SUPPORTING INFORMATION

Bora-amidinate as a cooperative ligand in group 2 metal catalysis

Benjamin Freitag,[a] Christian A. Fischer,[a] Johanne Penafiel,[a] Gerd Ballmann,[a] Holger Elsen,[a] Christian Färber,[a] Dirk F. Piesik[b] and Sjoerd Harder*[a]

[a]*Inorganic and Organometallic Chemistry, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 1, 91058 Erlangen, Germany.*

[b]*Inorganic Chemistry, Universität Duisburg-Essen, Universitätsstrasse 7, 45151 Essen, Germany.*

Contents **Page**

1. Crystal structures

Crystal structures have been measured on a SuperNova (Agilent) diffractometer with dual Cu and Mo microfocus sources and an Atlas S2 detector (^{DIPP}NBN-Mg·THF_3) and on Bruker SMART diffractometer with APEXII detector (^{DIPP}NBN-Ca·THF_4). Using Olex2,[1] the structures were solved by Direct Methods (ShelXT)[2] and refined with ShelXL[3] using Least Squares minimization. Geometric calculations and graphical presentations were done with the program PLATON.[4] Crystallographic data can be found below and have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1551537 (^{DIPP}NBN-Ca·THF_4) and 1551538 (^{DIPP}NBN-Mg·THF_3). 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).

1.1 Crystal structure of ^{DIPP}NBN-Mg·THF$_3$

All H atoms have been placed at idealized positions and were refined isotropically in a riding mode, except for the H atom attached to B. The latter was located in a difference Fourier map and refined isotropically. The correct chirality of the structure solution was confirmed by refinement of the Flack parameter to -0.04(3).

Table S1. Crystal data and structure refinement for ^{DIPP}NBN-Mg·THF$_3$.

Identification code	hasj161205b
Empirical formula	$C_{36}H_{59}BMgN_2O_3$
Formula weight	602.97
Temperature/K	100
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.5266(2)
b/Å	17.9167(3)
c/Å	18.7856(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3543.00(12)
Z	4
ρ_{calc}g/cm^3	1.130
μ/mm^{-1}	0.698
F(000)	1320.0
Crystal size/mm^3	0.425 × 0.28 × 0.164
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.818 to 136.23
Index ranges	-12 ≤ h ≤ 12, -21 ≤ k ≤ 21, -22 ≤ l ≤ 21
Reflections collected	17026
Independent reflections	6422 [R_{int} = 0.0486, R_{sigma} = 0.0457]
Data/restraints/parameters	6422/0/400
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0466, wR_2 = 0.1218
Final R indexes [all data]	R_1 = 0.0490, wR_2 = 0.1245
Largest diff. peak/hole / e Å^{-3}	0.42/-0.31
Flack parameter	-0.04(3)

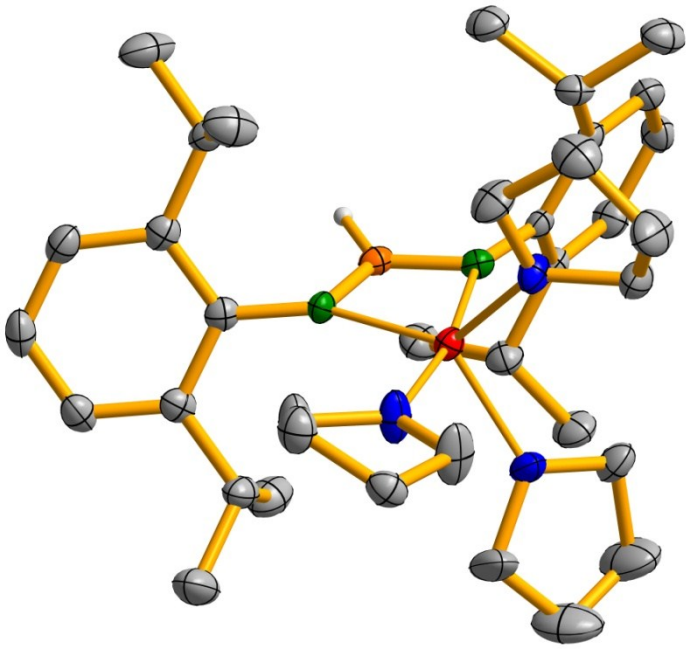


Figure S1. ORTEP plot for ^{DIPP}NBN-Mg·THF$_3$; 50% probability.

1.2 Crystal structure of ^{DIPP}NBN-Ca·THF$_4$

Only smaller weakly diffracting crystals could be obtained. All H atoms have been placed at idealized positions and were refined isotropically in a riding mode, except for the H atom attached to B. The latter was located in a difference Fourier map and refined isotropically. Slight disorder in the THF ligands was treated by refinement with high anisotropy. The correct chirality of the structure solution was confirmed by refinement of the Flack parameter to -0.01(5).

Table S2. Crystal data and structure refinement for ^{DIPP}NBN-Ca·THF$_4$.

Identification code	hasj180
Empirical formula	$C_{40}H_{67}BCaN_2O_4$
Formula weight	690.85
Temperature/K	173
Crystal system	triclinic
Space group	P1
a/Å	10.1263(10)
b/Å	10.1718(9)
c/Å	11.2367(6)
α/°	81.148(6)
β/°	66.376(6)
γ/°	74.572(6)
Volume/Å^3	1020.74(17)
Z	1
ρ_{calc}g/cm^3	1.124
μ/mm^{-1}	0.193
F(000)	378
Crystal size/mm^3	0.10 × 0.10 × 0.10
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.0 to 24.8
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -13 ≤ l ≤ 13
Reflections collected	17051
Independent reflections	6562 [R_{int} = 0.073, R_{sigma} = 0.0963]
Data/restraints/parameters	6562/0/446
Goodness-of-fit on F^2	1.12
Final R indexes [I>=2σ (I)]	R_1 = 0.0765, wR_2 = 0.1811
Final R indexes [all data]	R_1 = 0.0984, wR_2 = 0.1959
Largest diff. peak/hole / e Å^{-3}	0.77/-0.29
Flack parameter	-0.01(5)

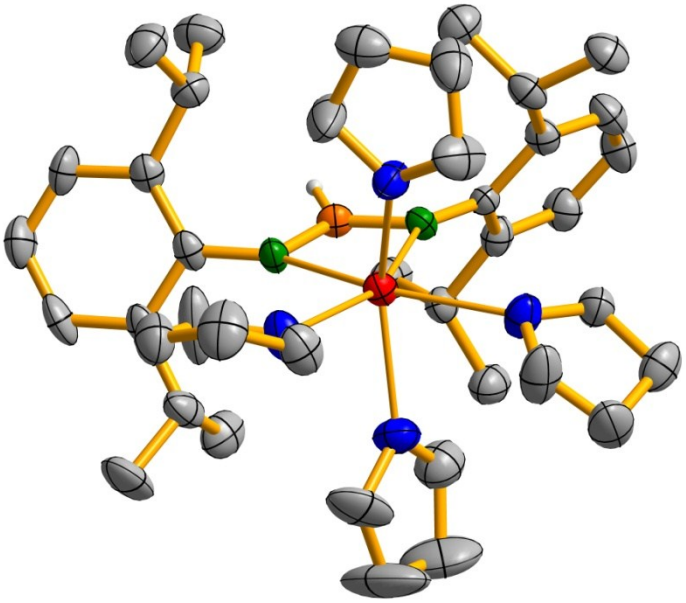


Figure S2. ORTEP plot for ^{DIPP}NBN-Ca·THF$_4$; 50% probability.

2. Selected ^{1}H and ^{13}C NMR spectra

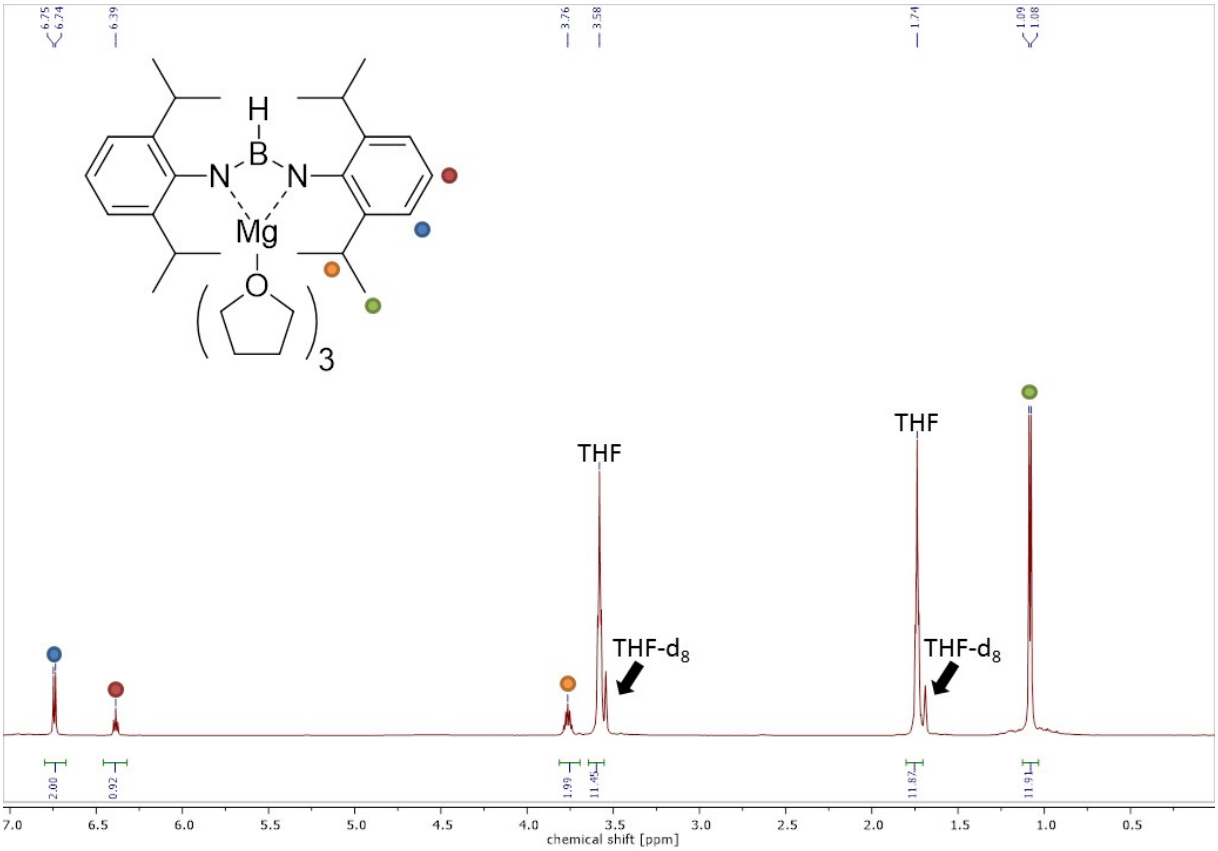


Figure S3. ^{1}H NMR spectrum of ^{DIPP}NBN-Mg·(THF)$_3$ in THF-d$_8$ (298K, 600 MHz).

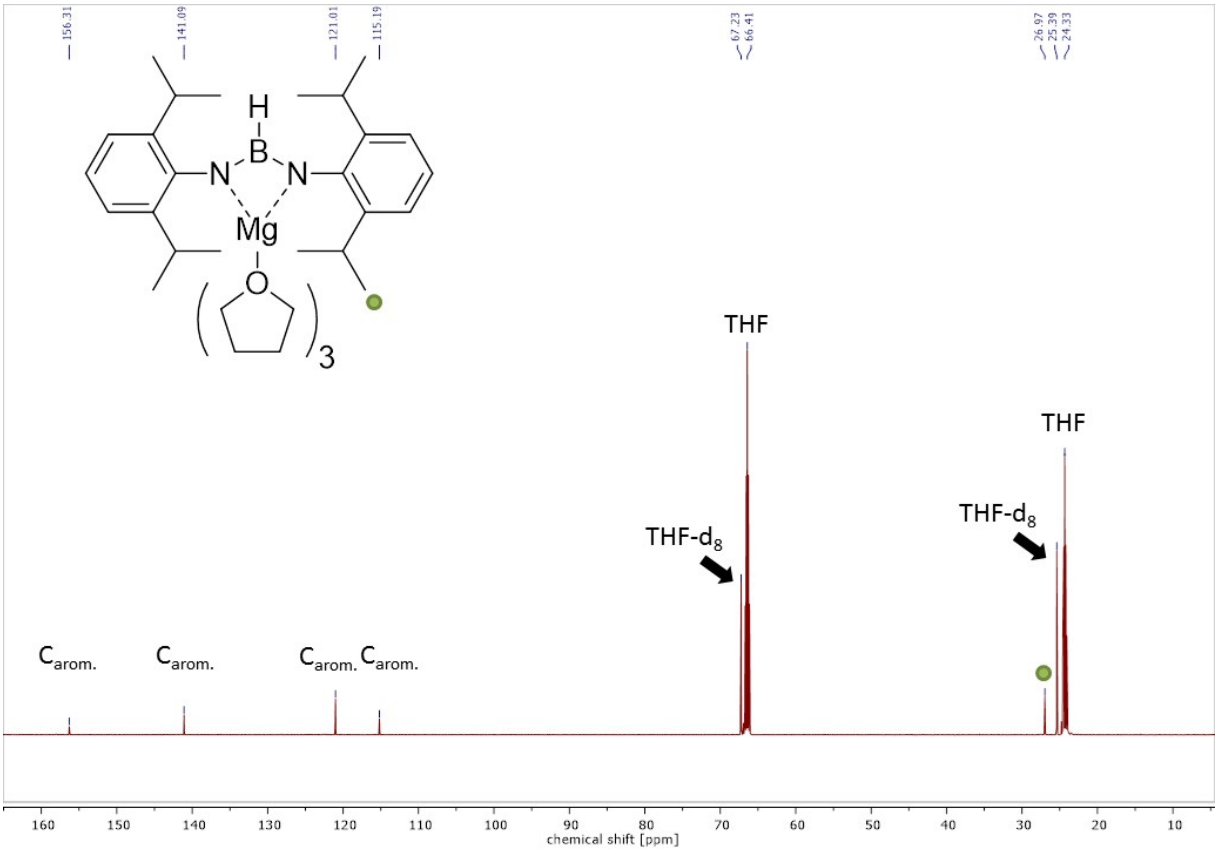


Figure S4. ^{13}C NMR spectrum of ^{DIPP}NBN-Mg·(THF)$_3$ in THF-d$_8$ (298K, 151 MHz).

