%} + 1a-c, e-g \text{ \%} \cdot F} \cdot 100$$

$$F = \frac{\text{molecular weight of } 3a-c, e-g}{\text{molecular weight of } 1a-c, e-g}$$

The results are collected in Table 5 and those achieved at 60 °C graphically represented in Figure 1.

**Proof of the Equilibria of Eq. (3)**: To the suspension of 1.0 g of **2** in 25 ml of THF the equimolar amounts of the respective compound **1a,b,f** were added, and the mixture was stirred at room temp. for 3 d. Thereafter, 0.5-ml samples were removed from the stirred suspension, protolyzed by the addition of 1.0 ml of toluene/CH<sub>3</sub>OH (25:1, vol/vol) and analyzed by gas chromatography. The results are given in Table 7.

Table 7. Proof of the equilibria of eq. (3)

Aromat. hydro-carbon	Reaction products (rel. %)			2/2a,b,f (molar ratio)
	<b>1</b>	DHA <sup>a)</sup>	<b>1a,b,f</b>	
<b>1a</b>	5.1	47.3	42.7	4.6
<b>1b</b>	5.0	50.0	40.4	4.4
<b>1f</b>	6.8	33.6	50.5	8.5

<sup>a)</sup> 9,10-Dihydroanthracene.

**Reaction of 2a,e, and f with Organic Halides in THF**: The reaction and the workup were performed according to the procedure described for the reaction of **2** with organic halides (RX)<sup>14)</sup>, except that RX was added at room temperature. The complete data concerning these experiments are collected in Table 6.

**Reaction of 2e with EtBr** (Table 6, Entry 1): The compounds **5e**, **5e'**, and **5e''** (R = Et, major isomers) were isolated from the "crude product mixture"<sup>14)</sup> (0.89 g) in 85–90% purity by preparative gas chromatography. — <sup>1</sup>H NMR of **5e** (CDCl<sub>3</sub>): δ = 0.16–0.49 (t; CH<sub>2</sub>CH<sub>3</sub>), 1.66 (s; CH<sub>3</sub>), 1.95–2.33 (q; CH<sub>2</sub>), 7.0–7.5 (m; H arom.). — MS of **5e** (70 eV): *m/z* = 249, 235, 206, 191. — <sup>1</sup>H NMR of **5e'** (CDCl<sub>3</sub>): δ = 0.66–1.00 (m; CH<sub>2</sub>CH<sub>3</sub>), 1.16–1.83 (m; CH<sub>2</sub>), 2.16–2.33 (m; 2-H), 2.66 (s; CH<sub>3</sub>), 3.16 (t; 1-H), 6.16 (dd; 3-H), 6.66 (d; 4-H), 7.50 (m; 6,7-H), 8.00 (m; 5,8-H). — MS of **5e'** (70 eV):

$m/z = 264 [M^+]$ , 235, 220, 206, 191. —  $^1\text{H NMR}$  of **5e''** ( $\text{CDCl}_3$ ):  $\delta = 0.2\text{--}0.5$  (t;  $\text{CH}_2\text{CH}_3$ ), 1.1 (m;  $\text{CH}_2$ ), 1.91 (m; 1,4-H), 2.66 (s;  $\text{CH}_3$ ), 3.66 (m; 1-H), 6.33 (dd; 2,3-H), 7.5 (m; 6,7-H), 8.0–8.16 (m; 5,8-H). — MS of **5e''** (70 eV):  $m/z = 264 [M^+]$ , 235, 220, 206, 191.

**Reaction of 2e with iPrBr** (Table 6, Entry 2): The compounds **5e**, **5e'**, and **5e''** ( $\text{R} = \text{iPr}$ ) were isolated from the "crude product mixture"<sup>14)</sup> (2.22 g) in 70–90% purity by preparative gas chromatography. —  $^1\text{H NMR}$  of **5e** ( $\text{CDCl}_3$ ):  $\delta = 0.5$  (d;  $\text{CHCH}_3$ ), 1.83 (s;  $\text{CH}_3$ ), 1.86–2.13 (m; CH), 7.0–7.5 (m; H arom.). — MS of **5e** (70 eV):  $m/z = 249, 207, 191$ . —  $^1\text{H NMR}$  of **5e'** ( $\text{CDCl}_3$ ):  $\delta = 0.75\text{--}1.0$  (d;  $\text{CHCH}_3$ ), 1.0–2.3 (m; 2-H, CH), 2.58 (s;  $\text{CH}_3$ ), 3.0–3.1 (d; 1-H), 5.88–6.1 (m; 3-H), 6.83 (d; 4-H), 7.25–7.33 (m; 6,7-H), 7.88–8.12 (m; 5,8-H). — MS of **5e'** (70 eV):  $m/z = 292 [M^+]$ , 249, 207, 191. —  $^1\text{H NMR}$  of **5e''** ( $\text{CDCl}_3$ ):  $\delta = 0.33\text{--}1.1$  (d;  $\text{CHCH}_3$ ), 1.83 (m; CH), 2.5 (s;  $\text{CH}_3$ ), 3.78 (m; 1,4-H), 5.91 (d; 2,3-H), 7.25–7.33 (m; 6,7-H), 7.85–8.0 (m; 5,8-H). — MS of **5e''** (70 eV):  $m/z = 292 [M^+]$ , 249, 207, 191.

