## Assessing the reactivity of sodium alkyl-magnesiates towards Quinoxaline: single electron transfer (SET) *vs* nucleophilic alkylation processes

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**General Remarks.** All reactions were performed under a protective argon atmosphere using standard Schlenk techniques. Hexane and THF were dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. [Na(THF)<sub>6</sub>]<sup>+</sup>[{Ph<sub>2</sub>Si(NAr\*)<sub>2</sub>}Mg(Bu)(THF)}]<sup>-</sup> and [NaMg(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>] were synthesized as described in the literature.<sup>1, 2</sup> Quinoxaline and 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) were purchased from Sigma Aldrich Chemicals and used as received.

All NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer, operating at 400.13 MHz for <sup>1</sup>H and 100.62 MHz for <sup>13</sup>C. All <sup>13</sup>C NMR spectra were proton decoupled. The NMR assignments were performed, in some cases, with the help <sup>13</sup>C{<sup>1</sup>H}-DEPT135, <sup>1</sup>H, <sup>1</sup>H-COSY, <sup>1</sup>H, <sup>13</sup>C-HSQC and <sup>1</sup>H, <sup>13</sup>C-HMBC experiments. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} chemical shifts are expressed in parts per million ( $\delta$ , ppm) and referenced to residual solvent peaks.

Magnetic susceptibility data for polycrystalline samples of the complex **2** were collected in the temperature range 2-300 K in an applied magnetic field of 1 T with a SQUID magnetometer (MPMS-7, Quantum Design). Experimental susceptibility data were corrected for the underlying diamagnetism using Pascal's constants. The temperature dependent magnetic contribution of the glassholder was experimentally determined and substracted from the measured susceptibility data.

EPR spectra of **2** in THF solutions (1 mmol/l) at room temperature and liquid N<sub>2</sub> temperature were collected on a Magnettech MiniScope MS300 benchtop cw EPR spectrometer (X-band, ~9.4 GHz microwave frequency). EPR simulations were performed using EasySpin 3.1.7.<sup>3</sup>

Elemental analyses were performed using a Perkin Elmer 2400 elemental analyzer.

Crystallographic data were measured at 123(2) K on Oxford Diffraction diffractometers<sup>4</sup> with Mo K $\alpha(\lambda = 0.71073 \text{ Å})$  or Cu K $\alpha(\lambda = 1.5418 \text{ Å})$  radiation, and on a Crystal Logic diffractometer with a Rigaku Saturn 724+ detector using synchrotron radiation ( $\lambda = 0.6889 \text{ Å}$ ) at beamline I19 of Diamond Light Source. Structures were refined to convergence on  $F^2$  for all independent reflections by the full-matrix least squares method using SHELXL-2014/7.<sup>5</sup> Selected crystallographic and refinement details are given in Table S1 (see the Supporting Information for details).

