

Supporting information for:

**Amine- and Dimeric Amino-Borane Complexes of the $\{\text{Rh}(\text{P}^i\text{Pr}_3)_2\}^+$ fragment and their
Relevance to the Transition Metal-Mediated Dehydrocoupling of Amine-Boranes**

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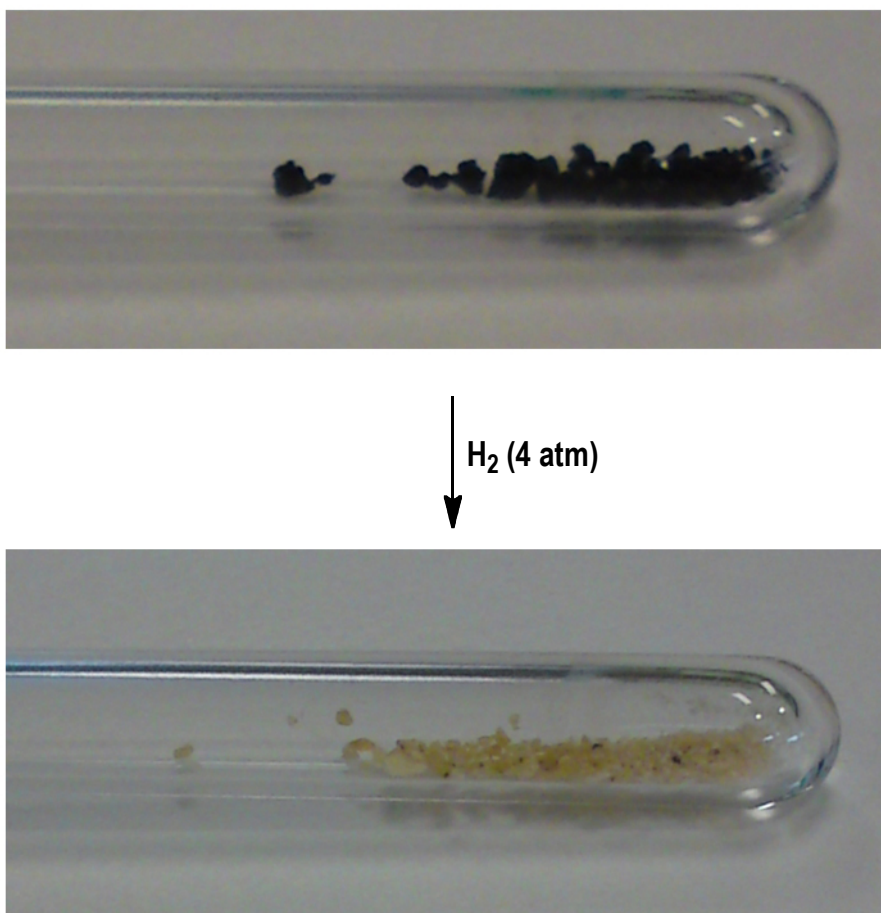


Figure S-1: Formation of **4** from **2** by solid-state hydrogenation (4 atm, 48 h).

