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Borane and alane reductions of bulky *N*,*N*′-diaryl-1,3-diimines: structural characterization of products and intermediates in the diastereoselective synthesis of 1,3-diamines †

David T. Carey, Francis S. Mair,* Robin G. Pritchard, John E. Warren and Rebecca J. Woods
Department of Chemistry, UMIST, PO Box 88, Manchester, UK M60 1QD.
E-mail: frank.mair@umist.ac.uk

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Two new C_2-symmetric diazaborinanes were prepared by diastereoselective intramolecular dihydroboration of bulky 1,3-diamines, the remarkably stable *l*-[HB(2,6-Pr^i_2-C_6H_3NCHMe)$_2$CMe$_2$], from which it was not possible to isolate free diimine, and the less bulky *l*-[HB(2-Pr^i-C_6H_4NCHMe)$_2$CMe$_2$], which yielded *l*-(2-Pr^i-C_6H_4NHCHMe)$_2$CMe$_2$ on acid work up. The BH_3 reductions were highly diastereoselective for *l*-products (*de* > 95%). Use of $AlCl_3$/$LiAlH_4$ mixtures in diethyl ether gave lower (*de* ≈ 75%) and opposite selectivity, yielding predominantly *u*-(2,6-Pr^i_2-C_6H_3NHCHMe)$_2$CMe$_2$ upon work up, *via* a *u*-[H_2Al(2,6-Pr^i_2-C_6H_3)NHCHMeCMe$_2$CHMeN(2,6-Pr^i_2-C_6H_3)] intermediate in a two-step reduction. All products were characterized crystallographically.

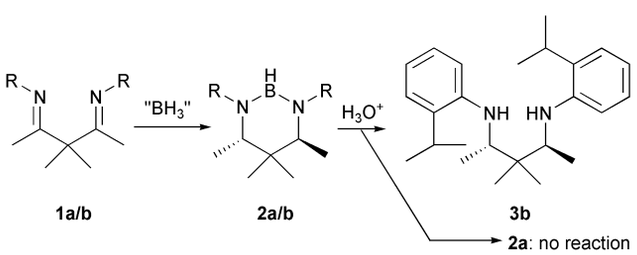
Introduction

Nitrogen donor ligands are as important and widely studied today as they have been for many years.[1] The mono-anionic, *N*,*N*′-bidentate diketiminate ligand class in particular has seen intensive use by main-group, co-ordination and catalytic chemists in the past few years.[2] We recently reported the dialkylation of bulky diaryl variants of this class, to yield neutral bulky 1,3-diimines.[3] As ligands, these 1,3-diimines were very much less effective than their 1,2 counterparts.[4] Our attention therefore turned to converting these 1,3-diimines to 1,3-diamines. The possibility that this may be done diastereoselectively suggests a route to bulky 1,3-diamines of C_2-symmetry. While C_2-symmetric 1,2-diamines have been widely studied as manifolds for asymmetric synthesis,[1] convenient stereocontrolled access to simple 1,3-diamines has been lacking. There is but a single prior report on the double reduction of diketimines: Pr^iNCMeCHCMeNHPr^i·HCl in reaction with $LiAlH_4$ gave *u*-(Pr^iNCHMe)$_2$CH$_2$ upon work up.[5] Reaction of all manner of hydride or alkyl Group 13 reagents with the free base diketimines has in almost all other cases resulted in simple acid–base chemistry, with no reduction of the imine functions.[5,6] Only in the reaction of BMe_3 with *p*-MeC_6H_4NCMeCHCMeNHC_6H_4Me has B–Me addition across a single C=N bond accompanied the acid–base reactivity.[7] This is in contrast to the case of 1,2-diimines, where diastereoselective (and enatioselective) double alkyl additions[8] and borane reductions[9] have precedent. Our strategy of removing the problematic C–H acidity of the diketimines by double alkylation[3] allows neutral hydride sources to be effective reducing agents of 1,3-diimines for the first time, and hence allows access to highly substituted diazaborinanes and alinanes, and in turn to the derived 1,3-diamines. Here we report the preparation of *u* and *l* diastereoisomers of diamines formed by reduction of the diimines (2,6-Pr^i_2-C_6H_3N=CMe)$_2$CMe$_2$ (**1a**) and (2-Pr^i-C_6H_4N=CMe)$_2$CMe$_2$ (**1b**) respectively, and the structural chemistry of the boron and aluminium intermediates. Structural characterization of these intermediates represents a significant addition to scant structural data on saturated six-membered C_3N_2B/Al rings. Furthermore, this approach of intermediate characterization has yielded much new mechanistic insight in other areas of metal–organic chemistry, not least in lithium chemistry,[10] and its application to hydroboration/hydroalumination is comparatively infrequent, at least in the case of imine reductions. The diamines produced offer promise as new C_2 and C_s-symmetric scaffolds for co-ordination chemistry.[1]