	-	-	-	
Energi i d	2	3	4	/b
formula	$C_{144}H_{212}Mg_2N_8Na_2O_{14}Si_2$	$C_{69}H_{110}MgN_3NaO_6Si$	$C_{59.8}H_{91.6}MgN_3NaO_{4.7}Si$	$C_{12}H_{20}N_2Si$
Molecular Weight	2429.98	1152.98	1003.15	220.39
Temperature (K)	120(2) K	150(2)	123(2) K	123(2)
Wavelength (Å)	synchrotron, 0.6889 Å	0.71073	0.71073	1.5418
Crystal system	monoclinic	orthorhombic	orthorhombic	Orthorhombic
Space group	P2 <sub>1</sub> /n	Pbcm	Pna2 <sub>1</sub>	Pca21
a (Å)	12.601(7)	13.3693(4)	24.4651(11)	10.1849(6)
b (Å)	15.449(8)	20.9222(6)	10.8289(4)	15.8617(13)
c (Å)	34.612(19)	24.8200(8)	22.8846(10)	8.2200(5)
α, β, γ (°)	α=γ= 90; β=92.851(8)	α=β=γ=90	a=b=g=90	$\alpha = \beta = \gamma = 90$
Cell volume (Å <sup>3</sup> )	6730(6)	6942.5(4)	6062.8(4)	1327.94(16)
Z	2	4	4	4
ρcalc (g.cm- 3)	1.199	1.103	1.099	1.102
μ (mm <sup>-1</sup> )	0.072	0.098	0.102	1.328
F (000)	2636	2520	2184	480
20 max(°)	42.6	53.4	56	146.19
	-8≤h≤13	-15≤h≤16	-32≤h≤23	-12≤h≤12
Index ranges	-15≤k≤15	-25≤k≤21	-13≤k≤12	-19≤ <i>k</i> ≤19
	-36≤/≤36	-31≤/≤26	- <b>2</b> 9≤/≤30	-7≤ <b>/</b> ≤10
Reflections collected	29380	18830	21243	7852
Reflections unique	8121	6943	11240	2398
Reflections obs.	3861	5114	8326	1991
R <sub>int</sub>	0.1625	0.0351	0.0416	0.0356
No. Parameters	1061	514	684	147
Goodnes-of- fit-on F <sup>2</sup> (GOF)	1.027	1.040	1.033	1.078
Final <i>R</i> indices [ <i>I</i> >2σ( <i>I</i> )]	0.0973	0.0672	0.0670	0.0524
R indices (all data)	0.3319	0.1919	0.1677	0.1369
Largest diff. peak and hole (e Å <sup>-3</sup> )	0.45 and -0.49	0.48 and –0.37	0.41 and -0.23	0.39 and - 0.19

Table S1. Selected crystallographic and refinement parameters.

Synthesis of  $[Na(THF)_6]^+{}_2[{Ph_2Si(NAr*_2)}_2Mg_2(Qx^*)_2]^{2-}$  (2). To a solution of 1 (1.14 g, 1 mmol) in 5 ml THF quinoxaline (0.13 g, 1 mmol) was added. The resulting yellow solution was stirred for one hour changing colour from yellow to green and finally blue. Hexane was added (3 ml) and the solution cooled at -30°C for twenty-four hours, depositing a batch of blue crystals (yield 0.67 g, 55%). Anal Calcd for C<sub>140</sub>H<sub>204</sub>Mg<sub>2</sub>N<sub>8</sub>Na<sub>2</sub>O<sub>13</sub>Si<sub>2</sub>: C, 71.31; H, 8.72; N, 4.75. Found: C, 70.26, H, 7.80; N, 5.38. Compound 2 co-crystallizes with one molecule of THF.



<sup>1</sup>H NMR ([D]<sub>8</sub>-THF, 298K) δ7.35 [m, 8H, CH, Ph], 6.90 [m, 12H, CH, Ph], 6.70 [m, 8H, CH, Ar\*], 6.40 [t, J = 7.4 Hz, 4H, CH, Ar\*], 5.89 [m, 4H, Hc, qunioxalyl], 5.35 [m, 8H, Ha+Hb, quinoxalyl], 4.16 [m, 4H, CH, <sup>i</sup>Pr, Ar\*], 4.02 [m, 4H, CH, <sup>i</sup>Pr, Ar\*], 3.62 [m, 44H, OCH<sub>2</sub>, THF], 1.77 [m, 44H, CH<sub>2</sub>, THF], 0.93 [m, 24H, CH<sub>3</sub>, <sup>i</sup>Pr, Ar\*], 0.76 [m, 12H, CH<sub>3</sub>, <sup>i</sup>Pr, Ar\*], 0.55 [m, 12H, CH<sub>3</sub>, <sup>i</sup>Pr, Ar\*], 0.31 [m, 12H, CH<sub>3</sub>, <sup>i</sup>Pr, Ar\*]. <sup>13</sup>C{<sup>1</sup>H} NMR ([D]<sub>8</sub>THF, 298K) δ154.48, 145.04, [C<sub>quarternary</sub>, Ar\*], 146.97 [C<sub>quarternary</sub>, quinoxalyl], 136.59 [CH, Ph], 136.25, 136.15 [C<sub>quaternary</sub>, Ph], 131.58 [CH<sub>α</sub>, quinoxalyl], 126.07 [CH+CHc, Ph+quinoxalyl], 123.78 [CH<sub>b</sub>, quinoxalyl], 122.56, 122.13, 116.05 [CH, Ar\*], 68.23 [OCH<sub>2</sub>, THF], 28.09, 28.02 [CH, <sup>i</sup>Pr, Ar\*], 26.39 [CH<sub>2</sub>, THF], [CH<sub>3</sub>, <sup>i</sup>Pr, Ar\*] overlap with signals of deuterated THF.

