Isolation of an intermediate in the insertion of a carbodiimide into a boron-aryl bond†

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A 1 : 1 Lewis acid–base complex between CyN=C=NCy and $PhBCl_2$ has been isolated and structurally characterized, heating of which in refluxing toluene results in the amidinate, $[PhC\{NCy\}_2]BCl_2$; the overall reaction has been modeled by DFT calculations.

Despite the fact that aluminium and gallium amidinates can serve as olefin polymerization catalysts[1] and as precursors for thin film deposition,[2] very little information is available regarding the congeneric amidinates of boron.[3] We have therefore embarked on synthetic, structural and reactivity studies of this class of compound.[4] One of the potential routes to the desired compounds features the insertion of a carbodiimide into a boron–carbon or boron–heteroatom bond of a boron(III) derivative. In fact, insertion reactions of this type represent part of a broader tapestry of heterocumulene insertion processes that includes commercially and environmentally important CO_2. In an early mechanistic study of the insertion of a variety of heterocumulenes into Zr–carbon bonds, Gambarotta *et al.*[5] proposed that the prerequisite initial step involves coordination of one of the terminal heteroatoms to the Lewis acidic zirconium centre. A similar conclusion has since been drawn by others.[6] Additional support for this proposal has also been forthcoming from theoretical studies of the insertion of CO_2 into the Rh(III)–H bond[7] and of carbodiimide insertions into Al–Me and Al–NMe_2 bonds.[8] Interestingly, and in contrast to $Al_2(NMe_2)_6$ and aluminium alkyls, our attempts to insert CyN=C=NCy (Cy = cyclohexyl) into $B(NMe_2)_3$ and BEt_3 were not successful. However, we have now succeeded in the isolation and structural characterization of an example of the putative initial Lewis acid–base complex (**1**) from the reaction of $PhBCl_2$ with CyN=C=NCy, subsequent heating of which in toluene furnishes the amidinate complex, $[PhC\{NCy\}_2]BCl_2$ (**2**). The experimental work is supported by a DFT study of the overall reaction mechanism. To the best of our knowledge, the present work represents (a) the first example of the preparation of a boron amidinate by means of carbodiimide insertion,[9] and (b) the first example of such a process occurring at a p-block element/aryl bond.

Treatment of $PhBCl_2$ with an equimolar quantity of CyN=C=NCy in hexane solution at ambient temperature results, after isolation and crystallization, in a 96% yield of **1**.[10] The X-ray crystal structure of **1** (Fig. 1) reveals that one of the nitrogen atoms of the carbodiimide, N(1), forms a donor–acceptor bond of length 1.583(3) Å to the boron atom of $PhBCl_2$. As a consequence of the donor action on the part of the carbodiimide, the C(13)–N(1)–C(7) angle becomes more acute than the corresponding angle at N(2) and the C(13)–N(1) bond distance is ~ 0.12 Å longer than that of the C(13)–N(2) bond. Although there is some departure from the ideal angles, the geometry at N(1) is trigonal planar (sum of angles = 359.9(2)°). The donor function is also evident from the fact that the sum of bond angles at B(1) is 334.0(2)°. In the case of $B(C_6F_5)_3$ as a reference Lewis acid, the departure of the sum of bond angles at boron from the ideal value of 360° has been taken as a measure of donor strength of the Lewis base.[12,13] Another significant structural feature is the close proximity of the *ipso* carbon of the phenyl ring to the carbodiimide carbon, a conformation that favours the migration of the phenyl group from B(1) to C(13) (the C(1)···C(13) distance is 2.796(7) ° and the C(1)–B(1)–N(1)–C(13) torsion angle is 7.5°). Upon migration of the phenyl group, formation of amidinate **2**[10] is accomplished by means of a rotation of the N(1)–C(13) bond followed by ring closure. Despite making several attempts, we were unable to isolate or detect the second intermediate by ^{11}B NMR. Compound **2** was prepared independently *via* the salt metathesis reaction of $[Ph\{NCy\}_2Li]$ with BCl_3 and characterized by X-ray crystallography.[11]

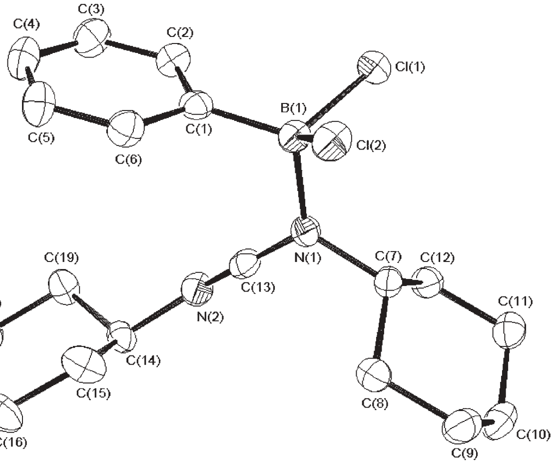

Fig. 1 View of **1** showing the atom numbering scheme and thermal ellipsoids at 40% probability with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): N(1)–B(1) 1.583(3), B(1)–C(1) 1.589(3), B(1)–Cl(1) 1.887(3), B(1)–Cl(2) 1.874(3) N(1)–C(13) 1.282(3), N(1)–C(7) 1.501(3), N(2)–C(13) 1.166(3), N(2)–C(14) 1.468(3), C(7)–N(1)–C(13) 116.91(17), C(13)–N(1)–B(1) 119.68(18), C(7)–N(1)–B(1) 123.34(17), C(13)–N(2)–C(14) 142.8(2), C(1)–B(1)–Cl(1) 112.99(17), C(1)–B(1)–Cl(2) 113.21(17), Cl(1)–B(1)–Cl(2) 107.78(13).