Results and discussion

Synthesis using borane

Reaction of **1a**, either with diborane generated *in situ* in dichloromethane,[11] or with borane in thf (Scheme 1), gave good yields of the stable diazaborinane, *l*-HB(2,6-$Pr^i_2C_6H_3$NCHMe)$_2$CMe$_2$, **2a**. A similar reaction with **1b** worked equally well to yield *l*-**2b** (Scheme 1). This represents a new route to diazaborinanes, previously made by hydrogen-elimination routes from amines.[12] The reduction route offers the possibility of diastereoselectivity, and this proved to be the case for **1**: both **2a** and **2b** were obtained as *l*-diastereoisomers after one crystallization, without the need for close temperature control. The compounds were pure by NMR, corresponding to a *de* in excess of 95%. This very high diastereoselectivity is ascribed to an intramolecular reduction, as expected from the 1 : 1 reaction stoichiometry, in which the chirality of the first-reduced carbon is efficiently transferred to the second by chelation-control.[13] The very high level of 1,3 stereoinduction achieved far surpasses that shown in borane reduction of the analogous diketone (O=CMe)$_2$CMe$_2$,[13] though similarly high levels of 1,3 induction have recently been seen in reduction of the bulkier diketone (O=CPh)$_2$CMe$_2$, using LiAl(OBu^t)$_2$H$_2$.[14] Conditions which precluded intramolecular reduction of both imine functions by the same boron species were demonstrably less-selective: reductions of **1b** with HBCl$_2$·SMe$_2$ in thf gave oily multi-component mixtures, inseparable by preparative flash

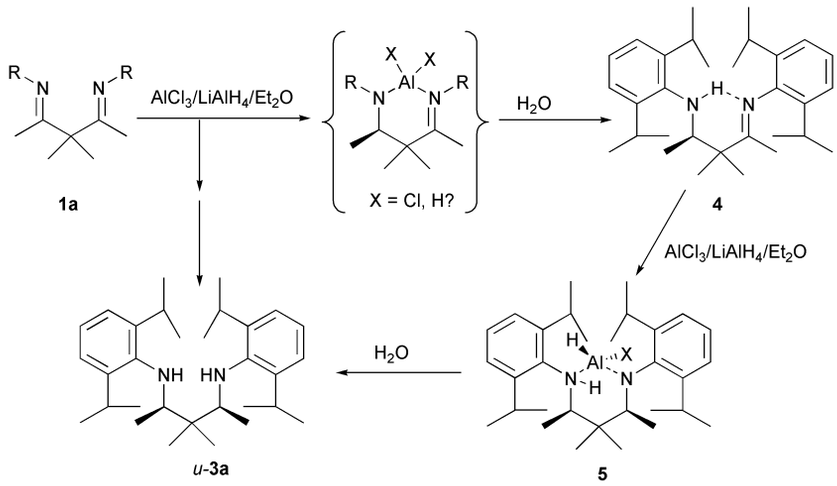


1a/2a/3a/4/5: R = $C_6H_3(Pr^i)_2$; **1b/2b/3b** R = $C_6H_4(Pr^i)$

Scheme 1

† Electronic supplementary information (ESI) available: preparative and characterization details; substructure of **5**. See http://www.rsc.org/suppdata/dt/b3/b306401h/

DOI: 10.1039/b306401h



Scheme 2

chromatography. The possibility that imine chloroboration competed with hydroboration in this case cannot be excluded,[15] however, it was clear that the reactions would not be preparatively useful.

In the case of **2b**, the *l*-diamine **3b** was obtained after acid-work up and neutralization, in equally high diastereomeric excess. Similar acid treatment of **2a** resulted in no change. Even after overnight reflux, no deboronated product was detectable. It appeared as though the 2,6-diisopropyl-phenyl substituents were blocking attack of protons on the nitrogen atoms. Furthermore, even KOH/H_2O_2 failed to dislodge the boron from **2a**.

In order to find a convenient route to the amine **3a**, alternative means of reduction were necessary given the difficulty of deboronation of **2a**, which, despite including a co-ordinatively unsaturated boron atom, is indefinitely stable in air and in solution.

Synthesis using alane

Attempted reaction of **1a** with a preformed alane complex $H_3AlN(Me)C_5H_8$[16] resulted in recovery of unchanged **1a**. The amine complex of the alane was apparently too stable, and did not allow pre-co-ordination of alane to the imine functions, therefore attention turned to *in-situ* alane preparations in weakly co-ordinating solvents: the *in-situ* reaction of $AlCl_3$ with $LiAlH_4$ in diethyl ether is reported to yield AlH_3, though temperature must be controlled to avoid ether-cleavage and polymerization of alane.[17] When the experiment was run at −70 °C, the major product from the reaction of the mixture with **1a** after aqueous work up was a mono-reduced imino-amine **4**, Scheme 2. This suggests that the reacting species was predominantly $HAlCl_2$, though in this case, crystallization of the intermediate aluminium species was unsuccessful. Conscious of the fact that the $AlCl_3/LiAlH_4$ reaction was substantially incomplete at −70 °C,[17] complete reduction was achieved by reaction of **4** with a further equivalent of the $AlCl_3/LiAlH_4$ mixture in diethyl ether at the higher temperature of −10 °C. In this case, isolation of the intermediate was possible by extraction of an aliquot of the reaction mixture. Structural analysis revealed the intermediate to be an amidodihydroaluminium species **5** with internal co-ordination of the previously reduced amino group, giving a four-co-ordinate aluminium. The crystal is contaminated with varying amounts of chloride in one of the hydride positions, indicating that, even after pre-contacting the $AlCl_3/LiAlH_4$ mixture for 1 hour at −10 °C, reaction was incomplete (a prior attempt using a shorter pre-contacting time yielded material with an identical structure, but with a higher Cl : H ratio in the disordered position). Hydrolysis of **5** gave the desired diamine **3a**. However, the *u*-isomer was shown to be present by NMR and structural characterization of derivatives.‡ Despite the predominance of *u*-**3a** in the hydrolysate, the crystal selected for structural characterization was in fact of *l*-**3a**, a minor contaminant, as judged from NMR analysis of the crude product. A further preparation of **3a** starting from **1a** in one pot from $AlCl_3/LiAlH_4$ in diethyl ether, but at −10 °C, also resulted in the isolation of *u*-**3a**, indicating that the *u*-diastereochemistry need *not* necessarily result from the pre-reduced amino-substituent, which would itself become a stereocentre once co-ordinated to aluminium. It seems, therefore, that while high diastereoselection for *l*-product is achievable near ambient temperatures with borane, a predominance of *u*-product, with lower selectivity (estimated by NMR at *de* = 75% in favour of *u*), is achieved with *in situ* 'alane'. This finding fits with the previously reported reduction of a less-bulky variant of **1**, $(Pr^iNCMeC)_2CH_2\cdot HCl$, in its reaction with an excess of $LiAlH_4$, which yielded *u*-product.[5] While the poor performance of $HBCl_2$ suggests that a key issue is intramolecular double reduction, the isolation of *u*-product from the second run with alane, using a higher reaction temperature, longer pre-reaction time of $LiAlH_4$ and $AlCl_3$, and alane : diimine ratio closer to 1 : 1, indicates that *u*-product predominates using aluminium in *any* case, as it does in the only other published study.[5]