**Synthesis of [Na(THF)\_6]^+[{Ph\_2Si(NAr\*\_2)}Mg(TMP)]^- (3)**. To a suspension of compound **1** (1.14 g, 1 mmol) in 10 ml of hexane TMP(H) (0.17 ml, 1 mmol) was added. The resulting suspension was allowed to stir for one hour, then 4ml of THF were introduced. Gentle heating of the mixture afforded a solution which upon cooling at -30°C during two days yielded colourless crystals identified as compound **3** (1.62 g, 70%). Anal Calcd for C<sub>69</sub>H<sub>110</sub>MgN<sub>3</sub>NaO<sub>6</sub>Si: C, 71.88; H, 9.62; N, 3.64. Found: C, 71.51, H, 9.17; N, 3.92.

<sup>1</sup>H NMR ( $C_6D_6$ , 298K)  $\delta$ 7.73 [d, J = 7.8 Hz, 4H, CH, Ph], 7.16 [m, 4H, CH, Ar\*], 7.05 [m, 6H, CH, Ph], 6.70 [t, 2H, CH, Ar\*], 4.40 [m, 4H, CH, <sup>i</sup>Pr, Ar\*], 3.32 [m, 24H, OCH<sub>2</sub>, THF], 1.83 [m, 2H, CH<sub>2</sub>,  $\gamma$ -TMP], 1.43 [bs, 4H +12H, , CH<sub>2</sub>,  $\beta$ -TMP; CH<sub>3</sub>, TMP], 1.33 [m, 24H, CH<sub>2</sub>, THF], 1.23 [d, J = 7.2 Hz, 24H, CH<sub>3</sub>, <sup>i</sup>Pr, Ar\*]. <sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_6$ , 298K)  $\delta$  152.33, 145.71, 144.06 [ $C_{quarternary}$ , Ph + Ar\*], 135.85 [CH, Ph], 126.98 [CH, Ar\*], 126.60 [CH, Ph], 122.89 [CH, Ar\*], 116.50 [CH, Ar\*], 68.87 [OCH<sub>2</sub>, THF], 51.37 [ $C_{\alpha}$ , TMP], 40.23 [ $C_{\beta}$ , TMP], 35.87 [CH<sub>3</sub>, TMP], 28.04 [CH, iPr, Ar\*], 25.41 [CH<sub>3</sub>, iPr, Ar\*], 25.07 [CH<sub>2</sub>, THF], 20.11 [ $C\gamma$ , TMP].

Synthesis of  $[(Ph_2Si(NAr^*)_2)Mg(TEMPO^-)Na(THF)_3]$  (4). Tempo (0.16 g, 1 mmol) was added to a solution of 1 (1.14 g, 1 mmol) in 5 ml of THF. The yellow solution allowed stirring for one hour, and then hexane (4 ml) was introduced. The Schlenk tube was transferred to the freezer at -30°C. After 24h a crop of colourless crystals of compound 4 were isolated (0.41 g, 41%). Anal Calcd for C<sub>61</sub>H<sub>94</sub>MgN<sub>3</sub>NaO<sub>5</sub>Si: C, 71.49; H, 9.25; N, 4.10. Found: C, 72.04, H, 9.66; N, 3.39. Compound 4 co-crystallizes with one molecule of THF.

