JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

COMMUNICATION

pubs.acs.org/JACS

Olefin–Borane "van der Waals Complexes": Intermediates in Frustrated Lewis Pair Addition Reactions

Xiaoxi Zhao and Douglas W. Stephan*

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada M5S 3H6

Ⓢ *Supporting Information*

ABSTRACT: The nature of the borane–olefin interactions that take place prior to frustrated Lewis pair addition reactions has been probed employing a Lewis acidic borane tethered to a vinyl group through an alkyl chain. $^1H\{^{19}F\}$ HOESY spectral data obtained at −50 °C demonstrated the spatial proximity of the boryl and vinyl groups and computational data support the initial formation of a van der Waals borane–olefin complex. Such species serve as intermediates undergoing facile addition reactions with phosphine bases to afford cyclic zwitterionic products.

Activation and transformation of small molecules had long been considered the domain of transition metal compounds. However, in recent years, there has been an increasing number of reports on nontransition metal systems that show reactivity traditionally characteristic of transition metal species.[1] Such systems offer considerable advantages in future applications from both economic and environmental viewpoints. One approach to achieve transition metal-free chemical transformations is the use of sterically encumbered pairs of Lewis acids and bases, or "frustrated Lewis pairs" (FLPs).[2] Besides mediating catalytic reduction of a range of polar substrates using H_2,[3] FLPs have also been shown to undergo intriguing addition reactions to a variety of substrates including olefins.[4] Unlike many transition metal-based systems where d-orbitals are accessible and back-bonding stabilizes η^2–olefin complexes, a combination of a Lewis acidic borane with an olefin does not show a detectable coordination complex. Thus, the nominally termolecular reaction of an FLP addition to an olefin raises interesting and important mechanistic questions. Computational studies by Papai and co-workers examined the reaction of tBu$_3$P and $B(C_6F_5)_3$ with ethylene.[5] These authors proposed an "encounter complex" in which steric congestion limits the P–B approach, affording a shallow energy minimum at P–B distance of 4.2 Å. It is this intermediate that is proposed to subsequently react with ethylene. In contrast, calculations of Guo and Li showed that the three-component reaction may be initiated by the formation of a weak association complex of $B(C_6F_5)_3$ with ethylene.[6] There is a paucity of direct experimental evidence that might illuminate the mechanism of action of FLPs, although an earlier argon matrix isolation study did describe IR data that suggested the formation of BF_3–ethylene and BF_3–propylene van der Waals complexes at 93–125 K.[7] Borane–olefin π-complexes are also believed to take a part in the noncatalyzed hydroboration reaction,[8] one of the most useful organic transformations. However, the nature of the intermediates has been overlooked due in part to rapidity of products formation. Identification of such intermediates may also provide mechanistic insights into allyl group abstraction reactions by boron-based Lewis acids.[9] In this communication, we probe the nature of the intramolecular interaction of olefinic and $B(C_6F_5)_2$ fragments, and provide the first NMR spectroscopic evidence of a weakly interacted olefin–borane van der Waals complex. Such systems are formed en route to zwitterionic FLP addition products.

In approaching the question of the mechanism of FLP-olefin addition reactions, we proposed to explore a tethered olefin–borane species to minimize entropic destabilization of complex formation by chelate effect. It is noted that a related strategy has been employed by the research groups of Casey[10] and Jordan[11] in probing group III and IV d^0 metal–olefin interactions important for olefin polymerization. We began by using DFT calculations to assess the feasibility of this idea. To this end, computations were performed at the M06 level of theory[12] (6-311++G(d,p) for B, C on B, olefinic C and H; 6-31G(d) for all other atoms), for two conformers of $B(C_6F_5)_2(CH_2CH_2CH_2CH{=}CH_2)$. The "open" form (**1a**) with the least steric congestion and the "closed" form (**1b**) in which the alkenyl group is oriented toward the B center were both found to be energy minima, with the "closed" form being lower in free energy by 3.3 kcal/mol (with thermal energy corrections at STP) (Figure 1). In contrast with the classical view of a coordination complex bearing a dative bond, **1b** does not show any sign of a chemical bond between B and the vinyl group. This includes minimum elongation of the C=C bond and no pyramidalization of the B center. Atomic charges and molecular orbital considerations also do not indicate notable charge transfer or p–π orbital overlap. Nonetheless, the B–C$_{vinyl}$ distances (3.04 and 3.26 Å) are within the sum of the van der Waals radii of B and C (3.62 Å),[13] consistent with the existence of a weakly interacted borane–olefin van der Waals complex, held in close proximity by noncovalent interactions. The use of the popular density functional B3LYP also displayed an energetic preference for the "closed" form, but to a lesser extent ($\Delta G_{1b-1a} = -1.9$ kcal/mol). This is consistent with the well-documented underestimation of medium-range exchange-correlation energies, such as van der Waals forces, by the B3LYP method.[12] Single point energy calculations at the B3LYP/def2-TZVP level of theory on the optimized structures gave a ΔE_{1b-1a} of 1.4 kcal/mol, while such calculations employing Zhao and Truhlar's M06-2X (improved performance for noncovalent interactions)[14] or Grimme's B97-D (inclusion of empirical dispersion correction)[15] method with the

