Electronic supplementary information (ESI)

Reactivity studies of a soluble LiH-complex and non-spectator behaviour of its stabilising phosphinoamide ligand

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1. NMR Spectroscopy

**Fig S1.** $^1$H NMR (300.13 MHz, C$_6$D$_6$, 303 K) spectrum of the in-situ reaction of [(LLi)$_4$(LiH)$_4$] 1 with DCC, after 20 minutes at room temperature. * denotes the newly formed HDCC$^-$ resonance; + shows the partially hidden, unreacted broad LiH resonance of 1; § toluene resonance.
**Fig S2.** $^3$P{$^1$H} NMR (121.51 MHz, C$_6$D$_6$, 303 K) spectrum of the *in-situ* reaction of [(LLi)$_4$(LiH)$_4$] 1 with DCC, after 25 minutes at room temperature. %: likely a DCC donor-stabilised Ph$_2$PN(Dip)Li species [c.f. the resonances of Ph$_2$PN(Dip)Li(THF)$_2$: $\delta$61.1 ppm, and Ph$_2$PN(Dip)Li(TMEDA): $\delta$60.3 ppm]$^1$; $\$: small amounts of Ph$_2$PN(H)Dip; 1: unreacted [(LLi)$_4$(LiH)$_4$] 1; A, B, C: newly formed products, likely from Ph$_2$PN(Dip)Li addition to DCC.
**Fig S3.** $^1$H NMR (300.13 MHz, C$_6$D$_6$, 303 K) spectrum of the *in-situ* reaction of [LLi] 2 with DCC, after 20 minutes at room temperature. (*) shows no HDCC$^-$ resonance.
Fig S4. $^{31}$P($^1$H) NMR (121.51 MHz, C₆D₆, 303 K) spectrum of the in-situ reaction of [LLi] 2 with DCC, after 25 minutes at room temperature. %: likely a DCC donor-stabilised Ph₂PN(Dip)Li species [c.f. the resonances of Ph₂PN(Dip)Li(THF)$_2$: δ61.1 ppm, and Ph₂PN(Dip)Li(TMEDA): δ60.3 ppm]$^1$; $$: small amounts of Ph₂PN(H)Dip; A, B, C: newly formed reaction products likely from Ph₂PN(Dip)Li addition to DCC and very similar to those in Fig. S2.
Fig S5. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.51 MHz, C$_6$D$_6$, 303 K) spectrum of the in-situ reaction of [LLi]$_2$ with DCC, after ca. 15 h at room temperature, showing different product ratios compared to Fig. S4. %: DCC donor-stabilised Ph$_2$PN(Dip)Li species; $\$: Ph$_2$PN(H)Dip; A, B, C: newly formed reaction products.
Fig S6. $^1$H NMR (400.17 MHz, C$_6$D$_6$, 303 K) spectrum (top: full spectrum, bottom: excerpt) of the in-situ reaction of [(LLi)$_4$(LiH)$_4$] 1 with PhN=NPh, after ca. 25 minutes at room temperature showing largely unreacted 1. #: PhN=NPh resonances; *: H$_2$; +: characteristic resonances of [(LLi)$_4$(LiH)$_4$] 1; § toluene resonance.
Fig S7. $^{31}$P{$^1$H} NMR (161.98 MHz, C$_6$D$_6$, 303 K) spectrum of the in-situ reaction of [($LLi$)$_4$($LiH$)$_4$] 1 with PhN=NPh, after ca. 30 minutes at room temperature. %: likely a DCC donor-stabilised Ph$_2$PN(Dip)Li species; $\$: small amounts of Ph$_2$PN(H)Dip; 1: [($LLi$)$_4$($LiH$)$_4$] 1; 5: [{$(LN(Ph)N(Ph)Li)}_2$] 5. The species showing the sharp singlet at $\delta$17.25 ppm has not yet been identified.