**Reaction of 2e with Acetone (Molar Ratio 1:2.5)**: A solution of 1.63 g (28.9 mmol) of acetone in 30 ml of THF was added dropwise during 0.5 h to a stirred suspension of 4.18 g (10.3 mmol) of **2e** in 70 ml of THF. The mixture was then stirred at room temp. for 14 h, the solvent removed in vacuo, and the residue hydrolyzed by addition of water, dilute HCl, and ether. The ether extracts were neutralized, dried with  $\text{Na}_2\text{SO}_4$ , and the ether was removed in vacuo; yield 2.95 g of an oil having the following composition (GC analysis): **1e** 49.6, **8** 30.5, **3e** 10.2%; mol. mass (%) 264 (2.1), 266 (4.2), 324 (3.2).

**8** was isolated from the oil in 91% purity by preparative gas chromatography. —  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 1.0\text{--}1.30$  (s;  $\text{H}_3\text{C-COH}$ ), 1.66 (s; OH), 2.66 (m; 2-H,  $\text{CH}_3$ ), 3.5 (t; 1-H), 6.0–6.16 (m; 3-H), 7.16 (d; 4-H), 7.5 (m; 6,7-H), 8.0–8.16 (m; 5,8-H). — MS (70 eV):  $m/z = 248, 207, 206, 193, 178, 59, 43$ .

**Reaction of 2e with Ethyl Acetate (Molar Ratio 1:2.4)**: The reaction was performed starting with 4.18 g (10.3 mmol) of **2e**, 2.17 g (24.6 mmol) of ethyl acetate, and 100 ml of THF in the same way as in the reaction of **2e** with acetone (see above). The hydrolytic workup, as described above, gave 2.60 g of a solid having the following composition (GC analysis): **9** 83.8, **3e** 3.1, **1e** 6.1%.

$\text{C}_{18}\text{H}_{18}\text{O}$  (250.3) Calcd. C 86.40 H 7.27 O 6.40  
Found C 86.29 H 7.28 O 6.44

$^1\text{H NMR}$  of crude **9** ( $\text{CDCl}_3$ ):  $\delta = 0.9$  (s;  $\text{H}_3\text{CCOH}$ ), 1.7 (s;  $\text{CH}_3$ ), 6.9–7.2 (m; H arom.). — MS of **9** (70 eV):  $m/z = 250 [M^+]$ , 235, 215, 207, 178, 43.

#### CAS Registry Numbers

**1a**: 613-12-7 / **1b**: 781-92-0 / **1c**: 779-02-2 / **1d**: 605-83-4 / **1e**: 781-43-1 / **1f**: 602-55-1 / **1g**: 1499-10-1 / **2a**: 126615-75-6 / **2b**: 98820-30-5 / **2c**: 110567-70-9 / **2d**: 126615-76-7 / **2e**: 126615-77-8 / **2f**: 126615-78-9 / **2g**: 126615-80-3 / **3a**: 948-67-4 / **3b**: 98800-27-2 / **3c**: 17239-99-5 / **3d**: 605-82-3 / **3e**: 22566-43-4 / **3f**: 13577-28-1 / **4g**: 126615-79-0 / **5** ( $\text{R} = \text{Et}$ ): 126615-66-5 / **5** ( $\text{R} = \text{iPr}$ ): 126615-69-8 / **5'** ( $\text{R} = \text{Et}$ ): 126615-67-6 / **5'** ( $\text{R} = \text{iPr}$ ): 126615-70-1 / **5''** ( $\text{R} = \text{Et}$ ): 126615-68-7 / **5''** ( $\text{R} = \text{iPr}$ ): 126615-71-2 / **7a**: 126615-72-3 / **8**: 126615-73-4 / **9**: 126615-74-5 / **Mg**: 7439-95-4 / **iPrBr**: 75-26-3 /  $\text{H}_2\text{C}=\text{CHCH}_2\text{Cl}$ : 107-05-1 /  $\text{HC}\equiv\text{CCH}_2\text{Cl}$ : 624-65-7 /  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ : 100-44-7 /  $\text{C}_6\text{H}_5\text{Br}$ : 108-86-1 /  $(\text{CH}_3)_2\text{CO}$ : 67-64-1 /  $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$ : 141-78-6

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