

# **Reductive Coupling of CO with Magnesium Anthracene Complexes: Formation of Magnesium Enediolates**

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## **Electronic Supplementary Information (11 pages)**

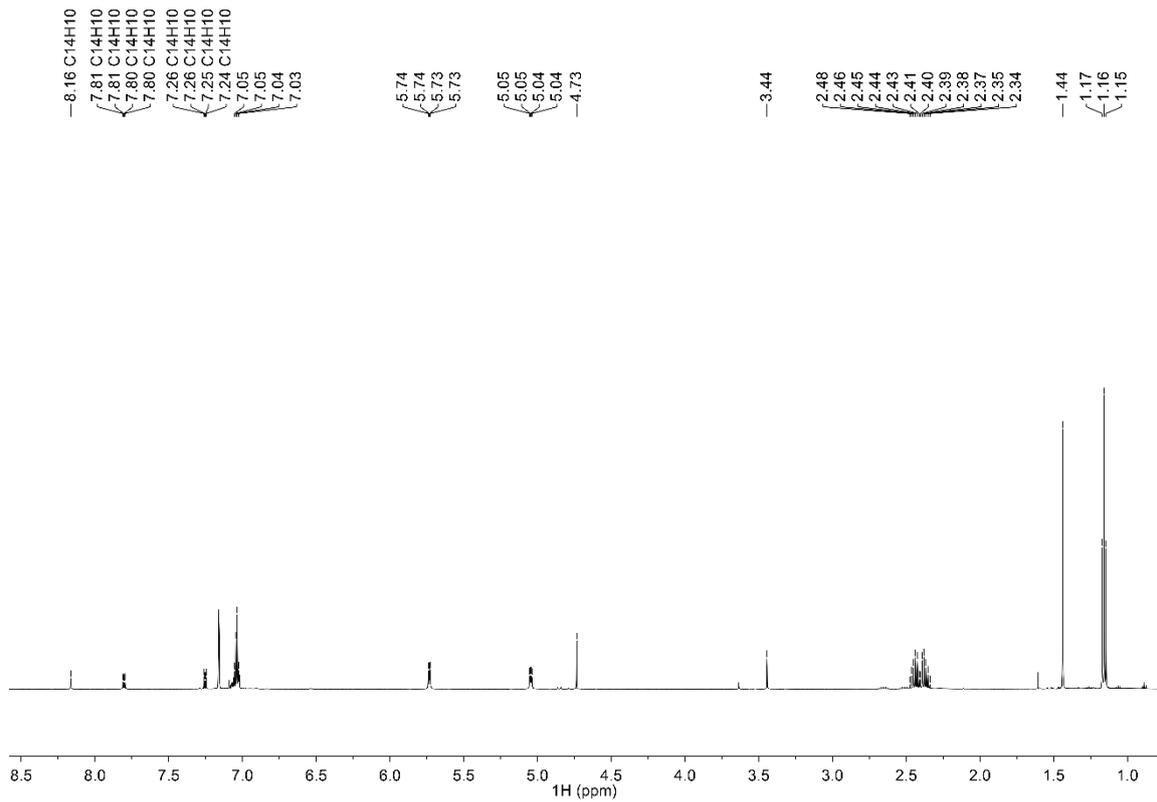
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## 1. Experimental

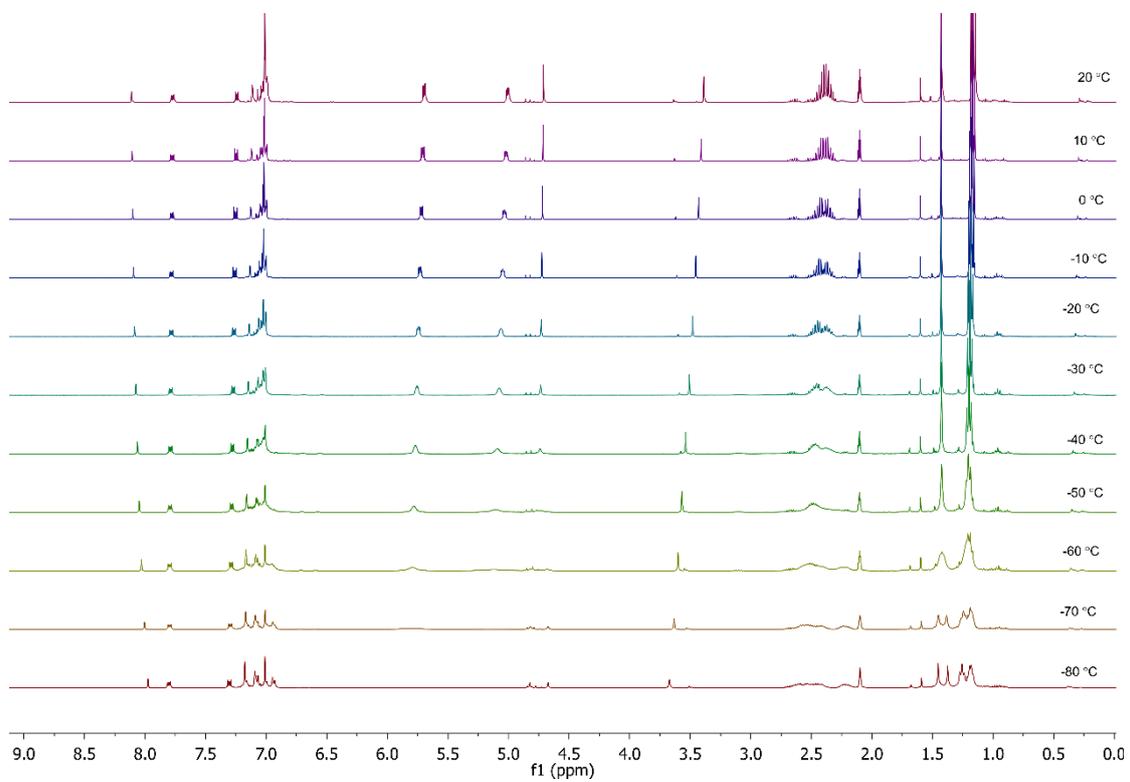
### General considerations.