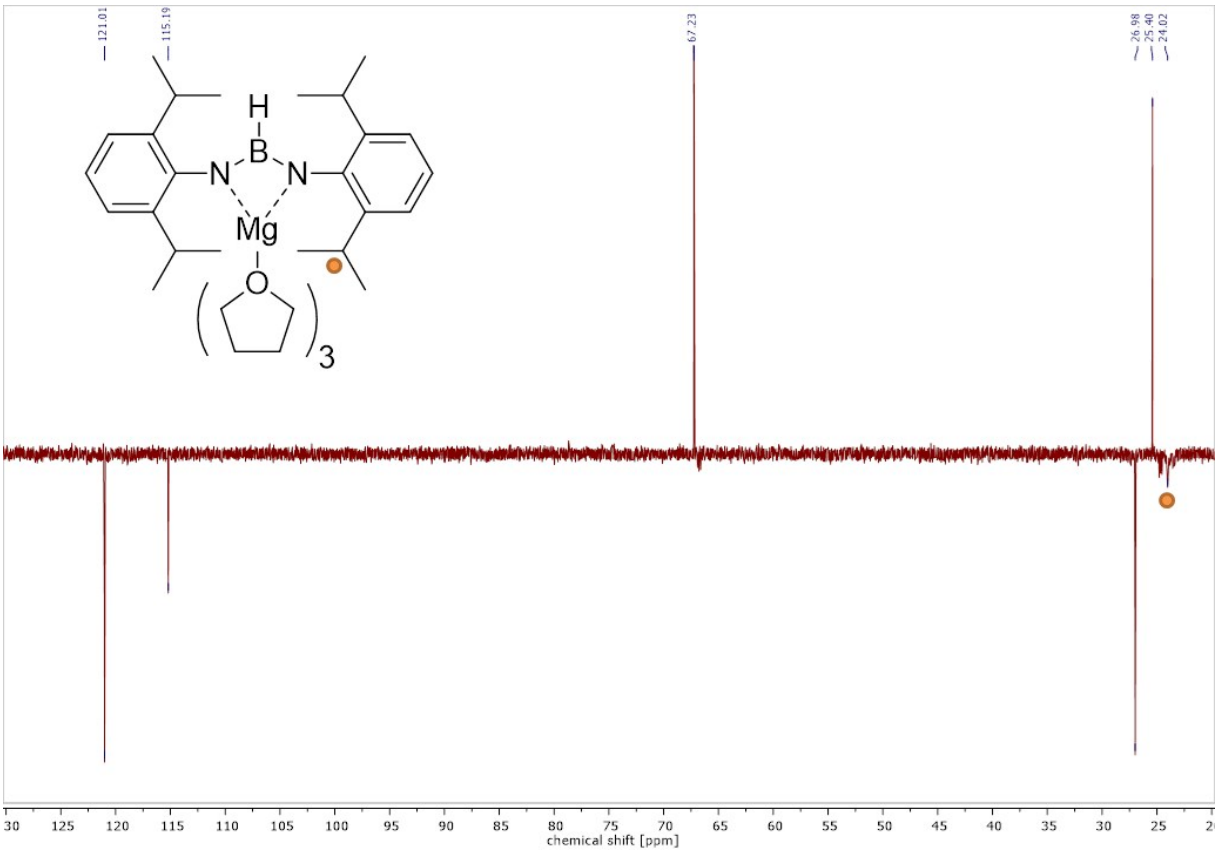


Figure S5. DEPT-135 spectrum of ^{DIPP}NBN-Mg·(THF)$_3$ in THF-d$_8$ (298K, 151 MHz) allows for detection of the iPr CH signal.

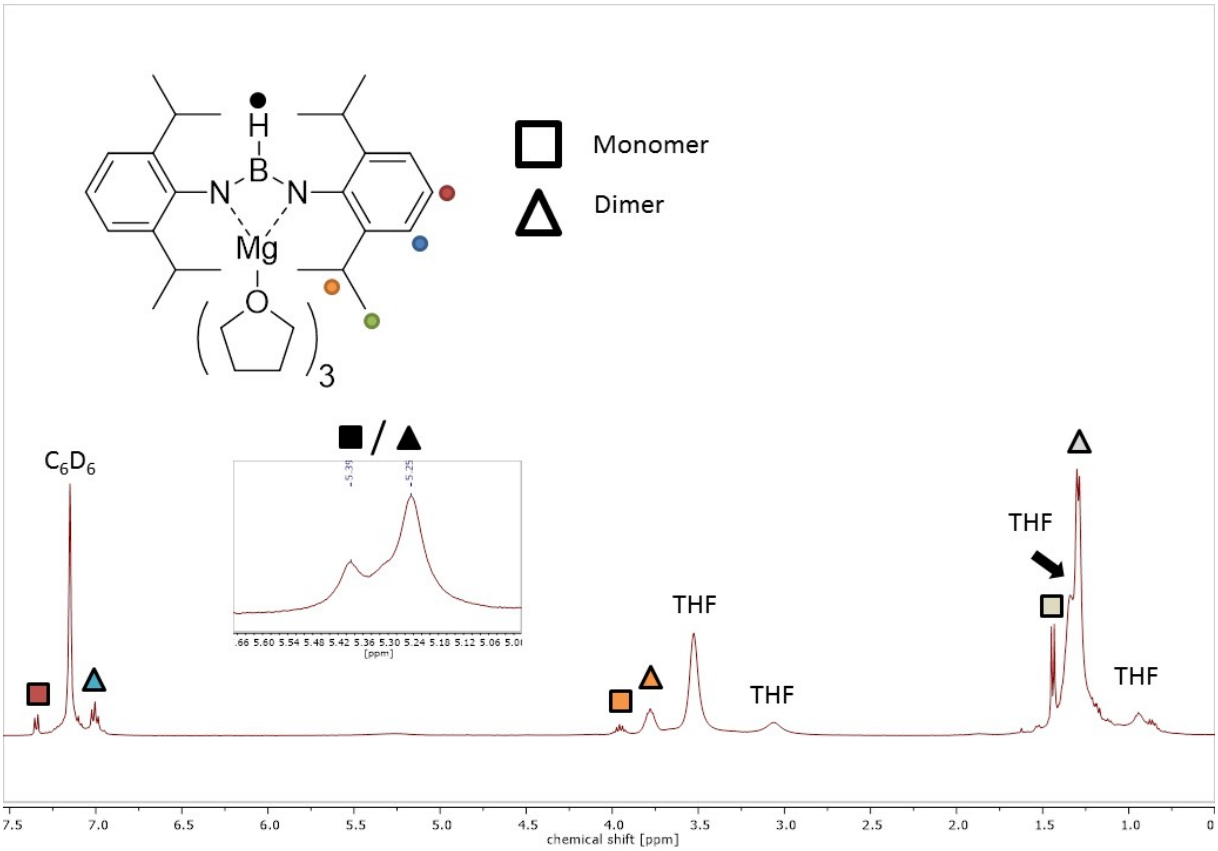


Figure S6. ^{1}H NMR spectrum of ^{DIPP}NBN-Mg·(THF)$_3$ in C$_6$D$_6$ (298K, 400 MHz)

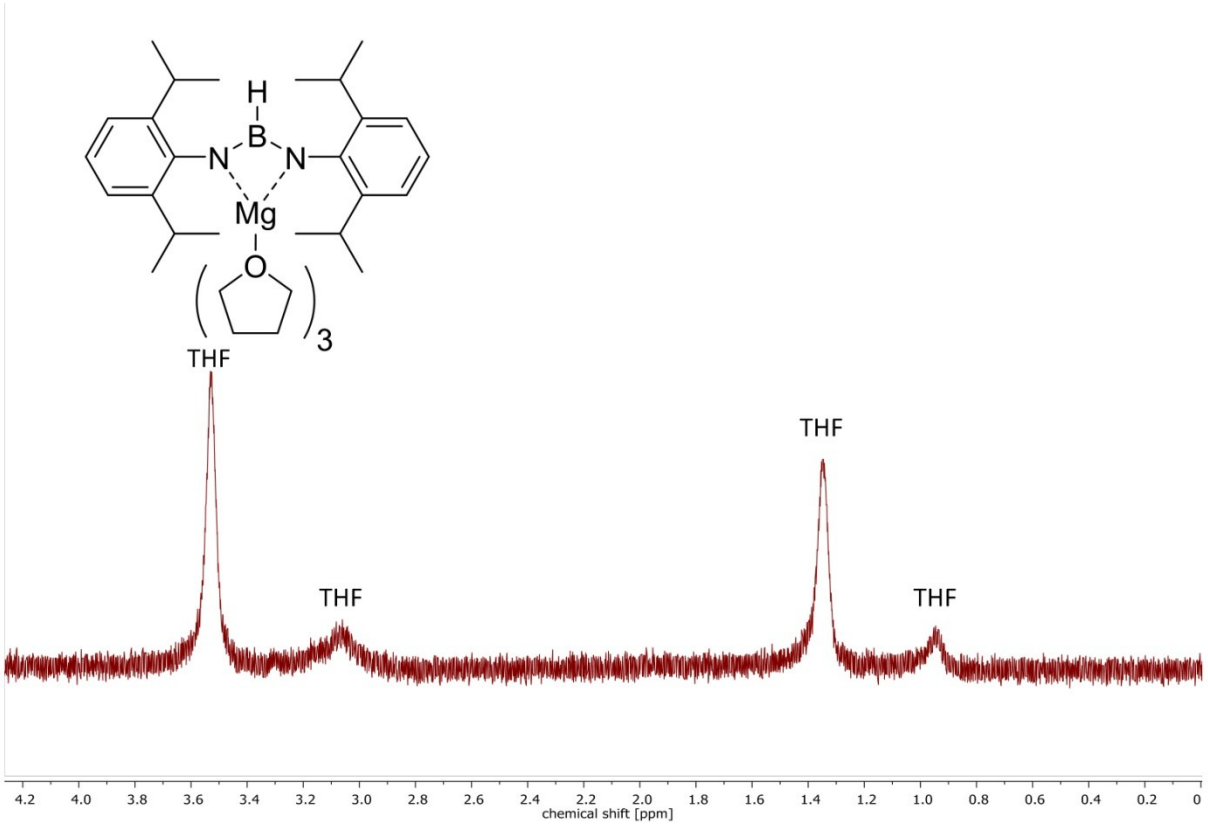


Figure S7. ^{1}H TOCSY NMR spectrum of ^{DIPP}NBN-Mg·(THF)$_3$ in C_6D_6 (298K, 100 MHz) with irradiation at the frequency for the smaller signal at 3.06 ppm showing exchange of THF bound to monomer (larger signal) and THF bound to dimer (smaller signal).

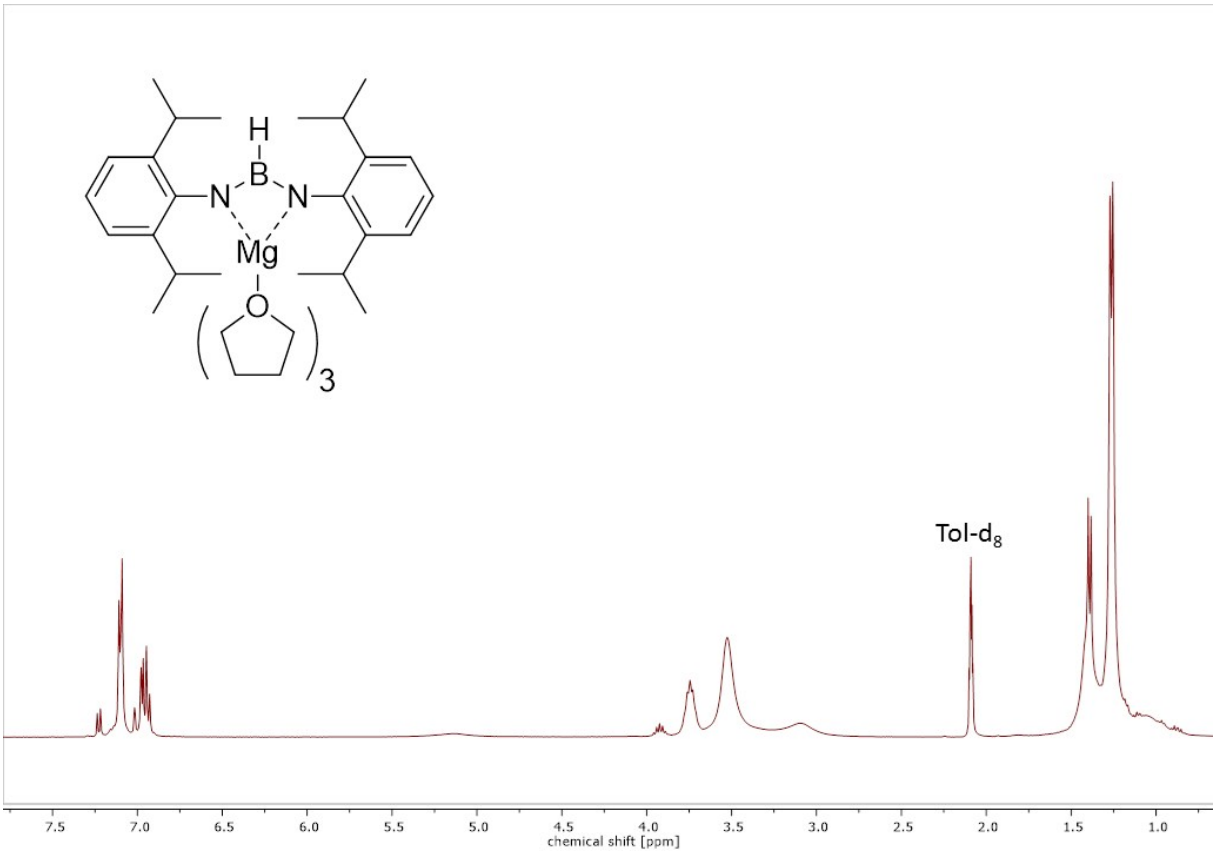


Figure S8. ^{1}H NMR spectrum of ^{DIPP}NBN-Mg·(THF)$_3$ in Tol-d_8 (298K, 400 MHz).