Please refer to Fig. 2 (main text) for the respective $^1$H and $^{31}$P{$^1$H} NMR spectra after ca. 16 h at room temperature.
Fig S8. $^1$H NMR (400.17 MHz, C$_6$D$_6$, 303 K) spectrum of the in-situ reaction of [(LLi)$_4$(LiH)$_4$] 1 with PhN=NPh, after ca. 2.8 days at room temperature. *: H$_2$; >: selected resonances of [((LN(Ph)N(Ph)Li)$_2$] 5; $\S$: toluene resonance.
Fig S9. $^{31}$P$^1$H NMR (161.98 MHz, C$_6$D$_6$, 303 K) spectrum of the in-situ reaction of [(LLi)$_4$(LiH)$_4$] 1 with PhN=NPh, after ca. 2.8 days at room temperature. 1: [(LLi)$_4$(LiH)$_4$] 1; 5: [(LN(Ph)N(Ph)Li)$_2$] 5.
Fig S10. $^1$H NMR (400.17 MHz, C$_6$D$_6$, 303 K) spectrum (top: full spectrum, bottom: excerpt) of the in-situ reaction of [LLi] 2 with PhN=NPh, after ca. 25 minutes at room temperature showing the predominant formation of $\left\{\left[\text{LN(Ph)N(Ph)Li}\right]_2\right\}$ 5. #: PhN=NPh resonances; (*): no (significant) H$_2$ formation; >: selected resonances of $\left\{\left[\text{LN(Ph)N(Ph)Li}\right]_2\right\}$ 5.
Fig S11. $^{31}$P($^1$H) NMR (161.98 MHz, C$_6$D$_6$, 303 K) spectrum of the in-situ reaction of [LLiH]$_2$ with PhN=NPh, after ca. 30 minutes at room temperature. $\$: small amounts of Ph$_2$PN(H)Dip; 5: [((LN(Ph)N(Ph)Li)$_2$] 5.
Fig S12. $^1$H NMR (300.13 MHz, C$_6$D$_6$) spectrum of isolated [((LN(Ph)N(Ph)Li)$_2$] 5, at 303 K (top) and 333 K (bottom). Note: once isolated by crystallisation, the sample shows limited solubility and could not be fully dissolved. § toluene resonance.
Fig S13. $^{31}$P($^1$H) NMR (121.50 MHz, C$_6$D$_6$) spectrum of isolated [(LN(Ph)N(Ph)Li)$_2$] 5 at 333 K.
2. Crystal Structures

**Fig S14.** Molecular structure of [LLi(THF)₃] (30% probability thermal ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)-N(1) 1.6649(10), P(1)-C(1) 1.8492(13), P(1)-C(7) 1.8646(12), O(1)-Li(1) 1.996(2), N(1)-C(13) 1.4164(14), N(1)-Li(1) 2.001(2), Li(1)-O(3) 1.982(2), Li(1)-O(2) 2.036(2); N(1)-P(1)-C(1) 105.86(5), N(1)-P(1)-C(7) 105.82(5), C(1)-P(1)-C(7) 96.18(6), P(1)-N(1)-Li(1) 129.25(8), O(3)-Li(1)-O(1) 95.79(9), O(3)-Li(1)-N(1) 121.01(11), O(1)-Li(1)-N(1) 113.71(10), O(3)-Li(1)-O(2) 100.38(9), O(1)-Li(1)-O(2) 98.75(10), N(1)-Li(1)-O(2) 122.13(10).
**Fig S15.** Molecular structure of compound 6 (30% probability thermal ellipsoids). Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)-N(1) 1.5797(18), P(1)-N(2) 1.6871(17), O(1)-Li(1) 1.892(4), N(1)-Li(1) 2.019(4), Li(1)-N(3) 1.932(4), N(2)-N(3) 1.462(2); N(1)-P(1)-N(2) 115.90(9), N(3)-N(2)-P(1) 101.48(11), N(3)-Li(1)-N(1) 92.91(17), O(1)-Li(1)-N(3) 143.9(2), O(1)-Li(1)-N(1) 118.8(2).

3. Reference: