Heterobimetallic metallation studies of \( \text{N,N-dimethylphenylethylamine (DMPEA)} \): benzylic C-H bond cleavage/dimethylamino capture or intact DMPEA complex†‡

Supporting Information

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Table of contents

Synthesis of Zn(TMP)$_2$

Figure S1. $^1$H NMR spectrum of [(TMEDA)Na(TMP)(NMe$_2$)Zn(Bu')$_2$] 3 in C$_6$D$_{12}$ solution.

Figure S2. $^{13}$C NMR spectrum of [(TMEDA)Na(TMP)(NMe$_2$)Zn(Bu')$_2$] 3 in C$_6$D$_{12}$ solution.

Figure S3. $^1$H NMR spectrum of [(PMDETA)Li(NMe$_2$)Zn(Bu')$_2$] 4 in C$_6$D$_{12}$ solution.

Figure S4. $^{13}$C NMR spectrum of [(PMDETA)Li(NMe$_2$)Zn(Bu')$_2$] 4 in C$_6$D$_{12}$ solution.

Figure S5. $^7$Li spectrum of [(PMDETA)Li(NMe$_2$)Zn(Bu')$_2$] 4 in C$_6$D$_{12}$ solution.

Figure S6. $^1$H NMR spectrum of [(THF)Li(TMP)(NMe$_2$)Al(Bu')$_2$] 5 in C$_6$D$_{12}$ solution.

Figure S7. $^{13}$C NMR spectrum of [(THF)Li(TMP)(NMe$_2$)Al(Bu')$_2$] 5 in C$_6$D$_{12}$ solution.

Figure S8. $^7$Li spectrum of [(THF)Li(TMP)(NMe$_2$)Al(Bu')$_2$] 5 in C$_6$D$_{12}$ solution.

Figure S9. $^1$H NMR spectrum of [DMPEA·Li(TMP)Zn(Me)$_2$] 6 in C$_6$D$_6$ solution.

Figure S10. $^{13}$C NMR spectrum of [DMPEA·Li(TMP)Zn(Me)$_2$] 6 in C$_6$D$_6$ solution.

Figure S11. $^7$Li NMR spectrum of [DMPEA·Li(TMP)Zn(Me)$_2$] 6 in C$_6$D$_6$ solution.

Figure S12. $^1$H NMR spectrum of [DMPEA·Li(TMP)Zn(Me)$_2$] 6 in C$_6$D$_{12}$ solution.

Figure S13. $^{13}$C NMR spectrum of [DMPEA·Li(TMP)Zn(Me)$_2$] 6 in C$_6$D$_{12}$ solution.

Figure S14. $^7$Li NMR spectrum of [DMPEA·Li(TMP)Zn(Me)$_2$] 6 in C$_6$D$_{12}$ solution.

Figure S15. $^1$H NMR spectrum of [DMPEA·Li(TMP)Zn(Me)$_2$] 6 in d$_8$-toluene solution.

Figure S16. $^7$Li NMR spectrum of [DMPEA·Li(TMP)Zn(Me)$_2$] 6 in d$_8$-toluene solution.

Figure S17. $^1$H NMR spectrum in C$_6$D$_6$ solution of crystals of 6 dissolved in THF solution showing the emergence of a new NMe$_2$ resonance (at 3 ppm) resulting from the metallation and subsequent $\beta$-elimination of DMPEA.
Synthesis of Zn(TMP)$_2$: TMP(H) (6.8 mL, 40 mmol) was added to hexane (40 mL) and the solution cooled to 0°C before nBuLi (25 mL, 1.6 M in hexanes, 40 mmol) was introduced. The resulting yellow suspension was stirred for 1 hour before all the solvent was removed \textit{in vacuo}. ZnCl$_2$ (2.72 g, 20 mmol) was then added followed by diethyl ether (50 mL). The suspension was then left to stir for 2 days after which the ether was removed \textit{in vacuo} and replaced by hexane (100 mL). The suspension was then filtered and the solid rinsed with hexane (80 mL). The solvent was then removed \textit{in vacuo} to provide the pale yellow solid (yield: 4.0 g, 58%).

Figure S1. $^1$H NMR spectrum of [(TMEDA)Na(TMP)(NMe$_2$)Zn(Bu')]$_3$ in C$_6$D$_{12}$ solution.
Figure S2. $^{13}$C NMR spectrum of [(TMEDA)Na(TMP)(NMe$_2$)Zn(Bu)$_3$] in C$_6$D$_{12}$ solution.

Figure S3. $^1$H NMR spectrum of [(PMDETA)Li(NMe$_2$)Zn(Bu')]$_2$ in C$_6$D$_{12}$ solution.
Figure S4. $^{13}$C NMR spectrum of [(PMDETA)Li(NMe$_2$)Zn(Bu')$_2$] 4 in C$_6$D$_{12}$ solution.

Figure S5. $^7$Li spectrum of [(PMDETA)Li(NMe$_2$)Zn(Bu')$_2$] 4 in C$_6$D$_{12}$ solution with an unidentified impurity at 1.31 ppm.
Figure S6. $^1$H NMR spectrum of [(THF)Li(TMP)(NMe$_2$)Al(Bu)$_2$]$_5$ in C$_6$D$_{12}$ solution.

Figure S7. $^{13}$C NMR spectrum of [(THF)Li(TMP)(NMe$_2$)Al(Bu')$_2$]$_5$ in C$_6$D$_{12}$ solution.
Figure S8. $^7$Li spectrum of [(THF)Li(TMP)(NMe$_2$)Al(Bu')$_2$] 5 in C$_6$D$_{12}$ solution.

Figure S9. $^1$H NMR spectrum of [DMPEA·Li(TMP)Zn(Me)$_2$] 6 in C$_6$D$_6$ solution.
Figure S10. $^{13}$C NMR spectrum of [DMPEA·Li(TMP)Zn(Me)$_2$] 6 in C$_6$D$_6$ solution.

Figure S11. $^7$Li NMR spectrum of [DMPEA·Li(TMP)Zn(Me)$_2$] 6 in C$_6$D$_6$ solution.
Figure S12. $^1$H NMR spectrum of [DMPEA·Li(TMP)Zn(Me)$_2$] 6 in C$_6$D$_{12}$ solution.

Figure S13. $^{13}$C NMR spectrum of [DMPEA·Li(TMP)Zn(Me)$_2$] 6 in C$_6$D$_{12}$ solution.
Figure S14. \(^7\text{Li}\) NMR spectrum of [DMPEA·Li(TMP)Zn(Me)\(_2\)] \(_6\) in C\(_6\)D\(_{12}\) solution.

Figure S15. \(^1\text{H}\) NMR spectrum of [DMPEA·Li(TMP)Zn(Me)\(_2\)] \(_6\) in d\(_8\)-toluene solution.
Figure S16. $^7$Li NMR spectrum of $[\text{DMPEA} \cdot \text{Li(TMP)}Zn(\text{Me})_2]$ 6 in d$_8$-toluene solution.

Figure S17. $^1$H NMR spectrum in C$_6$D$_6$ solution of crystals of $[\text{DMPEA} \cdot \text{Li(TMP)}Zn(\text{Me})_2]$ 6 dissolved in THF solution showing the emergence of a new NMe$_2$ resonance (at 3 ppm) resulting from the metallation and subsequent $\beta$-elimination of DMPEA.