Received: June 16, 2011
Published: July 19, 2011

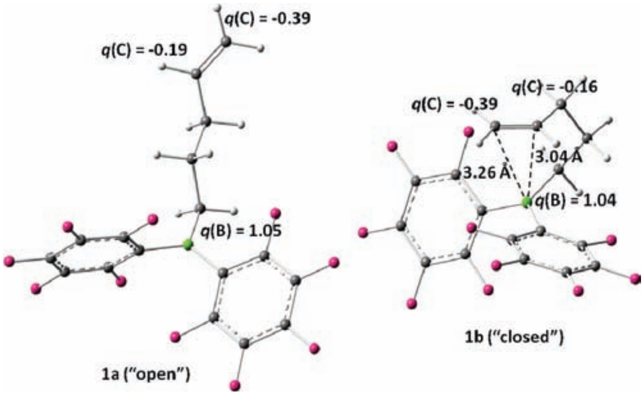
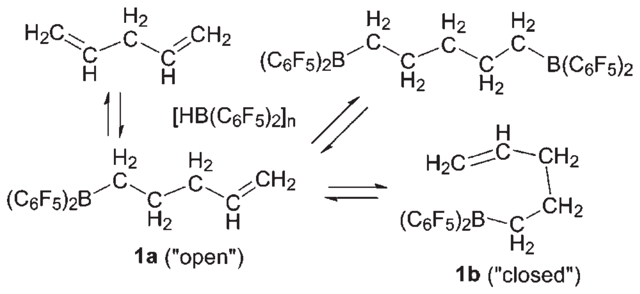


Figure 1. Optimized structures of **1a** and **1b** with pertinent distances and NPA charges.

Scheme 1. Equilibria Governing the Formation of 1a and 1b



same AO basis set gave $\Delta E_{1b-1a} = -5.0$ and -4.6 kcal/mol, respectively. This is an indication of van der Waals interactions that afford stabilization to **1b**. Despite the small free-energy difference of 3.3 kcal/mol, simple calculations show that the equilibrium should lie heavily toward **1b** ($K_{298} = 2.6 \times 10^2$; $K_{223} = 1.7 \times 10^3$), encouraging us to attempt to examine such van der Waals complex spectroscopically. It is noted that, using the IEF-PCM solvent model for dichloromethane, no significant deviation in the geometries and energies was identified ($\Delta G_{1b-1a} = -3.0$ kcal/mol).

The boryl-alkyl-alkene species (**1**) was generated in a NMR sample in CD_2Cl_2 by hydroboration of 1,4-pentadiene with 1 equiv of $[HB(C_6F_5)_2]_n$, commonly known as Piers borane.[16] Isolation of the target species $B(C_6F_5)_2(CH_2CH_2CH_2CH{=}CH_2)$ (**1**) was not possible due to the facility of retrohydroboration. Nonetheless, species **1** was indeed detected as the major species existing in equilibrium with the starting materials as well as some of the double hydroboration product $(CH_2)((CH_2)_2B(C_6F_5)_2)_2$ as assessed by ^1H and ^{19}F NMR spectra (Scheme 1).