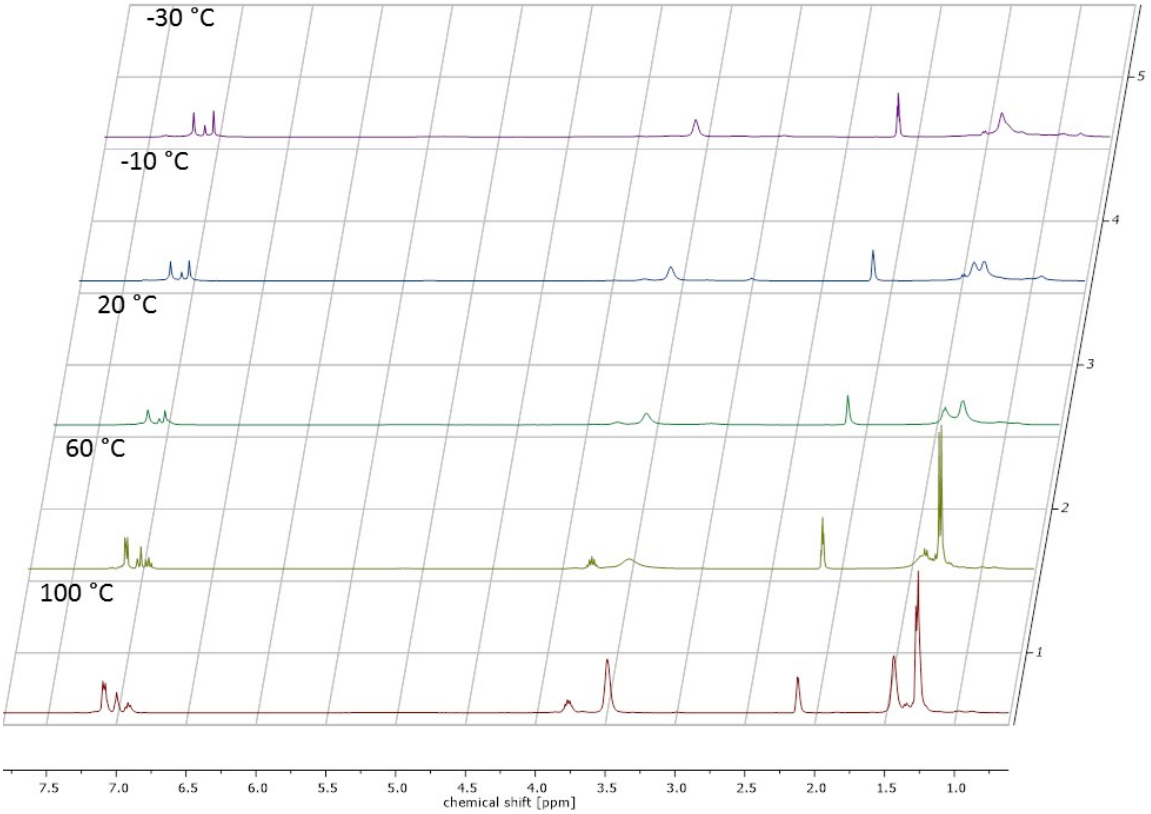


Figure S9. ^{1}H NMR spectrum of ^{DIPP}NBN-Mg·(THF)$_3$ in Tol-d$_8$ (298K, 400 MHz) at -30°C, -10°C, 20°C, 60°C and 100°C.

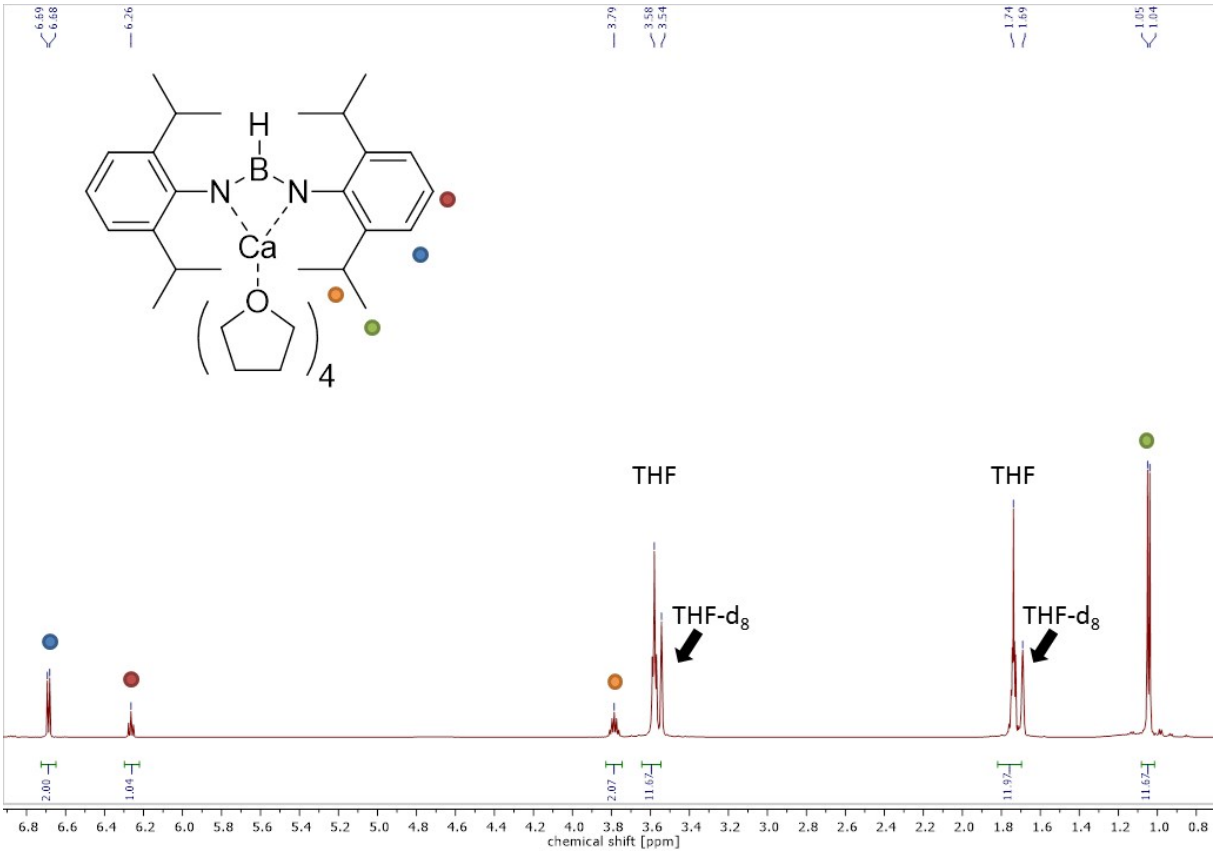


Figure S10. ^{1}H NMR spectrum of ^{DIPP}NBN-Ca·(THF)$_4$ in THF-d$_8$ (298K, 600 MHz).

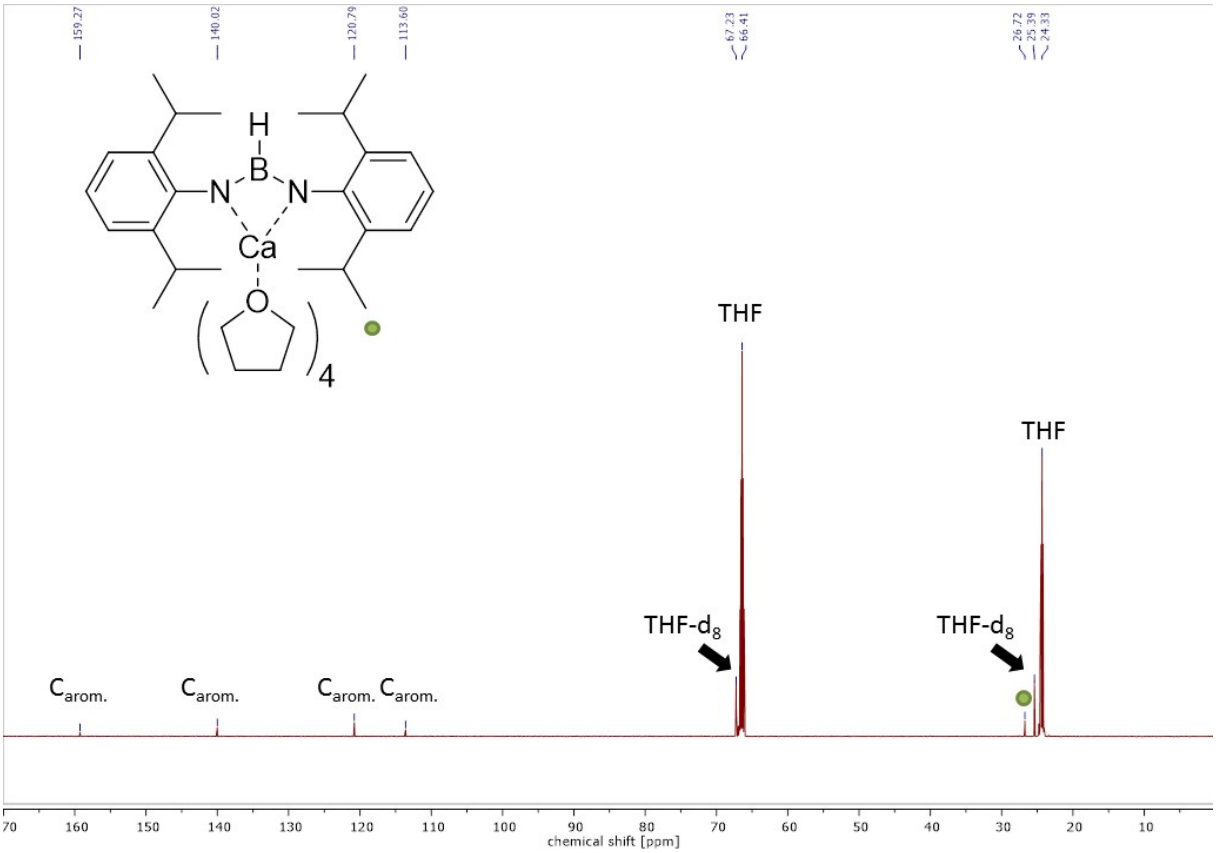


Figure S11. ^{13}C NMR spectrum of ^{DIPP}NBN-Ca·(THF)$_4$ in THF-d$_8$ (298K, 151 MHz).

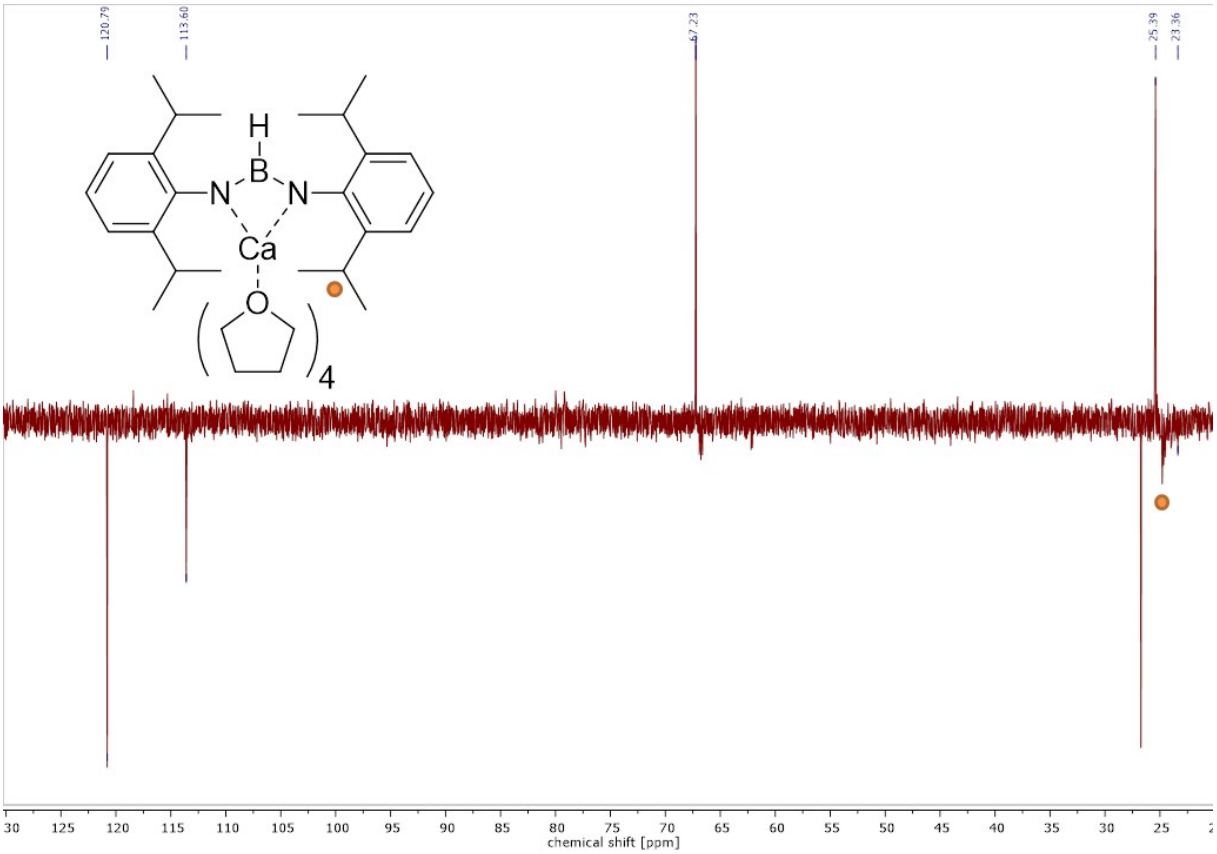


Figure S12. DEPT-135 spectrum of ^{DIPP}NBN-Ca·(THF)$_4$ in THF-d$_8$ (298K, 151 MHz) allows for detection of the iPr CH signal.

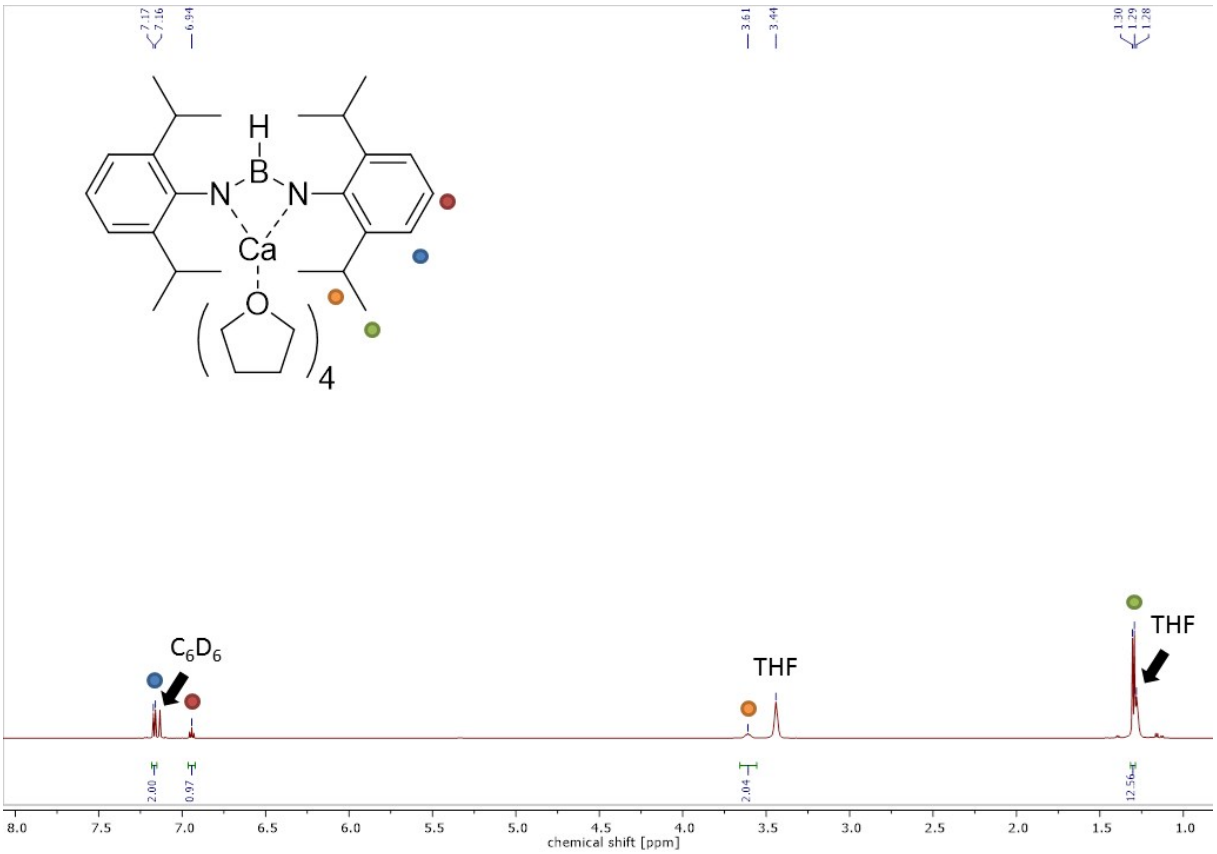


Figure S13. ^{1}H NMR spectrum of ^{DIPP}NBN-Ca·(THF)$_4$ in C_6D_6 (298K, 600 MHz).

