Dimethylamine borane dehydrogenation chemistry: syntheses, X-ray and neutron diffraction studies of 18-electron aminoborane and 14-electron aminoboryl complexes

Christina Y. Tang, Nicholas Phillips, Joshua I. Bates, Amber L. Thompson, Matthias J. Gutman, and Simon Aldridge

Supporting Information

General details of synthetic procedures and instrumentation

Materials: All reactions involving air- or moisture-sensitive compounds were carried out under an inert atmosphere by using Schlenk-type glassware or in a glovebox. Solvents were dried using an MBraun SPS800 prior to use. NMR-solvents were dried over molecular sieves and degassed before use when necessary. Solid starting materials were dried on high vacuum before use when necessary. Unless otherwise noted, all starting materials were commercially available and were used without further purification. $M(IMes)_2(H)_2Cl$ (**1a/b**) and $Na[BAr^f_4]$ were prepared via literature routes.[s1,s2]

Techniques: The following instruments were used for physical characterization of the compounds: IR: Nicolet Magna-IR 560; NMR: Bruker AVC500 (^{1}H: 500 MHz; ^{13}C: 125 MHz); Bruker DRX500 (^{11}B: 160 MHz), Varian Unity500 (^{1}H: 500 MHz; ^{13}C: 125 MHz, ^{11}B: 160 MHz), Varian Mercury VX-300 (^{31}P: 122 MHz, ^{19}F: 282 MHz, ^{11}B: 96 MHz). Details of the crystallographic studies are contained within the manuscript itself and within the respective CIFs.

Syntheses and characterizing data for new compounds

2: To a suspension of **1a** and $Na[BAr^f_4]$ (0.25 mmol of each) in fluorobenzene (50 cm^3) at -30^{o}C was added $Me_2NH{\cdot}BH_3$ (0.295g, 5 mmol) and the reaction mixture warmed to 20 ^{o}C over a period of 1 h. After stirring for a further 24 h, the resulting light yellow solution was filtered, concentrated in *vacuo* and light yellow crystals suitable for X-ray diffraction obtained by layering with pentane and storage at 20 ^{o}C. Isolated yield 0.33 g, 76 %. ^{1}H NMR (toluene-d_8, 300 MHz, 20 ^{o}C): δ_H -15.24 (s, 2H, IrH), -6.31 (br s, 2H, BH_2), 1.49 (s, 24H, *ortho*-Me of IMes), 1.61 (s, 6H, Me of NMe_2), 2.21 (s, 12H, *para*-Me of IMes), 5.98 (s, 4H, NCH of IMes), 6.63 (s, 8H, *meta*-CH of IMes), 7.69 (s, 4H, *para*-CH of $[BAr^f_4]^-$), 8.31 (s, 8H, *para*-CH of $[BAr^f_4]^-$). ^{13}C NMR (toluene-d_8, 75 MHz, 20 ^{o}C): (i) signals due to cation: δ_C 17.1 (*ortho*-Me of IMes), 17.9 (*para*-Me of IMes), 39.6 (Me of NMe_2), 121.6 (NCH of IMes), 129.1 (*ortho*-quaternary C of IMes) 134.4 (*meta*-CH of IMes), 138.8 (*para*-quaternary C of IMes), carbene quaternary of IMes and N-bound aryl quaternary signals not observed; (ii) signals due to anion: δ_C 117.6 (*para*-CH), 124.9 (q, $^1J_{CF}$ = 273.6 Hz, CF_3), 129.5 (q, $^2J_{CF}$ = 34.5 Hz, *meta*-quaternary C), 135.1 (*ortho*-CH), 162.2 (q, $^1J_{CB}$ = 50.3 Hz, *ipso*-quaternary C). ^{11}B NMR (toluene-d_8, 96 MHz, 20 ^{o}C): δ_B -6.1 ($[BAr^f_4]^-$ anion), 36 (br, H_2BNMe_2). ^{19}F NMR (toluene-d_8, 282 MHz, 20 ^{o}C): δ_F -61.3. IR (ν_{BH}, cm^{-1}): 2360, 2343. Elemental microanalysis: calcd for $C_{76}H_{70}N_5B_2F_{24}Ir$: C, 52.94; H, 4.09, N, 4.06; measd: C, 52.94; H, 3.92; N, 3.93. *Crystallographic data:* (X-ray) $C_{76}H_{70}N_5B_2F_{24}Ir$, M_r = 1723.2, monoclinic, *C1c1*, *a* = 22.8105(2), *b* = 19.0153(2), *c* = 19.9792(2) Å, β = 117.1045(4) ^{o}, *V* = 7714.2(1) Å^3, *Z* = 4, ρ_c = 1.484 Mg m^{-3}, T = 150(2) K, λ = 0.71073 Å. 66010 reflections collected, 17099 independent [R(int) = 0.051], which were used in all calculations. R_1 = 0.0360, wR_2 = 0.0813 for observed unique reflections [$F^2 > 2\sigma(F^2)$] and R_1 = 0.0423, wR_2 = 0.0866 for all unique reflections. Max. and min. residual electron densities 1.19 and –0.96 e Å^{-3}. CSD refs: 880791 (X-ray), 880792 (neutron).

