

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 $\text{CyN}=\text{C}=\text{NCy}$ and PhBCl_2 has been isolated and structurally characterized, heating of which in refluxing toluene results in the amidinate, $[\text{PhC}\{\text{NCy}\}_2]\text{BCl}_2$; the overall reaction has been modeled by DFT calculations.

Despite the fact that aluminium and gallium amidinates can serve as olefin polymerization catalysts¹ 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 bond⁷ and of carbodiimide insertions into Al–Me and Al–NMe₂ bonds.⁸ Interestingly, and in contrast to $\text{Al}_2(\text{NMe}_2)_6$ and aluminium alkyls, our attempts to insert $\text{CyN}=\text{C}=\text{NCy}$ (Cy = cyclohexyl) into $\text{B}(\text{NMe}_2)_3$ and $\text{B}(\text{Et})_3$ 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 $\text{CyN}=\text{C}=\text{NCy}$, subsequent heating of which in toluene furnishes the amidinate complex, $[\text{PhC}\{\text{NCy}\}_2]\text{BCl}_2$ (**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 $\text{CyN}=\text{C}=\text{NCy}$ 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 $\text{B}(\text{C}_6\text{F}_5)_3$ 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) Å 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 ¹¹B NMR. Compound **2** was prepared independently *via* the salt metathesis reaction of $[\text{Ph}\{\text{NCy}\}_2\text{Li}]$ with BCl_3 and characterized by X-ray crystallography.¹¹