<sup>1</sup>H NMR ([D]<sub>8</sub>THF, 298K) δ7.24 [m, 4H, CH, Ph], 6.92 [m, 6H, CH, Ph], 6.68 [d, *J* = 7.6 Hz, 4H, CH, Ar\*], 6.40 [t, *J* = 7.6 Hz, 2H, CH, Ar\*], 4.03 [m, 4H, CH, <sup>i</sup>Pr, Ar\*], 3.61 [m, 16H, OCH<sub>2</sub>, THF], 1.77 [m, 16H, CH<sub>2</sub>, THF], 1.60 [bs, 1H+2H,  $\gamma$ -CH<sub>2</sub>+ $\beta$ -CH<sub>2</sub>, TEMPO], 1.52 [bs, 2H,  $\beta$ -CH<sub>2</sub>, TEMPO], 1.34 [bs, 1H,  $\gamma$ -CH<sub>2</sub>, TEMPO], 1.05, 0.97 [m, 6H+6H, CH<sub>3</sub>, TEMPO], 0.74 [bs, 24H, CH<sub>3</sub>, <sup>i</sup>Pr, Ar\*]. <sup>13</sup>C{1H} NMR ([D]<sub>8</sub>THF, 298K) δ153.71, 148.49, 144.66 [C<sub>quarternary</sub>, Ph, Ar\*], 136.17 [CH, Ph], 126.37 [CH, Ph], 126.23 [CH, Ph], 122.20 [CH, Ar\*], 116.32 [CH, Ar\*], 68.21 [OCH<sub>2</sub>, THF], 59.57 [C<sub>α</sub>, TEMPO], 41.06 [C<sub>β</sub>, TEMPO], 34.83 [CH<sub>3</sub>, TEMPO], 28.18 [CH, <sup>i</sup>Pr, Ar\*], 26.36 [CH<sub>2</sub>, THF], [CH<sub>3</sub>, <sup>i</sup>Pr, Ar\*] overlap with signals of deuterated THF, 19.37 [CH<sub>3</sub>, TEMPO], 18.45 [C<sub>γ</sub>, TEMPO].

## Reaction of [NaMg(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>] (5) with quinoxaline

a) Reaction in Young tap NMR tube

 $[NaMg(CH_2SiMe_3)_3]$  (0.04 g, 0.13 mmol) and quinoxaline (0.017g, 0.13mmol) were weighed out in a Youngs tap NMR tube and  $[D_8]THF$  was added to form an orange solution containing compound  $[(THF)_xNa\{C_8H_6N_2(CH_2SiMe_3)\}Mg(CH_2SiMe_3)_2]$  **6** as the only organometallic product. The solution was then characterized by NMR spectroscopy (Fig S9-S15). Attempts to isolate compound **6** led to formation of an orange oil.