First described by Yu and Levy[17] and by Rinaldi[18] independently in 1983, the 2D heteronuclear NOE (HOESY) technique has provided valuable information in structural and conformational analysis of organic and biologically relevant molecules[19] and detection of ion pairing.[20] The $^1H\{^{19}F\}$ HOESY spectrum obtained on a sample of **1** in CD_2Cl_2 at −50 °C showed significant cross-peaks between each of the three olefinic protons, especially those on the terminal carbon, and the *ortho*-F atoms of C_6F_5 groups, inferring that the olefinic protons undergo a significant amount of cross-relaxation with the *ortho*-F nuclei. (Figure 2) It is noted that the mixing time was kept relatively short (400 ms) to minimize contribution from spin diffusion, and the temperature was maintained high enough so that the system stays in the positive NOE regime to avoid overestimation of enhancements.[21] It is noteworthy that no significant change in ^1H, ^{19}F, and ^{11}B NMR chemical shifts was observed at −50 °C. Interestingly, these cross-peaks were all but lost at 25 °C, consistent with the small dissociation energy of the van der Waals complex. Similarly, no NOE cross-peaks for olefinic protons and *ortho*-F atoms were observed upon addition of 1 equiv of acetonitrile to the sample. This was attributed to the facile formation of the stable borane−nitrile adduct. Such NOE cross-peaks were also not observed for saturated analogue $B(C_6F_5)_2(CH_2)_4(CH_3)$ (**2**), generated in situ from hydroboration of 1-pentene with $[HB(C_6F_5)_2]_n$, demonstrating that the presence of a vinyl group is essential to stabilizing the "closed" form. (Figure 2) Collectively, these data provide spectroscopic evidence of close proximity of the olefinic fragment in **1** to the B center, and thus, the van der Waals olefin−borane complex, or the "closed" form **1b**.

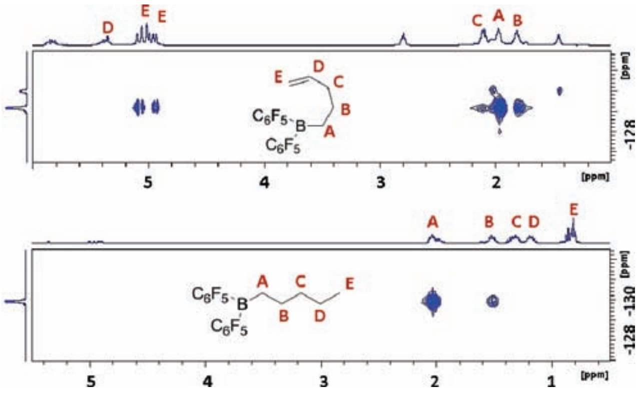


Figure 2. Partial $^1H\{^{19}F\}$ HOESY spectra of (top) **1** and (bottom) **2** (*X*-axis, ^1H spectrum; *Y*-axis, ^{19}F spectrum; 32 equally spaced contour levels).

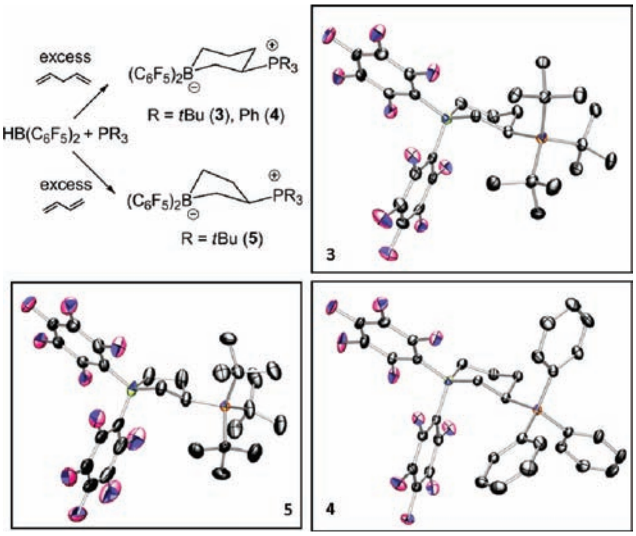


Figure 3. Syntheses and POV-ray depictions of **3**−**5**.