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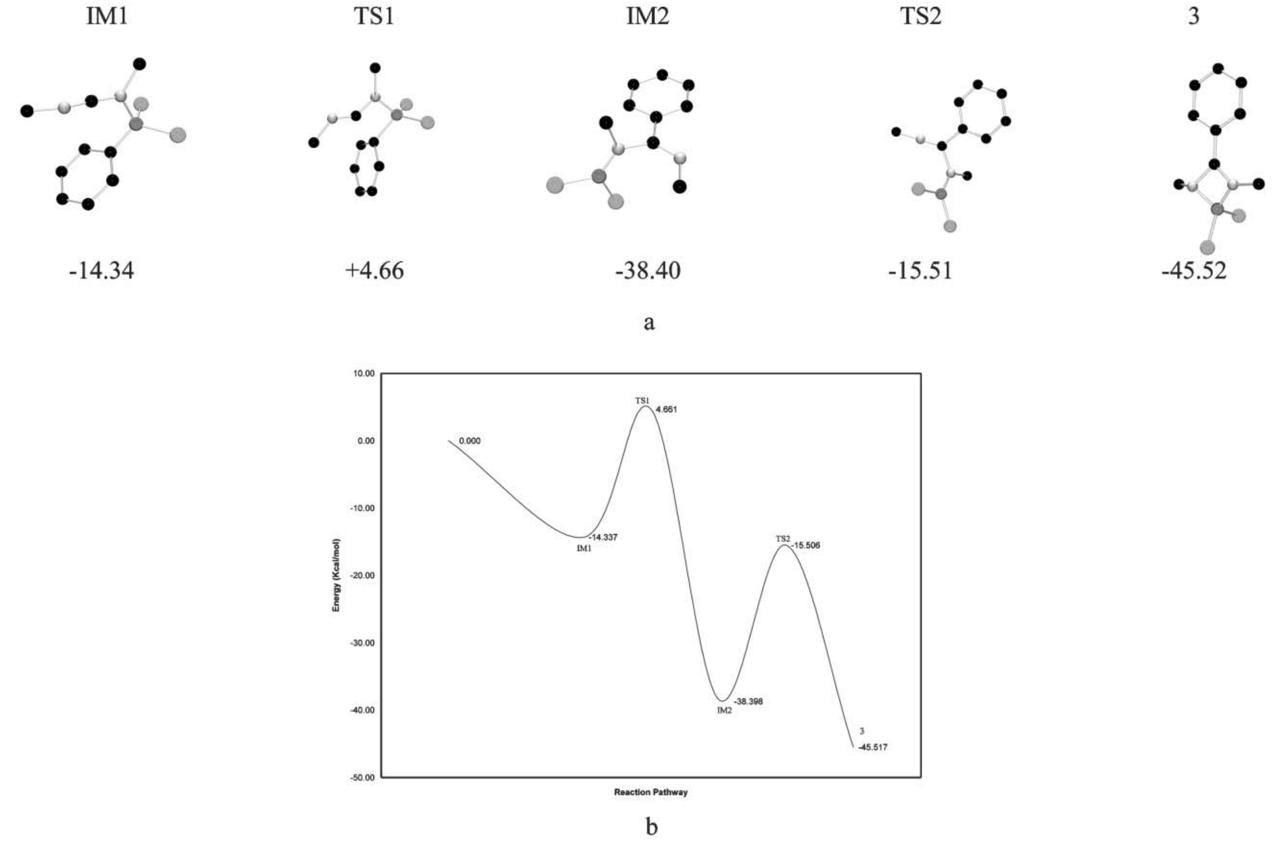

Fig. 2 (a) Structures and energies (kcal mol^{-1}) of intermediates **IM1** and **IM2**, transition states **TS1** and **TS2**, and amidinate **3** as calculated by DFT. (b) Graphical representation of the calculated energy profile of the reaction between $PhBCl_2$ and MeN=C=NMe.