3: was synthesized from **1b** as per the synthesis of **2**, and yellow crystals suitable for X-ray diffraction obtained from a fluorobenzene/pentane layering at 20 ^{o}C. Isolated yield 0.29 g, 71 %. ^{1}H NMR (toluene-d_8, 300 MHz, 20 ^{o}C): δ_H -23.59 (d, $^1J_{RhH}$ = 43.5 Hz, 1H, RhH), 0.51 (br s, 1H, BH), 1.41 (s, 3H, NMe), 1.51 (s, 24H, *ortho*-Me of IMes), 1.59 (s, 3H, NMe), 2.19 (s, 12H, *para*-Me of IMes), 6.01 (s, 4H, NCH of IMes), 6.65 (s, 8H, *meta*-CH of IMes), 7.68 (s, 4H, *para*-CH of $[BAr^f_4]^-$), 8.30 (s, 8H, *para*-CH of $[BAr^f_4]^-$). ^{13}C NMR (toluene-d_8, 75 MHz, 20 ^{o}C): (i) signals due to cation: δ_C 17.7 (*ortho*-Me of IMes), 21.8 (*para*-Me of IMes), 31.5 (Me of NMe_2), 41.3 (Me of NMe_2), 122.9 (NCH of IMes), 129.8 (*ortho*-quaternary C of IMes) 135.5 (*meta*-CH of IMes), 140.1 (*para*-quaternary C of IMes), 183.7 (d, $^1J_{RhC}$ = 46.5 Hz, carbene quaternary C), N-bound aryl quaternary signals not observed; (ii) signals due to anion: δ_C 118.3 (*para*-CH), 125.7 (q, $^1J_{CF}$ = 273.1 Hz, CF_3), 130.2 (q, $^2J_{CF}$ = 31.5 Hz, *meta*-quaternary C), 135.9 (*ortho*-CH), 163.0 (q, $^1J_{CB}$ = 49.1 Hz, *ipso*-quaternary C). ^{11}B NMR (toluene-d_8, 96 MHz, 20 ^{o}C): δ_B -6.0 ($[BAr^f_4]^-$ anion), 53 (br, H_2BNMe_2). ^{19}F NMR (toluene-d_8, 282 MHz, 20 ^{o}C): δ_F -62.2. IR (ν_{BH}, cm^{-1}): 2394. Elemental microanalysis: calcd for $C_{76}H_{68}B_2F_{24}N_5Rh$: C, 55.90; H, 4.20, N, 4.29; measd: C, 55.67; H, 3.99; N, 4.00. *Crystallographic data:* (X-ray) $C_{76}H_{68}B_2F_{24}N_5Rh$, M_r = 1631.9, monoclinic, $P2_1/n$, *a* = 12.7501(1), *b* = 14.1549(1), *c* = 21.1993(2) Å, β = 93.0899(3) ^{o}, *V* = 3820.4(1) Å^3, *Z* = 2, ρ_c = 1.419 Mg m^{-3}, T = 150(2) K, λ = 0.71073 Å. 61210 reflections collected, 8721 independent [R(int) = 0.024], which were used in all calculations. R_1 = 0.0666, wR_2 = 0.1801 for observed unique reflections [$F^2 > 2\sigma(F^2)$] and R_1 = 0.0824, wR_2 = 0.1922 for all unique reflections. Max. and min. residual electron densities 1.40 and –0.98 e Å^{-3}. CSD ref.: 880793 (X-ray), 880794 (neutron).