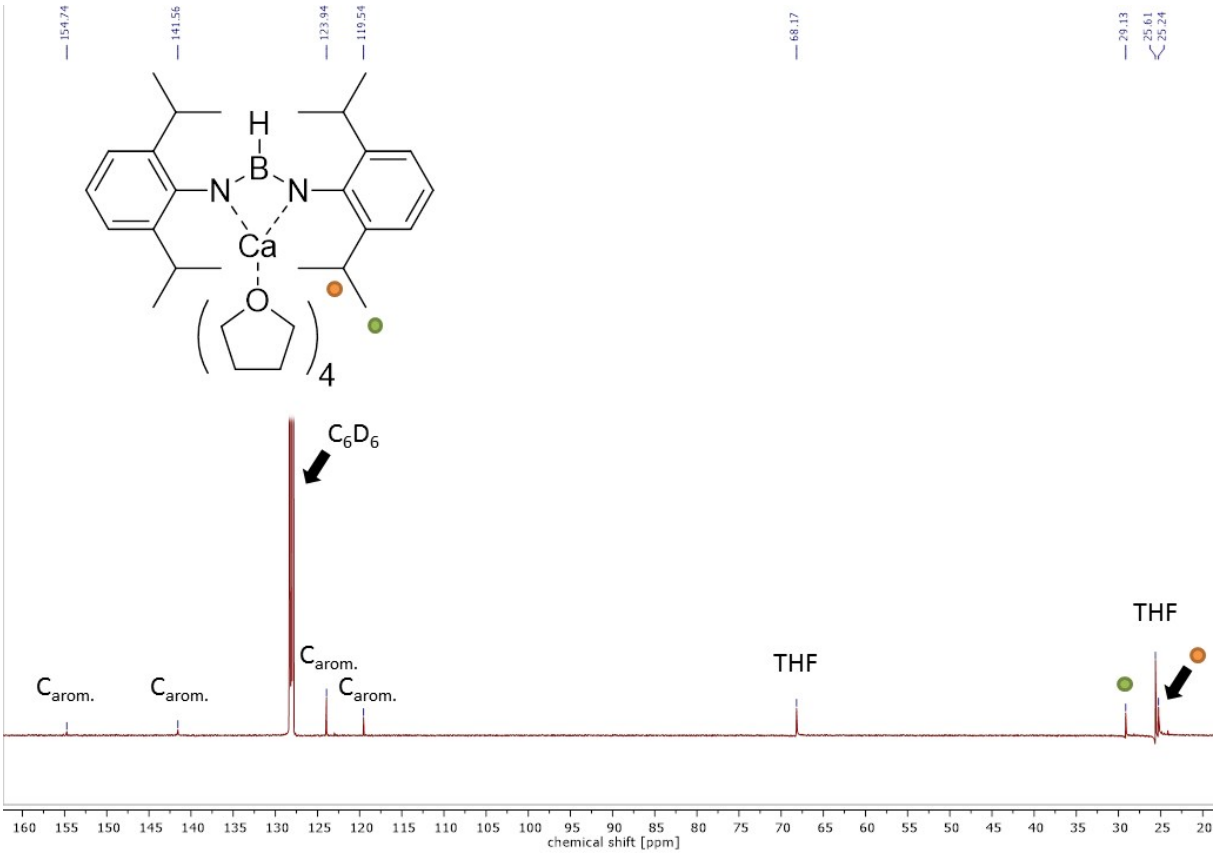


Figure S14. ^{13}C NMR spectrum of ^{DIPP}NBN-Ca·(THF)$_4$ in C_6D_6 (298K, 151 MHz).

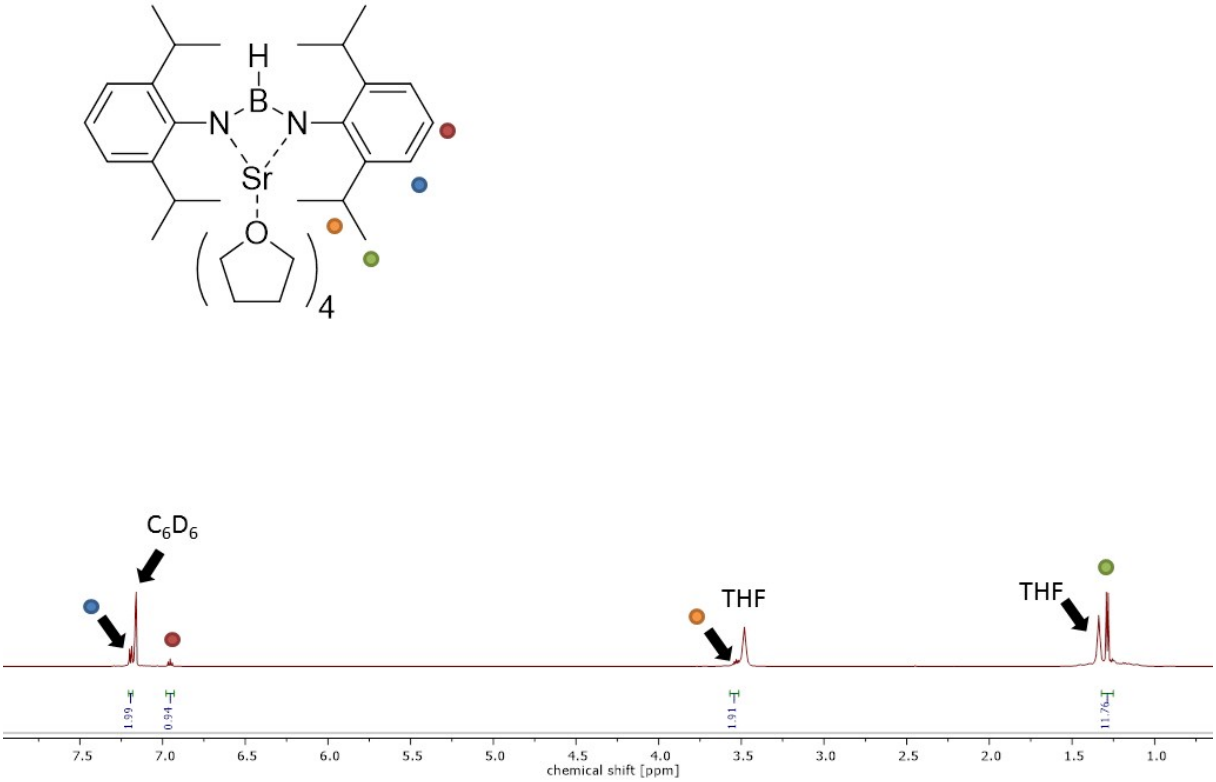


Figure S15. ^{1}H NMR spectrum of ^{DIPP}NBN-Sr·(THF)$_4$ in C_6D_6 (298K, 600 MHz).

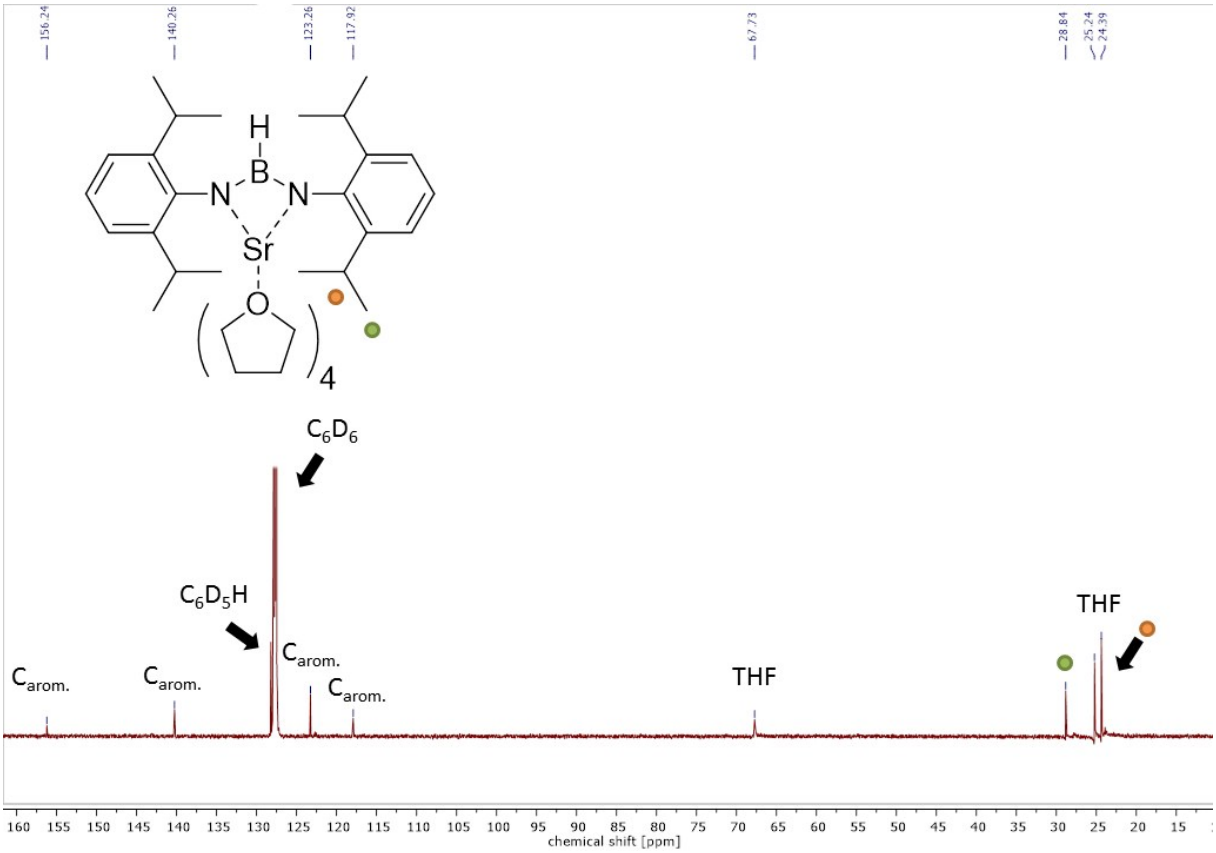
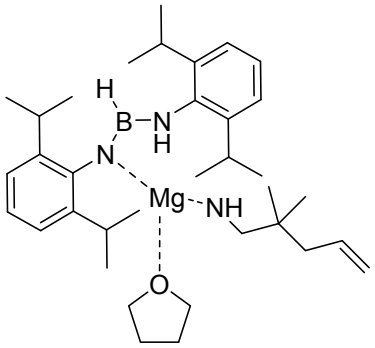


Figure S16. ^{13}C NMR spectrum of ^{DIPP}NBN-Sr·(THF)$_4$ in C_6D_6 (298K, 151 MHz).

3. Solution characterization of (^{DIPP}NBN-H)Mg-N(H)$CH_2CMe_2CH_2CH=CH_2$·$(THF)_x$



NMR scale experiment: In the glovebox, 2,2-dimethylpent-4-en-1-amine (7.2 mg, 0.0636 mmol) was dissolved in C_6D_6 (550 µl) and ^{DIPP}NBN-Mg·$(THF)_3$ (38.2 mg, 0.0636 mmol) was added to the solution at room temperature. This immediately resulted in a clear solution. The formation of (^{DIPP}NBN-H)Mg-N(H)$CH_2CMe_2CH_2CH=CH_2$·$(THF)_x$ could be directly observed via NMR measurements. No ring closure or decomposition could be observed even after heating to 100 °C for three days.

Evidence for the existence of the species (^{DIPP}NBN-H)Mg-N(H)$CH_2CMe_2CH_2CH=CH_2$·$(THF)_x$ is based on the following observations:

(i) The ^{1}H NMR spectrum shows a new set of signals for the substrate molecule (Figure S17); for comparison the ^{1}H NMR spectrum of the substrate $H_2NCH_2CMe_2CH_2CH=CH_2$ is also shown (Figure S23). The ^{1}H NMR spectrum of (^{DIPP}NBN-H)Mg-N(H)$CH_2CMe_2CH_2CH=CH_2$·$(THF)_x$ shows a high-field triplet which we assign to the negatively charged NH in the substrate (coupling with CH_2).

(ii) The ^{15}N HSQC (Figure S19) shows two different NH cross peaks and also enables assignment of the NBN NH signal.

(iii) The ^{13}C HSQC (Figure S21) shows no correlation between the NH fragments and any carbon which confirms their assignment.

(iv) A DOSY spectrum (Figure S20) shows that all aromatic, aliphatic and NH signals belong to one species that therefore must contain ^{DIPP}NBN and substrate fragments.

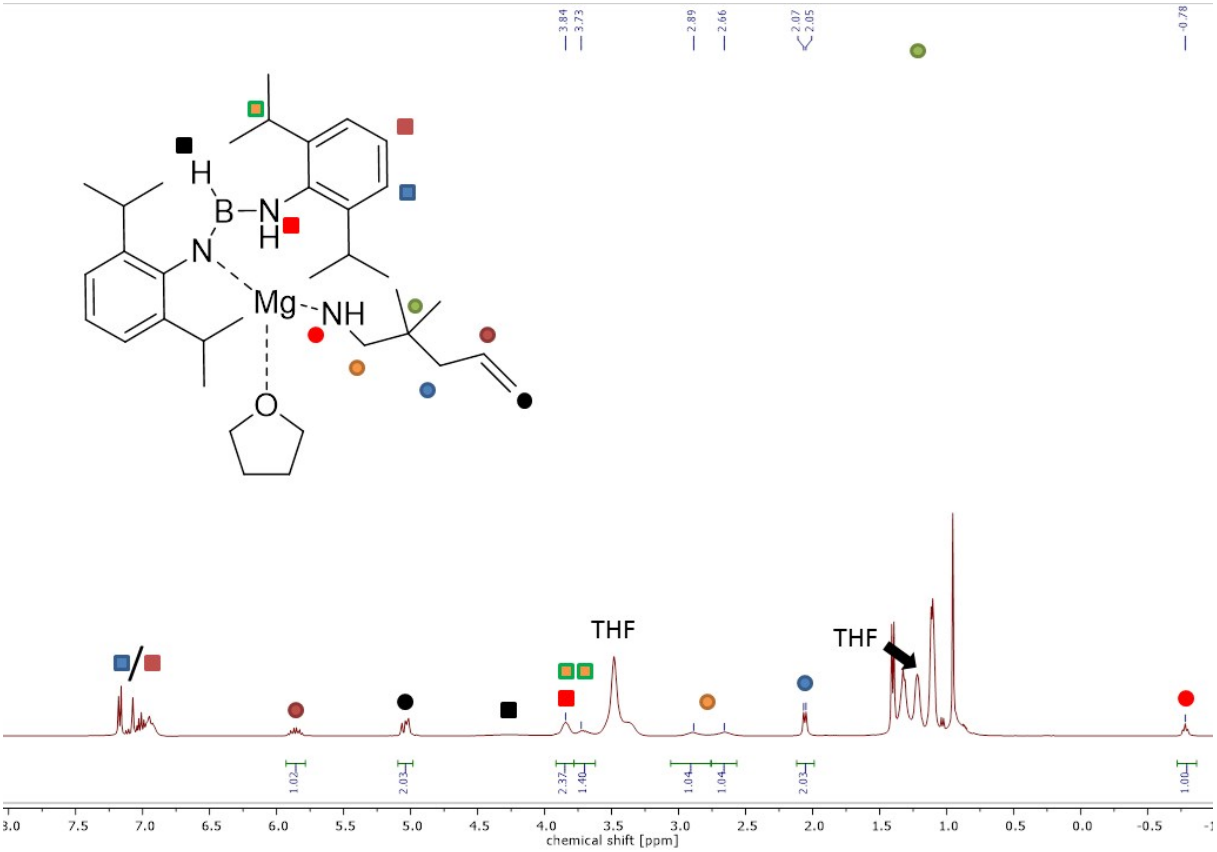


Figure S17. ^{1}H NMR spectrum of (^{DIPP}NBN-H)Mg-N(H)$CH_2CMe_2CH_2CH=CH_2$·$(THF)_x$ in C_6D_6 (298K, 400 MHz).

