Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information for:

Dehydrocoupling of Dimethylamine-Borane Promoted by Manganese(II) *m*-Terphenyl Complexes.

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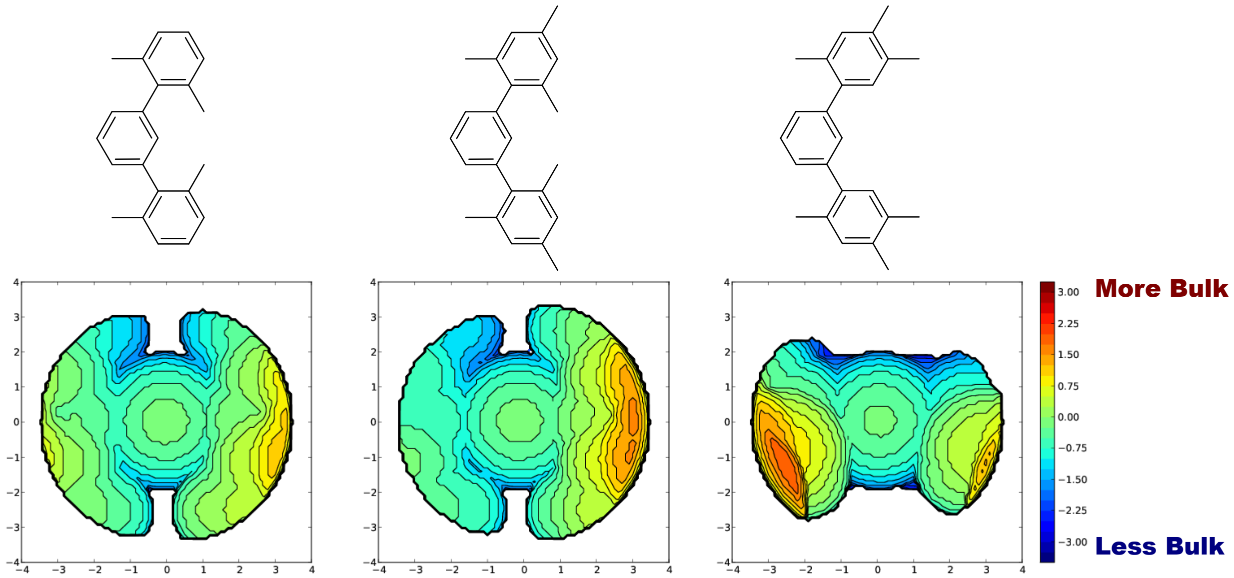
Table S1. Quantities of precatalyst (1-3) and $Me_2NH·BH_3$ used in reactions.

Precatalyst		$Me_2NH·BH_3$
Cat. (mol%)	mg, mmol	mg, mmol
1 (5)	10.0, 0.0160	18.9, 0.320
2 (5)	10.0, 0.0147	17.3, 0.294
3 (5)	10.0, 0.0133	15.7, 0,266
1 (2)	5.0, 0.00799	23.7, 0.400
2 (2)	5.0, 0.00733	21.5, 0.367
3 (2)	5.0, 0.00663	19.7, 0.322



%V_{Bur} = 42.0
2,6-Xyl

%V_{Bur} = 42.7
Mes

%V_{Bur} = 37.5
Tmp

Figure S1. Steric map representation and %V_{Bur} of *m*-terphenyl ligands with a sphere radius of 3.5 Å, mesh spacing 0.10, hydrogen atoms included.

Transmission electron microscopy (TEM)