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Hexane, cyclohexane, toluene and THF were distilled over molten potassium.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on either Bruker AvanceIII 600 or Bruker AvanceIII 400 spectrometers and were referenced to the resonances of the solvent used. FTIR spectra were collected for solid samples or Nujol mulls on an Agilent Cary 630 attenuated total reflectance (ATR) spectrometer. Microanalyses were carried out using a PerkinElmer- 2400 CHNS/O Series II System. Melting points were determined in sealed glass capillaries under dinitrogen, and are uncorrected. The starting materials  $[\{(\text{MesNacnac})\text{Mg}\}_2(\mu\text{-C}_{14}\text{H}_{10})]$ ,<sup>1</sup>  $[\{(\text{DepNacnac})\text{Mg}\}_2]$ <sup>2</sup> and  $[\text{Mg}(\text{THF})_3(\text{C}_{14}\text{H}_{10})]$ <sup>3</sup> were prepared by literature procedures. CO and H<sub>2</sub> were dried over P<sub>2</sub>O<sub>5</sub> prior to use. All other reagents were used as received.

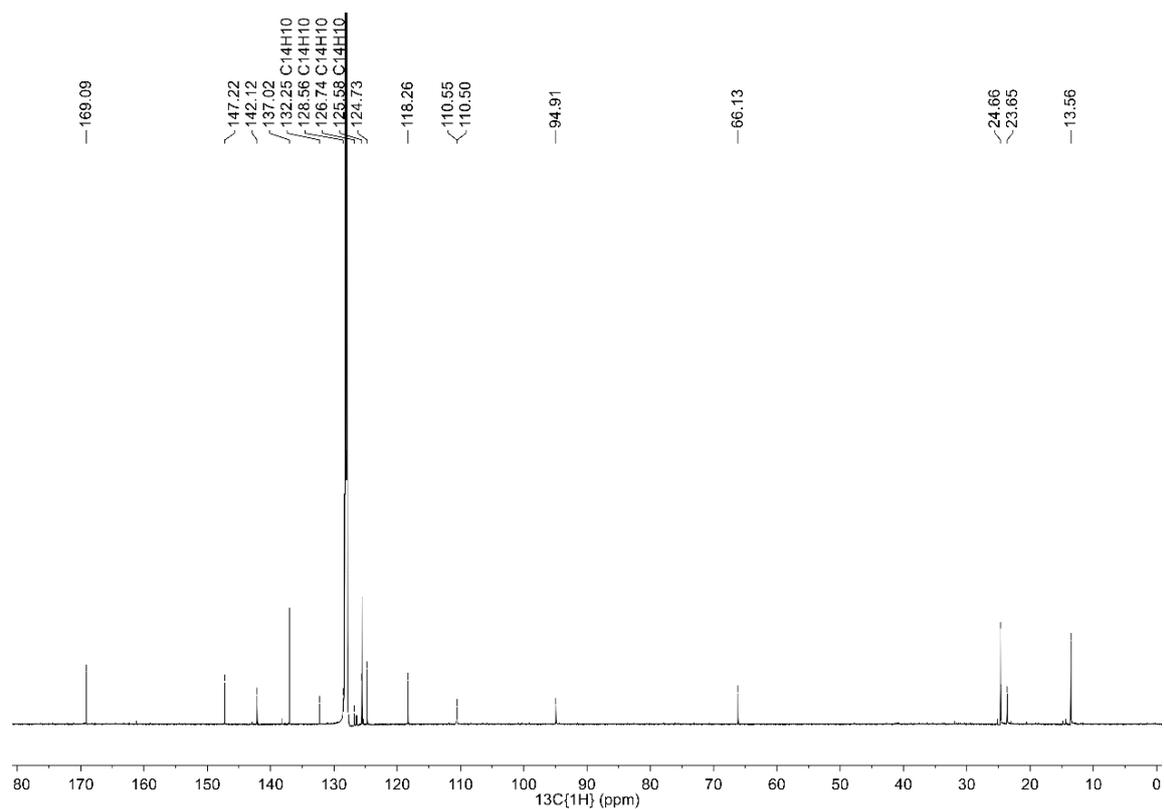
**$[\{(\text{DepNacnac})\text{Mg}\}_2(\mu\text{-C}_{14}\text{H}_{10})]$  2.**  $[\{(\text{DepNacnac})\text{Mg}\}_2]$  (500 mg, 0.648 mmol) and anthracene (140 mg, 0.790 mmol) were dissolved in 20 mL of toluene at room temperature. The reaction mixture was stirred for 1d at room temperature, resulting in a slow colour change of the solution from yellow to dark red. All the volatiles were then removed *in vacuo* and the residue was extracted with *ca.* 30 mL *n*-hexane. The extract was filtered, and the filtrate concentrated to *ca.* 5 mL, then placed at -30 °C for 2 d, after which time dark red blocks of **2** had deposited. These were isolated and the mother liquor was concentrated to *ca.* 4 mL, then placed at -30 °C for 1 d yielding a second crop (462 mg, 74 %). N.B the title compound persistently co-crystallized with a small amount of anthracene. M.p: 191–194°C;  $^1\text{H}$  NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  1.16 (t,  $J$  = 7.6 Hz, 24H, CH<sub>2</sub>CH<sub>3</sub>), 1.44 (s, 12H, NCCCH<sub>3</sub>), 2.41 (m, 16H, CH<sub>2</sub>CH<sub>3</sub>), 3.44 (s, 2H, 9,10-anthracene-CH), 4.73 (s, 2H,  $\beta$ -CH), 5.05 (dd,  $J$  = 5.3, 3.4 Hz, 4H, anthracene-CH), 5.73 (dd,  $J$  = 5.4, 3.3 Hz, 4H, anthracene-CH), 7.02–7.07 (m, 12H, Ar-H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  13.5 (CH<sub>2</sub>CH<sub>3</sub>), 23.6 (NCCCH<sub>3</sub>), 24.6 (CH<sub>2</sub>CH<sub>3</sub>), 66.1 (9,10-anthracene-C), 94.9 ( $\beta$ -CH), 110.5, 110.6, 118.2 (anthracene-C), 124.7, 137.0, 142.1, 147.2 (Ar-C), 169.0 (NCCCH<sub>3</sub>); IR  $\nu/\text{cm}^{-1}$  (Nujol): 1521 (s), 1260 (s), 1208 (m), 1179 (s), 1012 (m), 1008 (s), 935 (m), 852 (s), 761 (s), 726 (s). A reproducible microanalysis could not be obtained as the title compound persistently co-crystallized with a small amount of anthracene, which could not be separated after repeated recrystallisations.