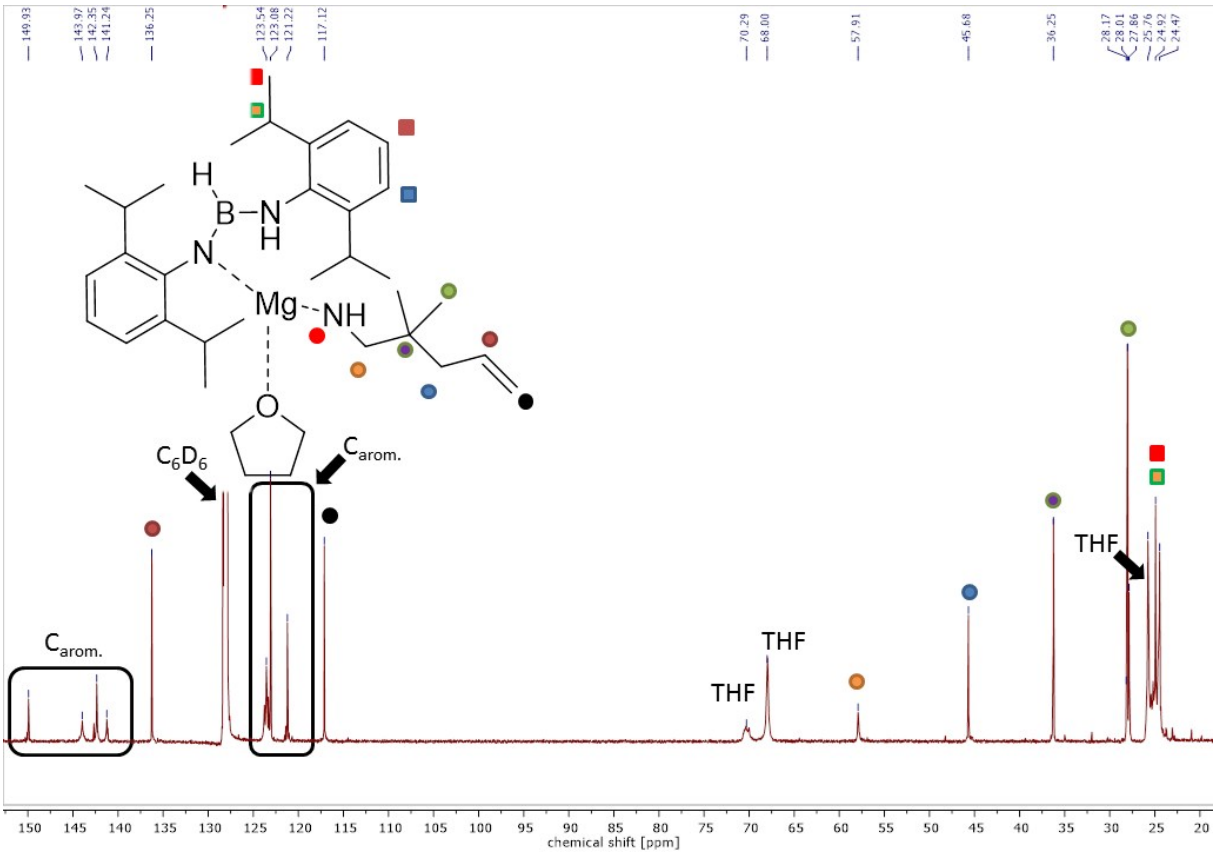


Figure S18. ^{13}C NMR spectrum of (^{DIPP}NBN-H)Mg-N(H)$CH_2CMe_2CH_2CH=CH_2$·$(THF)_x$ in C_6D_6 (298K, 151 MHz).

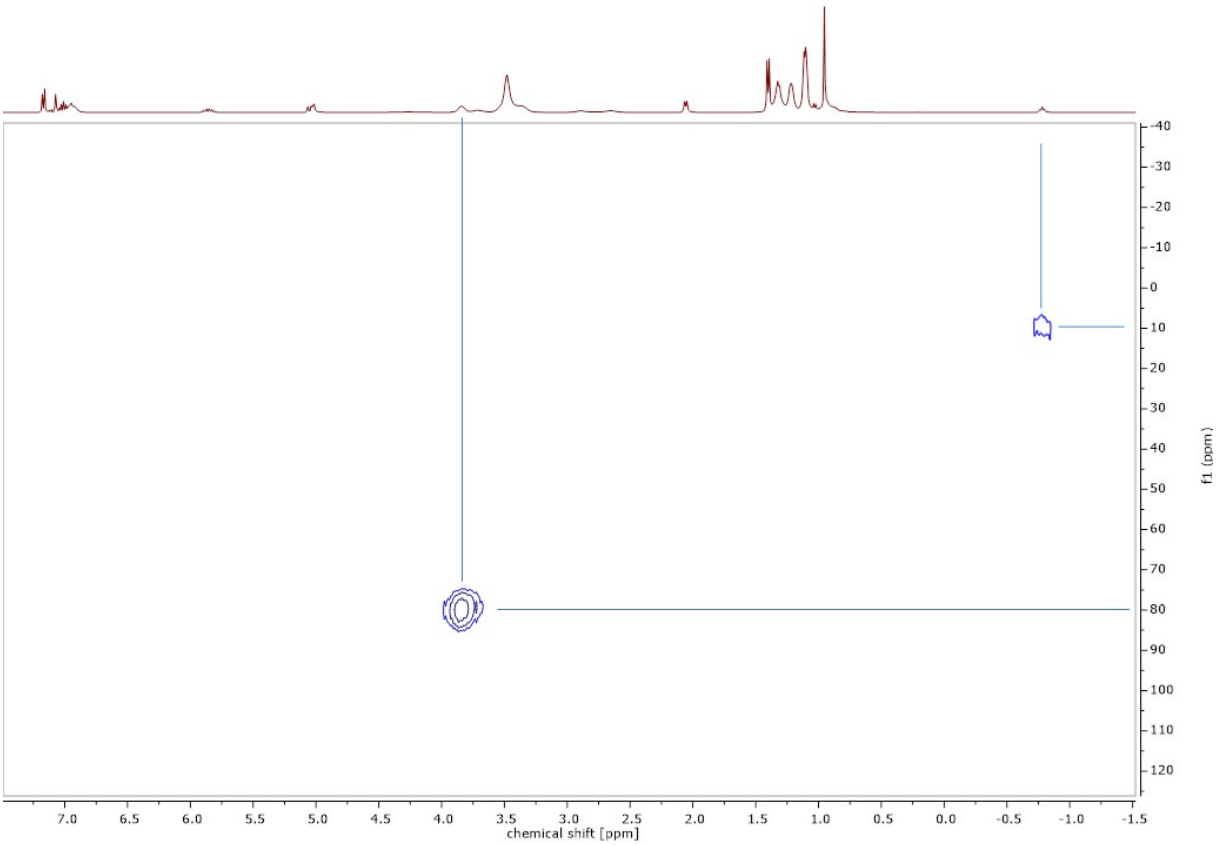


Figure S19. ^{15}N HSQC NMR spectrum of (^{DIPP}NBN-H)Mg-N(H)$CH_2CMe_2CH_2CH=CH_2$·$(THF)_x$ in C_6D_6 (298K, 600 MHz/ 61MHz).

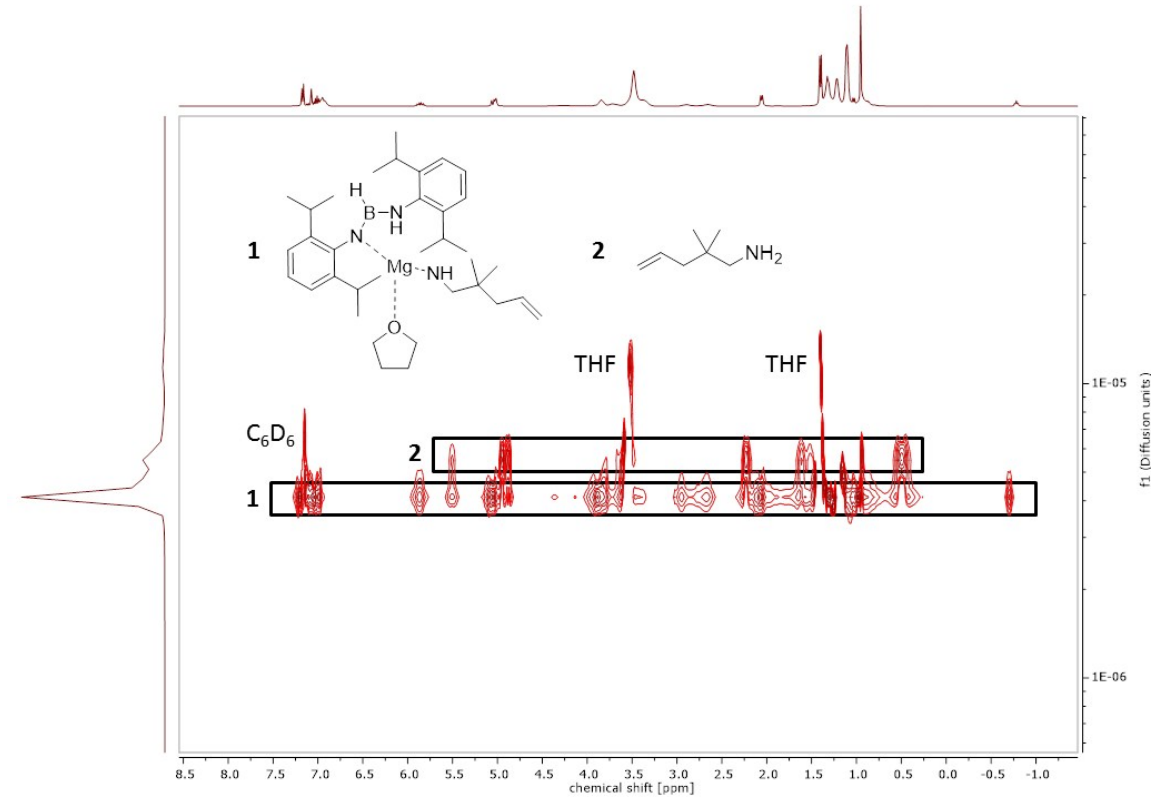


Figure S20. ^{1}H DOSY NMR spectrum of (^{DIPP}NBN-H)Mg-N(H)$CH_2CMe_2CH_2CH=CH_2$·$(THF)_x$ in C_6D_6 (298K, 600 MHz/ 61MHz) showing from top to bottom molecules of increasing size: THF < $NH_2CH_2CMe_2CH_2CH=CH_2$ < (^{DIPP}NBN-H)Mg-N(H)$CH_2CMe_2CH_2CH=CH_2$·$(THF)_x$.

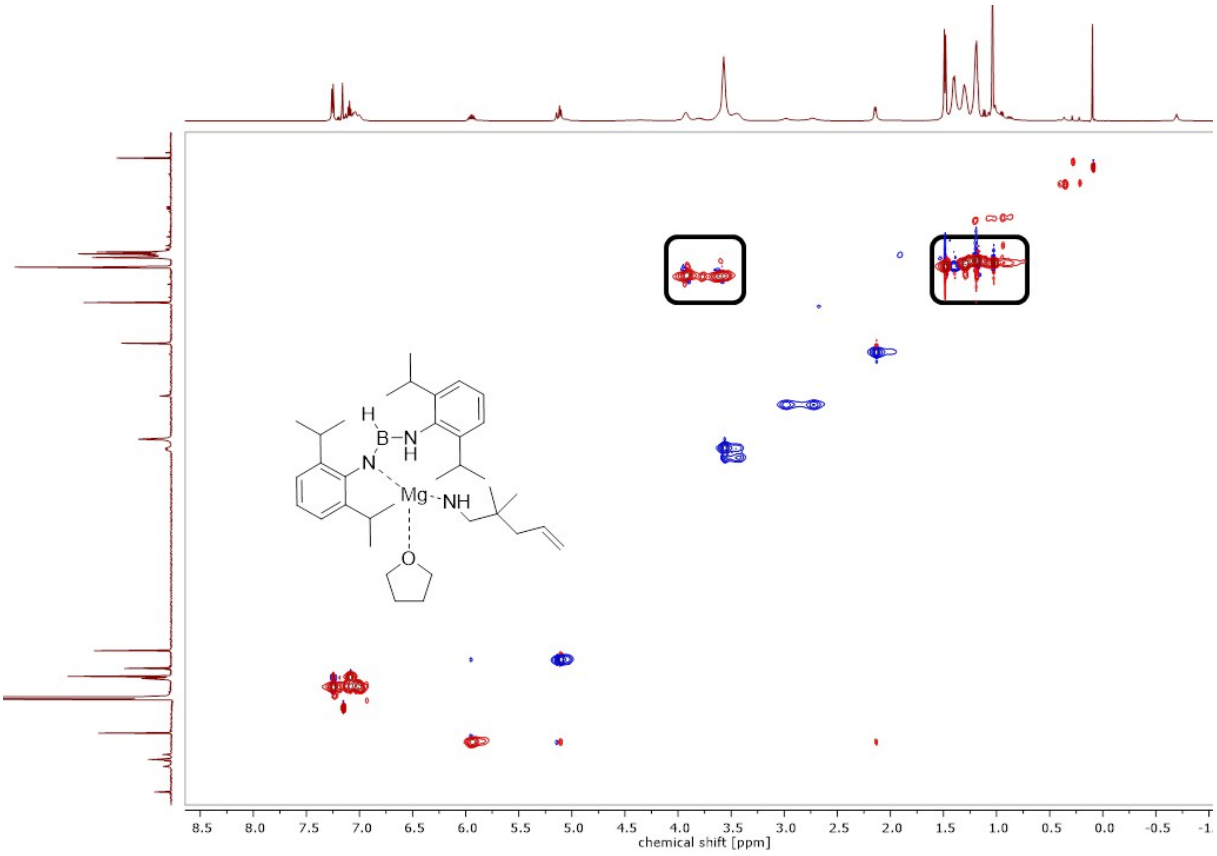


Figure S21. ^{13}C HSQC NMR spectrum of (^{DIPP}NBN-H)Mg-N(H)$CH_2CMe_2CH_2CH=CH_2$·$(THF)_x$ in C_6D_6 (298K, 600 MHz/ 151MHz).