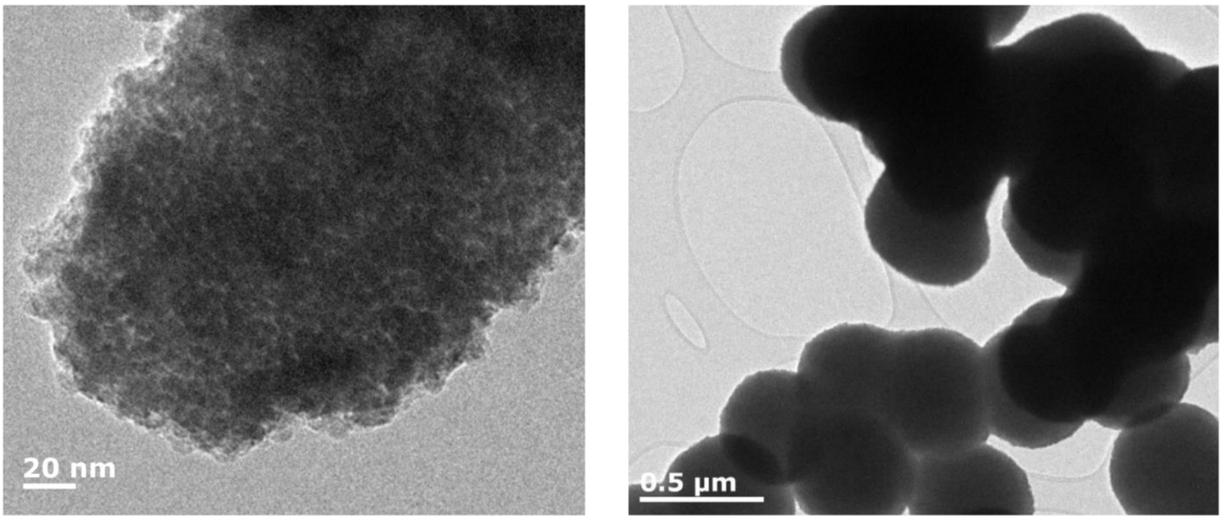


Figure S2. Bright field TEM micrograph of the nanoparticles afforded during the reaction of $Me_2NH{\cdot}BH_3$ and **3** in C_6D_6 (0.6 mL) after heating at 60 °C for 16 h. Large sub-micron aggregates of small ~10 nm nanoparticles can be observed.