<sup>1</sup>H NMR ([D]<sub>8</sub>THF, 298K)  $\delta$  6.89 [d, J= 8.4 Hz, 1H, CH, C<sub>8</sub>H<sub>6</sub>N<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)], 6.75 [m, 2H, CH + N=CH, C<sub>8</sub>H<sub>6</sub>N<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)] 6.58 [t, J = 8.4 Hz, 1H, CH, C<sub>8</sub>H<sub>6</sub>N<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)], 5.94 [t, J = 8.4 Hz, 1H, CH, C<sub>8</sub>H<sub>6</sub>N<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)], 4.35 [m, 1H, N-CHCH<sub>2</sub>SiMe<sub>3</sub>], 1.00, 0.37 [m, 1H + 1H, CH<sub>2</sub>SiMe<sub>3</sub>], 0.03 [s, 9H, CH<sub>2</sub>SiMe<sub>3</sub>], -0.13 [s, 18H, MgCH<sub>2</sub>SiMe<sub>3</sub>], -1.73, -1.75 [s, 2H + 2H, MgCH<sub>2</sub>SiMe<sub>3</sub>]. <sup>13</sup>C {<sup>1</sup>H} NMR ([D<sub>8</sub>]THF, 298K)  $\delta$ 151.19, 134.42 [C<sub>quarternary</sub>, C<sub>8</sub>H<sub>6</sub>N<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)], 146.39 [N=CH], 126.84, 125.84, 121.14, 108.70 [CH, C<sub>8</sub>H<sub>6</sub>N<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)], 51.23 [NCHR], 22.42 [NCH CH<sub>2</sub>SiMe<sub>3</sub>], 5.22 [MgCH<sub>2</sub>SiMe<sub>3</sub>], 0.20 [NCHCH<sub>2</sub>SiMe<sub>3</sub>], -5.71 [MgCH<sub>2</sub>SiMe<sub>3</sub>].

b) Hydrolysis studies of [(THF)<sub>x</sub>Na{C<sub>8</sub>H<sub>6</sub>N<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)}Mg(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>] (6)

To a pale yellow solution of NaMgR<sub>3</sub> (0.31 g, 1mmol) in THF (5 mL) was added quinoxaline (0.13g, 1mmol) dissolved in THF (5 mL). The resulting orange solution was stirred for 1h before being quenched with a saturated aq NH<sub>4</sub>Cl solution (5 mL). The product was extracted with dichloromethane (3 x 5 mL) and the combined organic phases dried (MgSO<sub>4</sub>), filtered and concentrated under reduced pressure. Yield (**7a** 46%, **7b** 47%)<sup>a</sup> was determined by integration of the products resonances relative to the resonance of ferrocene (10%) as internal standard in the <sup>1</sup>H NMR spectrum (Figure S16-S19). Single crystals of compound **7b** were grown by slow evaporation of a dichloromethane solution containing a mixture of compounds **7a** and **7b**.



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 298K) of **7a**  $\delta$ 8.59 [s, 1H,  $H_a$ ], 8.05, 7.99 [d, J = 8 Hz, 1H + 1H,  $H_b$  +  $H_e$ ], 7.71, 7.65 (t, J = 8 Hz, 1H + 1H,  $H_c$ + $H_d$ ) 2.60 (s, 2H,  $CH_2$ SiMe<sub>3</sub>), 0.10 (s, 9H,  $CH_2$ Si $Me_3$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298K)  $\delta$ 158.15 ( $C_{quaternary}$ , NCCH<sub>2</sub>SiMe<sub>3</sub>), 146.65 (CH, CH<sub>a</sub>), 143.27, 141.11 ( $C_{quaternary}$ , NCCH), 130.74, 130.02, 129.36, 128.98 (CH<sub>b</sub>-CH<sub>e</sub>), 29.76 (CH<sub>2</sub>, CH<sub>2</sub>SiMe<sub>3</sub>), 0.27 (CH<sub>3</sub>, CH<sub>2</sub>SiMe<sub>3</sub>).

<sup>&</sup>lt;sup>a</sup> Note that maximum yield for **7a** and **7b** is 50%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 298K) of **7b**  $\delta$  6.6, 6.5 [m, 2H + 2H,  $H_d$ - $H_g$ ], 3.51 (m, 1H,  $H_a$ ), 3.2 (bs, 2H, NH) 3.33 (d, J = 10.8 Hz, 1H,  $H_c$ ), 3.03 (m, 1H,  $H_b$ ) 0.83 (d, J = 6.8 Hz, 2H,  $CH_2$ SiMe<sub>3</sub>), 0.11 (s, 9H, CH<sub>2</sub>SiMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR ([D]<sub>8</sub>THF, 298K)  $\delta$ 134.42, 134.09 (C<sub>quaternary</sub>, NCCH), 119.67, 119.57, 115.57, 115.30 (CH<sub>d</sub>-CH<sub>g</sub>), 50.05 (CH<sub>b</sub>+CH<sub>c</sub>), 48.64 (CH<sub>a</sub>), 23.86 (CH<sub>2</sub>, CH<sub>2</sub>SiMe<sub>3</sub>), -0.62 (CH<sub>3</sub>, CH<sub>2</sub>SiMe<sub>3</sub>).