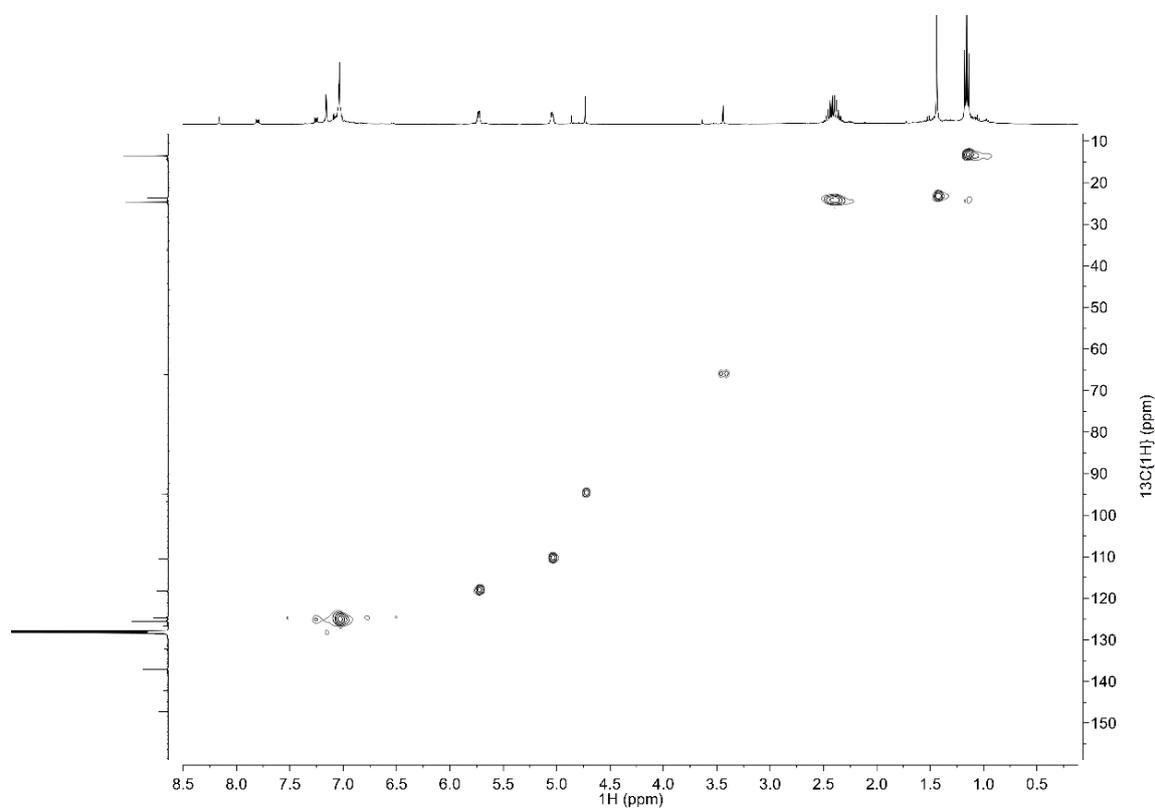
**Figure S1.** <sup>1</sup>H NMR spectrum (600 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>) of **2** (C<sub>14</sub>H<sub>10</sub>: free anthracene).



**Figure S2.** Variable temperature <sup>1</sup>H NMR spectrum (400 MHz, toluene-*d*<sub>8</sub>) of **2**.



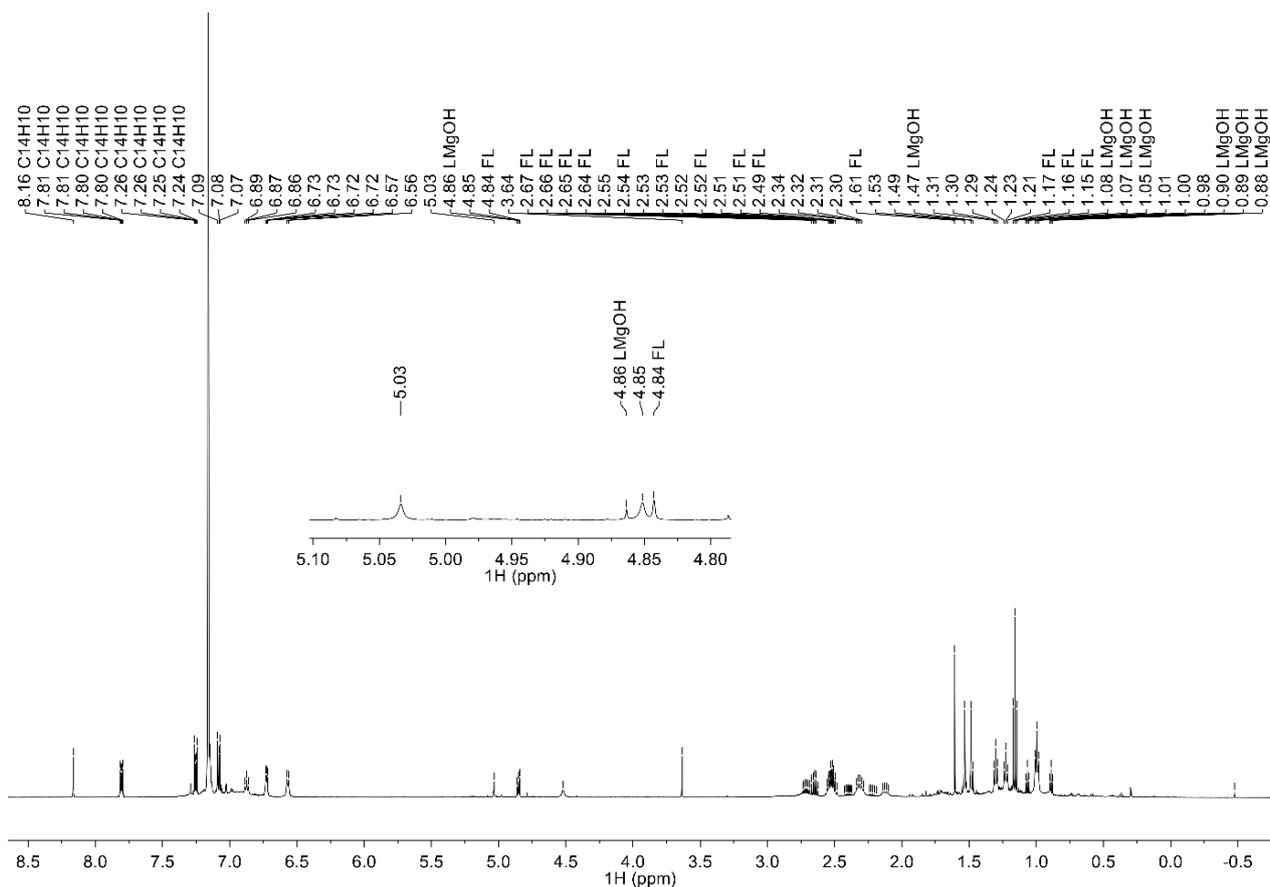
**Figure S3.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (151 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) of **2** ( $\text{C}_{14}\text{H}_{10}$ : free anthracene).



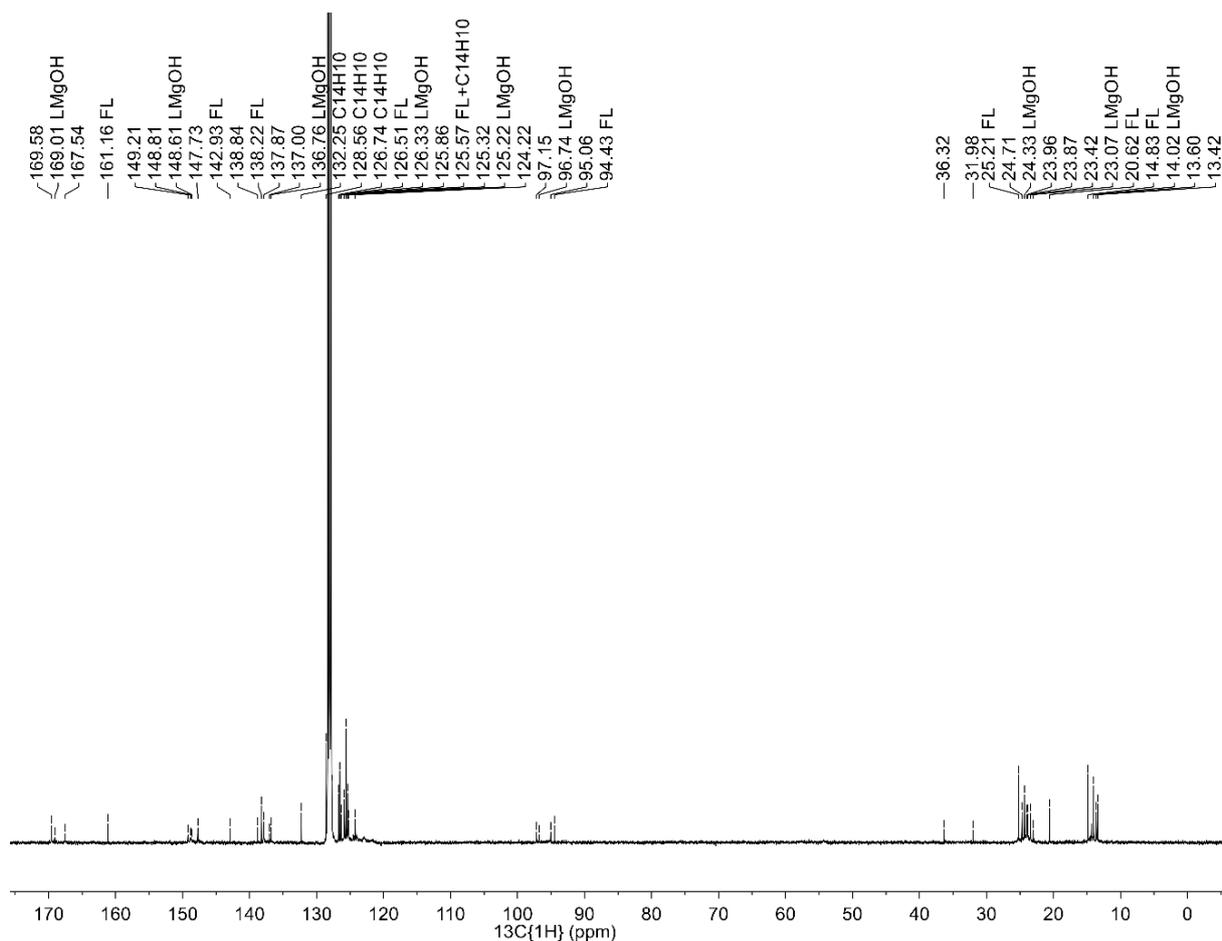
**Figure S4.** HMQC spectrum ( $^1\text{H}$ : 600 MHz;  $^{13}\text{C}$ : 151 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) of **2**.