NMR Reaction Monitoring

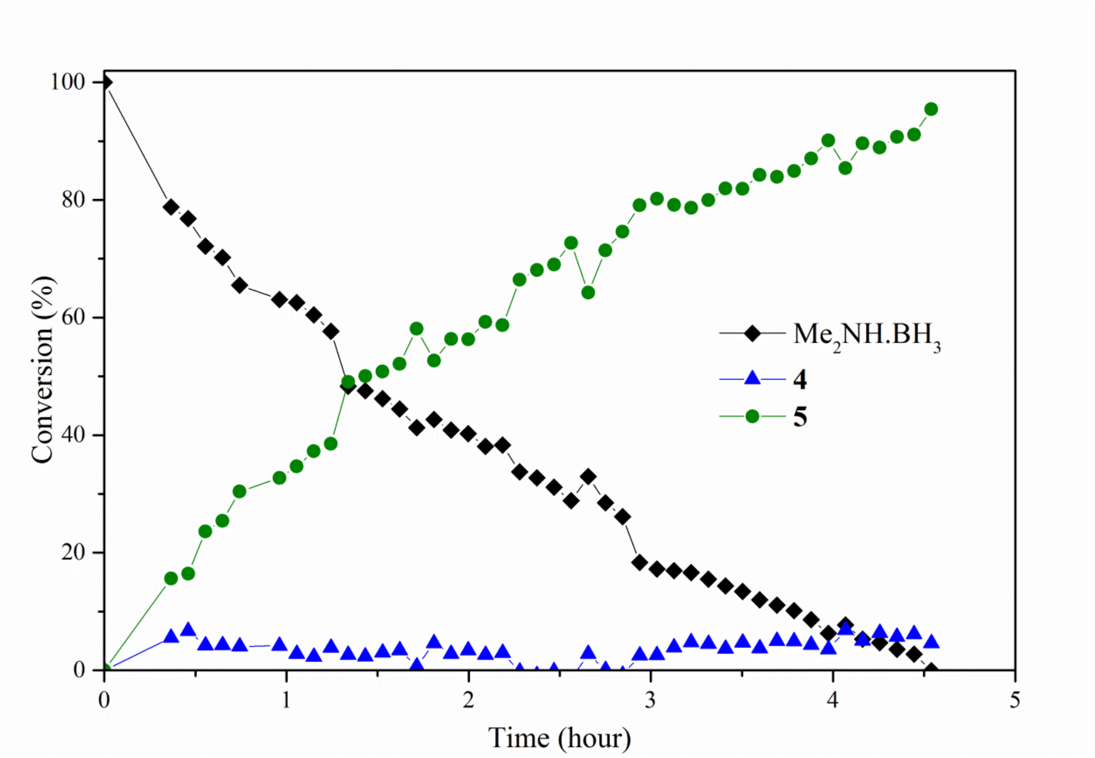


Figure S3. Conversion (%) *vs.* time (hour) for the dehydrocoupling of $Me_2HN{\cdot}BH_3$ with 5 mol% cat. of **2** in C_6D_6 at 60 °C.

Selected NMR Spectra

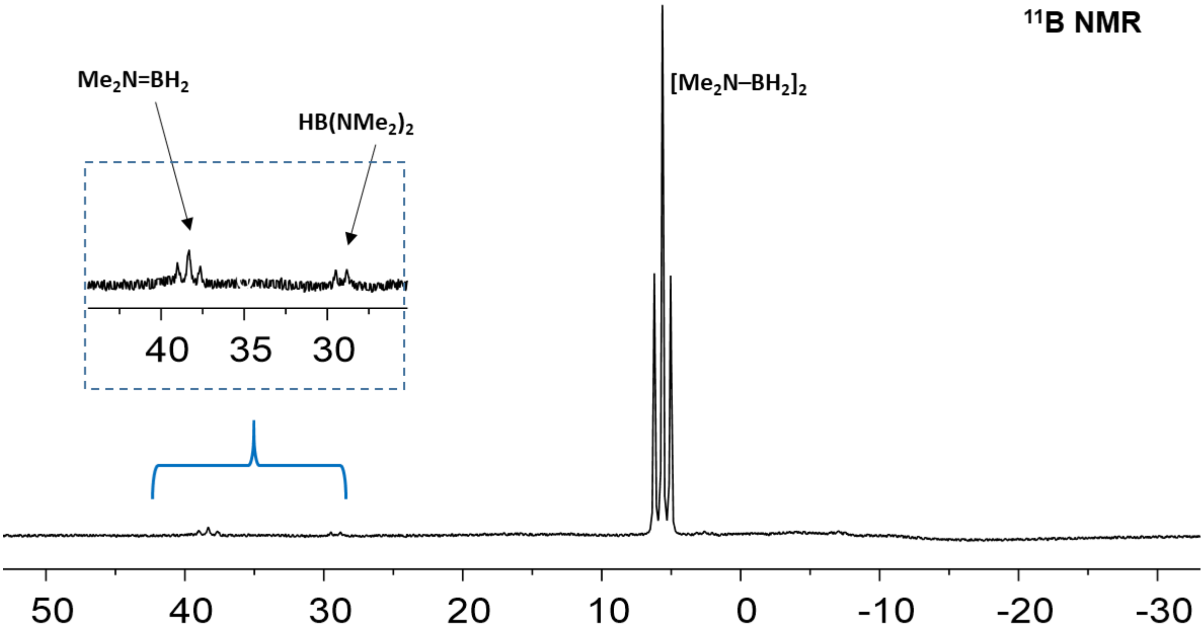


Figure S4. ^{11}B NMR spectrum for the dehydrocoupling of $Me_2HN \cdot BH_3$ with 5 mol% cat. **1** in C_6D_6 after 72 min. at 60 °C.

