
SUPPORTING INFORMATION

Reversible Addition and Hydrogenation of 1,1-Diphenylethylene with Barium Complex

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1. Experimental section

General remarks

All reactions were carried out under a dry and oxygen-free nitrogen atmosphere using Schlenk techniques and a Vigor glovebox. The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves (4 Å) catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by O₂ (GE) / H₂O (Xentaur) to ensure both were always below 0.1 ppm. Toluene, and hexane were purified by use of a Vigor VSPS-5 solvent purification system, and dried over fresh Na chips in the glovebox. THF and C₆D₆ were distilled from Na/K alloy/benzophenone ketyl, degassed by the freeze-pump-thaw method (three times), and dried over fresh Na chips in the glovebox. [(Tp^{Ad,iPr})Ba(μ-H)]₂ (**1**) was prepared according to the published work^[1]. 1,1-Diphenylethylene was obtained commercially, dried over CaH₂ (92 %) at 45°C for 18 h and distilled before using. Other commercially available reagents were used without purification.

Samples for NMR spectroscopic measurements were prepared in the glovebox by use of J. Young valve NMR tubes. ¹H and ¹³C NMR spectra were recorded on a Bruker AV400, AV500 or AV600 spectrometer. ¹H and ¹³C NMR spectra of complexes were recorded using TMS as internal standard. Conversion was determined by integration of characteristic signals in the NMR spectra of substrate and product. The elemental analyses were performed on Elementar Vario EL cube (WO₃ was used as pro-oxidant) at National Analytical Research Centre of Changchun Institute of Applied Chemistry (CIAC).

Synthesis of [(Tp^{Ad,iPr})Ba(η⁶-Ph)C(Ph)Me] (**2**)

A solution of 1,1-diphenylethylene (21 mg, 0.116 mmol) and [(Tp^{Ad,iPr})Ba(μ-H)]₂ (100 mg, 0.057 mmol) in hexane (10 mL) was stirred for 10 minutes at room temperature and then filtered. The deep-red solution was concentrated to ~2 mL, slowly cooled to -30 °C to give complex **2** as dark-red crystals (108 mg, 0.102 mmol, 90% yield). Single crystals of **2**•hexane suitable for X-ray analysis, were grown from hexane at -30 °C. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ = 1.20 (d, ³J_{HH} = 7.2 Hz, 18H, CH(CH₃)₂), 1.62 (dd, ³J_{HH} = 12.8, 15.4 Hz, 18H AdCH₂), 1.84 (br, 18H, AdCH₂), 1.91 (br, 9H, AdCH), 2.03 (s, 3H, CH₃), 3.29 (sept, ³J_{HH} = 6.8 Hz, 3H, CH(CH₃)₂), 6.01 (s, 3H, 4-pz-H), 6.21 (t, ³J_{HH} = 6.8 Hz, 2H, Ph), 6.93 (dd, ³J_{HH} = 6.8, 8.4 Hz, 4H, Ph), 7.02 (d, J = 7.2 Hz, 4H, Ph). ¹³C{¹H} NMR (100 MHz, C₆D₆, 25 °C): δ = 20.77 (s, CH₃), 23.45 (s, CH(CH₃)₂), 26.74 (s, CH(CH₃)₂), 28.90 (s, Ad-γ), 34.94 (s, Ad-α), 36.88 (s, Ad-δ), 43.87 (s, Ad-β), 85.74 (s, CPh₂), 99.30 (s, pz-4C),

110.22 (s, Ph), 118.96 (s, Ph), 131.06 (s, Ph), 144.46 (s, Ph), 158.40 (s, pz-3C), 164.09 (s, pz-5C). Anal. calcd. for (2) C₆₂H₈₃B₁Ba₁N₆ (1060.49): C, 70.22; H, 7.89; N, 7.92; found: C, 70.13; H, 7.97; N, 7.81.

Synthesis of [(Tp^{Ad,iPr})Ba(η^6 -Ph)C(Ph)-CH₂-C(Ph)₂Me] (3)

A solution of 1,1-diphenylethylene (410 mg, 2.28 mmol) and [(Tp^{Ad,iPr})Ba(μ -H)]₂ (100 mg, 0.057 mmol) in hexane (6 mL) was stirred for 3 h at room temperature and then filtered. The resulting deep-red solution was slowly volatilized at room temperature for 3 days to give complex **3** as dark-red crystals (65.7 mg, 0.053 mmol, 46.3% yield). Single crystals of **3** suitable for X-ray analysis, were grown from hexane at room temperature. ¹H NMR (600 MHz, C₆D₆, 25 °C): δ = 1.24 (d, ³J_{HH} = 6.6 Hz, 18H, CH(CH₃)₂), 1.58 (dd, ³J_{HH} = 12.6, 20.4 Hz, 18H, AdCH₂), 1.78 (s, 3H, CH₃), 1.82 (br, 18H, AdCH₂), 1.88 (br, 9H, AdCH), 3.36 (sept, ³J_{HH} = 6.6 Hz, 3H, CH(CH₃)₂), 3.41 (s, 2H, CH₂), 6.07 (t, ³J_{HH} = 6.6 Hz, 2H, Ph), 6.10 (s, 3H, 4-pz-H), 6.70 (dd, ³J_{HH} = 6.6, 8.4 Hz, 4H, Ph), 6.80 (d, ³J_{HH} = 7.8 Hz, 4H, Ph), 7.07 (t, ³J_{HH} = 7.2 Hz, 2H, Ph), 7.17 (t, ³J_{HH} = 8.4 Hz, 4H, Ph), 7.45 (d, ³J_{HH} = 7.2 Hz, 4H, Ph). ¹³C{¹H} NMR (150 MHz, C₆D₆, 25 °C): δ = 23.45 (s, CH₃), 23.54 (s, CH(CH₃)₂), 26.82 (s, CH(CH₃)₂), 28.87 (s, Ad- γ), 34.92 (s, Ad- α), 36.83 (s, Ad- δ), 43.94 (s, Ad- β), 44.70 (s, CPh₂CH₃), 50.58 (s, CH₂), 91.06 (s, CPh₂CH₂), 98.93 (s, pz-4C), 109.98 (s, Ph), 119.90 (s, Ph), 125.63 (s, Ph), 128.57 (s, Ph), 130.90 (s, Ph), 145.14 (s, Ph), 151.38 (s, Ph), 158.45 (s, pz-3C), 164.00 (s, pz-5C). Anal. calcd. for (3) C₇₆H₉₅B₁Ba₁N₆ (1240.72): C, 73.57; H, 7.72; N, 6.77; found: C, 73.44; H, 7.87; N, 6.64.

Typically experiments:

Reactions of $[(\text{Tp}^{\text{Ad},i\text{Pr}})\text{Ba}(\mu\text{-H})]_2$ with excess amount of DPE

In the glovebox, $[(\text{Tp}^{\text{Ad},i\text{Pr}})\text{Ba}(\mu\text{-H})]_2$ (5.3 mg, 3 μmol) was dissolved in dry C_6D_6 (1.0 mL) in a dried J. Young valve NMR tube and excess DPE was added. The reaction was allowed to proceed at 25°C for a certain time, during which time the color of the solution changed from colorless to dark red. Conversions of the mono-DPE adduct **2** and di-DPE adduct **3** were determined by integration of characteristic signals in the NMR spectra.

Catalytic hydrogenation of DPE with 5 % catalyst

In a stainless steel autoclave (25 mL) containing a glass tube charged with a magnetic stir bar, the catalyst $[(\text{Tp}^{\text{Ad},i\text{Pr}})\text{Ba}(\mu\text{-H})]_2$ (3 μmol , 5 mol%) was dissolved into dry C_6D_6 (1.0 mL) and the DPE (0.12 mmol) was added to the solution. The autoclave was sealed, brought out of the nitrogen-filled glovebox, and pressurized with H_2 to 6 atm after degassed twice. The reaction was carried out in a 30 °C oil bath for the time indicated and monitored by ^1H NMR spectroscopy.

2. Selected NMR Spectra

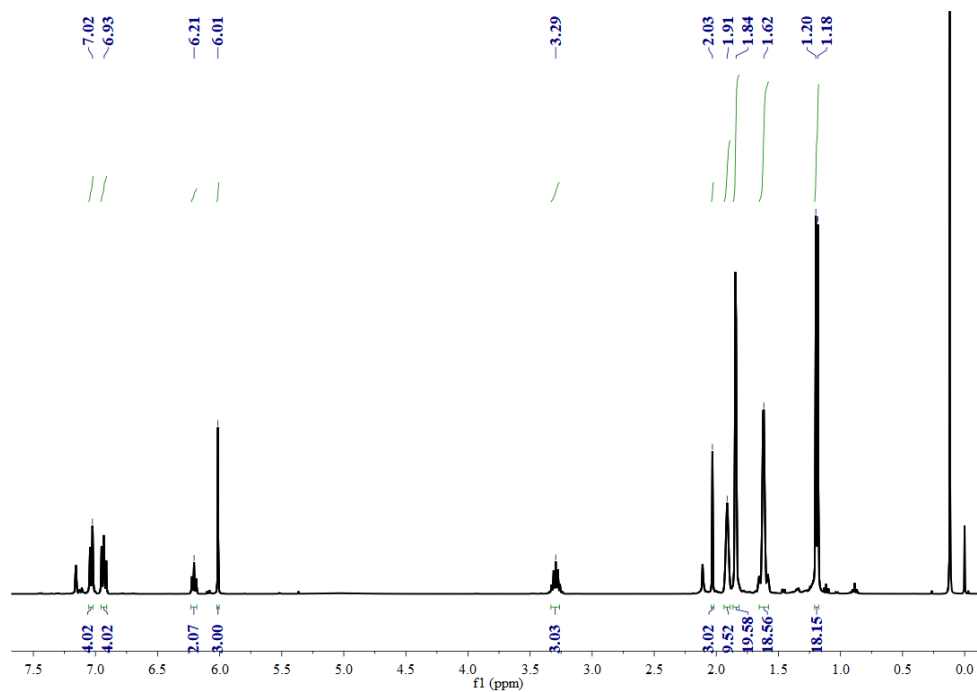


Figure S1. ¹H NMR spectrum (400 MHz) of [(Tp^{Ad,iPr})Ba(η⁶-Ph)C(Ph)Me] (**2**) in C₆D₆ at 25 °C.

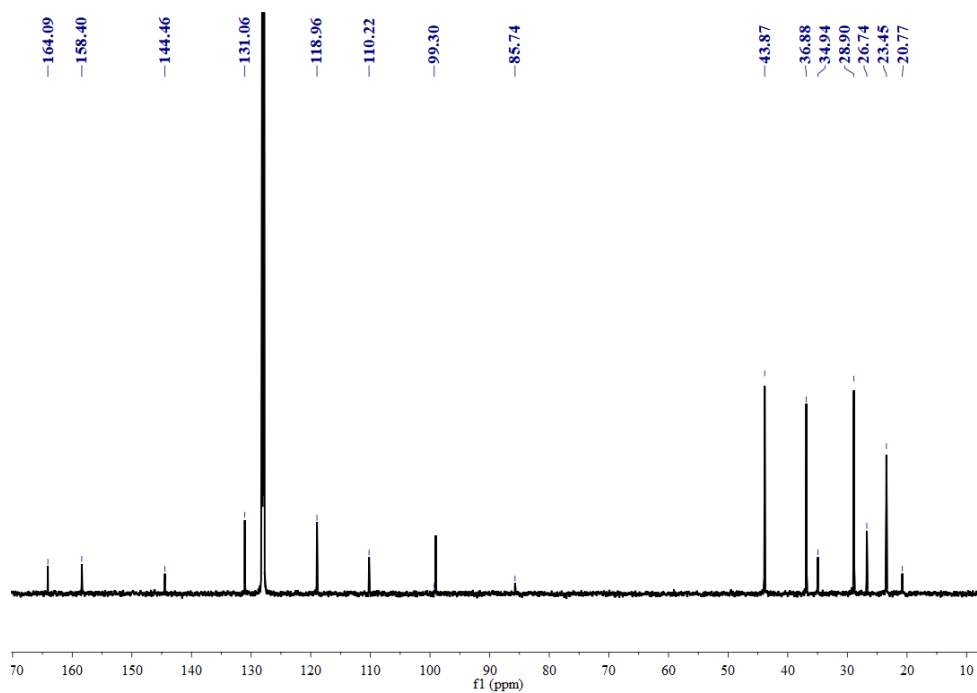


Figure S2. ¹³C NMR spectrum (100 MHz) of [(Tp^{Ad,iPr})Ba(η⁶-Ph)C(Ph)Me] (**2**) in C₆D₆ at 25 °C.

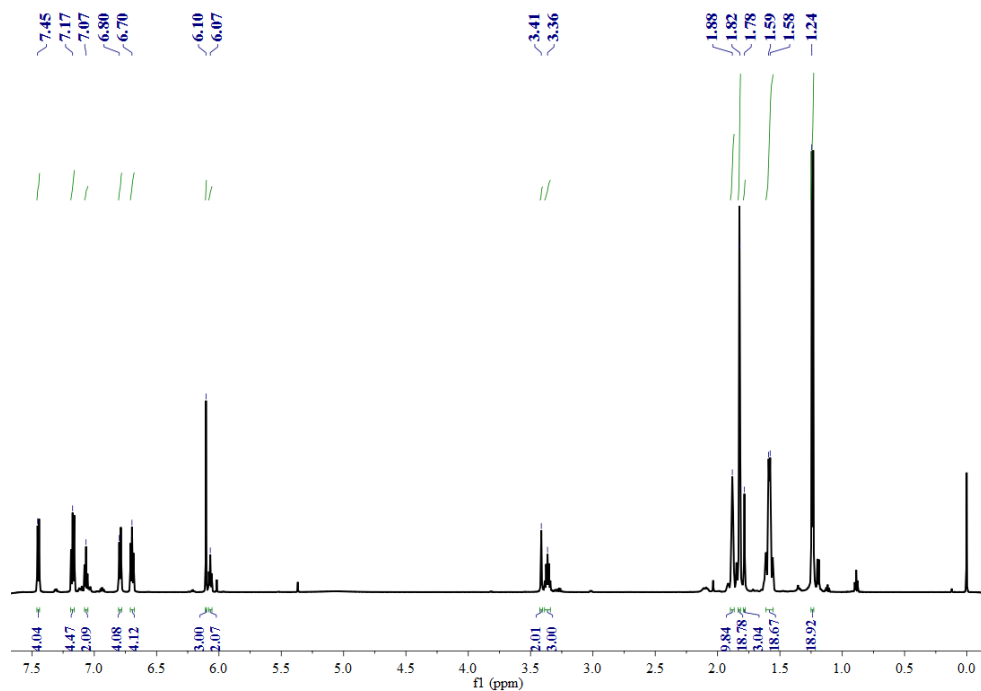


Figure S3. ^1H NMR spectrum (600 MHz) of $[(\text{Tp}^{\text{Ad,Pr}})\text{Ba}(\eta^6\text{-Ph})\text{C}(\text{Ph})\text{-CH}_2\text{-C}(\text{Ph})_2\text{Me}]$ (**3**) in C_6D_6 at 25 °C.

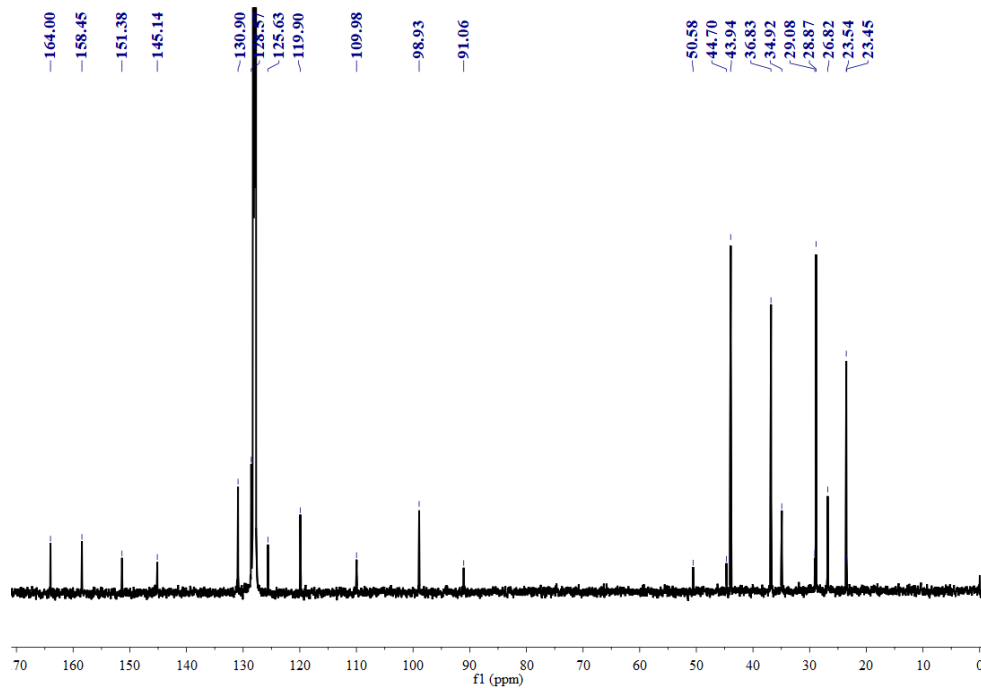


Figure S4. ^{13}C NMR spectrum (150 MHz) of $[(\text{Tp}^{\text{Ad,Pr}})\text{Ba}(\eta^6\text{-Ph})\text{C}(\text{Ph})\text{-CH}_2\text{-C}(\text{Ph})_2\text{Me}]$ (**3**) in C_6D_6 at 25 °C.

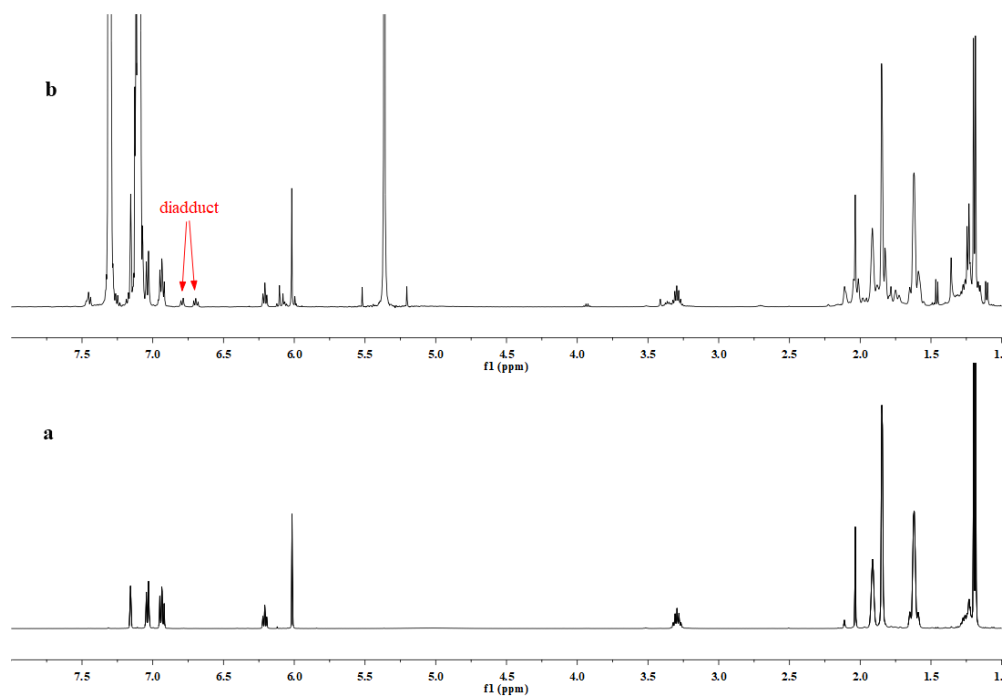


Figure S5. Stacked ¹H NMR spectrum (400 MHz, C₆D₆, 25 °C) of (a) complex **2** and (b) the reaction of complex **2** with 20 mol-eq. DPE after 27 h.

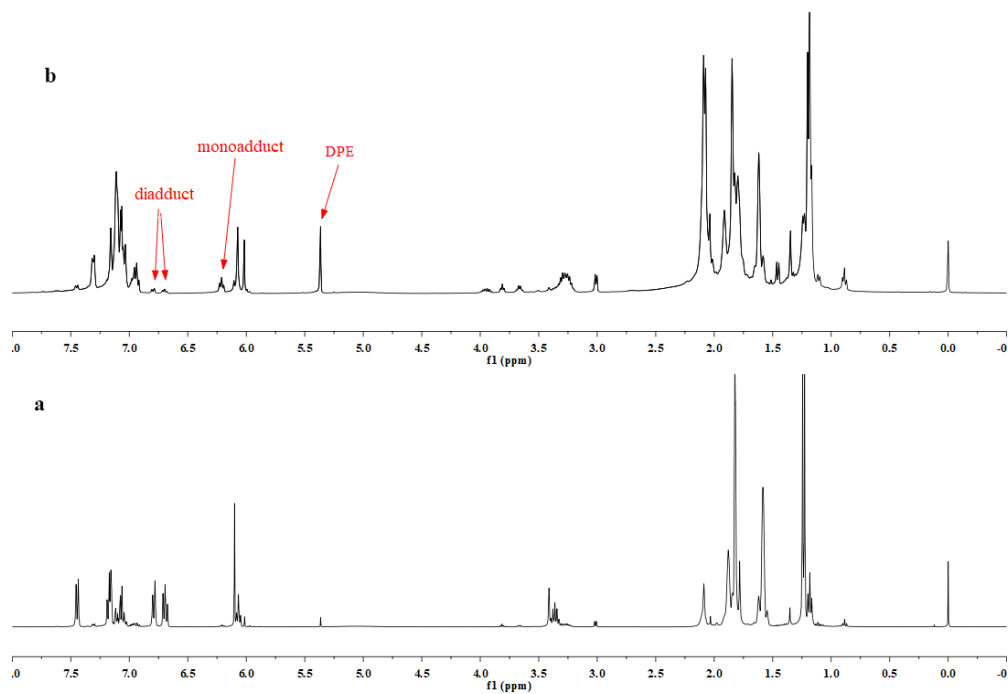


Figure S6. Stacked ¹H NMR spectrum (600 MHz, C₆D₆, 25 °C) of complex **3** after (a) 0 day and (b) 6 days.

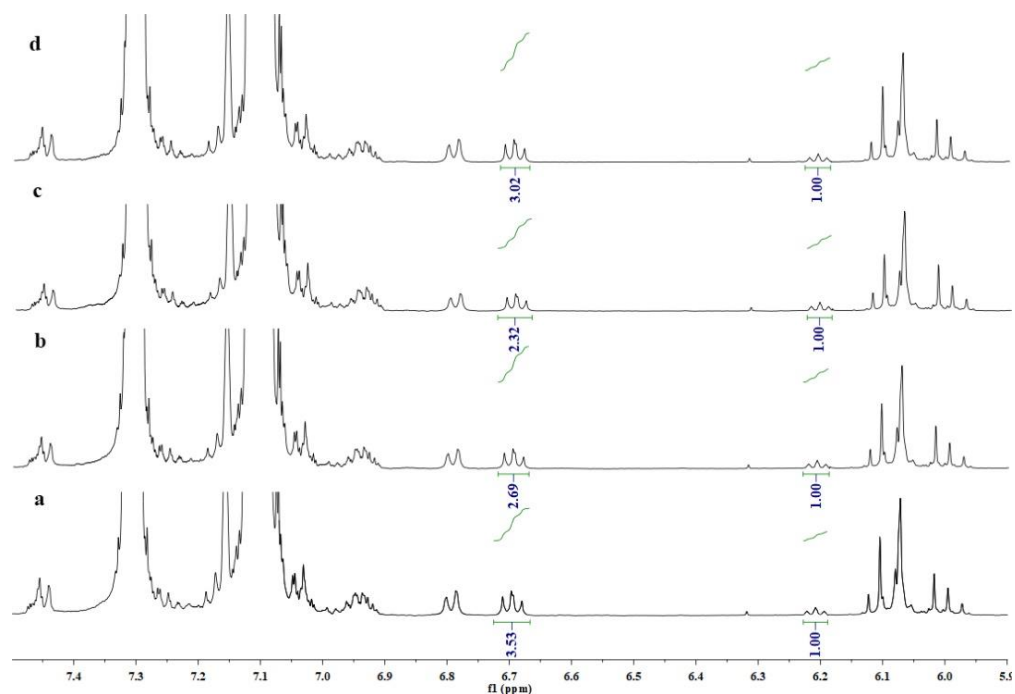


Figure S7. Stacked ^1H NMR spectrum (500 MHz, C_6D_6) of the reaction of $[(\text{Tp}^{\text{Ad},i\text{Pr}})\text{Ba}(\mu\text{-H})]_2$ with DPE (Table 1, entry 6) after (a) 0 h (25 °C); (b) 1 h (50 °C); (c) 2 h (50 °C); (d) 27 h (25 °C) in turn.

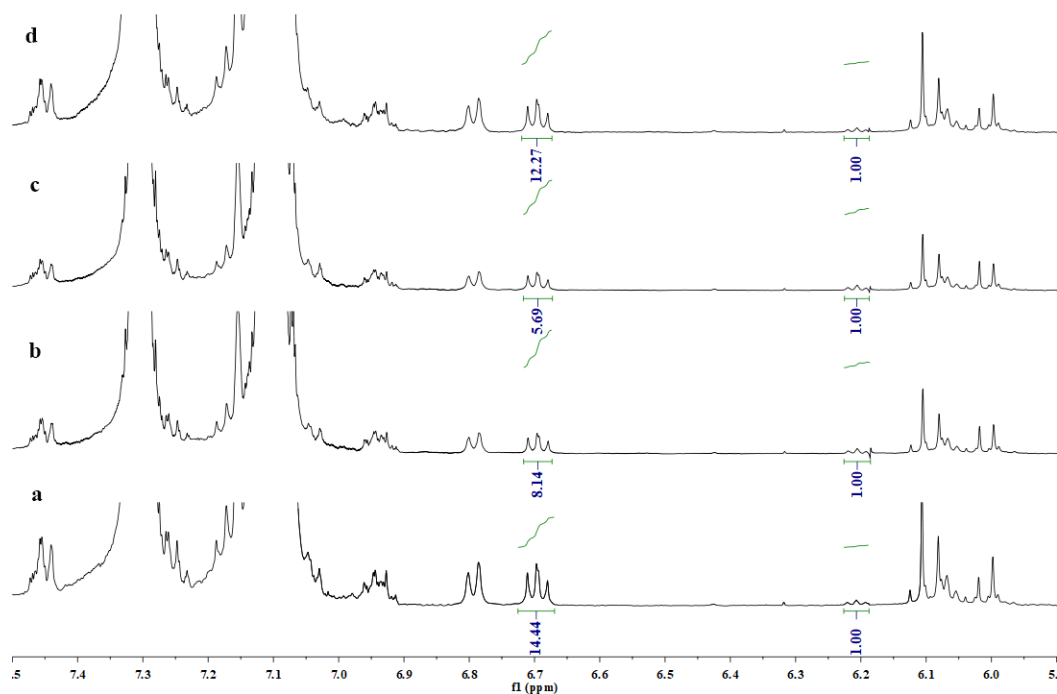


Figure S8. Stacked ^1H NMR spectrum (500 MHz, C_6D_6) of the reaction of $[(\text{Tp}^{\text{Ad},i\text{Pr}})\text{Ba}(\mu\text{-H})]_2$ with DPE (Table 1, entry 11) after (a) 0 h (25 °C); (b) 1 h (50 °C); (c) 2 h (50 °C); (d) 27 h (25 °C) in turn.

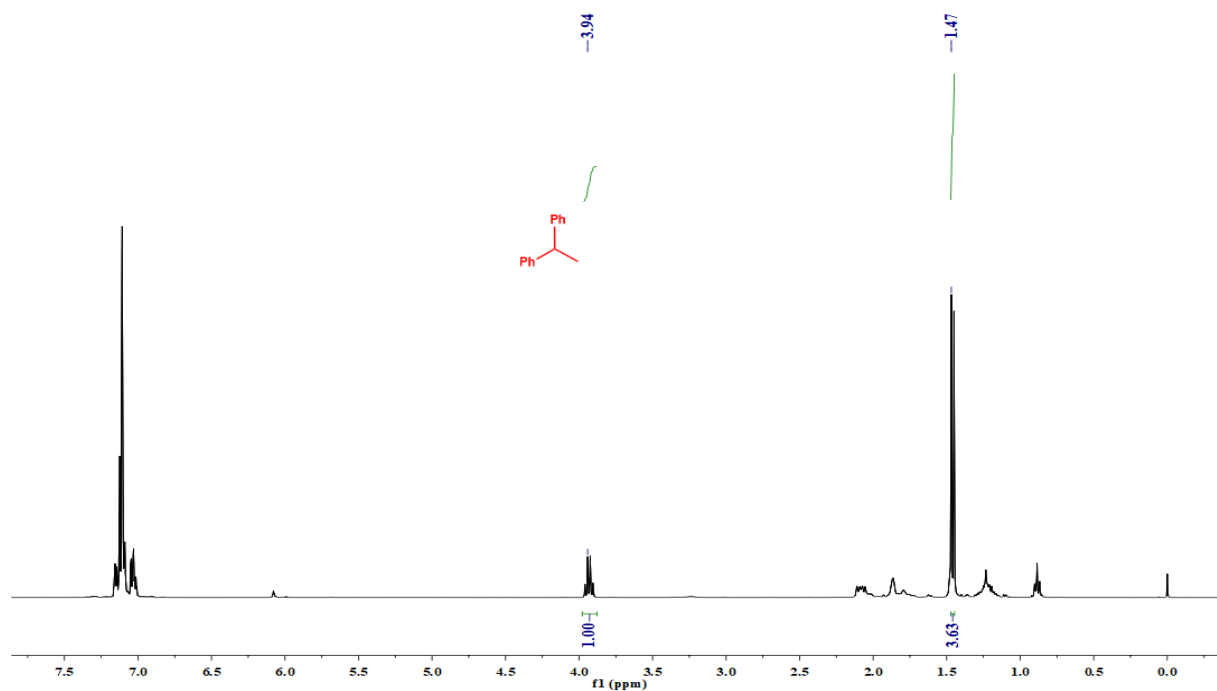


Figure S9. ^1H NMR spectrum (500 MHz, C_6D_6 , 25 $^\circ\text{C}$) of 1,1-diphenylethane after catalytic hydrogenation with $[(\text{Tp}^{\text{Ad},\text{Pr}})\text{Ba}(\mu\text{-H})_2]$ (5 mol%) and H_2 (6 atm) at 30 $^\circ\text{C}$ (Table 2, entry 3).

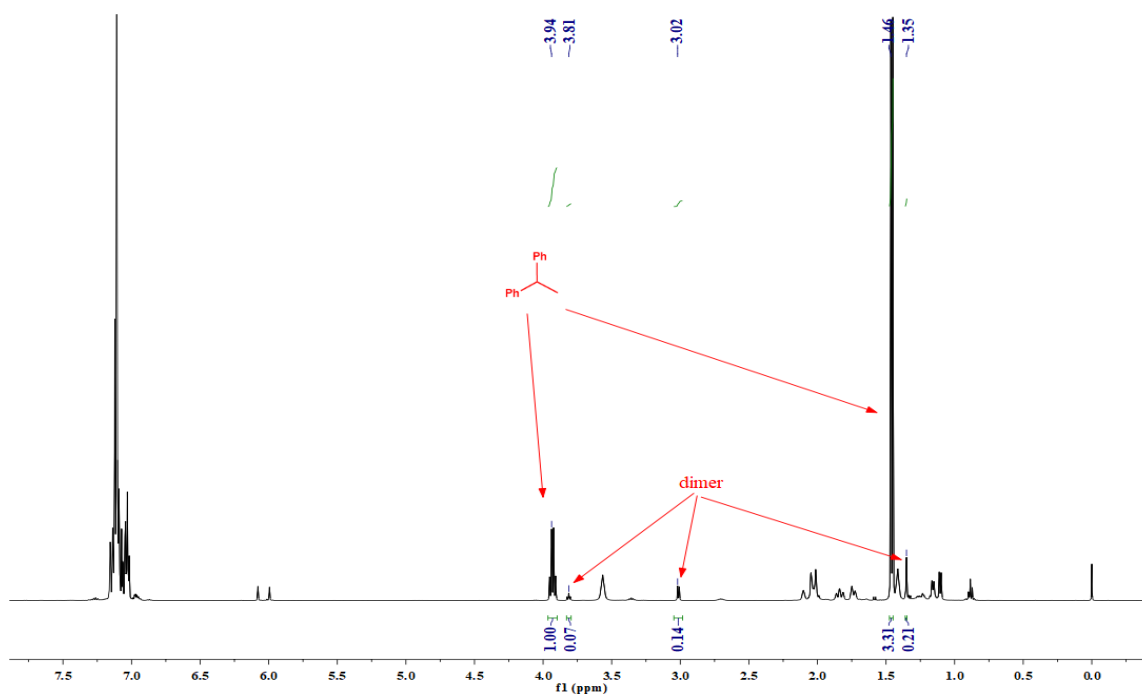


Figure S10. ^1H NMR spectrum (500 MHz, C_6D_6 , 25 $^\circ\text{C}$) of 1,1-diphenylethane after catalytic hydrogenation with $[(\text{Tp}^{\text{Ad},\text{Pr}})\text{Ba}(\mu\text{-H})_2]$ (5 mol%) and H_2 (6 atm) at 30 $^\circ\text{C}$ (Table 2, entry 6).

3. X-ray Crystallographic Studies

Single crystals suitable for X-ray analysis were obtained as described in the preparation. The crystals were manipulated in the glovebox under a microscope in the glovebox, data collection was performed at -80 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The determination of the crystal class and unit cell parameters was carried out by the SMART program packages^[2]. The raw frame data were processed using SAINT^[3] and absorption corrections using SADABS^[4] to yield the reflection data file. The structures were solved by using SUPERFLIP^[5] in the WinGX program package^[6]. Refinements were performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method using SHELXL-2018 program^[7]. The SQUEEZE^[8] routine of the program PLATON^[9] was implemented to remove the contributions of the disordered solvents to the observed structure factors. The hydrogen (H1B1) bonded to the boron atom was located by Difference Fourier Syntheses, and refined isotropically. Other hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. The residual electron densities were of no chemical significance. Crystal data and analysis results are listed in STable 1-2.

Refinement of **2**: The SQUEEZE^[8] routine of the program PLATON^[9] was implemented to remove the contributions of the disordered hexane to the observed structure factors. Two adamantyl groups in the pyrazolyl rings (N1, N2 and N5, N6) were disordered. C27~C35 and C27'~C35' disordered over two sites with occupancies 0.579:0.421. C67~C75 and C67'~C75' disordered over two sites with occupancies 0.555:0.445.

CCDC number 1863149 (**2**) and 1569762 (**3**) contain the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

4. References

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5. Tables of crystal data and structure refinement

STable 1. Crystal data and structure refinement for Complex 2.

Identification code	C121
Empirical formula	C ₆₂ H ₈₃ B ₁ Ba ₁ N ₆
Formula weight	1060.49
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
a	12.3228(19) Å
b	15.352(3) Å
c	17.272(3) Å
α	90.219(2) °
β	101.569(2) °
γ	104.232(3) °
Volume	3098.0(8) Å ³
Z, Calculated density	2, 1.137 Mg/m ³
Absorption coefficient	0.680 mm ⁻¹
F(000)	1116
Crystal size	0.230 x 0.170 x 0.120 mm
Theta range for data collection	1.774 to 25.000 °
Limiting indices	-14<=h<=14, -18<=k<=10, -20<=l<=19
Reflections collected / unique	15398 / 10595 [R(int) = 0.0436]
Completeness to theta	(25.00 °) 97.0 %
Absorption correction	Empirical
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	10595 / 102 / 607
Goodness-of-fit on F ²	0.953
Final R indices [I>2σ(I)]	R1 = 0.0709, wR2 = 0.1711
R indices (all data)	R1 = 0.0989, wR2 = 0.1873
Largest diff. peak and hole	2.044 and -1.048 e. Å ⁻³

STable 2. Crystal data and structure refinement for Complex 3.

Identification code	C085
Empirical formula	C ₇₆ H ₉₅ B ₁ Ba ₁ N ₆
Formula weight	1240.72
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
a	12.9194(19) Å
b	15.110(2) Å
c	18.808(3) Å
α	81.415(3) °
β	85.327(2) °
γ	66.844(3) °
Volume	3336.8(8) Å ³
Z, Calculated density	2, 1.235 Mg/m ³
Absorption coefficient	0.642 mm ⁻¹
F(000)	1308
Crystal size	0.250 x 0.150 x 0.120 mm
Theta range for data collection	1.715 to 25.000 °
Limiting indices	-11 ≤ h ≤ 15, -17 ≤ k ≤ 16, -22 ≤ l ≤ 22
Reflections collected / unique	15929 / 11459 [R(int) = 0.0486]
Completeness to theta	(25.00 °) 97.5 %
Absorption correction	Empirical
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	11459 / 0 / 761
Goodness-of-fit on F ²	0.964
Final R indices [I > 2σ(I)]	R1 = 0.0635, wR2 = 0.1195
R indices (all data)	R1 = 0.0983, wR2 = 0.1367
Largest diff. peak and hole	1.419 and -0.519 e. Å ⁻³