**[{(MesNacnac)Mg}<sub>4</sub>(O<sub>2</sub>C<sub>16</sub>H<sub>10</sub>)<sub>2</sub>] 3.** Compound **1** (150 mg, 0.165 mmol) was dissolved in 6 mL of toluene at room temperature. The orange-red solution was cooled to -78 °C for 30 minutes, then the reaction vessel placed under vacuum, and backfilled with excess CO gas. The resultant solution was stirred for 1h, warmed to room temperature, and left for 12h, during which time the product precipitated as colourless solid. The orange suspension was then filtered, and the colourless solid washed with hexane, then dried *in vacuo* (81 mg, 52 %). N.B. Once crystallised compound **3** has negligible solubility in THF-*d*<sub>8</sub>, so meaningful solution state spectroscopic data could not be obtained. **Crystallization:** Compound **1** (40 mg, 0.044 mmol) was placed in a long, thin layering Schlenk tube, then dissolved in 3 mL of toluene at room temperature. The orange-red solution was then layered with 5 mL of toluene. High purity CO (*ca.* 1 atm) was then introduced to the head space of the tube, then the tube placed at room temperature for 3 weeks, after which time colourless needles of **3** had deposited. M.p: 221–224 °C; IR  $\nu/\text{cm}^{-1}$  (Nujol): 1660 (m), 1605 (w), 1283 (m), 1230 (m), 1192 (m), 1143 (m), 1071 (w), 1015 (m), 854 (m), 732 (m); anal. calc. for C<sub>124</sub>H<sub>134</sub>Mg<sub>4</sub>N<sub>8</sub>O<sub>4</sub>: C 78.48 %, H 7.12 %, N 5.90 %: found: 78.53 %, H 7.28 %, N 5.85 %.

**[{(DepNacnac)Mg}<sub>4</sub>(O<sub>2</sub>C<sub>16</sub>H<sub>10</sub>)<sub>2</sub>] 4.** Compound **2** (150 mg, 0.155 mmol) was dissolved in 6 mL of toluene at room temperature. The orange-red solution was cooled to -78 °C for 30 minutes, then the reaction vessel placed under vacuum, and backfilled with excess CO gas. The solution was stirred for 1h, warmed to room temperature, and left 12h to yield an orange solution. The mixture was then filtered, and the filtrate concentrated to *ca.* 2 mL *in vacuo* and layered with *ca.* 4 mL of cyclohexane in a long, thin Schlenk flask. This was then placed at room temperature for 5 d, after which time colourless crystals of **4** had deposited. These were isolated and a second crop obtained from the mother liquor (42 mg, 27 %). M.p: 199–201 °C; <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  1.00 (t, *J* = 7.5 Hz, 24H, CH<sub>2</sub>CH<sub>3</sub>), 1.23 (t, *J* = 7.3 Hz, 12H, CH<sub>2</sub>CH<sub>3</sub>), 1.30 (t, *J* = 7.6 Hz, 12H, CH<sub>2</sub>CH<sub>3</sub>), 1.49 (s, 12H, NCCH<sub>3</sub>), 1.53 (s, 12H, NCCH<sub>3</sub>), 2.03 – 2.15 (m, 8H, CH<sub>2</sub>CH<sub>3</sub>), 2.28 – 2.34 (m, 8H, CH<sub>2</sub>CH<sub>3</sub>), 2.50 – 2.55 (m, 8H, CH<sub>2</sub>CH<sub>3</sub>), 2.69 – 2.74 (m, 8H, CH<sub>2</sub>CH<sub>3</sub>), 3.64 (s, 4H, 9,10-anthracene-CH), 4.85 (br. s, 2H,  $\beta$ -CH), 5.03 (br, 2H,  $\beta$ -CH), 6.57 (m, 8H, anthracene-CH), 6.73 (dd, *J* = 5.3, 3.0 Hz, 8H, anthracene-CH), 6.87 (t, *J* = 7.5 Hz, 8H, Ar-H), 7.07 – 7.15 (m, 16H, Ar-H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  13.4, 13.6 (CH<sub>2</sub>CH<sub>3</sub>), 23.4, 23.8 (NCCH<sub>3</sub>), 23.9, 24.7, 31.9, 36.3 (CH<sub>2</sub>CH<sub>3</sub>), 95.0, 97.1 ( $\beta$ -CH), 124.2, 125.3, 125.8 (Ar-C) 137.0 (OHC=CHO), 137.8, 138.8, 147.7, 148.8, 149.2 (Ar-C), 167.5, 169.8 (NCCH<sub>3</sub>); IR  $\nu/\text{cm}^{-1}$  (Nujol): 1673 (w), 1651 (m), 1290 (m), 1245 (m), 1167 (s), 1109 (m), 1073 (m), 1018 (m), 869 (m), 803 (s), 744 (s); A reproducible microanalysis could not be obtained as the title compound persistently co-crystallized with a small amount of <sup>Dep</sup>NacnacH and anthracene, which could not be separated after repeated recrystallisations.