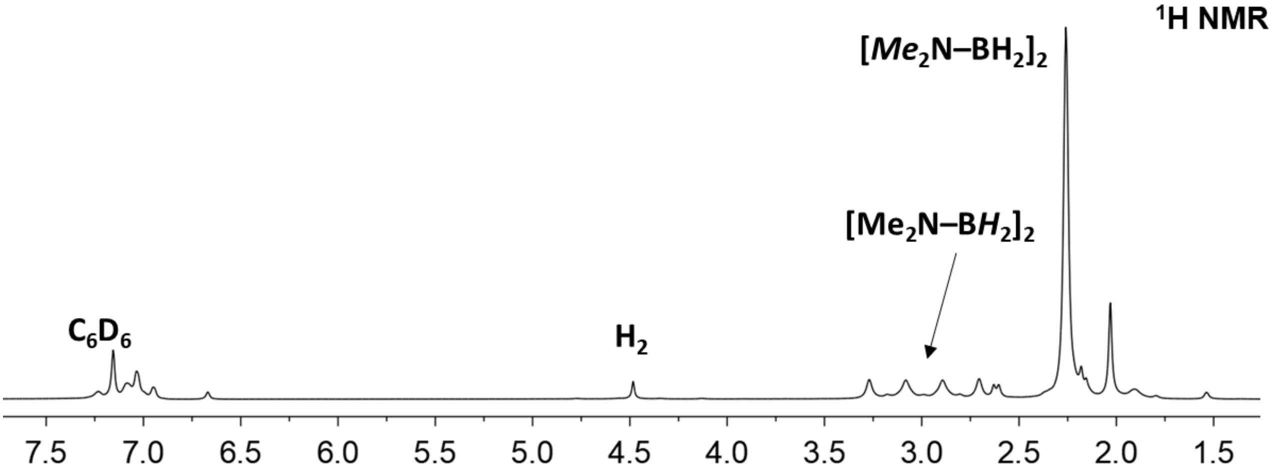


Figure S5. ^{1}H NMR spectrum for the dehydrocoupling of $Me_2HN \cdot BH_3$ with 5 mol% cat. **1** in C_6D_6 after 72 min. at 60 °C.

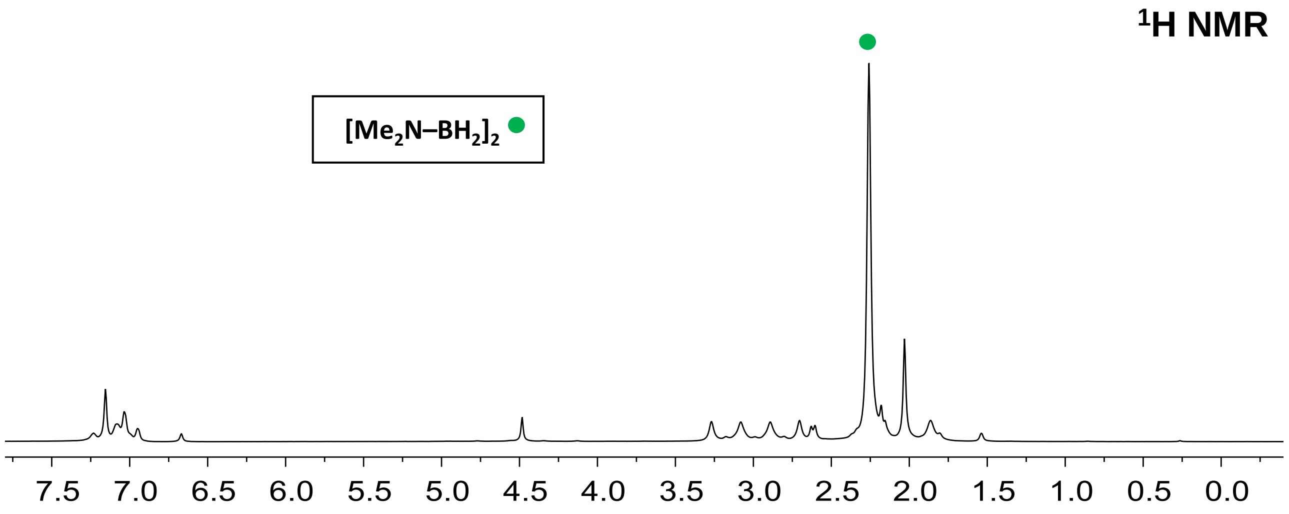


Figure S6. ^{1}H NMR spectrum for the dehydrocoupling of $Me_2HN{\cdot}BH_3$ with 5 mol% cat. **2** in C_6D_6 after 5 h at 60 °C.