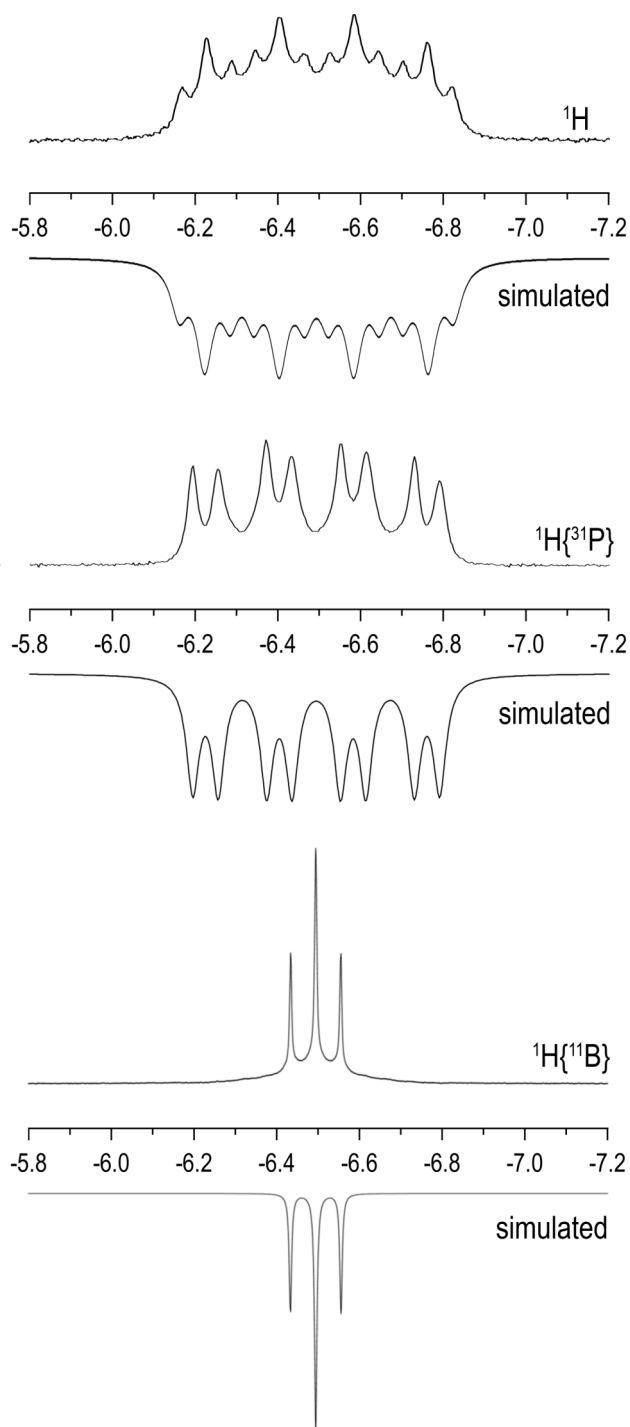


Figure S-2: ^1H NMR spectra of **2** (hydride region, CD_2Cl_2 , 500 MHz).

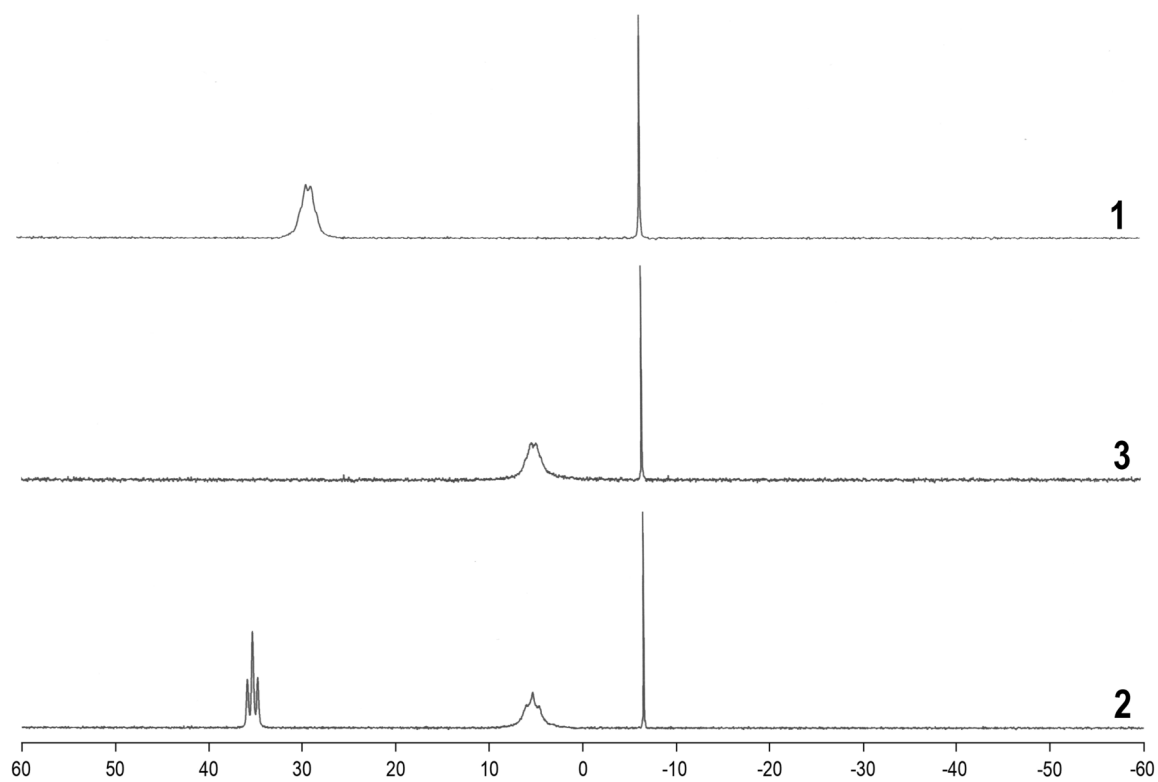


Figure S-3: Selected ^{11}B NMR spectra (CD_2Cl_2 , 160 MHz).