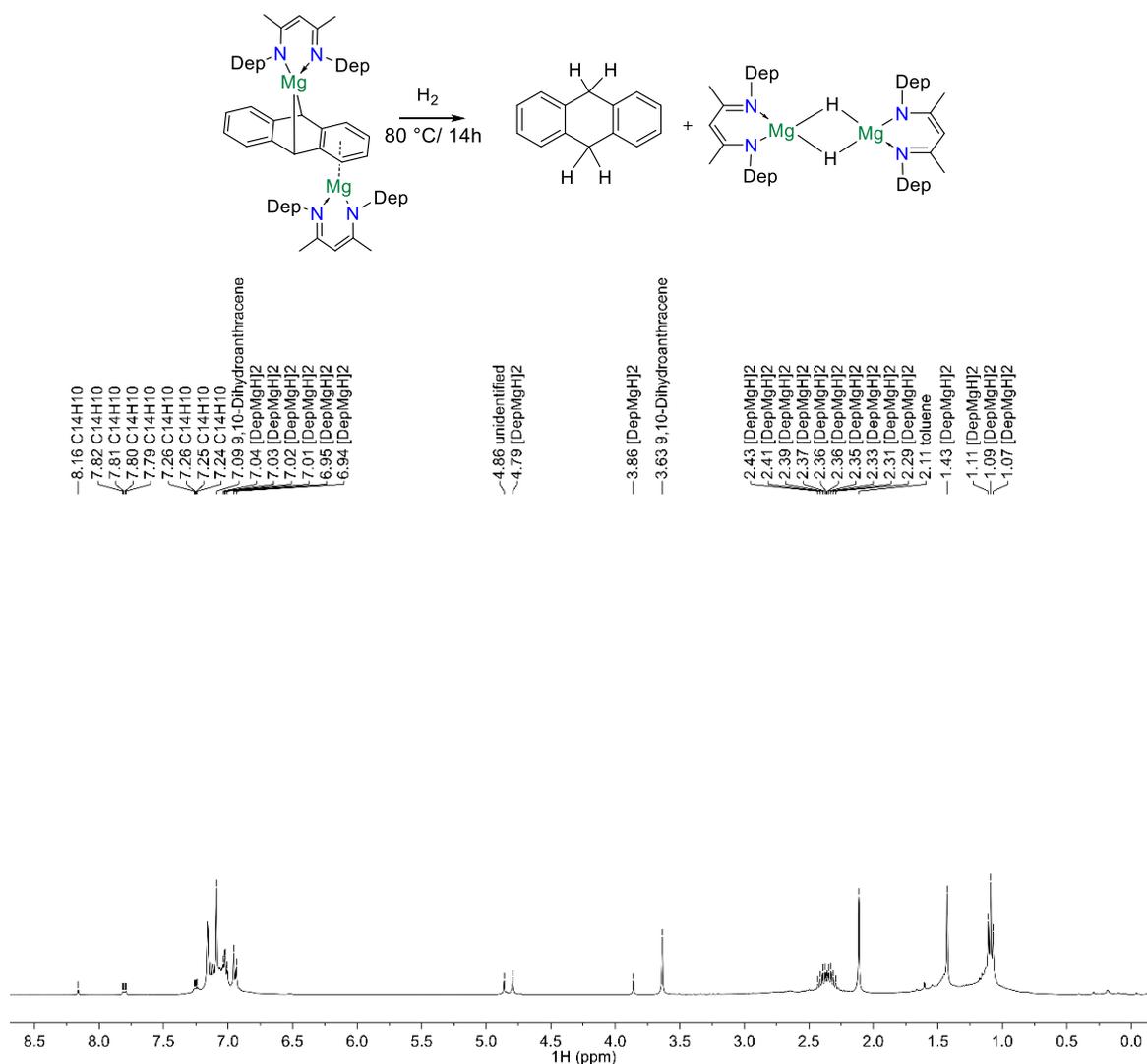
**Figure S5.**  $^1\text{H}$  NMR spectrum (400 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) of the total reaction mixture that gave **4**, showing impurities ( $\text{C}_{14}\text{H}_{10}$ : free anthracene; FL:  $^{\text{Dep}}\text{NacnacH}$ ; LMgOH:  $\{(^{\text{Dep}}\text{Nacnac})\text{Mg}(\text{OH})\}_2$ ). N.B. NMR spectra of the total reaction mixture, before crystallisation, were recorded as compound **4** has poor solubility once crystallised.



**Figure S6.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) of the total reaction mixture that gave **4** showing impurities ( $\text{C}_{14}\text{H}_{10}$ : free anthracene; FL:  $^{\text{Dep}}\text{NacnacH}$ ; LMgOH:  $\{(^{\text{Dep}}\text{Nacnac})\text{Mg}(\text{OH})_2\}$ ).

**[Mg<sub>4</sub>(O<sub>2</sub>C<sub>30</sub>H<sub>20</sub>)(OC<sub>15</sub>H<sub>10</sub>)<sub>2</sub>(THF)<sub>6</sub> 5.** [Mg(THF)<sub>3</sub>(C<sub>14</sub>H<sub>10</sub>)] (150 mg, 0.358 mmol) was suspended in 6 mL of THF at room temperature. The orange suspension was cooled to -78 °C for 30 minutes, then the reaction vessel placed under vacuum, and backfilled with excess CO gas. The solution was stirred for 1h, warmed to room temperature, and left for 1 d to yield an orange-red suspension. The orange-red solution was then filtered off, and the filtrate concentrated to *ca.* 2 mL *in vacuo*. This was placed at -30 °C for 2 d to give a few orange crystals of **5**. N.B. Due to the negligible solubility of **5**, even in THF, meaningful solution state spectroscopic data could not be obtained for the compound. Moreover, the compound could not be separated from similarly insoluble orange [Mg(THF)<sub>3</sub>(C<sub>14</sub>H<sub>10</sub>)], thus precluding the acquisition of a suitable microanalysis for **5**. IR  $\nu/\text{cm}^{-1}$  (Nujol): 1599 (m), 1578 (m), 1554 (w), 1298 (w), 1240 (s), 1217 (w), 1177 (s), 1065 (s), 1032 (m), 1000 (m), 895 (m), 863 (m), 833 (m), 757 (s), 737 (s).