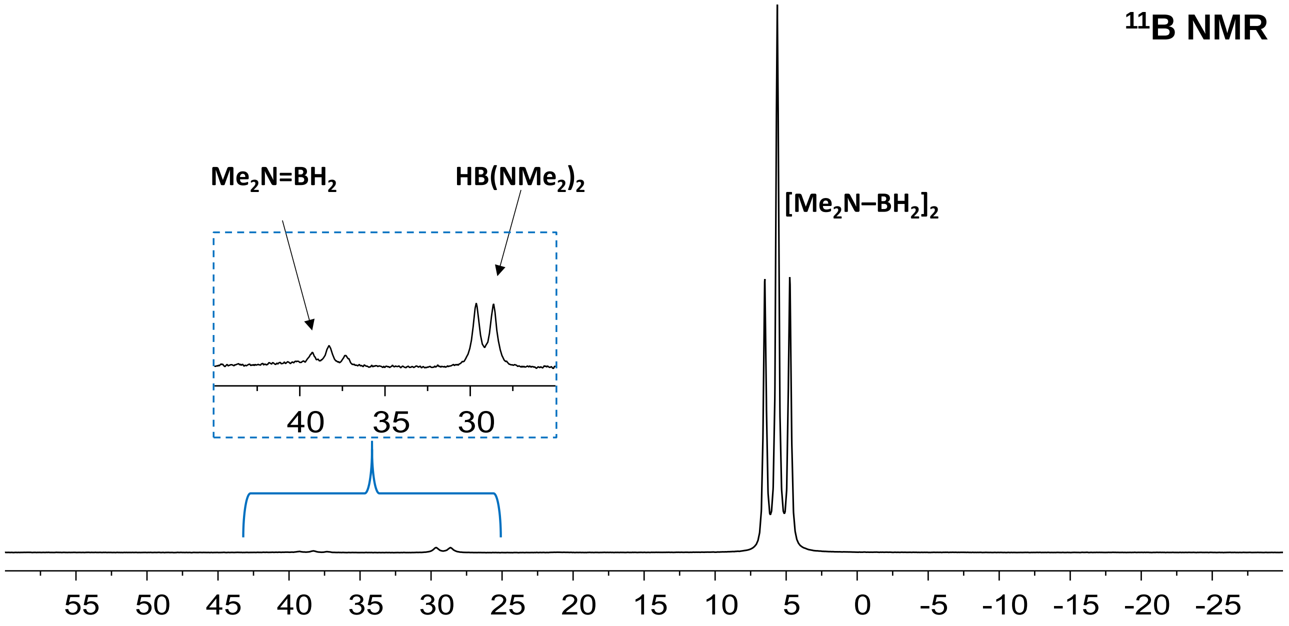


Figure S7. ^{11}B NMR spectrum for the dehydrocoupling of $Me_2HN{\cdot}BH_3$ with 5 mol% cat. **2** in C_6D_6 after 5 h at 60 °C.