When the structures of the six-membered ring intermediates are considered, a possible reason for this difference becomes apparent; in this way, the structural data inform further mechanistic discussion.

Structural characterization of borane and alane intermediates

Six structures in all have been characterized, those of *l*-**2a**, *l*-**2b**, *l*-**3a**, *l*-**3b**, **4**, and *u*-**5**. The metrical parameters for these are given in Table 1. **2a** (Fig. 1) and **2b** (Fig. 2) exhibit very similar structures. Despite the fact that each molecule is chiral, both crystallize in achiral space groups. In **2b**, the single isopropyl groups are pointing to one side of the molecule (*syn*), the side opposite to that of the envelope tilt of the C(3) atom. The other five atoms of the central six-membered C_3N_2B ring are coplanar (**2a**: rms deviation = 0.012 Å; C(3) lies 0.657 Å out of the mean plane), in order to optimise B–N pπ–pπ interactions, as judged from the B–N bond lengths of around 1.40 Å. Selected bond lengths and angles are given in Table 1. There is no previous crystallographic data on diazaborinanes as such; in fact, crystallographically characterized saturated C_3N_2B rings of any

‡ In addition to the *u*-diastereochemistry exhibited in crystals of **5**, and by NMR of bulk samples, subsequent use of the bulk material has yielded a number of crystalline complexes, all structurally characterized as being of *u*-diastereochemistry.

Table 1 Selected bond lengths (Å) and angles (°) in **2a**, **2b**, **3a**, **4** and **5**