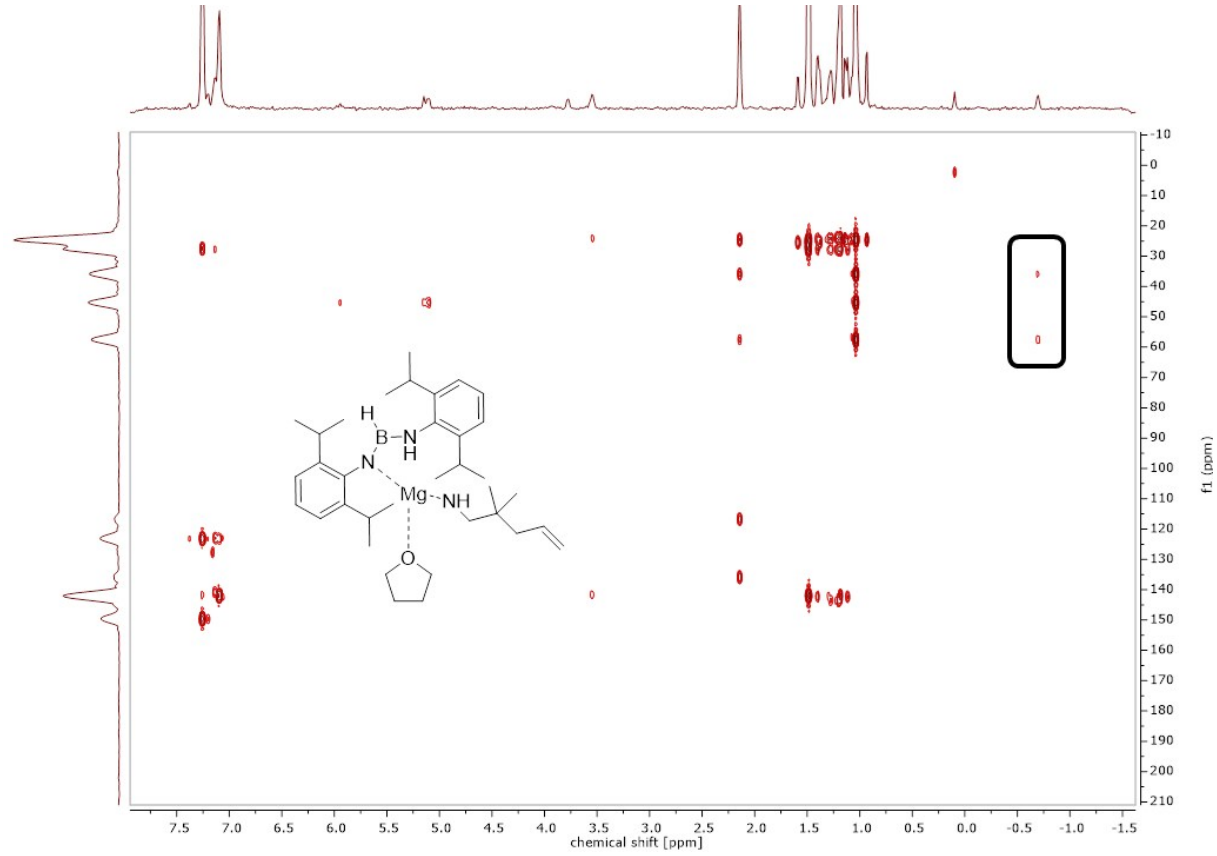


Figure S22. ^{13}C HMBC NMR spectrum of (^{DIPP}NBN-H)Mg-N(H)$CH_2CMe_2CH_2CH=CH_2$·$(THF)_x$ in C_6D_6 (298K, 600 MHz/ 151MHz).

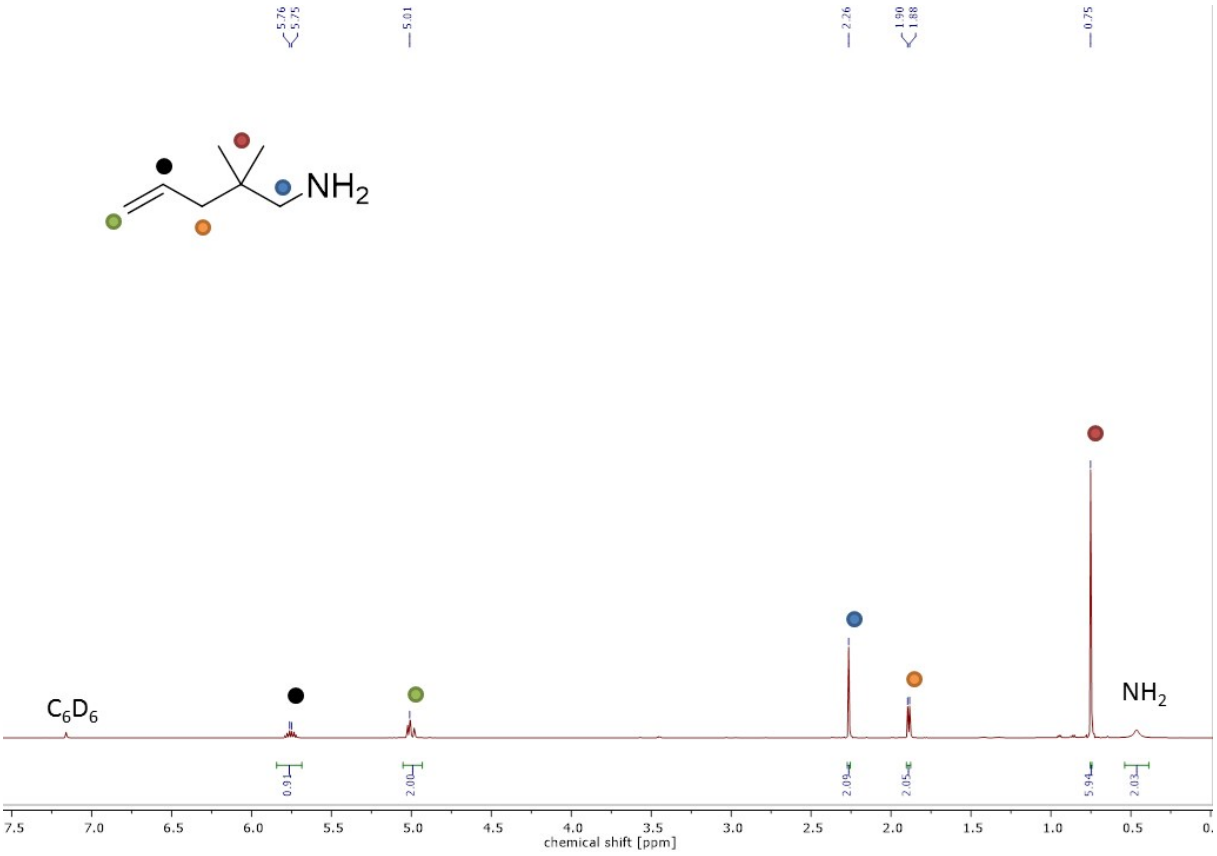


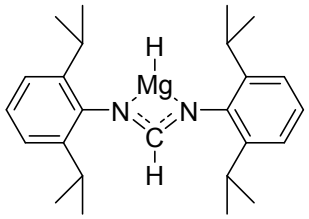
Figure S23. ^{1}H NMR spectrum of intramolecular hydroamination substrate (Me,Me) in C_6D_6 (298K, 600 MHz).

4. Theoretical calculations

General

All calculations were carried out using Gaussian 09 Rev. D.[5] All methods were used as implemented. All molecules were fully optimized on a B3PW91/6-311++G** level[6-10] of theory without any symmetry constraints. All structures were determined to be true minima (NIMAG=0). Charges were calculated using NBO analysis.[11] Structures were drawn using Molecule V2.3.[12] Topological analysis was carried out using AIMAll V16,[13, 14] using the wavefunctions of the optimization. The electron densities in the bond critical point r are given in au which is $e{\cdot}r_{Bohr}^{-3}$ (1 $e{\cdot}r_{Bohr}^{-3}$ = 6.755 $e{\cdot}Å^{-3}$). B3PW91 energies are given in Hartree, zero point energies (ZPE) in kcal/mol.

XYZ coordinates

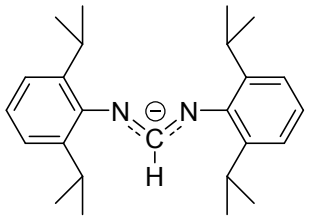


64

ZPE=345.8

$HC(N\text{-}DIPP)_2MgH$	B3PW91=-1283.82861		21
C	0.000004	0.000048	-0.033641
N	1.124570	0.121635	0.655816
N	-1.124545	-0.121653	0.655824
C	2.366135	0.321221	0.008954
C	-2.366116	-0.321235	0.008974
C	-3.375095	0.655075	0.180573
C	-4.611703	0.458374	-0.429029
C	-4.863426	-0.669700	-1.199947
C	-2.622018	-1.486627	-0.745874
C	-3.874451	-1.628261	-1.349452
C	-3.128482	1.881504	1.042728
H	-5.391433	1.203180	-0.309783
H	-5.829742	-0.801730	-1.676019
C	-1.611286	-2.614411	-0.889010
H	-4.080567	-2.516051	-1.939899
C	2.621979	1.486611	-0.745905
C	3.874396	1.628290	-1.349506
C	4.863413	0.669769	-1.200004
C	3.375150	-0.655056	0.180544

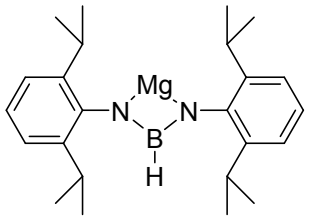
C	4.611744	-0.458308	-0.429074
C	1.611167	2.614319	-0.889062
H	4.080465	2.516076	-1.939975
H	5.829716	0.801832	-1.676094
C	3.128604	-1.881489	1.042712
H	5.391505	-1.203083	-0.309832
H	-0.000005	0.000117	-1.129830
C	1.161401	2.805694	-2.343013
C	2.153770	3.927260	-0.307711
H	1.389491	4.709970	-0.350523
H	2.457122	3.803240	0.735522
H	3.024273	4.284162	-0.866179
C	3.766378	-3.159233	0.490919
C	3.586647	-1.625841	2.486255
H	2.046189	-2.044531	1.060104
H	3.358682	-2.482731	3.128569
H	4.667426	-1.455072	2.521598
H	3.103208	-0.743448	2.916030
H	3.449655	-4.022902	1.083720
H	3.475991	-3.335459	-0.548512
H	4.859303	-3.125107	0.533676
H	0.405327	3.594163	-2.413165
H	2.001050	3.092696	-2.983591
H	0.733283	1.888134	-2.756617
H	0.726844	2.351827	-0.303565
C	-3.766209	3.159273	0.490939
C	-3.586508	1.625885	2.486281
H	-2.046059	2.044497	1.060097
C	-1.161522	-2.805831	-2.342956
H	-0.726951	-2.351994	-0.303503
C	-2.154004	-3.927307	-0.307664
H	-3.358490	2.482767	3.128586
H	-4.667294	1.455166	2.521646
H	-3.103101	0.743471	2.916051
H	-3.449432	4.022931	1.083726
H	-3.475837	3.335477	-0.548500
H	-4.859135	3.125198	0.533721
H	-1.389792	-4.710082	-0.350469
H	-2.457355	-3.803261	0.735566
H	-3.024533	-4.284134	-0.866140
H	-0.405506	-3.594357	-2.413095
H	-2.001186	-3.092775	-2.983539
H	-0.733332	-1.888306	-2.756565
Mg	0.000018	0.000007	2.418145
H	0.000019	0.000024	4.125381



62

$HC(N\text{-}DIPP)_2^-$	B3PW91=-1083.17521		ZPE=339.375
C	0.000001	0.000001	0.169144
N	-1.164865	-0.077241	0.777762
N	1.164866	0.077243	0.777763
C	-2.309493	-0.332488	0.051980
C	2.309494	0.332489	0.051982
C	3.374613	-0.612961	0.110009
C	4.567842	-0.356672	-0.558474
C	4.753756	0.816295	-1.284383
C	2.517680	1.549074	-0.662936
C	3.730899	1.757010	-1.320264
C	3.176541	-1.873213	0.932643
H	5.369298	-1.089404	-0.524841
H	5.686355	0.996925	-1.811641
C	1.473160	2.655480	-0.595557
H	3.888170	2.679978	-1.870685
C	-2.517676	-1.549074	-0.662939
C	-3.730894	-1.757012	-1.320267
C	-4.753754	-0.816299	-1.284385
C	-3.374613	0.612959	0.110008
C	-4.567842	0.356668	-0.558474
C	-1.473154	-2.655478	-0.595561
H	-3.888164	-2.679979	-1.870689
H	-5.686352	-0.996930	-1.811643
C	-3.176546	1.873210	0.932645
H	-5.369300	1.089398	-0.524839
H	0.000001	0.000001	-0.942957
C	-1.565545	-3.683039	-1.724027
C	-1.537492	-3.345045	0.775373
H	-0.760551	-4.113675	0.865014
H	-1.390366	-2.611500	1.571812
H	-2.512649	-3.824843	0.918636
C	-4.024628	3.061916	0.478909
C	-3.400723	1.579938	2.423185
H	-2.121179	2.144640	0.825131
H	-3.200921	2.469953	3.032659
H	-4.435978	1.267182	2.604933
H	-2.728349	0.783060	2.747924

H	-3.738783	3.961392	1.035475
H	-3.892625	3.267642	-0.588181
H	-5.093567	2.898776	0.659716
H	-0.718418	-4.375038	-1.668053
H	-2.478884	-4.285524	-1.660013
H	-1.546129	-3.203948	-2.708135
H	-0.485473	-2.194660	-0.668867
C	4.024640	-3.061913	0.478924
C	3.400689	-1.579938	2.423187
H	2.121178	-2.144651	0.825111
C	1.565551	3.683041	-1.724024
H	0.485478	2.194664	-0.668862
C	1.537500	3.345048	0.775376
H	3.200883	-2.469954	3.032658
H	4.435938	-1.267174	2.604953
H	2.728302	-0.783065	2.747913
H	3.738790	-3.961391	1.035485
H	3.892657	-3.267641	-0.588169
H	5.093574	-2.898765	0.659750
H	0.760559	4.113679	0.865018
H	1.390373	2.611503	1.571815
H	2.512658	3.824844	0.918639
H	0.718425	4.375041	-1.668050
H	2.478892	4.285524	-1.660011
H	1.546134	3.203950	-2.708132