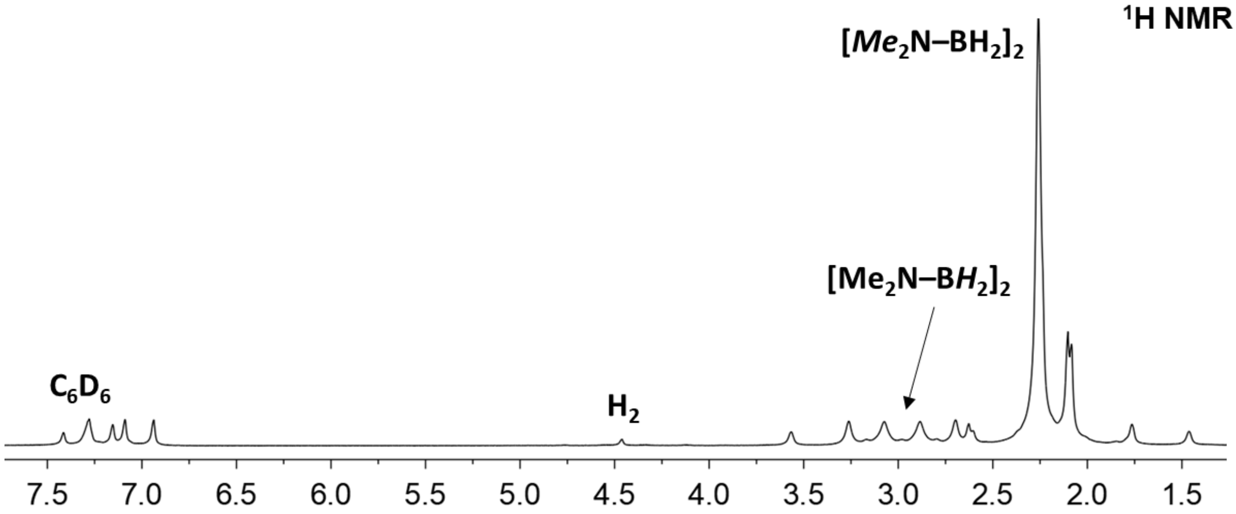


Figure S8. ^{1}H NMR spectrum for the dehydrocoupling of $Me_2HN{\cdot}BH_3$ with 5 mol% cat. **3** in C_6D_6 after 12 h at 60 °C.

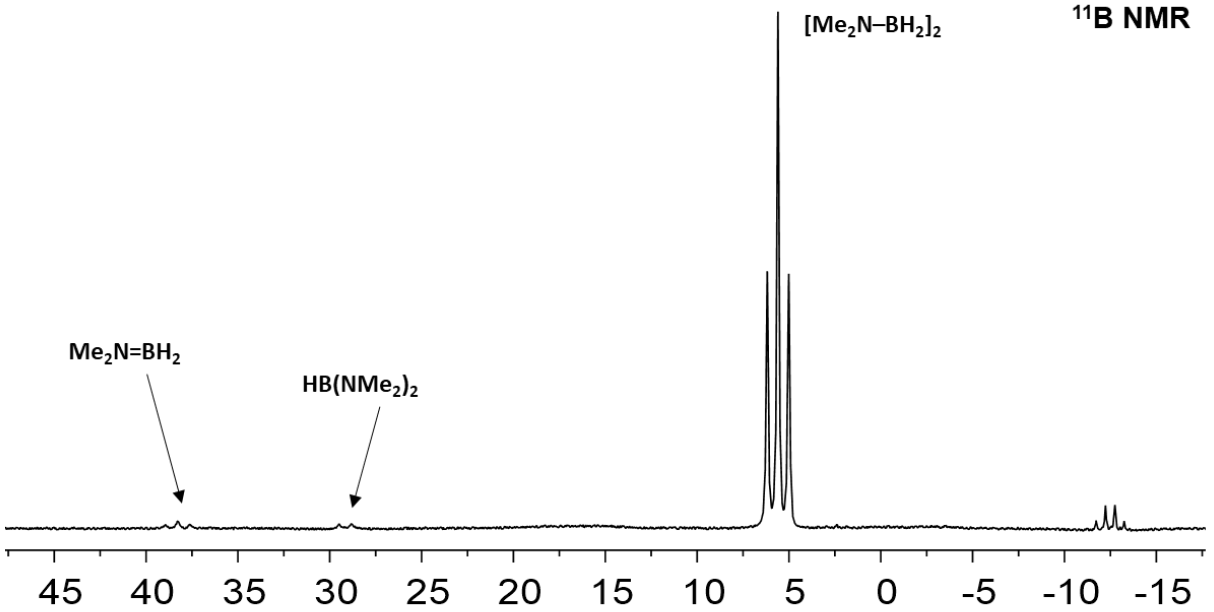


Figure S9. ^{11}B NMR spectrum for the dehydrocoupling of $Me_2HN{\cdot}BH_3$ with 5 mol% cat. **3** in C_6D_6 after 12 h at 60 °C.