2a		**2b**		**3a**		**4**		**5**	
B(1)–N(2)	1.396(4)	N(1)–B(1)	1.399(4)	C(1)–C(2)	1.519(5)	N(1)–C(20)	1.425(3)	Al(1)–N(2)	1.808(2)
B(1)–N(1)	1.413(5)	N(2)–B(1)	1.414(5)	C(2)–N(1)	1.486(5)	N(1)–C(2)	1.445(3)	Al(1)–N(1)	1.992(2)
N(1)–C(20)	1.445(4)	N(1)–C(4)	1.474(4)	C(2)–C(3)	1.545(6)	N(2)–C(4)	1.283(3)	Al(1)–Cl(1)	2.116(2)
N(1)–C(2)	1.475(4)	N(1)–C(17)	1.436(4)	C(3)–C(7)	1.520(5)	N(2)–C(8)	1.428(3)	N(1)–C(8)	1.484(3)
N(2)–C(6)	1.444(4)	N(2)–C(8)	1.441(4)	C(3)–C(6)	1.525(6)	C(1)–C(2)	1.526(5)	N(1)–C(2)	1.527(3)
N(2)–C(4)	1.480(4)	N(2)–C(2)	1.481(4)	C(3)–C(4)	1.544(5)	C(2)–C(3)	1.546(4)	N(2)–C(20)	1.433(3)
C(1)–C(2)	1.529(5)	C(1)–C(2)	1.526(5)	C(4)–N(2)	1.466(5)	C(3)–C(4)	1.521(4)	N(2)–C(4)	1.476(3)
C(2)–C(3)	1.545(5)	C(2)–C(3)	1.530(5)	C(4)–C(5)	1.497(6)	C(3)–C(7)	1.531(4)	C(1)–C(2)	1.527(4)
C(3)–C(18)	1.527(5)	C(3)–C(6)	1.529(5)			C(3)–C(6)	1.548(5)	C(2)–C(3)	1.558(3)
C(3)–C(19)	1.536(4)	C(3)–C(7)	1.537(5)			C(4)–C(5)	1.500(4)	C(3)–C(6)	1.534(4)
C(3)–C(4)	1.542(5)	C(3)–C(4)	1.548(4)					C(3)–C(7)	1.545(4)
C(4)–C(5)	1.524(5)	C(4)–C(5)	1.522(5)					C(3)–C(4)	1.559(3)
								C(4)–C(5)	1.535(4)
N(2)–B(1)–N(1)	121.4(3)	N(1)–B(1)–N(2)	121.5(3)	N(1)–C(2)–C(1)	111.5(3)	C(20)–N(1)–C(2)	117.7(2)	N(2)–Al(1)–N(1)	99.22(9)
B(1)–N(1)–C(20)	121.4(3)	B(1)–N(1)–C(17)	124.0(3)	N(1)–C(2)–C(3)	109.5(3)	C(4)–N(2)–C(8)	122.6(2)	N(2)–Al(1)–Cl(1)	123.01(9)
B(1)–N(1)–C(2)	120.8(3)	B(1)–N(1)–C(4)	119.5(3)	C(1)–C(2)–C(3)	114.6(3)	N(1)–C(2)–C(1)	114.6(3)	N(1)–Al(1)–Cl(1)	98.39(8)
C(20)–N(1)–C(2)	117.3(2)	C(17)–N(1)–C(4)	116.5(2)	C(7)–C(3)–C(6)	106.8(3)	N(1)–C(2)–C(3)	111.8(2)	C(8)–N(1)–C(2)	117.55(18)
B(1)–N(2)–C(6)	119.6(3)	B(1)–N(2)–C(8)	119.5(3)	C(7)–C(3)–C(4)	108.1(3)	C(1)–C(2)–C(3)	114.4(2)	C(8)–N(1)–Al(1)	115.29(13)
B(1)–N(2)–C(4)	121.0(3)	B(1)–N(2)–C(2)	121.5(3)	C(6)–C(3)–C(4)	108.7(3)	C(4)–C(3)–C(7)	110.2(2)	C(2)–N(1)–Al(1)	114.96(14)
C(6)–N(2)–C(4)	118.8(2)	C(8)–N(2)–C(2)	119.0(3)	C(7)–C(3)–C(2)	108.0(4)	C(4)–C(3)–C(2)	114.4(2)	C(20)–N(2)–C(4)	114.48(19)
N(1)–C(2)–C(1)	110.3(3)	N(2)–C(2)–C(1)	111.3(3)	C(6)–C(3)–C(2)	112.0(3)	C(7)–C(3)–C(2)	108.9(3)	C(4)–N(2)–Al(1)	129.08(16)
N(1)–C(2)–C(3)	110.7(3)	N(2)–C(2)–C(3)	109.7(3)	C(4)–C(3)–C(2)	113.0(3)	C(4)–C(3)–C(6)	107.0(3)	N(1)–C(2)–C(1)	109.5(2)
C(1)–C(2)–C(3)	114.2(3)	C(1)–C(2)–C(3)	113.2(3)	N(2)–C(4)–C(5)	113.3(3)	C(7)–C(3)–C(6)	107.5(3)	N(1)–C(2)–C(3)	109.84(19)
N(2)–C(4)–C(3)	110.3(3)	N(1)–C(4)–C(3)	109.8(3)	N(2)–C(4)–C(3)	111.8(3)	C(2)–C(3)–C(6)	108.5(2)	C(1)–C(2)–C(3)	114.4(2)
C(5)–C(4)–C(3)	113.7(3)	C(5)–C(4)–C(3)	115.2(3)	C(5)–C(4)–C(3)	114.3(3)	N(2)–C(4)–C(5)	122.8(2)	N(2)–C(4)–C(3)	113.40(19)
N(2)–C(4)–C(5)	111.4(3)	N(1)–C(4)–C(5)	110.5(3)	C(17)–N(1)–C(2)	119.3(3)	N(2)–C(4)–C(3)	119.6(2)	N(2)–C(4)–C(5)	110.7(2)
				C(8)–N(2)–C(4)	117.7(3)	C(5)–C(4)–C(3)	117.5(2)	C(5)–C(4)–C(3)	112.63(19)

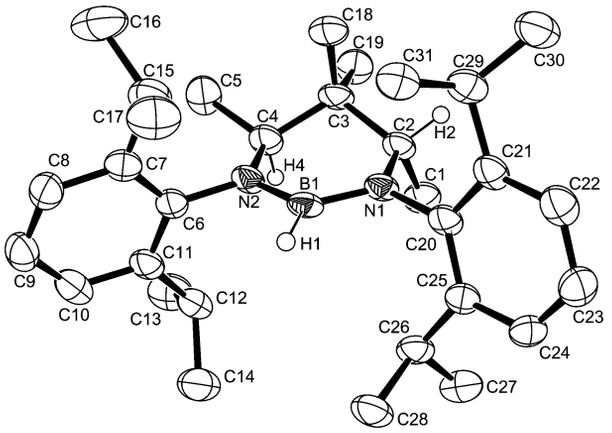


Fig. 1 Crystal and molecular structure of **2a**. Those hydrogens originating from the borane reagent are shown; others are omitted.

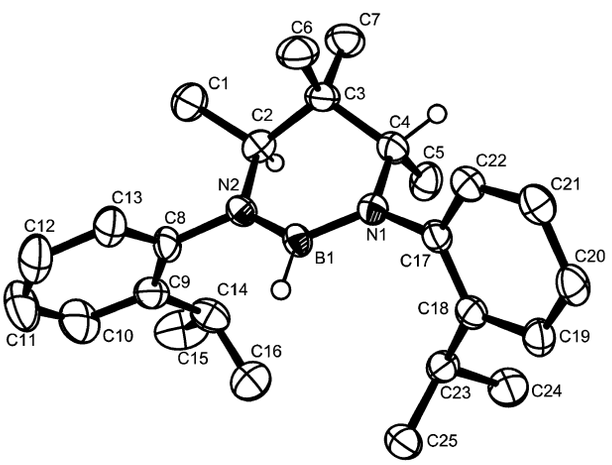


Fig. 2 Crystal and molecular structure of **2b**. Those hydrogens originating from the borane reagent are shown; others are omitted.