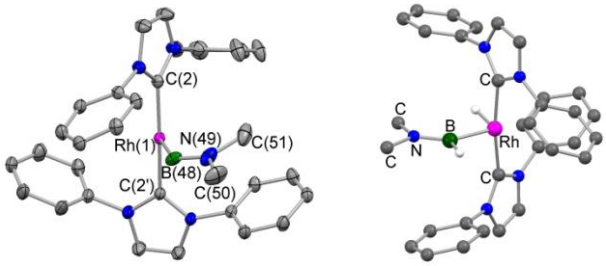

Fig. S1 Molecular structure of the cationic component of **3** as determined by X-ray diffraction (left; one disorder component only) and Density Functional Theory (right). Counter-ion, mesityl Me groups and H atoms (except Rh- and B-bound Hs for DFT structure) omitted for clarity. Thermal ellipsoids set at the 30 % probability level for X-ray structure.

Details of Density Functional Theory Calculations

The DFT calculations were performed using the Amsterdam Density Functional (ADF) Package Software 2012.[s3] Calculations were performed using the Vosko-Wilk-Nusair local density approximation with exchange from Becke[s4] and correlation corrections from Lee-Yang-Parr[s5] (BLYP). Slater-type orbitals (STOs)[s6] were used for the triple zeta basis set with an additional set of polarization functions (TZP). The large frozen core basis set approximation was applied with no molecular symmetry. The general numerical integration was 6 for geometry optimization and 4 for frequency calculation. No significant imaginary frequencies were observed for the optimized geometry of complex **3**. See below for the run file for frequency calculation which contain coordinates for the optimized geometry of complex **3**.

```
#! /bin/sh

# ==============================
# Frequency Calc Compound 3
# ==============================

"$ADFBIN/adf" <<eor
ATOMS
1 Rh     -0.006125429118     -0.027217775330      0.045532657890
2 C      -0.347814967700      3.910035828000     -5.439113937000
3 C       0.456697240700      1.609860997000     -4.702633100000
4 C       0.359996748300      2.987759853000     -4.462716764000
5 C      -4.756390872000     -2.717360417000     -4.645773388000
6 C       1.225367630000     -0.738996855800     -4.138374314000
7 C       1.131299223000      0.742480521300     -3.826637080000
8 C       0.962485715800      3.500739148000     -3.302468699000
9 C      -3.864550748000     -0.620473104100     -3.518319656000
10 C     -4.355474127000     -1.929990108000     -3.411211915000
11 C      1.714641870000      1.297860992000     -2.670532548000
12 C      1.653124495000      2.682156689000     -2.395769653000
13 C     -2.987132119000      1.553835047000     -2.565148214000
14 C     -3.472233582000      0.126759632200     -2.395495767000
15 C      3.855225311000      0.234356210300     -1.935132752000
16 C     -0.729365160200     -3.482593207000     -1.060408095000
17 C     -4.459402292000     -2.493549198000     -2.129994161000
18 C      2.332433666000      3.295008934000     -1.183194657000
19 C      4.260458128000     -0.547759129700     -0.903088642600
20 C     -3.567121511000     -0.490082852200     -1.130749454000
21 C     -4.076730574000     -1.795758414000     -0.973345398600
22 C      2.004663037000     -0.208019996000     -0.646924563500
23 C      3.255119416000     -3.728409136000     -0.283115072500
24 C     -0.555091472600     -4.321471920000      1.242436772000
25 C     -4.227680189000     -2.440908956000      0.392465967700
26 C     -1.986201028000      0.502824282600      0.603129394600
27 C     -0.972054812700      3.845986838000      0.853118235500
28 C      3.305731403000     -2.988451236000      1.041503235000
29 C     -4.221208332000      0.976673873000      0.777429089700
30 C      3.223707877000     -1.582166670000      1.115926993000
31 C     -3.595951284000      1.637795264000      1.784950874000
32 C      3.461279597000     -3.700652053000      2.241471975000
33 C     -0.604445841900      3.140759805000      2.146720031000
34 C      3.329410560000     -0.893447930400      2.342150366000
35 C      3.298462141000      0.621182223700      2.426030589000
36 C     -1.213398293000      1.926027947000      2.537158098000
37 C      0.338946049000      3.710254958000      3.015323070000
38 C      3.546692711000     -3.057518098000      3.485809962000
39 C      3.483429404000     -1.656392261000      3.510646993000
40 C     -0.921410766900      1.310105900000      3.772140497000
41 C      0.669449897400      3.123342996000      4.247611544000
42 C     -1.612585318000      0.035739561340      4.219049811000
43 C      3.694297540000     -3.854128695000      4.769685969000
44 C      0.029136606560      1.927746401000      4.603083085000
45 C      1.662357513000      3.790611381000      5.182049068000
46 N      2.481012612000      0.436390609500     -1.774515673000
47 N     -0.489724363900     -3.144360249000      0.352528086500
48 N      3.130784403000     -0.813318596100     -0.121759401700
49 N     -3.236300877000      0.287315493600      0.060582083110
50 N     -2.233876434000      1.342404647000      1.671846811000
51 B     -0.191839034300     -1.875087929000      0.860393786200
52 H     -0.926140970600      3.345209314000     -6.178378389000
```