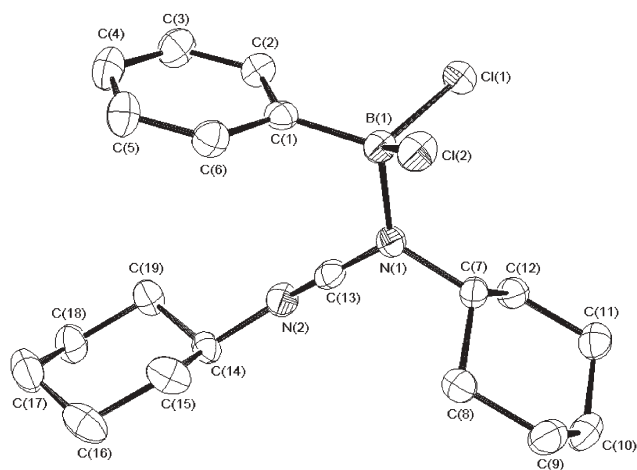


Fig. 1 View of **1** showing the atom numbering scheme and thermal ellipsoids at 40% probability with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): N(1)–B(1) 1.583(3), B(1)–C(1) 1.589(3), B(1)–Cl(1) 1.887(3), B(1)–Cl(2) 1.874(3), N(1)–C(13) 1.282(3), N(1)–C(7) 1.501(3),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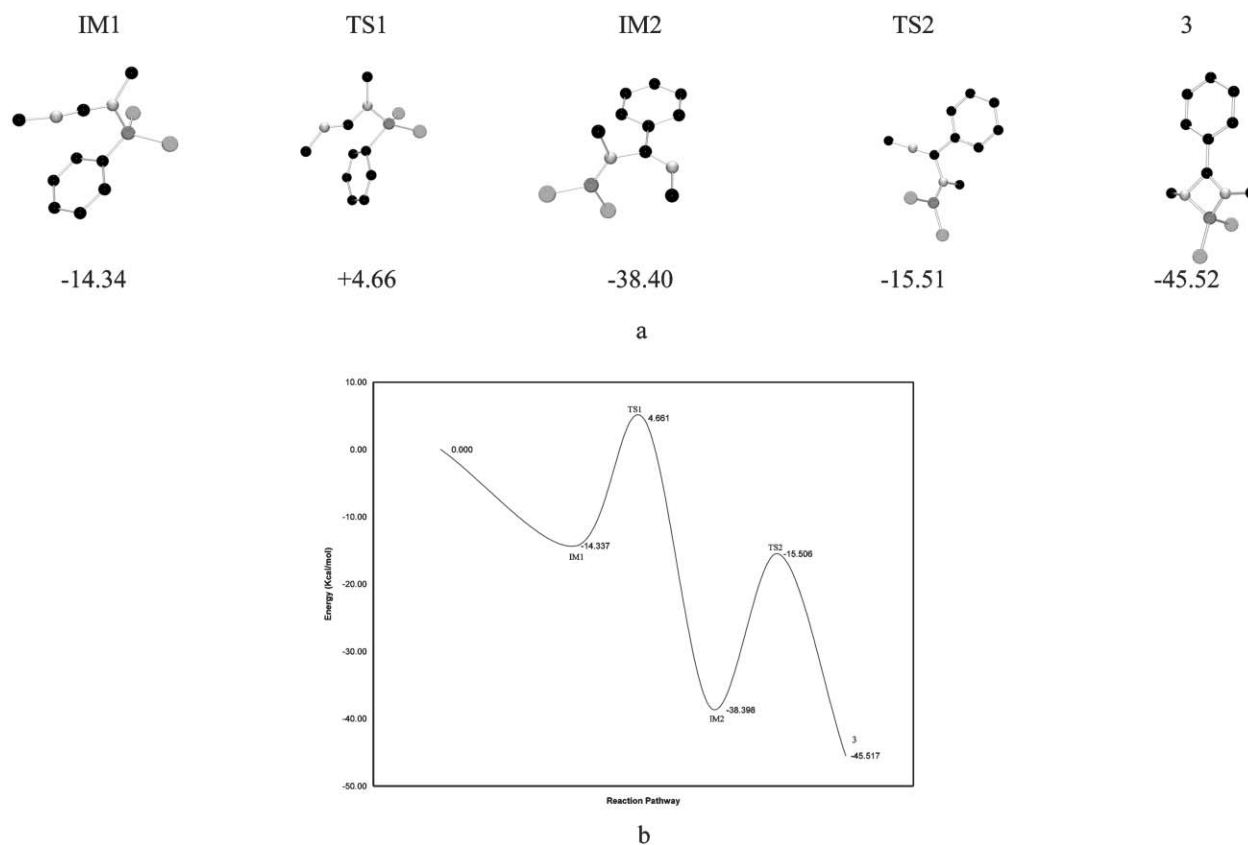


Fig. 2 (a) Structures and energies (kcal mol⁻¹) of intermediates **IM1** and **IM2**, transition states **TS1** and **TS2**, and amidinate **3** as calculated by DFT. (b) Graphical representation of the calculated energy profile of the reaction between PhBCl₂ and MeN=C=NMe.

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 PhBCl₂ 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 PhBCl₂. 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 BCl₂ moiety completes the formation of the boron amidinate, [PhC{NMe}₂]BCl₂, (**3**). We also computed the ¹¹B 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–C⁸ and Al–N⁸ bonds.

In summary, we have isolated and structurally characterized a 1 : 1 Lewis acid–base complex of CyN=C=NCy and PhBCl₂. 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

- M. P. Coles, D. C. Swenson, R. F. Jordan and V. G. Young, Jr., *Organometallics*, 1997, **16**, 5183.
- J. Barker, N. C. Blacker, P. R. Phillips, N. W. Alcock, W. Errington and M. G. H. Wallbridge, *J. Chem. Soc., Dalton Trans.*, 1996, 431.
- (a) C. Ergezinger, F. Weller and K. Dehnicke, *Z. Naturforsch.*, 1988, **43b**, 1621; (b) P. Blais, T. Chivers, A. Downard and M. Parvez, *Can. J. Chem.*, 2000, **78**, 10.
- N. J. Hill, M. Findlater and A. H. Cowley, *Dalton Trans.*, 2005, 3329.
- S. Gambarotta, S. Strologo, C. Floriani, A. Chiesi-Villa and C. Guastini, *Inorg. Chem.*, 1985, **24**, 654.
- (a) P. Braunstein and D. Nobel, *Chem. Rev.*, 1989, **89**, 1927; (b) J. A. Tunge, C. J. Czerwinski, D. A. Gately and J. R. Norton, *Organometallics*, 2001, **20**, 254.