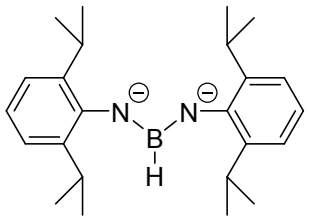


63

^{DIPP}NBN-Mg	B3PW91=-1269.99268		ZPE=338.735
B	-0.000001	0.576190	-0.300631
N	-1.191763	-0.078097	0.186862
N	1.191763	-0.078094	0.186861
C	-2.541909	0.050640	-0.043538
C	2.541909	0.050640	-0.043538
C	3.302625	-1.150902	-0.204002
C	4.679007	-1.094000	-0.392624
C	5.345336	0.125779	-0.429650
C	3.234886	1.290364	-0.063798
C	4.615254	1.294295	-0.264073
C	2.567784	-2.481096	-0.190580

H	5.246764	-2.009116	-0.526310
H	6.418416	0.162203	-0.585293
C	2.516373	2.609792	0.152271
H	5.138421	2.246413	-0.283266
C	-3.302625	-1.150901	-0.204012
C	-4.679006	-1.093998	-0.392635
C	-5.345335	0.125782	-0.429652
C	-3.234886	1.290364	-0.063789
C	-4.615253	1.294297	-0.264066
C	-2.567785	-2.481096	-0.190600
H	-5.246764	-2.009112	-0.526329
H	-6.418415	0.162208	-0.585296
C	-2.516372	2.609790	0.152293
H	-5.138420	2.246415	-0.283252
H	-0.000003	1.464481	-1.107770
C	-3.291606	-3.638583	-0.877272
C	-2.181730	-2.902485	1.248177
H	-1.381128	-3.662819	1.274587
H	-1.934002	-2.039018	1.887407
H	-3.034315	-3.364839	1.754157
C	-2.447258	3.433902	-1.139202
C	-3.135846	3.428230	1.292347
H	-1.491179	2.374260	0.447611
H	-2.547686	4.333766	1.474915
H	-4.158073	3.744049	1.060790
H	-3.168119	2.851596	2.221355
H	-1.883587	4.359551	-0.980737
H	-1.958628	2.871745	-1.938891
H	-3.449626	3.707529	-1.486113
H	-2.654793	-4.529053	-0.905796
H	-4.209711	-3.912519	-0.348817
H	-3.556735	-3.379336	-1.904763
H	-1.645309	-2.310431	-0.772960
C	3.291606	-3.638589	-0.877242
C	2.181728	-2.902474	1.248200
H	1.645310	-2.310436	-0.772944
C	2.447255	3.433889	-1.139233
H	1.491181	2.374265	0.447595
C	3.135849	3.428246	1.292315
H	1.381129	-3.662810	1.274616
H	3.034314	-3.364821	1.754185
H	1.933998	-2.039002	1.887423
H	2.654793	-4.529059	-0.905758
H	3.556735	-3.379351	-1.904736
H	4.209711	-3.912521	-0.348785

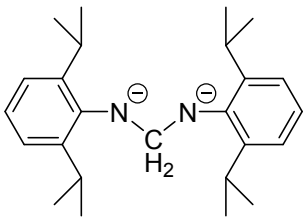
H	2.547687	4.333783	1.474872
H	3.168125	2.851624	2.221329
H	4.158074	3.744065	1.060751
H	1.883583	4.359539	-0.980778
H	3.449622	3.707513	-1.486150
H	1.958623	2.871722	-1.938915
Mg	0.000001	-1.477618	0.846881



62

$^{DIPP}NBN^{2-}$	B3PW91=-1069.89048		ZPE=333.516
B	0.000000	0.000000	-0.397818
N	-1.254631	0.118437	0.242078
N	1.254631	-0.118437	0.242078
C	-2.509629	-0.152708	-0.061643
C	2.509629	0.152708	-0.061643
C	3.551687	-0.840327	0.161229
C	4.887460	-0.548819	-0.067399
C	5.309116	0.704262	-0.526983
C	2.977276	1.442249	-0.551577
C	4.330340	1.677708	-0.754772
C	3.100580	-2.188128	0.684126
H	5.637701	-1.320407	0.106658
H	6.360626	0.910898	-0.712520
C	1.951358	2.546893	-0.724704
H	4.648548	2.658517	-1.108503
C	-2.977276	-1.442249	-0.551577
C	-4.330340	-1.677708	-0.754772
C	-5.309116	-0.704262	-0.526983
C	-3.551687	0.840327	0.161229
C	-4.887460	0.548819	-0.067399
C	-1.951358	-2.546893	-0.724704
H	-4.648548	-2.658517	-1.108503
H	-6.360626	-0.910897	-0.712519
C	-3.100580	2.188128	0.684126
H	-5.637701	1.320408	0.106658
H	0.000000	0.000000	-1.644414
C	-2.326148	-3.612848	-1.755275
C	-1.626162	-3.190440	0.631501
H	-0.827748	-3.939205	0.540355

H	-1.289325	-2.418862	1.328475
H	-2.516252	-3.680659	1.048035
C	-4.023892	3.354914	0.330774
C	-2.851947	2.129315	2.198679
H	-2.119752	2.362852	0.223691
H	-2.432183	3.073520	2.574313
H	-3.787745	1.929807	2.737862
H	-2.138889	1.327922	2.407738
H	-3.574643	4.306133	0.644911
H	-4.208834	3.403651	-0.747966
H	-4.997942	3.277011	0.831715
H	-1.490459	-4.308686	-1.902813
H	-3.192443	-4.209369	-1.439822
H	-2.567967	-3.159817	-2.722883
H	-1.031543	-2.065381	-1.070785
C	4.023893	-3.354914	0.330774
C	2.851948	-2.129315	2.198679
H	2.119752	-2.362853	0.223691
C	2.326147	3.612848	-1.755275
H	1.031543	2.065381	-1.070785
C	1.626162	3.190440	0.631501
H	2.432184	-3.073520	2.574313
H	3.787745	-1.929807	2.737862
H	2.138889	-1.327922	2.407738
H	3.574644	-4.306133	0.644911
H	4.208835	-3.403651	-0.747966
H	4.997943	-3.277011	0.831715
H	0.827747	3.939205	0.540355
H	1.289325	2.418861	1.328475
H	2.516252	3.680659	1.048035
H	1.490458	4.308686	-1.902812
H	3.192442	4.209370	-1.439822
H	2.567966	3.159818	-2.722883

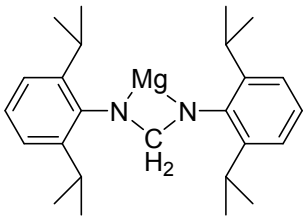


63

$H_2C(N\text{-}DIPP)_2^{2-}$	B3PW91=-1083.64798		ZPE=342.982
C	-0.000001	-0.313026	-0.000005
N	-1.171949	0.518365	0.115383
N	1.171948	0.518366	-0.115392

C	-2.414249	0.089985	-0.019822
C	2.414247	0.089986	0.019821
C	3.422428	1.138332	0.242972
C	4.728858	0.830120	0.559947
C	5.191927	-0.494748	0.635013
C	2.961596	-1.271703	-0.041765
C	4.292583	-1.506171	0.298194
C	2.931935	2.569847	0.167877
H	5.427520	1.639223	0.771015
H	6.218642	-0.721302	0.912120
C	2.152795	-2.393451	-0.679887
H	4.664511	-2.529443	0.274474
C	-2.961600	-1.271703	0.041768
C	-4.292589	-1.506169	-0.298179
C	-5.191936	-0.494746	-0.634991
C	-3.422431	1.138332	-0.242969
C	-4.728864	0.830122	-0.559931
C	-2.152794	-2.393453	0.679880
H	-4.664519	-2.529441	-0.274455
H	-6.218654	-0.721299	-0.912088
C	-2.931935	2.569847	-0.167881
H	-5.427526	1.639225	-0.770995
C	-2.683205	-3.807959	0.429439
C	-2.025851	-2.147552	2.192709
H	-1.355964	-2.880039	2.665419
H	-1.625994	-1.147196	2.378437
H	-3.011402	-2.213329	2.671967
C	-3.800576	3.589018	-0.905490
C	-2.715940	3.004518	1.289418
H	-1.932423	2.548972	-0.622797
H	-2.274799	4.010195	1.344707
H	-3.666740	3.014819	1.839587
H	-2.027436	2.303624	1.766947
H	-3.318451	4.575254	-0.894094
H	-3.958601	3.299441	-1.950329
H	-4.788642	3.706523	-0.439759
H	-1.983419	-4.546229	0.840198
H	-3.654856	-3.977234	0.909669
H	-2.798437	-4.007838	-0.641458
H	-1.138285	-2.377997	0.275305
C	3.800570	3.589019	0.905491
C	2.715955	3.004515	-1.289427
H	1.932418	2.548974	0.622782
C	2.683207	-3.807957	-0.429450
H	1.138283	-2.377998	-0.275319

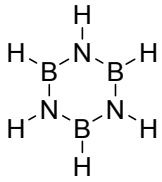
C	2.025861	-2.147543	-2.192715
H	2.274816	4.010191	-1.344723
H	3.666762	3.014813	-1.839585
H	2.027457	2.303620	-1.766961
H	3.318447	4.575256	0.894086
H	3.958581	3.299446	1.950334
H	4.788642	3.706519	0.439772
H	1.355977	-2.880027	-2.665433
H	1.626006	-1.147185	-2.378441
H	3.011415	-2.213317	-2.671968
H	1.983425	-4.546226	-0.840217
H	3.654861	-3.977229	-0.909674
H	2.798432	-4.007843	0.641447
H	0.128374	-0.988402	0.879879
H	-0.128374	-0.988400	-0.879891



64

$H_2C(N\text{-}DIPP)_2Mg$	B3PW91=-1283.76101		ZPE=348.153
C	-0.000019	0.759113	-0.105520
N	-1.147242	-0.128251	0.133042
N	1.147222	-0.128256	0.132940
C	-2.474031	0.061799	-0.121883
C	2.474016	0.061812	-0.121916
C	3.261985	-1.141022	-0.228657
C	4.632313	-1.076215	-0.455263
C	5.283197	0.141372	-0.591558
C	3.161430	1.309948	-0.256817
C	4.533898	1.307410	-0.492428
C	2.566528	-2.486055	-0.146967
H	5.207160	-1.992210	-0.542463
H	6.351500	0.182711	-0.773588
C	2.455090	2.638188	-0.021767
H	5.046100	2.258460	-0.590076
C	-3.261963	-1.141034	-0.228838
C	-4.632280	-1.076222	-0.455517
C	-5.283175	0.141372	-0.591695
C	-3.161458	1.309941	-0.256641
C	-4.533908	1.307415	-0.492353
C	-2.566476	-2.486062	-0.147309
H	-5.207105	-1.992215	-0.542880

H	-6.351466	0.182715	-0.773794
C	-2.455143	2.638144	-0.021309
H	-5.046126	2.258467	-0.589900
C	-3.344250	-3.672665	-0.716017
C	-2.111268	-2.827038	1.293894
H	-1.337444	-3.617503	1.325292
H	-1.794036	-1.936397	1.857761
H	-2.948819	-3.230702	1.868755
C	-3.122656	3.842430	-0.691070
C	-2.300959	2.890509	1.486723
H	-1.454936	2.574916	-0.452609
H	-1.718374	3.798248	1.678861
H	-3.284907	3.013497	1.951756
H	-1.802828	2.053000	1.982541
H	-2.481782	4.723798	-0.589203
H	-3.291009	3.668767	-1.757847
H	-4.083972	4.092718	-0.231515
H	-2.727595	-4.577557	-0.702859
H	-4.242381	-3.882859	-0.127821
H	-3.649705	-3.485422	-1.747718
H	-1.670989	-2.387938	-0.802176
C	3.344375	-3.672727	-0.715432
C	2.111233	-2.826817	1.294261
H	1.671083	-2.388067	-0.801917
C	3.122520	3.842322	-0.691892
H	1.454856	2.574820	-0.452978
C	2.301011	2.890944	1.486210
H	1.337419	-3.617289	1.325735
H	2.948756	-3.230383	1.869231
H	1.793951	-1.936094	1.857970
H	2.727746	-4.577635	-0.702166
H	3.649892	-3.485642	-1.747144
H	4.242473	-3.882796	-0.127142
H	1.718404	3.798711	1.678153
H	1.802953	2.053549	1.982295
H	3.284989	3.014095	1.951137
H	2.481629	4.723698	-0.590213
H	4.083861	4.092760	-0.232471
H	3.290804	3.668379	-1.758634
Mg	0.000002	-1.658084	0.495088
H	-0.000077	1.143476	-1.139835
H	0.000024	1.615298	0.583081



12

Borazine	B3PW91=242.6.513		ZPE=58.514
N	1.252497	-0.642488	-0.000282
B	0.071784	-1.447097	-0.000221
N	-1.182791	-0.763359	0.000541
B	-1.289676	0.661631	-0.000143
B	1.217731	0.785786	0.000276
N	-0.069713	1.405709	-0.000428
H	-2.029371	-1.310762	0.000263
H	-2.352965	1.207294	-0.000440
H	-0.119216	2.412650	0.000454
H	0.131332	-2.640868	-0.000373
H	2.149349	-1.103159	0.000017
H	2.221719	1.434209	0.001701

H_3C-CH_3

8

Ethane	B3PW91=-79.82452		ZPE=46.717
C	0.762339	-0.000004	-0.000003
C	-0.762334	0.000010	0.000006
H	-1.161827	-0.934684	0.404597
H	-1.161790	0.817752	0.607142
H	1.161825	0.934900	-0.404110
H	1.161841	-0.117518	1.011674
H	1.161797	-0.817393	-0.607599
H	-1.161876	0.116906	-1.011718

$H_2C=CH_2$

6

Ethene	B3PW91=-78.58047		ZPE=31.899
C	0.000000	0.000000	0.663740
C	0.000000	0.000000	-0.663740
H	0.000000	0.923426	-1.235289
H	0.000000	-0.923426	-1.235289
H	0.000000	-0.923426	1.235289
H	0.000000	0.923426	1.235289

H_2N-CH_3

7

H2NCH3	B3PW91=-95.85628		ZPE=40.164
C	0.704328	0.000000	0.017659
N	-0.746718	0.000000	-0.118860
H	-1.155155	0.814583	0.323742
H	1.115062	-0.878784	-0.486915
H	1.115062	0.878784	-0.486915
H	-1.155155	-0.814583	0.323742
H	1.081247	0.000000	1.052412