53 H	0.376890889400	4.529219129000	-5.986224200000
54 H	0.000585073622	1.191555771000	-5.600383003000
55 H	-1.030334334000	4.594919466000	-4.919755678000
56 H	-5.063434779000	-2.052736810000	-5.461470265000
57 H	0.682237498900	-0.972564020700	-5.059550862000
58 H	-3.915704676000	-3.323763372000	-5.013661771000
59 H	-5.584617989000	-3.402970763000	-4.431994518000
60 H	-3.803542942000	-0.152312789900	-4.501504702000
61 H	2.268082300000	-1.057258528000	-4.271881573000
62 H	0.804303985300	-1.343675661000	-3.326354873000
63 H	0.907641953900	4.571581397000	-3.101075205000
64 H	-3.176185361000	1.900374639000	-3.586274508000
65 H	4.408732570000	0.665786066300	-2.756738191000
66 H	0.029214327900	-4.195236377000	-1.420689275000
67 H	-1.716743732000	-3.950068121000	-1.186981152000
68 H	-0.690186144200	-2.577463358000	-1.667764784000
69 H	-1.908665084000	1.632790451000	-2.376075913000
70 H	-3.493116931000	2.240234902000	-1.874505120000
71 H	-4.860804360000	-3.501889193000	-2.021419885000
72 H	3.423856768000	3.181935722000	-1.236086387000
73 H	2.112161790000	4.365821637000	-1.123941937000
74 H	4.169951716000	-3.567360597000	-0.870393659200
75 H	5.237848865000	-0.929838518300	-0.646775915500
76 H	-0.514298088900	-0.429755931400	-1.366602946000
77 H	2.412024784000	-3.394759614000	-0.898818160300
78 H	-1.550268390000	-4.788330162000	1.193599420000
79 H	2.007391960000	2.825271564000	-0.246872173600
80 H	3.158280637000	-4.806174801000	-0.116101709600
81 H	0.187516288200	-5.076146249000	0.943970403200
82 H	-0.814340325900	3.208477220000	-0.025284223330
83 H	-4.602523036000	-3.464656207000	0.291727784600
84 H	-0.371674626000	4.752963087000	0.729978593600
85 H	-5.264309593000	0.937028822400	0.499253266200
86 H	-0.354859368700	-4.021145384000	2.272709188000
87 H	-2.029958810000	4.141294494000	0.847661129300
88 H	-4.933808469000	-1.889403587000	1.027613678000
89 H	-3.268595483000	-2.473350438000	0.924640031800
90 H	0.014063006520	-1.727725270000	2.040415894000
91 H	3.938736430000	1.085828723000	1.666337333000
92 H	3.529101055000	-4.788367538000	2.197126531000
93 H	2.282557088000	1.014030685000	2.281907401000
94 H	-3.985427591000	2.286018916000	2.556921366000
95 H	0.816114577400	4.647253527000	2.725095231000
96 H	3.642645284000	0.953581427000	3.410776490000
97 H	-1.452542731000	-0.779517203800	3.503352220000
98 H	-2.697260514000	0.179175961200	4.313673424000
99 H	4.222834306000	-4.798680697000	4.596921044000
100 H	3.575287869000	-1.135066778000	4.464285085000
101 H	2.516186987000	4.204370887000	4.631492455000
102 H	2.709330057000	-4.101035191000	5.192445261000
103 H	4.244143729000	-3.287702119000	5.530338677000
104 H	1.188810666000	4.624190131000	5.720067945000
105 H	-1.230277620000	-0.283964767000	5.193700159000
106 H	0.265069513500	1.460232585000	5.559459398000
107 H	2.043264092000	3.088692524000	5.932055198000