To gain additional mechanistic insights, the overall process was modeled by DFT calculations.[14–16] In the interest of computational efficiency, the carbodiimide MeN=C=NMe was used instead of CyN=C=NCy. The profile for the reaction of MeN=C=NMe with $PhBCl_2$ features two intermediates (**IM1** and **IM2**) and two transition states (**TS1** and **TS2**) leading to product **3** as depicted in Fig. 2. The overall reaction is exergic by −45.5 kcal mol^{-1}. The first intermediate, **IM1**, is a donor–acceptor complex between MeN=C=NMe and $PhBCl_2$. Comparison of the metrical parameters for **1** with those of the model complex, **IM1**, reveals that they are in good agreement (<2%) with the exception of the N→B bond distance which is overestimated by 3.7%. The first transition state, **TS1**, features a four-centre interaction between boron, nitrogen, the carbodiimide carbon and the *ipso* carbon of the phenyl ring (C···C = 1.871 Å). The phenyl migration is completed by cleavage of the Ph–B bond in concert with mutation of the N→B dative bond into an N–B σ-bond. Transition state **TS2**, which is lower in energy than **TS1**, involves rotation around a C–N bond such that the two nitrogen atoms attain a conformation that will permit chelation. Finally, chelation of both nitrogen atoms to the BCl_2 moiety completes the formation of the boron amidinate, $[PhC\{NMe\}_2]BCl_2$, (**3**). We also computed the ^{11}B chemical shifts for **IM1**, **IM2**, and **3**. The calculated (GAIO) values of δ 10.5 and 8.5 for **IM1** and **3**, respectively, are in good agreement with those obtained experimentally for **1** and **2**, while the calculated value of δ 33.8 for **IM2** falls within the range observed for similar three-coordinate boron compounds.[17] The general features of this mechanism are similar to those discussed for the insertion of heterocumulenes into Rh–H,[7] Al–C[8] and Al–N[8] bonds.

In summary, we have isolated and structurally characterized a 1 : 1 Lewis acid–base complex of CyN=C=NCy and $PhBCl_2$. Complexes of this general type have long been postulated as representing the first step in a variety of heteroallene insertion reactions. In the present case the acid–base complex **1** is readily converted to the boron amidinate **2** upon heating in toluene solution. The overall mechanism has been modeled satisfactorily by DFT calculations.

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Notes and references

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9 We have recently prepared $[FcC\{NCy\}_2]BBr_2$ by this method ($Fc = (C_5H_5)_2Fe$) (ref. 4).

10 Spectroscopic data for **1** (1.71 g, 97% yield): ^1H NMR (C_6D_6): δ 7.39–7.19 (s, 5H); 3.13 (br s, 2H); 2.17 (br s, 4H); 1.68–0.95 (br m, 16H); ^{13}C NMR (C_6D_6): δ 154.34; 136.28; 133.93; 133.11; 58.52; 55.68; 33.95; 32.57; 31.26; 26.51; 26.37; 25.38; 25.04; 24.40; ^{11}B NMR (C_6D_6): δ 8.17 (s). MS (CI^+, CH_4): *m*/*z* 364 (M^+), 207 (100%, CyN=C=NCy + H^+); HRMS (CI, CH_4) calcd for $C_{19}H_{27}N_2BCl_2$, 364.1644; found 364.1671. Spectroscopic data for **2** (1.03 g, 88% yield): ^1H NMR (C_6D_6): δ 3.49 (s, 2H); 2.09 (s, 4H); 1.67–1.45 (m, 10H); 1.14–1.05 (m, 6H); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 176.17; 132.55; 129.79; 127.99; 54.95; 33.70; 27.23; 25.94; ^{11}B NMR (C_6D_6): δ 6.25 (s). MS (CI^+, CH_4): *m*/*z* 364 (M^+), 329 (100%, M–Cl); HRMS (CI, CH_4) calcd for $C_{19}H_{27}N_2BCl_2$, 364.1644; found 364.1642.

11 *Crystal data* for **1**: $C_{19}H_{27}BCl_2N_2$, monoclinic, space group $C2/c$, a = 37.418(5), b = 6.561(5), c = 15.964(5) Å, β = 100.318(5)°, V = 3856(3) $Å^3$, Z = 4, D_c = 1.258 g cm^{-3}, μ (Mo–Kα) = 0.340 mm^{-1}, R_1 = 0.0480, wR_2 = 0.1018, GOF = 1.031. For **2**: $C_{19}H_{27}BCl_2N_2$, triclinic, space group $P\bar{1}$, a = 10.355(5), b = 11.914(5), c = 16.592(5) Å, α = 73.933(5), β = 83.657(5), γ = 80.431(5)°, V = 1935.1(14) $Å^3$, Z = 2, D_c = 1.250 g cm^{-3}, μ (Mo–Kα) = 0.338 mm^{-1}, R_1 = 0.0562, wR_2 = 0.1362, GOF = 0.979. Both data sets were collected at 153(2) K on a Nonius-Kappa CCD diffractometer. There are two independent molecules in the asymmetric unit of **2**. CCDC 278056 (**1**) and 278734 (**2**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b511080g.

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13 Preliminary DFT modeling of the $B(NMe_2)_3$/CyN=C=NCy system suggests that there is no interaction between the amidoborane and the carbodiimide, in agreement with the observed lack of reaction between these two compounds, even in refluxing toluene solution.

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