Fig S2.(a) Structure of the anion of **2** with displacement ellipsoids at the 30%; (b) Chemdraw representation of **2**; (c) Space filling model for solid state structure of compound **2**.



Fig S5. <sup>1</sup>H NMR spectrum of  $[Na(THF)_6]^+[{Ph_2Si(NAr_2)}Mg(TMP)]^-$  (3) in  $[D_8]THF$  at 298K.



Fig S3. <sup>1</sup>H NMR spectrum of  $[Na(THF)_6]^+_2[{Ph_2Si(NAr^*_2)}_2Mg_2(Qx^{\bullet})_2]^{2-}$  (2) in  $[D_8]THF$  at 298K.





Fig S6. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of  $[Na(THF)_6]^+[{Ph_2Si(NAr_2)}Mg(TMP)]^-$  (3) in  $[D_8]THF$  at 298K.



Fig S7. <sup>1</sup>H NMR spectrum of  $[(Ph_2Si(NAr^*)_2)Mg(TEMPO^-)Na(THF)_3]$  (4) in  $[D_8]THF$  at 298K.



Fig S8  ${}^{13}C{}^{1}H$  NMR spectrum of [(Ph<sub>2</sub>Si(NAr\*)<sub>2</sub>)Mg(TEMPO<sup>-</sup>)Na(THF)<sub>3</sub>] (4) in [D<sub>8</sub>]THF at 298K.



Figure S9. <sup>1</sup>H NMR spectrum of  $[(THF)_xNa\{C_8H_6N_2(CH_2SiMe_3)\}Mg(CH_2SiMe_3)_2]$  (6) in  $[D_8]THF$  at 298K.



Figure S10. Expanded <sup>1</sup>H NMR spectrum of  $[(THF)_xNa\{C_8H_6N_2(CH_2SiMe_3)\}Mg(CH_2SiMe_3)_2]$  (6) in  $[D_8]THF$  at 298K.



Figure S11. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of reaction of  $[(THF)_xNa\{C_8H_6N_2(CH_2SiMe_3)\}Mg(CH_2SiMe_3)_2]$  (6) in  $[D_8]THF$  at 298K.



Figure S12. <sup>1</sup>H, <sup>1</sup>H-COSY NMR spectrum of  $[(THF)_xNa\{C_8H_6N_2(CH_2SiMe_3)\}Mg(CH_2SiMe_3)_2]$  (6) in  $[D_8]THF$  at 298K.



Figure S13. <sup>1</sup>H, <sup>1</sup>H-COSY NMR spectrum of reaction of  $[(THF)_xNa\{C_8H_6N_2(CH_2SiMe_3)\}Mg(CH_2SiMe_3)_2]$ (6) in  $[D_8]THF$  at 298K.



Figure S14. <sup>13</sup>C{<sup>1</sup>H}-DEPT 135 NMR spectrum of  $[(THF)_xNa\{C_8H_6N_2(CH_2SiMe_3)\}Mg(CH_2SiMe_3)_2]$  (6) in  $[D_8]THF$  at 298K.



Figure S15. Comparison of <sup>1</sup>H NMR spectra of a)  $[(THF)_xNa\{C_8H_6N_2(CH_2SiMe_3)\}Mg(CH_2SiMe_3)_2]$  (6) and b) quinoxaline in  $[D_8]THF$  at 298K.



