Supporting Information

Alkali Metal and Stoichiometric Effects in Intermolecular Hydroamination Catalysed by Lithium, Sodium and Potassium Magnesiates

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<tr>
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<tr>
<td>Empirical formula</td>
<td>C_{54}H_{108}Mg_2N_6Na_2O_6</td>
<td>C_{32}H_{72}Mg_1N_8Na_2</td>
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<tr>
<td>Mol. Mass</td>
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<td>Crystal system</td>
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<td>Monoclinic</td>
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<td>a/ Å</td>
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<td>10.4760(14)</td>
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<tr>
<td>b/ Å</td>
<td>11.7398(7)</td>
<td>19.224(2)</td>
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<td>c/ Å</td>
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<td>19.864(2)</td>
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<td>α/ °</td>
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<tr>
<td>β/ °</td>
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<td>93.733(10)</td>
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<td>γ/ °</td>
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<td>V/ Å³</td>
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<td>3991.9(8)</td>
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<tr>
<td>Z</td>
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<td>4</td>
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<tr>
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<td>Measured reflections</td>
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<td>Unique reflections</td>
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<td>R_{int}</td>
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<td>Observed rflns [I&gt;2σ(I)]</td>
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<td>4183</td>
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<td>GooF</td>
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<td>R [on F, obs rflns only]</td>
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<td>ωR [on F^2, all data]</td>
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<td>Largest diff. Peak/hole. e/ Å³</td>
<td>0.486 / -0.363</td>
<td>0.613 / -0.381</td>
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</table>

**Figure S1** X-ray diffraction structures of 15-18. 17 and 18 provide general connectivity information only, due to poor data quality.
Catalysis - NMR Spectra

**Figure S2** Hydroamination of diphenylacetylene with piperidine, catalysed by LiMg(CH$_2$SiMe$_3$)$_3$ (1) (5 mol%) in $d_8$-THF.

**Figure S3** Hydroamination of diphenylacetylene with piperidine, catalysed by NaMg(CH$_2$SiMe$_3$)$_3$ (2) (5 mol%) in $d_8$-THF.
Figure S4  Hydroamination of diphenylacetylene with piperidine, catalysed by KMg(CH₂SiMe₃)₃ (3) (5 mol%) in d₈-THF.

Figure S5  Hydroamination of diphenylacetylene with piperidine, catalysed by NaMg(CH₂SiMe₃)₃ (2) (10 mol%) in d₈-THF.
Figure S6  Hydroamination of diphenylacetylene with piperidine, catalysed by NaMg(CH$_2$SiMe$_3$)$_3$ (2) (2 mol%) in $d_8$-THF.

Figure S7  Hydroamination of diphenylacetylene with piperidine, catalysed by [(TMEDA)$_2$Li$_2$Mg(CH$_2$SiMe$_3$)$_4$] (5) (5 mol%) in $d_8$-THF.
Figure S8  Hydroamination of diphenylacetylene with piperidine, catalysed by \([\text{TMEDA}]_2\text{Na}_2\text{Mg(CH}_2\text{SiMe}_3)_4\) (6) (5 mol%) in \(d_8\)-THF.

Figure S9  Hydroamination of diphenylacetylene with piperidine, catalysed by \([\text{PMDTA}]_2\text{K}_2\text{Mg(CH}_2\text{SiMe}_3)_4\) (7) (5 mol%) in \(d_8\)-THF.
Figure S10  Hydroamination of diphenylacetylene with piperidine, catalysed by \([\text{PMDTA}]_2\text{K}_2\text{Mg(CH}_2\text{SiMe}_3)_4\] (7) (5 mol\%) and 10 mol\% of 18-crown-6 in \(d_8\)-THF.

Figure S11  Hydroamination of diphenylacetylene with pyrrolidine, catalysed by \([\text{PMDTA}]_2\text{K}_2\text{Mg(CH}_2\text{SiMe}_3)_4\] (7) (5 mol\%) in \(d_8\)-THF.
Figure S12  Hydroamination of diphenylacetylene with morpholine, catalysed by 
[(PMDTA)$_2$K$_2$Mg(CH$_2$SiMe$_3$)$_4$] (7) (5 mol%) in $d_8$-THF.

Before catalyst addition

24 h room temp

Figure S13  Hydroamination of diphenylacetylene with dibenzylamine, catalysed by 
[(PMDTA)$_2$K$_2$Mg(CH$_2$SiMe$_3$)$_4$] (7) (5 mol%) in $d_8$-THF.

Before catalyst addition

24 h 80 °C
Figure S14  Hydroamination of diphenylacetylene with diphenylamine, catalysed by [(PMDTA)$_2$K$_2$Mg(CH$_2$SiMe$_3$)$_4$] (7) (5 mol%) in $d_8$-THF.

Figure S15  Hydroamination of styrene with piperidine, catalysed by [(PMDTA)$_2$K$_2$Mg(CH$_2$SiMe$_3$)$_4$] (7) (5 mol%) in $d_8$-THF.
Figure S16  Hydroamination of styrene with pyrrolidine, catalysed by [(PMDTA)$_2$K$_2$Mg(CH$_2$SiMe$_3$)$_4$] (7) (5 mol%) in $d_8$-THF.

Figure S17  Hydroamination of styrene with morpholine, catalysed by [(PMDTA)$_2$K$_2$Mg(CH$_2$SiMe$_3$)$_4$] (7) (5 mol%) in $d_8$-THF.
Amide complexes 15-18 NMR Spectra

Figure S18 $^1$H NMR spectrum of $[\text{(THF)}_2\text{NaMg(NC}_5\text{H}_{10})_3]_2$ (15) in C$_6$D$_6$.

Figure S19 $^{13}$C NMR spectrum of $[\text{(THF)}_2\text{NaMg(NC}_5\text{H}_{10})_3]_2$ (15) in C$_6$D$_6$. 
Figure S20  $^1$H NMR DOSY spectrum of [(THF)$_2${NaMg(NC$_5$H$_{10}$)$_3$}]$_2$ (15) in $d_8$-THF.

Figure S21  $^1$H NMR spectrum of [(THF)$_3${KMg(NC$_5$H$_{10}$)$_3$}]$_2$ (16) in C$_6$D$_6$. 
Figure S22  $^{13}$C NMR spectrum of [(THF)$_3$K(Mg(NC$_{5}$H$_{10}$)$_3$)$_2$ (16) in C$_6$D$_6$.

Figure S23  $^1$H NMR DOSY spectrum of [(THF)$_3$K(Mg(NC$_{5}$H$_{10}$)$_3$)$_2$ (16) in d$_8$-THF.
Figure S24 $^1$H NMR spectrum of [(TMEDA)$_2$Na$_2$Mg(NC$_5$H$_{10}$)$_4$] (17) in C$_6$D$_6$.

Figure S25 $^{13}$C NMR spectrum of [(TMEDA)$_2$Na$_2$Mg(NC$_5$H$_{10}$)$_4$] (17) in C$_6$D$_6$. 
Figure S26  $^1$H NMR spectrum of [(PMDETA)$_2$K$_2$Mg(NC$_5$H$_{10}$)$_4$] (18) in C$_6$D$_6$.

Figure S27  $^{13}$C NMR spectrum of [(PMDETA)$_2$K$_2$Mg(NC$_5$H$_{10}$)$_4$] (18) in C$_6$D$_6$. 