As isolation of **1** was not possible, it was reacted with phosphine bases in attempt to form stable adducts. Addition of 1,4-pentadiene to $HB(C_6F_5)_2 \cdot PtBu_3$ in toluene gave a colorless mixture that upon standing at 25 °C for 2 days gave a crystalline product **3** in 85% yield (Figure 3). Resonances attributable to the vinyl group of **1** were not observed in the ^1H NMR spectrum of **3**, while new ^{11}B and ^{31}P{^{1}H} resonances appeared at −12.8 and 50.1 ppm, respectively. ^{19}F signals corresponding to two inequivalent C_6F_5 groups suggest the formation of a substituted cyclic borate. Crystallography confirmed compound **3** to be the six-membered borate ring with a phosphonium substituent $(C_6F_5)_2B(CH_2CH_2CH_2CH(PtBu_3)CH_2)$ rather than the simple Lewis-acid−base adduct. It is noteworthy that the P adds to the substituted carbon of the olefin fragment, affording a substituent that adopts an equatorial position on the chair confirmation of the six-membered ring. The metric parameters of this zwitterion are unexceptional. In a similar fashion, the significantly less sterically encumbered and less nucleophilic PPh_3 was used to give the analogous species $(C_6F_5)_2B(CH_2CH_2CH_2CH(PPh_3)CH_2)$ (**4**) in 90% yield.

In a related reaction, a mixture of $[HB(C_6F_5)_2]_n$ and tBu_3P in toluene was exposed to an atmosphere of 1,3-butadiene and heated at 60 °C for 18.5 h in a closed vessel, during which time a microcrystalline solid **5** precipitated. NMR spectroscopic and crystallographic studies affirmed the nature of **5** as the zwitterion $(C_6F_5)_2B(CH_2CH_2CH(PtBu_3)CH_2)$, which was isolated in 62% yield. This cyclic borate product is analogous to **3** and **4** with a phosphonium fragment also adopting a pseudoequatorial position on the puckered five-membered borate-ring.

DFT calculations of the reaction profile confirmed **1b** as an intermediate en route to **3** (see Supporting Information). It is noteworthy that Erker, Grimme, and co-workers[22] have described the addition of a linked P/B system to norbornene, providing experimental and computational evidence for an asynchronously concerted process. These authors concluded that B−C bond formation occurs to a larger extent in the transition state, although the evidence for B−olefin or P−olefin interactions was necessarily indirect. In the present study, using a tethering approach, we have detected an interaction of a Lewis acidic B center with a pendant alkenyl group by 2D heteronuclear NOE techniques. This provides a compelling piece of evidence that the addition reaction of a sterically encumbered Lewis pair to a pendant vinyl group first forms a borane−olefin van der Waals complex. Subsequent nucleophilic attack by a Lewis base was used to afford the novel zwitterionic cyclic borate species **3**−**5**. While studies continue to target further insights into the mechanistic details of FLP reactions, the utility of this reactivity as a tool in developing new synthetic strategies is also ongoing.

■ ASSOCIATED CONTENT

S Supporting Information. Experimental, computational, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

dstephan@chem.utoronto.ca

■ ACKNOWLEDGMENT

D.W.S. gratefully acknowledges the financial support of NSERC of Canada, the award of a Canada Research Chair and a Killam Research Fellowship. X.Z. is grateful for the support of an NSERC-CGS Scholarship. The authors thank Dr. Edwin Otten and Dr. Zach Heiden for fruitful discussions. The peer-reviewers of the manuscript are also thanked for insightful suggestions. We would like to dedicate this paper to Professor Gerhard Erker on the occasion of his 65th birthday.

■ REFERENCES

(1) (a) Power, P. P. *Organometallics* **2007**, *26*, 4362–4372. (b) Nagendran, S.; Roesky, H. W. *Organometallics* **2008**, *27*, 457–492. (c) Martin, D.; Soleilhavoup, M.; Bertrand, G. *Chem. Sci.* **2011**, *2*, 389–399. (d) Power, P. P. *Nature* **2010**, *463*, 171–177.

(2) Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 46–76.