**Reaction of  $\{[(\text{Dep}^{\text{Nacnac}})\text{Mg}]_2(\mu\text{-C}_{14}\text{H}_{10})\}$  **2** with  $\text{H}_2$ .** Compound **2** (100 mg, 0.110 mmol) was dissolved in 3 mL of toluene at room temperature, then the reaction vessel placed under vacuum, and backfilled with excess  $\text{H}_2$  gas. The orange-red solution was stirred for 1h at room temperature, then placed at  $80\text{ }^\circ\text{C}$  for 12h, after which time the solution had turned yellow. The  $^1\text{H}$  NMR spectrum of the reaction mixture showed that **2** was consumed and the new resonances matched those of 9,10-dihydroanthracene and  $\{(\text{Dep}^{\text{Nacnac}})\text{Mg}(\mu\text{-H})\}_2$ ,<sup>4</sup> with near quantitative conversion.



**Figure S7.**  $^1\text{H}$  NMR spectrum (400 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) of the reaction mixture resulting from treating compound **2** with  $\text{H}_2$  gas at  $80\text{ }^\circ\text{C}$ . ([DepMgH]2:  $\{(\text{Dep}^{\text{Nacnac}})\text{Mg}(\mu\text{-H})\}_2$ ).

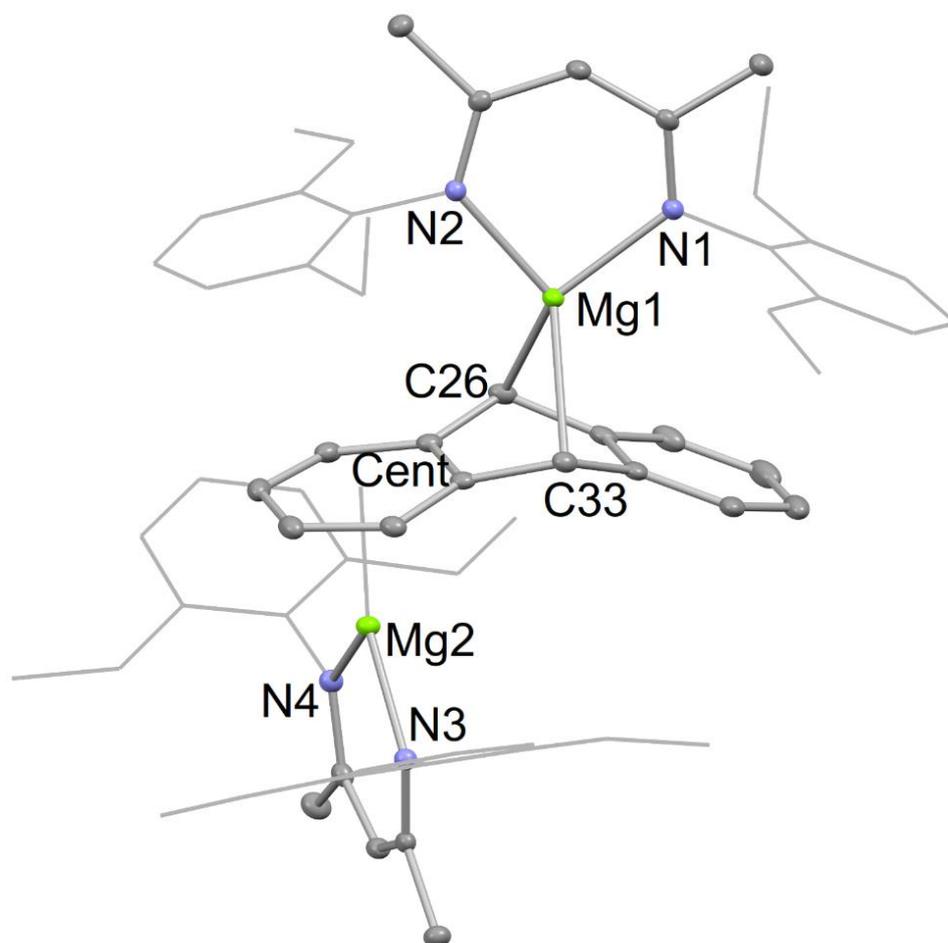
## 2. X-Ray Crystallography

Crystals of compounds suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using a Rigaku Xtalab Synergy Dualflex using a graphite monochromator with Cu  $\text{K}\alpha$  radiation ( $1.54180\text{ \AA}$ ) or the MX2 beamline of the Australian Synchrotron ( $\lambda = 0.71090\text{ \AA}$ ). The software package Blu-Ice<sup>5</sup> was used for synchrotron data