END

```
GUIBONDS
1 1 76 1.0
2 1 51 3
3 1 22 2.0
4 1 26 2.0
5 2 55 1.0
6 2 53 1.0
7 2 52 1.0
8 2 4 1.0
9 3 54 1.0
10 3 4 1.5
11 3 7 1.5
12 4 8 1.5
13 5 59 1.0
14 5 56 1.0
15 5 58 1.0
16 5 10 1.0
17 6 61 1.0
18 6 57 1.0
19 6 62 1.0
20 6 7 1.0
21 7 11 1.5
22 8 63 1.0
23 8 12 1.5
24 9 60 1.0
25 9 10 1.5
26 9 14 1.5
27 10 17 1.5
28 11 12 1.5
29 11 46 1.0
30 12 18 1.0
31 13 70 1.0
32 13 69 1.0
33 13 64 1.0
34 13 14 1.0
35 14 20 1.5
36 15 65 1.0
37 15 19 2.0
38 15 46 1.0
39 16 66 1.0
40 16 68 1.0
41 16 67 1.0
42 16 47 1.0
43 17 71 1.0
44 17 21 1.5
45 18 72 1.0
46 18 73 1.0
47 18 79 1.0
48 19 75 1.0
49 19 48 1.0
50 20 21 1.5
51 20 49 1.0
52 21 25 1.0
53 22 48 1.0
54 22 46 1.0
55 23 74 1.0
56 23 80 1.0
57 23 77 1.0
58 23 28 1.0
59 24 81 1.0
60 24 78 1.0
61 24 86 1.0
62 24 47 1.0
63 25 88 1.0
64 25 83 1.0
65 25 89 1.0
66 26 49 1.0
67 26 50 1.0
68 27 87 1.0
69 27 84 1.0
70 27 82 1.0
71 27 33 1.0
72 28 30 1.5
73 28 32 1.5
74 29 85 1.0
75 29 31 2.0
76 29 49 1.0
77 30 34 1.5
78 30 48 1.0
79 31 94 1.0
80 31 50 1.0
81 32 92 1.0
82 32 38 1.5
83 33 37 1.5
84 33 36 1.5
85 34 39 1.5
86 34 35 1.0
87 35 91 1.0
88 35 93 1.0
89 35 96 1.0
90 36 40 1.5
91 36 50 1.0
92 37 95 1.0
93 37 41 1.5
94 38 39 1.5
95 38 43 1.0
96 39 100 1.0
97 40 44 1.5
98 40 42 1.0
99 41 44 1.5
100 41 45 1.0
101 42 98 1.0
102 42 105 1.0
103 42 97 1.0
104 43 99 1.0
105 43 103 1.0
106 43 102 1.0
107 44 106 1.0
108 45 101 1.0
109 45 104 1.0
110 45 107 1.0
111 47 51 1.0
112 51 90 1.0
END

CHARGE 1.0

BASIS
type TZP
core Large
```

```
createoutput None
END

XC
GGA BLYP
END


SCANFREQ -1000 0

AnalyticalFreq
END

SAVE  TAPE21 TAPE13

FULLSCF
INTEGRATION 4.0

NOPRINT LOGFILE

eo
```