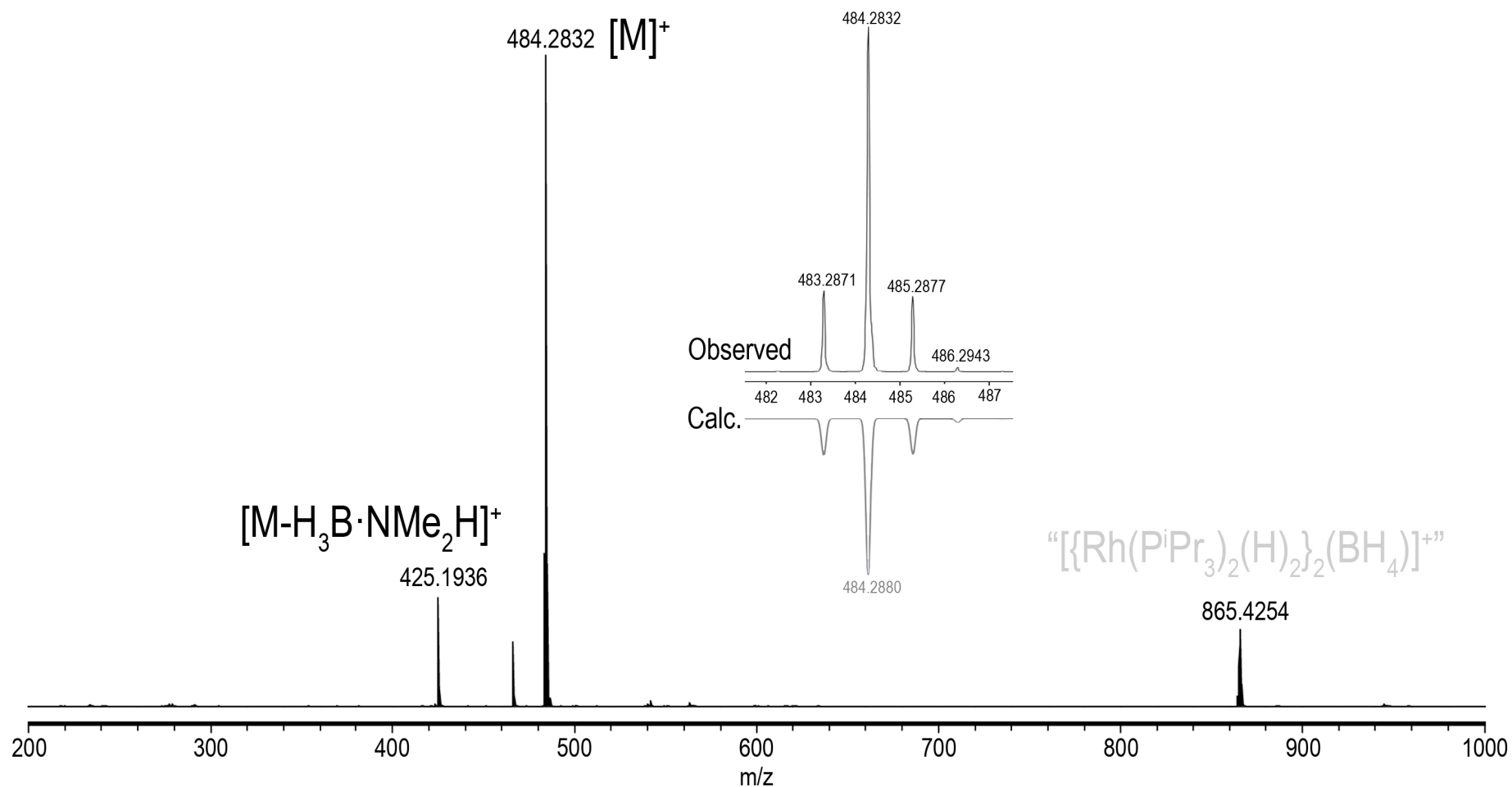


Figure S-4: ESI-MS (1,2- $C_6H_4F_2/CH_2Cl_2$, 60°C, 4.5 kV) of $H_3B \cdot NMe_2H$ dehydrocoupling with $[Rh(C_6H_5F)(PiPr_3)_2][BAr^F_4]$ (10 mol%, 1,2- $C_6H_4F_2$, 298 K, sealed system) after ca. 96 h; showing the presence of $[Rh(H)_2(PiPr_3)_2(\eta^2-H_3B \cdot NMe_2H)][BAr^F_4]$.