$HN=CH_2$

5

HN=CH2	B3PW91=-94.62131		ZPE=31.899
C	-0.585205	0.028821	-0.000365
N	0.666897	-0.154162	0.000161
H	1.164727	0.738838	-0.000356
H	-1.244378	-0.842302	0.000506
H	-1.077398	1.009670	0.000917

$H_3N^{-}-BH_3$

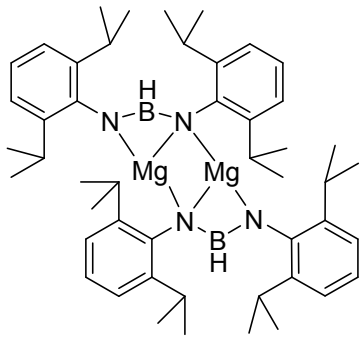
8

H3NBH3	B3PW91=-83.21339		ZPE=43.787
B	0.926417	-0.000056	0.000021
N	-0.725832	-0.000030	-0.000001
H	1.241501	-0.540299	1.037348
H	1.241546	-0.628202	-0.986627
H	-1.091575	0.437810	-0.841193
H	-1.091767	0.509652	0.799632
H	-1.092050	-0.947317	0.041468
H	1.241086	1.168846	-0.050726

H_2N-BH_2

6

H2NBH2	B3PW91=-82.03437		ZPE=30.059
B	0.778353	-0.000030	0.000096
N	-0.611254	-0.000065	0.000156
H	1.356583	1.046696	-0.000155
H	1.357477	-1.046267	-0.000454
H	-1.163758	-0.843330	-0.000296
H	-1.163288	0.843506	-0.000666



126

NBN-Dimer B3PW91=-2540.09987 ZPE=

B	1.965200	-1.733554	-0.102540
N	0.604777	-1.487561	0.389170
N	2.716354	-0.582972	-0.429262
C	-0.167700	-2.521386	0.983179
C	3.993706	-0.545805	-0.993886
C	5.046148	0.108903	-0.296295
C	6.314372	0.175988	-0.868994
C	6.578048	-0.386605	-2.111589
C	4.259863	-1.099373	-2.271585
C	5.550270	-1.013518	-2.797462
C	4.802883	0.684288	1.087783
H	7.118192	0.671357	-0.334726
H	7.573847	-0.331665	-2.539767
C	3.181870	-1.763872	-3.111450
H	5.752317	-1.445078	-3.774055
C	-0.010833	-2.889177	2.349847
C	-0.899032	-3.802916	2.911479
C	-1.942518	-4.357660	2.180036
C	-1.212716	-3.131446	0.218831
C	-2.089777	-4.025749	0.845212
C	1.142162	-2.357511	3.178833
H	-0.777004	-4.086946	3.951900
H	-2.628303	-5.055505	2.649014
C	-1.283672	-2.962288	-1.300069
H	-2.884546	-4.483195	0.267241
H	2.389611	-2.858243	-0.159533
C	2.278382	-3.390018	3.228739
C	0.733108	-1.939626	4.594580
H	1.572085	-1.450042	5.098062
H	-0.110437	-1.244339	4.586433
H	0.450681	-2.800006	5.208930
C	-0.381758	-4.018363	-1.958885
C	-2.696763	-3.011607	-1.885013
H	-0.841583	-1.992336	-1.578342

H	-2.657474	-2.792273	-2.955243
H	-3.145038	-4.003865	-1.780702
H	-3.369326	-2.282329	-1.425128
H	-0.377518	-3.894702	-3.046021
H	0.645853	-3.946557	-1.597495
H	-0.752703	-5.022532	-1.730666
H	3.129342	-2.999572	3.795219
H	1.941557	-4.310613	3.716856
H	2.625090	-3.649776	2.225980
H	1.525444	-1.472096	2.662680
C	4.880497	-0.417366	2.153311
C	5.719051	1.851322	1.459507
H	3.774700	1.074665	1.098039
C	3.484495	-3.246114	-3.360492
H	2.247364	-1.708637	-2.547840
C	2.955999	-1.021483	-4.435417
H	5.388253	2.301034	2.400619
H	6.753840	1.526312	1.605673
H	5.716048	2.629720	0.691432
H	4.631623	-0.025143	3.145939
H	4.197411	-1.236791	1.920975
H	5.894002	-0.828994	2.197562
H	2.135501	-1.477653	-4.999751
H	2.706654	0.029315	-4.262384
H	3.847594	-1.048319	-5.069894
H	2.677195	-3.717668	-3.930939
H	4.409889	-3.372470	-3.931719
H	3.600294	-3.787994	-2.418172
Mg	1.263708	0.559472	0.235249
B	-1.965199	1.733565	-0.102248
N	-0.604783	1.487488	0.389440
N	-2.716361	0.583037	-0.429144
C	0.167717	2.521219	0.983584
C	-3.993714	0.545966	-0.993771
C	-5.046145	-0.108891	-0.296301
C	-6.314373	-0.175874	-0.869003
C	-6.578066	0.386962	-2.111483
C	-4.259887	1.099781	-2.271359
C	-5.550299	1.014019	-2.797242
C	-4.802865	-0.684554	1.087660
H	-7.118184	-0.671356	-0.334825
H	-7.573868	0.332099	-2.539664
C	-3.181908	1.764449	-3.111110
H	-5.752356	1.445767	-3.773749
C	0.010890	2.888800	2.350315

C	0.899119	3.802436	2.912067
C	1.942595	4.357278	2.180683
C	1.212722	3.131383	0.219305
C	2.089813	4.025575	0.845803
C	-1.142103	2.357025	3.179234
H	0.777127	4.086302	3.952536
H	2.628404	5.055036	2.649753
C	1.283641	2.962461	-1.299623
H	2.884576	4.483099	0.267884
H	-2.389598	2.858266	-0.159088
C	-2.278414	3.389436	3.229076
C	-0.733112	1.939177	4.595010
H	-1.572065	1.449462	5.098404
H	0.110536	1.244014	4.586934
H	-0.450877	2.799591	5.209402
C	0.381741	4.018663	-1.958255
C	2.696721	3.011837	-1.884589
H	0.841521	1.992564	-1.578036
H	2.657404	2.792670	-2.954851
H	3.145021	4.004069	-1.780134
H	3.369278	2.282474	-1.424830
H	0.377477	3.895173	-3.045411
H	-0.645865	3.946827	-1.596857
H	0.752717	5.022787	-1.729885
H	-3.129368	2.998923	3.795519
H	-1.941684	4.310060	3.717204
H	-2.625096	3.649162	2.226300
H	-1.525276	1.471578	2.663052
C	-4.880459	0.416887	2.153410
C	-5.719035	-1.851657	1.459162
H	-3.774685	-1.074940	1.097825
C	-3.484550	3.246733	-3.359873
H	-2.247396	1.709120	-2.547520
C	-2.956043	1.022306	-4.435216
H	-5.388225	-2.301560	2.400179
H	-6.753819	-1.526670	1.605410
H	-5.716049	-2.629900	0.690930
H	-4.631571	0.024463	3.145956
H	-4.197372	1.236354	1.921227
H	-5.893961	0.828510	2.197760
H	-2.135557	1.478590	-4.999474
H	-2.706683	-0.028520	-4.262378
H	-3.847645	1.049247	-5.069678
H	-2.677262	3.718401	-3.930242
H	-4.409952	3.373188	-3.931065

H	-3.600342	3.788438	-2.417451
Mg	-1.263717	-0.559521	0.235173

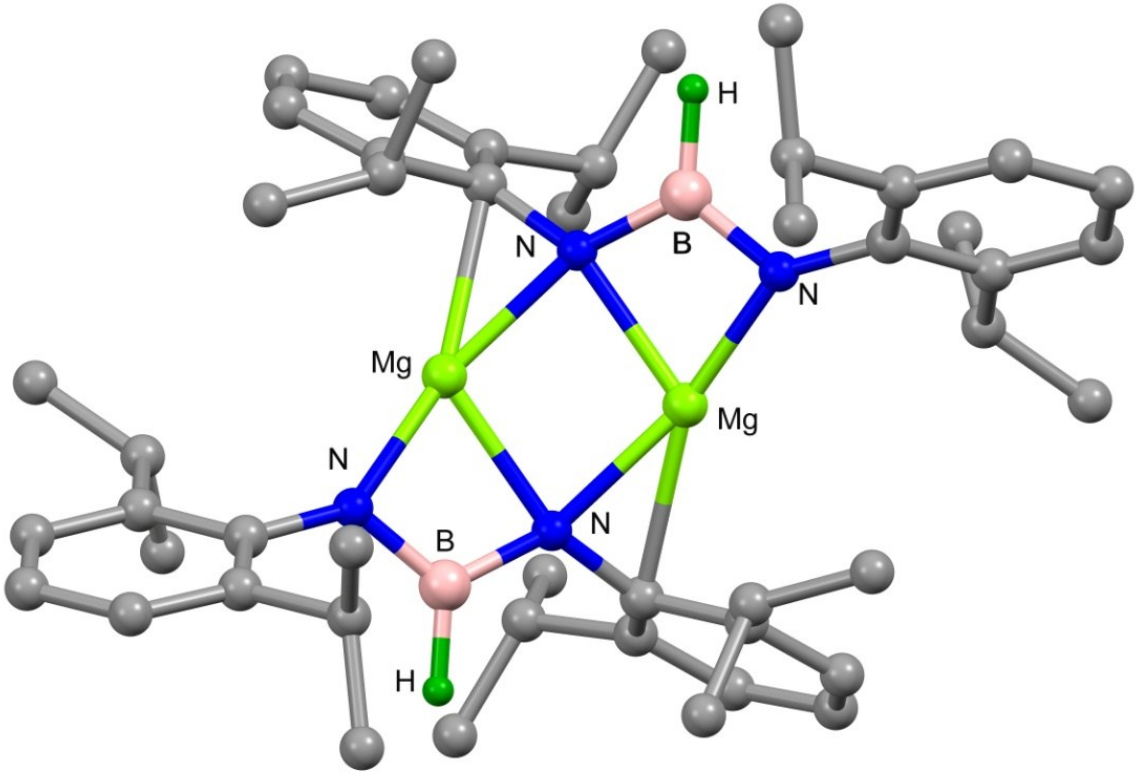


Figure S24. Optimized structure of (^{DIPP}NBN-Mg)$_2$ at the B3PW91/6-311++G** level (C1). The frequency calculation has been done at the B3PW91/6-311G* level (NIMAG=0). The dimerization energy (corrected for ZPE) is 76.9 kcal/mol.

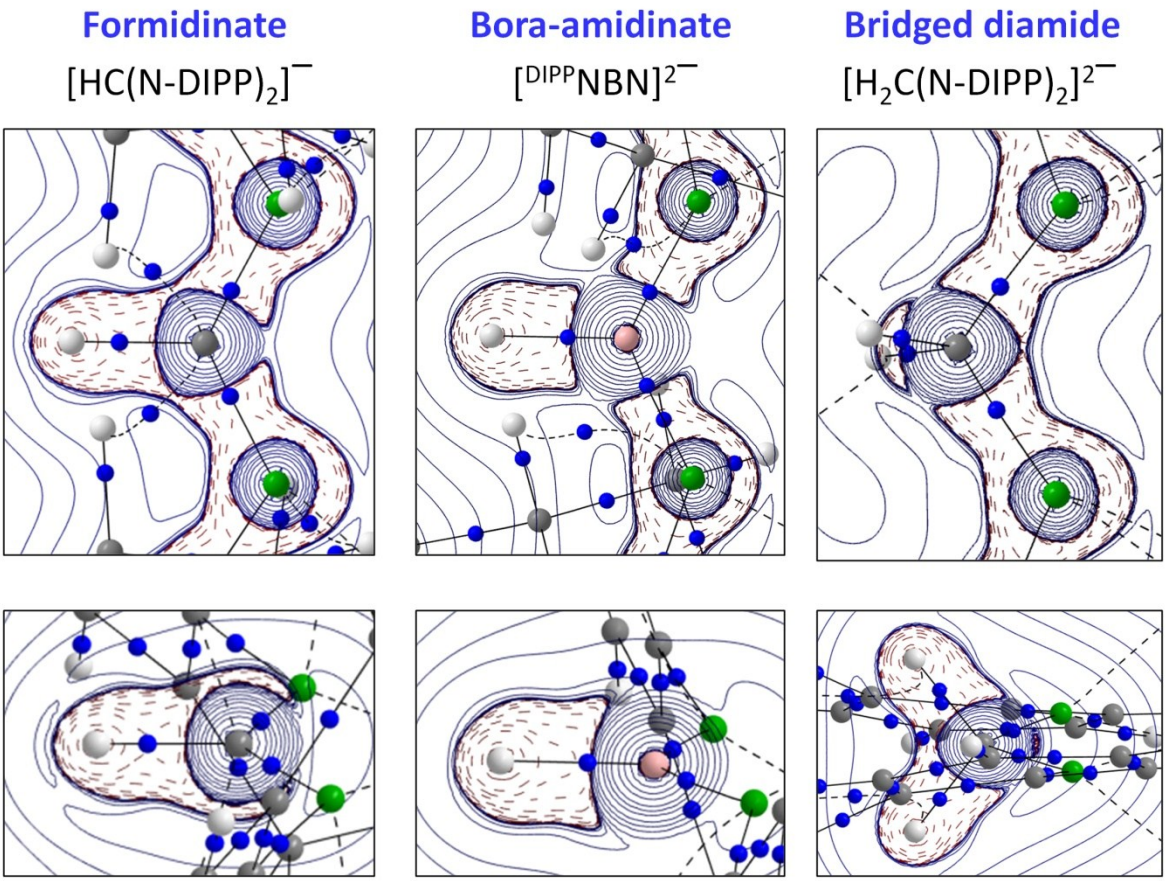


Figure S25. AIM analysis of the electron density in formidinate, bora-amdinate and bridged diamide anions. Top: intersection through the N-C-N or N-B-N planes. Bottom: Intersection through central H-C or H-B unit perpendicular to the N-C-N or N-B-N planes.

4. References

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339-341.
2. G. M. Sheldrick, *Acta Cryst.* **2015**, *A71*, 3-8.
3. G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122.
4. A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool* **2000**, Utrecht University, Utrecht, The Netherlands.
5. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, P. H. Hratchian, A. F. Izmaylof, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Makajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogilaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. E. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrezewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09 Rev. D.* **2013**, Wallingford, Connecticut, USA.
6. A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372–1377.
7. J. P. Perdew, *Electronic Structure of Solids*, Akademie Verlang, Berlin, **1991**.
8. K. B. Wiberg, *J. Comput. Chem.* **1986**, *7*, 379–379.
9. T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. v. R. Schleyer, *J. Comp. Chem.* **1983**, *4*, 294–301.
10. R. C. Binning, L. A. Curtiss, *J. Comput. Chem.* **1990**, *11*, 1206–1216.
11. A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735–746.
12. N. van Eikema Hommes, *Molecule V2.3* **2016**, University Erlangen-Nürnberg, Erlangen, Germany.
13. R. F. W. Bader, *Chem. Rev.* **1991**, *91*, 893–928.
14. T. A. Keith, *AIMAll V16* **2016**, TK Gristmill Software, Overland Park KS, USA.