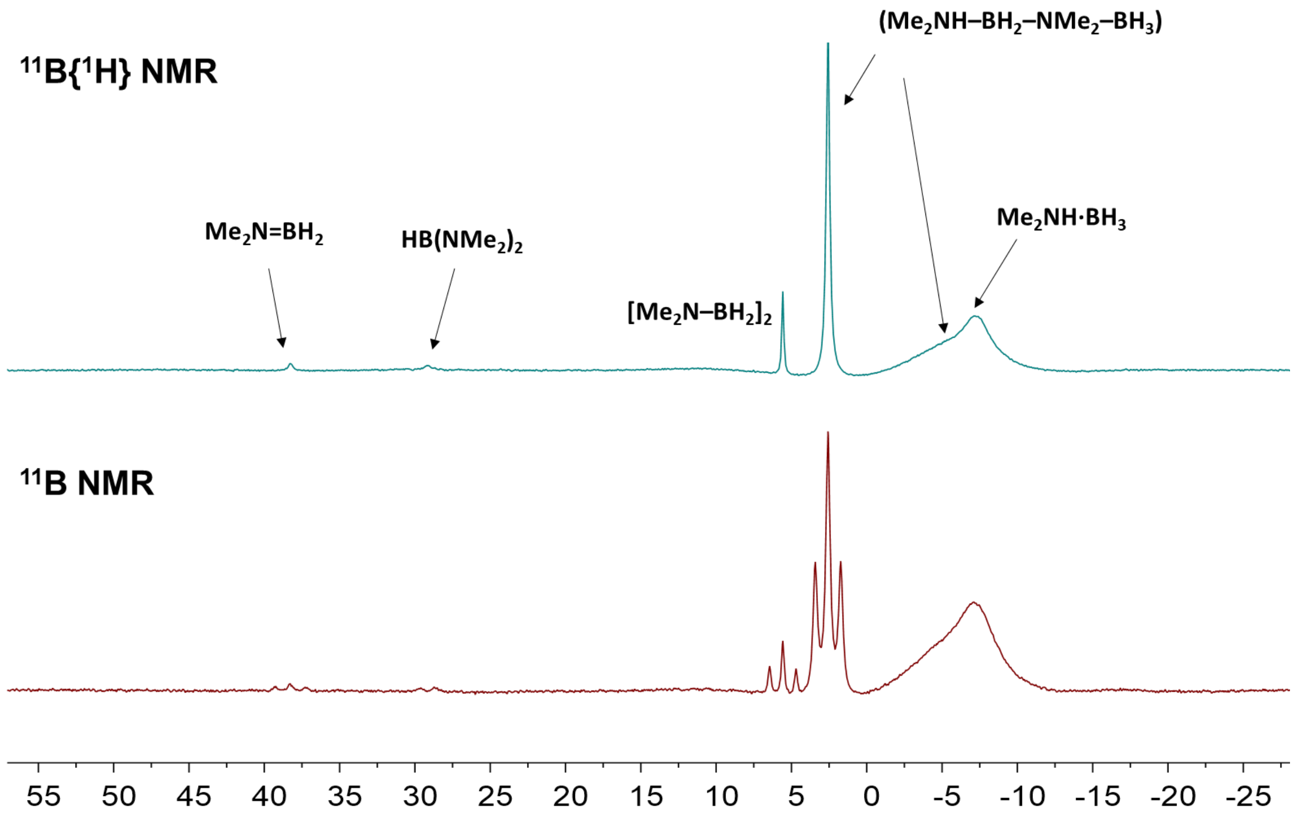


Figure S10. ^{11}B NMR (red) and ^{11}B{^{1}H} NMR (blue) spectrum for the dehydrocoupling of $Me_2HN\cdot BH_3$ with 5 mol% cat. **2** in C_6D_6 after 16 h at rt.