References

s1. J. Huang, E.D. Stevens and S.P. Nolan, *Organometallics*, 2000, **19**, 1194.
s2. D.L. Reger, T.D. Wright, C.A. Little, J.J.S. Lamba and M.D. Smith, *Inorg. Chem.*, 2001, **40**, 3810.
s3. (a) G. te Velde, F. M. Bickelhaupt, S. J. A. van Gisbergen, C. Fonseca Guerra, E. J. Baerends, J. G. Snijders and T. Ziegler, *J. Comput. Chem.*, 2001, **22**, 931; (b) C. Fonseca Guerra, J. G. Snijders, G. te Velde and E. J. Baerends, *Theor. Chem. Acc.* 1998, **99**, 391; (c) E.J. Baerends, T. Ziegler, J. Autschbach, D. Bashford, A. Bérces, F.M. Bickelhaupt, C. Bo, P.M. Boerrigter, L. Cavallo, D.P. Chong, L. Deng, R.M. Dickson, D.E. Ellis, M. van Faassen, L. Fan, T.H. Fischer, C. Fonseca Guerra, A. Ghysels, A. Giammona, S.J.A. van Gisbergen, A.W. Götz, J.A. Groeneveld, O.V. Gritsenko, M. Grüning, S. Gusarov, F.E. Harris, P. van den Hoek, C.R. Jacob, H. Jacobsen, L. Jensen, J.W. Kaminski, G. van Kessel, F. Kootstra, A. Kovalenko, M.V. Krykunov, E. van Lenthe, D.A. McCormack, A. Michalak, M. Mitoraj, J. Neugebauer, V.P. Nicu, L. Noodleman, V.P. Osinga, S. Patchkovskii, P.H.T. Philipsen, D. Post, C.C. Pye, W. Ravenek, J.I. Rodríguez, P. Ros, P.R.T. Schipper, G. Schreckenbach, J.S. Seldenthuis, M. Seth, J.G. Snijders, M. Solà, M. Swart, D. Swerhone, G. te Velde, P. Vernooijs, L. Versluis, L. Visscher, O. Visser, F. Wang, T.A. Wesolowski, E.M. van Wezenbeek, G. Wiesenekker, S.K. Wolff, T.K. Woo and A.L. Yakovlev, ADF2012, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam. The Netherlands. http://www.scm.com.
s4. A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098.
s5. (a) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1998, **37**, 785; (b) B.G. Johnson, P.M.W. Gill and J. A. Pople, *J. Chem. Phys.*, 1993, **98**, 5612; (c) T.V. Russo, R.L. Martin and P.J. Hay, *J. Chem. Phys.*, 1994, **101**, 7729.
s6. J. G. Snijders, P. Vernooijs and E. J. Baerends, *At. Data Nucl. Data Tables*, 1982, **26**, 483.