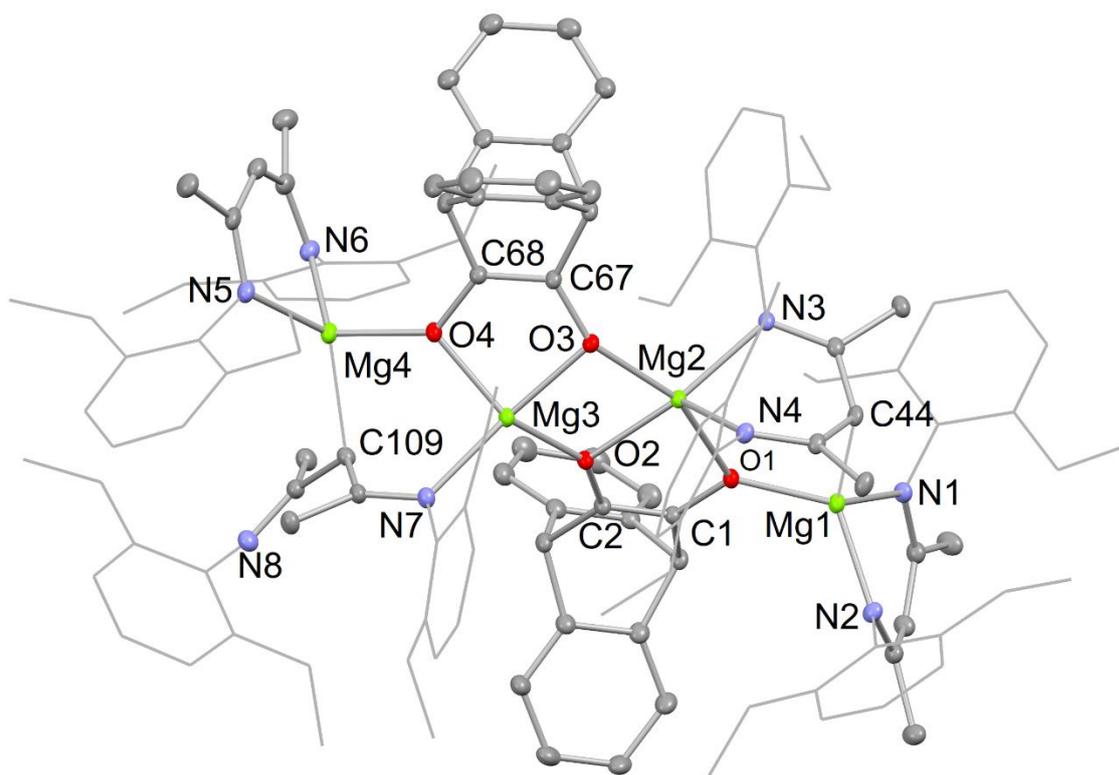
acquisition, while the program XDS<sup>6</sup> was employed for synchrotron data reduction. All structures were solved by direct methods and refined on F<sup>2</sup> by full matrix least squares (SHELX16<sup>7</sup>) using all unique data. Hydrogen atoms are typically included in calculated positions (riding model). Crystal data, details of data collections and refinements for all structures can be found in their CIF files and are summarized in Table S1.

**Table S1.** Crystal data for compounds **2-5**.

	<b>2</b>	<b>3</b> ·(C <sub>7</sub> H <sub>8</sub> ) <sub>3</sub>	<b>4</b> ·(C <sub>6</sub> H <sub>12</sub> ) <sub>3</sub> (C <sub>7</sub> H <sub>8</sub> ) <sub>1.5</sub>	<b>5</b> ·(THF) <sub>2.5</sub>
empirical formula	C <sub>64</sub> H <sub>76</sub> Mg <sub>2</sub> N <sub>4</sub>	C <sub>145</sub> H <sub>160</sub> Mg <sub>4</sub> N <sub>8</sub> O <sub>4</sub>	C <sub>321</sub> H <sub>412</sub> Mg <sub>8</sub> N <sub>16</sub> O <sub>8</sub>	C <sub>94</sub> H <sub>108</sub> Mg <sub>4</sub> O <sub>12.5</sub>
formula weight	949.90	2176.04	4817.12	1535.04
crystal system	monoclinic	triclinic	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
a (Å)	17.5346(2)	13.301(3)	33.1446(7)	21.3094(2)
b (Å)	13.3406(2)	19.539(4)	18.8553(3)	14.5347(2)
c (Å)	23.6839(3)	25.912(5)	23.5022(5)	26.9566(3)
α (°)	90	88.26(3)	90	90
β (°)	98.365(1)	86.73(3)	109.114(2)	100.011(1)
γ (°)	90	83.85(3)	90	90
V (Å <sup>3</sup> )	5481.25(13)	6683(2)	1378.0(5)	8222.03(17)
Z	4	2	2	4
T (K)	123(2)	100(2)	150(2)	123(2)
ρ <sub>calcd</sub> (g·cm <sup>3</sup> )	1.151	1.081	1.153	1.240
μ (mm <sup>-1</sup> )	0.709	0.081	0.680	0.913
F(000)	2048	2332	5220	3280
reflns collected	55099	157055	153548	81366
unique reflns	10161	24085	28946	15238
R <sub>int</sub>	0.0321	0.0880	0.1360	0.0448
R1 [I > 2σ(I)]	0.0395	0.0788	0.0756	0.0467
wR2 (all data)	0.1072	0.2456	0.1832	0.1210
largest peak and hole (e·Å <sup>-3</sup> )	0.62, -0.58	0.46, -0.36	0.33, -0.34	0.46, -0.36
CCDC no.	2097136	2097137	2097139	2097138



**Figure S8.** Molecular structure of **2** (20% ellipsoids; Dep substituents shown as wire frame for clarity; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Mg(1)-N(2) 2.0452(12), Mg(1)-N(1) 2.0455(11), Mg(1)-C(26) 2.3095(14), Mg(1)-C(33) 2.3322(13), Mg(2)-N(4) 2.0233(12), Mg(2)-N(3) 2.0272(11), Mg(2)-cent. 2.079 (10), N(2)-Mg(1)-N(1) 92.60(5), C(26)-Mg(1)-C(33) 71.78(5), N(4)-Mg(2)-N(3) 93.21(5).



**Figure S9.** Molecular structure of **4** (20% ellipsoids; Dep substituents shown as wire frame for clarity; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Mg(1)-O(1) 1.9360(19), Mg(1)-N(2) 2.080(3), Mg(1)-N(1) 2.083(2), Mg(2)-O(3) 2.0378(19), Mg(2)-O(2) 2.0716(19), Mg(2)-N(4) 2.115(2), Mg(2)-N(3) 2.143(2), Mg(2)-O(1) 2.2160(19), Mg(3)-O(2) 1.9241(19), Mg(3)-O(4) 2.008(2), Mg(3)-O(3) 2.036(2), Mg(3)-N(7) 2.128(2), Mg(4)-O(4) 1.957(2), Mg(4)-N(6) 2.056(3), Mg(4)-N(5) 2.066(3), Mg(4)-C(109) 2.333(3), O(1)-Mg(1)-C(44) 88.39(9), O(2)-Mg(2)-O(1) 79.88(7), O(4)-Mg(3)-O(3) 88.22(8), O(4)-Mg(4)-C(109) 88.20(9).

### 3. References

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