kind are only three in number: a tricyclic triaminoborane (1,5,9,13-triazaboratricyclotridecane),[18] a bicyclic triaminoborane (1,8,10,9-triazaboradecalin)[19] and, the closest analogy, monocyclic *N,N′*-bis{bis(dimethylamino)boryl}-2-phenyl-1,3,2-diazaboracyclohexane,[20] all of which possess similar half-boat conformations. The B–N bonds in **2** are comparable to those in all these cases. From a preparative viewpoint, the closest analogy lies with an unusual octaaza macrocycle, in which four C_3N_2B rings were formed by a combined hydrogen-elimination/imine reduction on the *o*-iminoanilino macrocyclic precursor.[21] Even in that example, the imine involved was an aldimine, and the resultant six-membered ring was annulated with an aromatic ring, hence the example addresses neither the conformational nor the diasereoselectivity issues in **2**. The structures of **2** represent the first crystallographic study concerning reduction of di-*ket*imines, and hence the first to address issues of stereoselectivity.

The 2,6-diisopropylphenyl groups lie at 81 ° and 105 ° to the CNBNC plane in **2a**, protecting the boron above and below the plane from protolysis.

In both **2a** and **2b**, one of the ring methyls attached to the reduced carbons is axial, the other equatorial, with respect to the C_3N_2B ring. Axial/equatorial exchange of their conformation would accompany flexing of the CMe_2 bow unit of the half-boat between the two equivalent positions by boat inversion. This is a relatively low-energy process, as judged from the ^{1}H NMR data, which for **2a** showed a single resonance for the two methyls of the CMe_2 unit, and for the two methyls attached to the reduced carbon atoms (one sharp doublet). Cooling of a deuterotoluene solution of **2a** to −80 °C revealed no evidence of decoalescence in the ^{1}H NMR spectrum. Importantly, in the *u*-diastereomer of such a species, the rapid boat inversion process would *not* render the two methyls of the CMe_2 bow unit equivalent.

Because of the fact that the ring boron is planar, there is minimal *A*-strain (1,3 axial repulsion) resulting from the axial position of one of the ring methyls. Indeed, because of the *l*-relation of the two stereocentres, there is little option but to place one methyl in an axial site; the only other viable conformation would be a twist-boat, which would increase 1,2 repulsions with the CMe_2 unit. In **2b** there is the additional issue of *syn*/*anti* interconversion of isopropyl environments by aryl rotation. General broadness of all ^{1}H NMR lines at room temperature in **2b** (not shown by **2a**) would suggest that this process was slowing at that temperature; all resonances sharpened at 80 °C. The observance of two isopropyl methine environments in the ^{1}H NMR spectrum of **2a** indicates that in this bulkier variant, aryl rotation was frozen on the NMR timescale at room temperature.

Given that there are no previous entries in the crystallographic database with the $XCHMeCMe_2CHMeX$ hydrocarbon unit present, it was deemed worthwhile to record crystallographic data on the product amines **3**. In the case of **3b** (Fig. 3), this reconfirmed the *l*-diasteromeric assignment, and showed that an intramolecular hydrogen bond maintained the ring conformation in the crystal. In the interests of brevity, bond length and angle data for the ring in **3b** are not listed in Table 1, they being essentially the same as those for **3a** (Fig. 4), except where noted below.

The key factor controlling conformation is the intramolecular hydrogen bond, which is rather weak (N ⋯ N separations: **3a**, 2.81 Å; **3b**, 2.84 Å).[22]

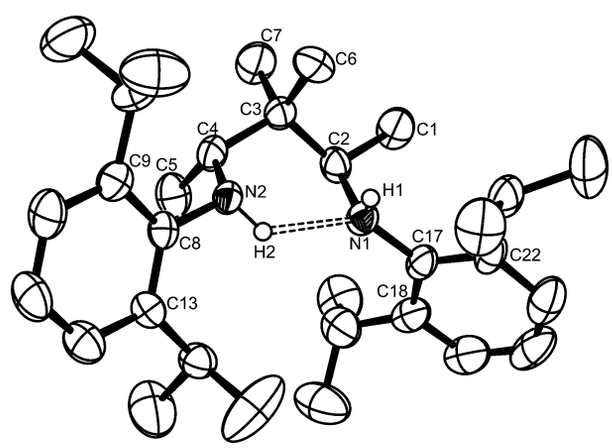


Fig. 3 Crystal and molecular structure of **3b**. Only NH hydrogens are shown.

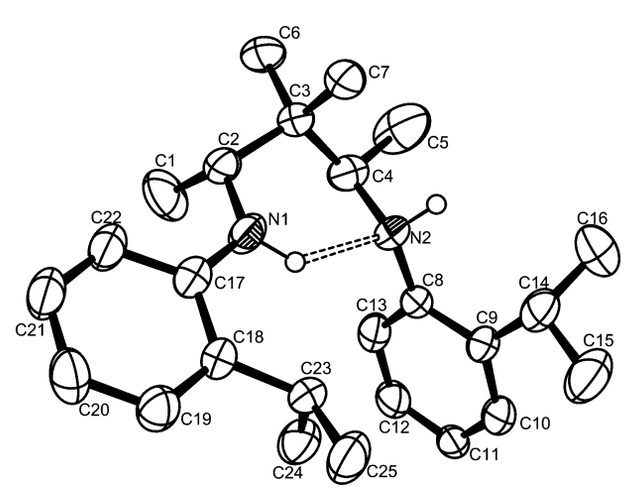


Fig. 4 Crystal and molecular structure of **3a**. NH hydrogens are shown; others are omitted.