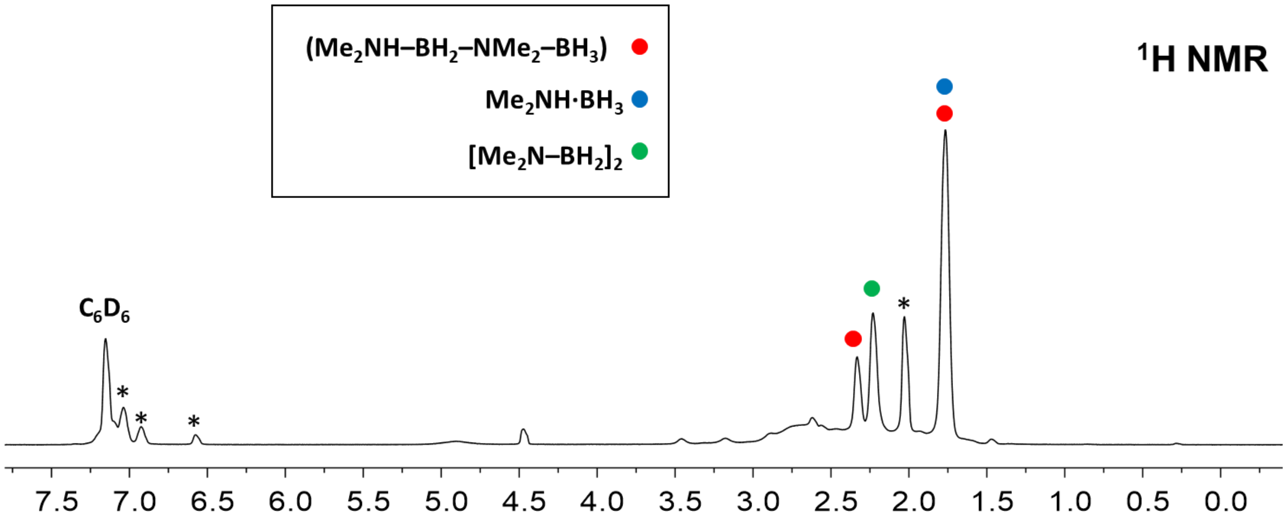


Figure S11. ^{1}H NMR spectrum for the dehydrocoupling of $Me_2HN\cdot BH_3$ with 5 mol% cat. **2** in C_6D_6 after 16 h at rt, asterisk (*) indicates protonated ligand ($2,6\text{-}Mes_2C_6H_4$).

Crystallographic Methods

Under a flow of nitrogen, crystals suitable for analysis by X-ray diffraction were quickly removed from the crystallisation vessel and covered in YR-1800 perfluoropolyether oil. Crystals were mounted on a MiTeGen MicroMount™ and cooled rapidly in a cold stream of nitrogen using an Oxford Cryostreams open flow cryostat.[1] Single crystal X-ray diffraction data were collected on Rikagu Oxford Diffraction SuperNova diffractometer (mirror-monochromated Cu-Kα radiation source; λ = 1.54184 Å; ω scans), equipped with a TitanS1 CCD detector. Cell parameters were refined from the observed positions of all strong reflections in each data set and absorption corrections were applied using a Gaussian numerical method with beam profile correction (CrysAlisPro).[2] The structure was solved either by direct methods and all non-hydrogen atoms refined by full-matrix least-squares on all unique F^2 values with anisotropic displacement parameters. Hydrogen atoms were refined with constrained geometries and riding thermal parameters. Programs used include CrysAlisPro (control of Supernova, data integration and absorption correction), SHELXL[3] (structure refinement), SHELXS[4] (structure refinement), OLEX2[5] (molecular graphics). CIF files were checked using the online checkCIF service.[6] CCDC-1548834 contains the supplementary data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for $(2,6\text{-Xyl}_2C_6H_3)_2Mn$ (1)

$C_{44}H_{42}Mn$ (M = 625.71 g/mol): tetragonal, space group $P4_3$ (no. 78), a = 10.52378(8) Å, c = 30.7376(4) Å, V = 3404.19(7) Å^3, Z = 4, T = 120(2) K, μ(CuKα) = 3.359 mm^{-1}, D_{calc} = 1.221 g/cm^3, 37850 reflections measured (8.402° ≤ 2Θ ≤ 147.666°), 6818 unique (R_{int} = 0.0309, R_{sigma} = 0.0168) which were used in all calculations. The final R_1 was 0.0372 (I > 2σ(I)) and wR_2 was 0.0999 (all data). Flack parameter 0.003(3). Largest diff. peak/hole = 0.20/-0.30 eÅ^{-3}.

References

1. Cosier, J.; Glazer, A. M., *J. Appl. Crystallogr.* **1986**, *19*, 105–107.
2. CrysAlisPRO Oxford Diffraction/Agilent Technologies UK Ltd Yarnton England.
3. Sheldrick, G. M., *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3–8.

4. G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.* **2008**, *64*, 112–122.
5. O. V Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst*. **2009**, *42*, 339–341.
6. http://checkcif.iucr.org/