Fig S16. <sup>1</sup>H NMR spectrum of hydrolysis of  $[(THF)_xNa\{C_8H_6N_2(CH_2SiMe_3)\}Mg(CH_2SiMe_3)_2]$  (6) using 10% of  $[FeCp_2]$  as an internal standard in CDCl<sub>3</sub> at 298K.



Fig S17.Expanded <sup>1</sup>H NMR spectrum of hydrolysis of  $[(THF)_xNa\{C_8H_6N_2(CH_2SiMe_3)\}Mg(CH_2SiMe_3)_2]$  (6) using 10% of  $[FeCp_2]$  as an internal standard in CDCl<sub>3</sub> at 298K.



Fig S18. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of hydrolysis of  $[(THF)_xNa{C_8H_6N_2(CH_2SiMe_3)}Mg(CH_2SiMe_3)_2]$  (6) using 10% of  $[FeCp_2]$  as an internal standard in CDCl<sub>3</sub> at 298K.



Fig S19. <sup>1</sup>H NMR spectrum of hydrolysis of  $[(THF)_xNa\{C_8H_6N_2(CH_2SiMe_3)\}Mg(CH_2SiMe_3)_2]$  (6) in CDCl<sub>3</sub> at 298K used to obtain yield.



Fig S20. <sup>1</sup>H NMR spectra of a) **2** and b) reaction of **3** and quinoxaline in  $[D_8]$ THF at 298K.

## **DFT Calculations**

Density Functional Theory (DFT) calculations<sup>6</sup> were performed using the Gaussian computational package G03.<sup>7</sup> In this series of calculations the geometries of the molecules and ions were optimised by employing the B3LYP density functionals<sup>8,9</sup> and the 6-311G\*\* basis set.<sup>10,11</sup> Calculations for models **1B**, **quinoxaline**, and **2** (singlet state) were restricted while for **2C**, **2C-THF** and **2** (triplet state) were unrestricted.



Figure S21. Optimized geometry of a) **1B** and b) quinoxaline.



Figure S22. Optimized geometry of **2** a) with a singlet state configuration and b) triplet state configuration.







Figure S24 Calculated SOMO for model **2C-THF** (left), LUMO of free **Qx** (right) and spin densities in Qx\* ring in **2C-THF** (bottom)

Bond	2	2A (Singlet)	<b>2B</b> (Triplet)	2C	2C·THF	1B	Quinoxaline
Mg-N <sub>quinoxaline</sub> (Å)	2.103(7)	2.150	2.174	2.020	26 2.080		
	2.115(6)	2.165	2.194	2.020			
N-C (Å)	1.347(9)	1.368	1.363	1.380	1.377		
	1.350(9)	1.389	1.392	1.392	1.387		1.313 1.363
	1.360(9)	1.387	1.395	1.348	1.349		
	1.394(9)	1.365	1.367	1.375	1.373		
C-C (Å)	1.364(10)	1.374	1.374	1.376	1.377		1.420 1.428
	1.432(10)	1.430	1.431	1.434	1.438		
N…N (Å)	2.825(9)	2.821	3.063				
C…C (Å)	$C_{1}C_{1}(h) = 2.024(11)$	3.072	3.331				
	3.034(11)	3.066	3.337				
Mg-N (Å)	2.028(6)	2.112	2.120	2.015	2.069	2.119	
	2.042(6)	2.075	2.072	2.014	2.050	2.081	
Mg-C (Å)						2.173	
Mg-O (Å)						2.223	

Table S2	Comparison o	of calculated and e	vnorimontall	v found structural	narameters for c	omnound <b>7</b>
I able 32.	Companson C	n calculateu allu e	лрепшенцан	y iounu structurar	parameters for c	ompound <b>z</b> .

In agreement with the lack of paramagnetism observed for **2** experimentally, the singlet state model **2A** shows better agreement with the experimental values found for **2** than that computed for **2B** with a triplet state configuration. Overall these data suggest that single state configuration for the **Qx**<sup>•</sup> radicals in compound **2**.

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