Compound **4**, isolated from a hydrolysate of a low-temperature reduction using $LiAlH_4$ and $AlCl_3$ in which the reaction had failed to go to completion,[17] has one remaining double bond, and this has a large influence on the conformation, as shown in Fig. 5. It can best be described as an envelope conformation, but instead of C(3) jutting upwards from the mean plane as in all other cases, it remains co-planar with N(2), C(4) and N(1), in order to minimise *gauche* interactions between C(5) and C(6)/C(7). Instead, it is the newly reduced carbon which forms the flap of the envelope, and, furthermore, it directs its methyl group into an axial orientation, when an equatorial one would seem equally viable. Here, though, there is no 1,3 *A*-strain between C(1) and C(4), remaining as it does, sp^2 hybridised, and there is clearly no 1,3 strain from C(1) to the N–H proton, so in fact in this unusual case the axial position of the six-membered ring is the most favourable, allowing C(1) to distance itself from 1,2 interaction with C(6). The presence of a permanent chiral centre in the molecule allows the solution behaviour to be probed in detail. Particularly, it appears that the aryl attached to the imine remains prevented from rotating by the closely bound C(5), as the two sides are distinguishable by NMR spectroscopy. That it is the imino-aryl which remains locked was confirmed by NOE experiments.

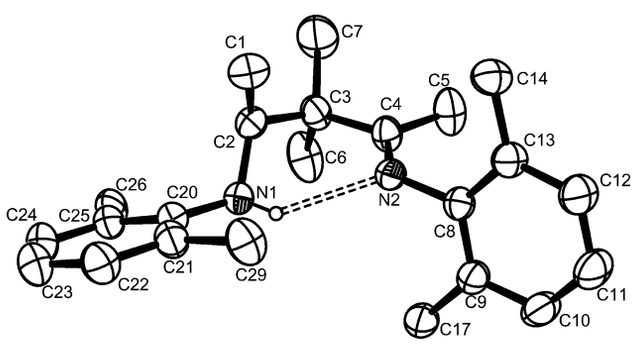


Fig. 5 Crystal and molecular structure of **4**. The NH hydrogen is shown; other hydrogens, and the isopropyl methyl groups, have been removed for clarity.

Further reaction of **4** with $LiAlH_4/AlCl_3$ produced a good crop of *u*-**3a** upon aqueous work up; from an aliquot withdrawn prior to work up, a few crystals of the aluminium intermediate **5**, Fig. 6, were obtained. Though the crystals were predominantly of the composition shown in Fig. 6, the dihydroaluminium species co-crystallised with an isostructural chlorohydroaluminium species (see ESI†). Occupancies of the disordered site refined to 72% H, 28% Cl. In **5**, one NH proton remains. It is not unusual for co-ordinated NH to co-exist with AlH bonds, provided that temperatures do not climb too high.

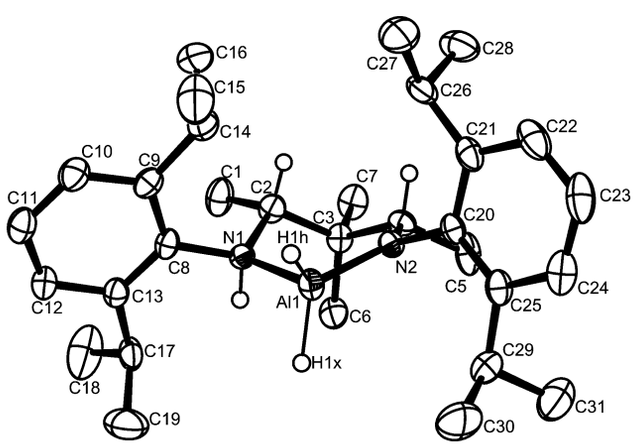


Fig. 6 Crystal and molecular structure of **5**. Those hydrogens bound to the central six-membered ring are shown; other hydrogens, and the minor occupancy of the co-ordination site H1*x* by chloride, are omitted.

The co-existence of amino and amido groups too has some precedent, though the route to $[Cl(H)Al\{NHBu^tCH_2CH_2NBu^t]$ was from hydrogen elimination, rather than imine reduction.[23] Another paper reports alane reduction of an α-diimine, but this was an aldimine, and hence stereochemical issues did not arise.[24] The mixed halide/hydride co-ordination seen in **5** has also been seen before, arising from use of ClH_2AlNMe_3 as a starting material.[25] In fact, a similar partial occupancy H/Cl site results from co-crystallization of $[(Me_3Si)_2NAlClH.NMe_3]$ with $[(Me_3Si)_2NAlH_2.NMe_3]$, just as it does in **5**, and this molecule crystallizes in the chiral space group $P2_12_12_1$, just as does **5**.[25] In **5**, in addition to the two chiral centres generated by the reduction, the amino nitrogen, and the aluminium (in the chloro-case) are also chiral. It is ironic that of the six structures, the only one to spontaneously resolve in the crystal was **5**, which yields optically inactive *u*-**3a** upon hydrolysis. All bond lengths and angles around aluminium are in keeping with these precedents. Amido nitrogen N(2) is rigorously planar, whereas the amino nitrogen N(1) is distorted tetrahedral. This leads to a rather puckered and slightly twisted boat, with the Al(1) lying only slightly above the mean ring plane. The most notable feature of the conformation is the mutually equatorial arrangement of the two ring methyls, also seen in $[Al_2H_4(Pr^iNCHMe)_2CH_2]_2$.[5] The alternative mutually axial arrangement would be prohibited by excessive 1,3 *A* strain. No amount of such ring flipping would render the two methyls of the CMe_2 unit equivalent, in either the aluminium complex or the free amine *u*-**3a**, and indeed they are sharp and distinct separate signals in *u*-**3a**. The spectrum of the mixture **5**, with all its possible diastereomers due to the tetrahedral Al(1) and N(1) sites, for both components, proved too crowded and broad to decipher.