(3) (a) Chen, D.; Wang, Y.; Klankermayer, J. *Angew. Chem., Int. Ed.* **2010**, *49*, 9475–9478. (b) Wang, H.; Frohlich, R.; Kehr, G.; Erker, G. *Chem. Commun.* **2008**, 5966–5968. (c) Chase, P. A.; Jurca, T.; Stephan, D. W. *Chem. Commun.* **2008**, 1701–1703. (d) Chase, P. A.; Welch, G. C.; Jurca, T.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 8050–8053. (e) Spies, P.; Schwendemann, S.; Lange, S.; Kehr, G.; Fröhlich, R.; Erker, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 7543–7546. (f) Geier, S. J.; Chase, P. A.; Stephan, D. W. *Chem. Commun.* **2010**, *46*, 4884–4886. (g) Sumerin, V.; Schulz, F.; Atsumi, M.; Wang, C.; Nieger, M.; Leskelö, M.; Repo, T.; Pyykkö, P.; Rieger, B. *J. Am. Chem. Soc.* **2008**, *130*, 14117–14119.

(4) (a) Sortais, J.-B.; Voss, T.; Kehr, G.; Frohlich, R.; Erker, G. *Chem. Commun.* **2009**, 7417–7418. (b) Voss, T.; Chen, C.; Kehr, G.; Nauha, E.; Erker, G.; Stephan, D. W. *Chem.—Eur. J.* **2010**, *16*, 3005–3008. (c) McCahill, J. S. J.; Welch, G. C.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 4968–4971.

(5) Stirling, A.; Hamza, A.; Rokob, T. A.; Papai, I. *Chem. Commun.* **2008**, 3148–3150.

(6) Guo, Y.; Li, S. *Eur. J. Inorg. Chem.* **2008**, *2008*, 2501–2505.

(7) Herrebout, W. A.; van der Veken, B. J. *J. Am. Chem. Soc.* **1997**, *119*, 10446–10454.

(8) Jones, P. R. *J. Org. Chem.* **1972**, *37*, 1886–1889.

(9) Blackwell, J. M.; Piers, W. E.; McDonald, R. *J. Am. Chem. Soc.* **2002**, *124*, 1295–1306.

(10) (a) Casey, C. P.; Hallenbeck, S. L.; Wright, J. M.; Landis, C. R. *J. Am. Chem. Soc.* **1997**, *119*, 9680–9690. (b) Casey, C. P.; Klein, J. F.; Fagan, M. A. *J. Am. Chem. Soc.* **2000**, *122*, 4320–4330. (c) Casey, C. P.; Carpenetti, D. W.; Sakurai, H. *J. Am. Chem. Soc.* **1999**, *121*, 9483–9484. (d) Casey, C. P.; Hallenbeck, S. L.; Pollock, D. W.; Landis, C. R. *J. Am. Chem. Soc.* **1995**, *117*, 9770–9771.

(11) (a) Carpentier, J.-F.; Wu, Z.; Lee, C. W.; Strömberg, S.; Christopher, J. N.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 7750–7767. (b) Wu, Z.; Jordan, R. F.; Petersen, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 5867–5868. (c) Carpentier, J.-F.; Maryin, V. P.; Luci, J.; Jordan, R. F. *J. Am. Chem. Soc.* **2001**, *123*, 898–909.

(12) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157–167.

(13) Mantina, M.; Chamberlin, A. C.; Valero, R.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. A* **2009**, *113*, 5806–5812.

(14) Zhao, Y.; Truhlar, D. *Theor. Chem. Acc.* **2008**, *120*, 215–241.

(15) Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787–1799.

(16) Parks, D. J.; Piers, W. E.; Yap, G. P. A. *Organometallics* **1998**, *17*, 5492–5503.

(17) Yu, C.; Levy, G. C. *J. Am. Chem. Soc.* **1983**, *105*, 6994–6996.

(18) Rinaldi, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 5167–5168.

(19) (a) Ampt, K. A. M.; Aspers, R. L. E. G.; Jaeger, M.; Geutjes, P. E. T. J.; Honing, M.; Wijmenga, S. S. *Magn. Reson. Chem.* **2011**, *49*, 221–230. (b) Li, D.; Sun, C.; Williard, P. G. *J. Am. Chem. Soc.* **2008**, *130*, 11726–11736.

(20) Pregosin, P. S.; Kumar, P. G. A.; Fernández, I. *Chem. Rev.* **2005**, *105*, 2977–2998.

(21) Neuhaus, D.; Williamson, M. P. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*; Wiley-VCH: New York, 2000.

(22) Mömming, C. M.; Frömel, S.; Kehr, G.; Fröhlich, R.; Grimme, S.; Erker, G. *J. Am. Chem. Soc.* **2009**, *131*, 12280–12289.