- 7 Y. Musashi and S. Sakaki, *J. Chem. Soc., Dalton Trans.*, 1998, 577.
- 8 C. N. Rowley, G. N. Dilabio and S. T. Berry, *Inorg. Chem.*, 2005, **44**, 1983.
- 9 We have recently prepared $[\text{Fc}\{\text{NCy}\}_2]\text{BBr}_2$ by this method ($\text{Fc} = (\text{C}_5\text{H}_5)_2\text{Fe}$) (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 (Cl^+ , CH_4): m/z 364 (M^+), 207 (100%, $\text{CyN}=\text{C}=\text{NCy} + \text{H}^+$); HRMS (Cl^+ , CH_4) calcd for $\text{C}_{19}\text{H}_{27}\text{N}_2\text{BCl}_2$, 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); $^{13}\text{C}\{^1\text{H}\}$ 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 (Cl^+ , CH_4): m/z 364 (M^+), 329 (100%, $\text{M}-\text{Cl}$); HRMS (Cl^+ , CH_4) calcd for $\text{C}_{19}\text{H}_{27}\text{N}_2\text{BCl}_2$, 364.1644; found 364.1642.
- 11 Crystal data for **1**: $\text{C}_{19}\text{H}_{27}\text{BCl}_2\text{N}_2$, monoclinic, space group $C2/c$, $a = 37.418(5)$, $b = 6.561(5)$, $c = 15.964(5)$ Å, $\beta = 100.318(5)^\circ$, $V = 3856(3)$ Å³, $Z = 4$, $D_c = 1.258$ g cm⁻³, μ (Mo-K α) = 0.340 mm⁻¹, $R_1 = 0.0480$, $wR_2 = 0.1018$, GOF = 1.031. For **2**: $\text{C}_{19}\text{H}_{27}\text{BCl}_2\text{N}_2$, triclinic, space group $P\bar{1}$, $a = 10.355(5)$, $b = 11.914(5)$, $c = 16.592(5)$ Å, $\alpha = 73.933(5)$, $\beta = 83.657(5)$, $\gamma = 80.431(5)^\circ$, $V = 1935.1(14)$ Å³, $Z = 2$, $D_c = 1.250$ g cm⁻³, μ (Mo-K α) = 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.
- 12 H. Jacobsen, H. Berke, S. Döring, G. Kehr, G. Erker, H. Fröhlich and O. Meyer, *Organometallics*, 1999, **18**, 1724.
- 13 Preliminary DFT modeling of the $\text{B}(\text{NMe}_2)_3/\text{CyN}=\text{C}=\text{NCy}$ 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.
- 14 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03, (Revision B.04)*, Gaussian, Inc., Pittsburgh PA, 2003.
- 15 All calculations were performed at the RB3LYP level of theory and 6-311++G(d,p) basis set using the Gaussian 03 suite of programs. Points on the potential energy surface were confirmed by the calculation of the vibrational frequencies, with no imaginary frequencies for **IM1**, **IM2** and **3** and one imaginary frequency for **TS1** and **TS2**. Graphical representations of the calculated molecular orbitals were produced using the Molden program¹⁶ and the POV-ray windows program.
- 16 G. Shafteenaar, *MOLDEN 3.4*; CAOS/CAMM Center Nijmegen: Toernooiveld, Nijmegen, The Netherlands, 1991.
- 17 H. Nöth and B. Wrackmeyer in *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*, Springer Verlag, Berlin, 1978, ch. 7, pp. 74–101.