Taking into account all of the structural data, a possible explanation of the selectivities with borane emerges from consideration of two possible cases of intramolecular hydride transfer.

In the first case, the intermediate of monoreduction, shown in Chart 1, proceeds to **2** *via* a boat-like transition state, of which there are two possible forms. In the first of these, **I**, the first asymmetric centre points its methyl group in an equatorial orientation in order to avoid a pseudo-axial hindrance from the isopropyl substituents on both aryls (examination of the boat structure of $[Br_2Ni(Pr^i_2C_6H_3NCMe)_2CH_2]$ lends credence to this postulate;[26] other complexes of ligands **1a** and **1b** have also demonstrated boat conformations where the co-ordinated fragment is four-co-ordinate).[4] Consequently, intermediate **I** predominates, and leads to *l*-product. Intermediate **II**, which would lead to *u*-product, does not attain sufficient concentration to contribute significantly because of the afore-

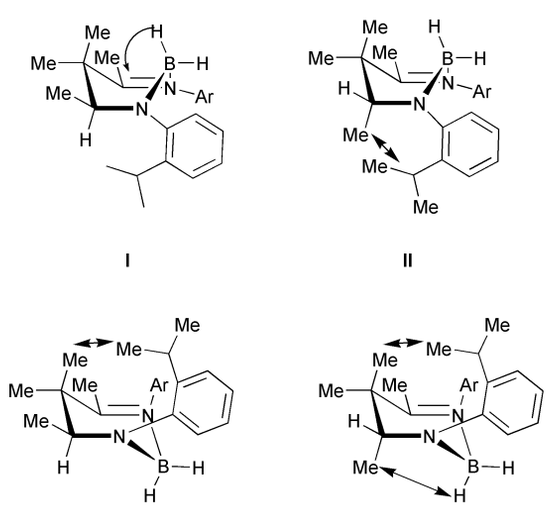


Chart 1 Proposed borane intermediates.

Table 2 X-Ray data collection and refinement details

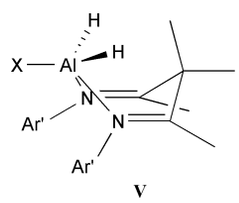
Compound	**2a**	**2b**	**3b**	**3a**	**4**	**5**
Formula	$C_{31}H_{49}BN_2$	$C_{25}H_{37}BN_2$	$C_{25}H_{38}N_2$	$C_{31}H_{50}N_2$	$C_{31}H_{48}N_2$	$C_{31}H_{50.6}AlCl_{0.4}N_2$
M	460.53	376.38	366.57	450.73	448.71	492.07
Crystal system	Triclinic	Triclinic	Monoclinic	Orthorhombic	Triclinic	Orthorhombic
a/Å	8.539(8)	11.0205(2)	13.111(2)	16.086(2)	10.802(4)	11.9491(3)
b/Å	9.459(7)	12.6758(2)	11.650(3)	11.236(2)	15.950(5)	12.7126(4)
c/Å	19.457(7)	17.0392(3)	15.729(3)	16.069(3)	10.464(4)	19.7892(6)
α/°	102.29(5)	77.6970(10)	(90)	(90)	103.83(3)	(90)
β/°	94.25(5)	84.2240(10)	109.31(3)	(90)	118.92(3)	(90)
γ/°	112.19(7)	89.6990(10)	(90)	(90)	70.67(3)	(90)
Space group	$P\bar{1}$, no. 2	$P\bar{1}$, no. 2	$P2_1/n$, no. 14	$Pca2_1$, no. 29	$P\bar{1}$, no. 2	$P2_12_12_1$, no. 19
Z	2	4	4	4	2	4
T/K	223(2)	150(2)	203(2)	203(2)	293(2)	150(2)
μ/mm^{-1}	0.062	0.062	0.062	0.059	0.427[c]	0.132
Reflns. measd.	5200	14788	12063	5196	5161	18526
Reflns. obsd[a] (R_{int})	4879 (0.0292)	9001 (0.1054)	3954 (0.2799)	2657 (0.0501)	4590 (0.0229)	6820 (0.0908)
R_1(observed)	0.0793	0.0886	0.1074	0.0531	0.0611	0.0572
wR_2(all data)[b]	0.2562	0.2372	0.3275	0.1281	0.2159	0.1203

[a] I = $I > 2\sigma(I)$. [b] $wR_2 = \{\sigma[w(F_o^2 - F_c^2)^2]/\sigma[w(F_o^2)^2]\}^{1/2}$. [c] High absorption due to use of Cu-Kα radiation; other datasets used Mo-Kα.

mentioned pseudo-axial 1,4 and pseudo-*gauche* 1,2 interaction of methyl with bulky aryls. Against this postulate is the fact that there would be substantial 1,4 strain introduced from interaction of the axial methyl of the CMe_2 bow unit with the BH_2 stern, however, it may be that displacement of the reacting BH group to one side, in order to relieve this 1,4 strain, is the key to reactivity; such sideways displacement would be required to place the hydride above the C=N plane.

The second possibility of a chair-like transition state seems strongly disfavoured on the basis of what is known of conformational preferences of similar systems,[2,4,26] and examination of postulated intermediates **III** and **IV**, both of which would suffer significantly stronger pseudo 1,3 axial strain between the CMe_2 unit and the bulky aryls, and (in the case of **IV**) more classical 1,3 axial strain between the B–H group and the axial methyl. Such a model satisfactorily explains the high *R*,*R*/*S*,*S* (*l*) selectivity of the 1 : 1 borane reductions.

This begs the question: how do the 'alane' reductions differ? It is true that the Al–N and Al–H bonds are significantly longer, and less covalent, and hence less directional. These factors alone would fit with reductions in selectivity, but not with reversal of it. In the case of the stepwise reduction, proceeding through **4**, an explanation is readily apparent: inspection of **4** reveals clearly that, whether by pre-co-ordination to N(1), direct addition across C=N, or pre-co-ordination to N(2), attack of the reducing species shall occur from the least hindered face, opposite to that of the axial methyl C(1), thus leading to *u*-product. Explanation in the direct syntheses, with no isolation of hemi-reduced material, is less certain. It may lie in the accessibility of a five-co-ordinate intermediate. While in the case of boron, co-ordination of both nitrogens of the diimines **1** to the boron atom would seem to require prior transfer of one hydride ligand, for the larger aluminium, there is ample precedent for N_2AlH_3 co-ordination spheres, albeit most of them exhibiting axial disposition of the two nitrogen donors about the trigonal bipyramidal aluminium.[5,27] The chelating nature of the ligands **1** prevents this disposition, and thus leads to a five-co-ordinate intermediate **V** in which two hydrides are disposed to the same side of the diimine. Rapid double reduction to ultimately yield *u*-**3a** would result, and is entirely plausible for the highly reactive alane fragment.



V

Chart 2 Proposed alane intermediate.

Conclusions

In summary, some interesting conformational issues arising in this first diastereoselective synthesis of diazaborinanes were employed to rationalise the selectivity. The ill-defined nature of $LiAlH_4/AlCl_3$ mixtures in diethyl ether caused some problems, but high-yielding routes to bulky C_2-symmetric 1,3-diamine *l*-**3b**, and yet bulkier C_s symmetric *u*-1,3-diamine **3a** have been found. These highly crystalline proligands offer much promise, judging by the pedigree of their parent diketiminates.[2] The co-ordination chemistry of the derived diamido ligands will be the subject of future papers in this series.[28]

Experimental

General procedures, solvent purifications, *etc*., were as previously described.[3] Starting materials **1a**, **1b**,[3] B_2H_6[11] and $AlH_3{\cdot}MeNC_5H_8$[16] were prepared by literature methods. Other reagents were used as supplied by commercial vendors. Elemental analyses were performed by the UMIST Microanalysis Service. Preparative and characterization details for the following compounds have been deposited as ESI †: 1,3-(2-isopropylphenyl)-4,5,5,6-tetramethyl-1,3,2-diazaborinane, **2b**; *N*,*N*′-bis-(2-isopropylphenyl)-3,3′-dimethylpentane-2,4-diamine, **3b**; 1,3-(2,6-diisopropylphenyl)-4,5,5,6-tetramethyl-1,3,2-diazaborinane, **2a**; 2-(2,6-diisopropyl)phenylamino-4-(2,6-diisopropyl)phenylimino-3,3-dimethyl-pentane, **4**; *N*,*N*′-bis-(2,6-diisopropylphenyl)-3,3′-dimethylpentane-2,4-diamine, **3a**, and aluminium intermediate, **5**.

Attempts to reduce **1a** using previously successful imine reduction methods involving $LiAlH_4$ in diethyl ether, $NaBH_4$ in thf,[29] or $ZnBH_4$ in dimethoxyethane,[30] or polymethylhydrosiloxane catalysed by $(Bu_2SnOAc)_2O$ or Bu_4NF,[31] all resulted in recovery of unchanged **1a**, as did an attempt using $AlH_3{\cdot}MeNC_5H_8$ in diethyl ether.[16] Reaction of **1b** with excess $HBCl_2{\cdot}SMe_2$ in diethyl ether at −10 °C, followed by aqueous base wash, produced no crystalline material. Acid work up gave an oil from the organic layer, which had three major bands of product by TLC. These proved inseparable by preparative flash chromatography, yielding oily mixtures with uninterpretable ^{1}H NMR.

X-Ray data were acquired using various techniques on three different diffractometers: Bruker CCD (**2b**, **3b** and **5**), Nonius MACH 3 (**2a**, **3a**), and Rigaku 4-circle (**4**). Collection and refinement methods and software for these have been fully discussed elsewhere.[4] Hydrogen atoms attached to carbon were

placed in calculated positions and refined using a riding model. Those attached to boron, aluminium and four-co-ordinate nitrogen were similarly treated but allowed to refine the A–H length freely. Hydrogens on three-co-ordinate nitrogen were allowed to refine freely. A summary of experimental parameters for all six data collections is shown in Table 2.

CCDC reference numbers 212230–212235.

See http://www.rsc.org/suppdata/dt/b3/b306401h/ for crystallographic data in CIF or other electronic format.

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