DOI: 10.1002/chem.200903483

Cyclizations via Frustrated Lewis Pairs: Lewis Acid Induced Intramolecular Additions of Amines to Olefins and Alkynes

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An emerging strategy for the activation and reaction of small molecules is based on the concept of "frustrated Lewis pairs" (FLPs).[1–3] Such systems exploit steric congestion that frustrates classical Lewis acid–base adduct formation. In this fashion the unquenched Lewis acidity and basicity is available for reaction with a third component. This concept was first employed to effect the heterolytic cleavage of H_2 by sterically frustrated combinations of phosphines and boranes.[4–7] This reactivity has subsequently been applied to develop a "metal-free" approach to hydrogenation catalysis of imines,[8,9] enamines,[10] and silylenol ethers.[11] This strategy of FLP activation of H_2 is not limited to P/B combinations. Indeed, suitably sterically hindered carbenes,[12,13] amines,[8,14,15] and pyridines[16] have been shown to generate FLPs that react with H_2. Moreover the nature of the Lewis acid can be adjusted so as to impart reversibility to the H_2 uptake.[6,11] FLPs have also been exploited to effect the activation of a variety of small molecules including olefins,[17] dienes,[18] alkynes,[19,20] B–H bonds,[21] disulfides,[22] PhNCO,[3,23,24] CO_2,[25] and N_2O.[26]

In the case of olefins and alkynes, Stephan and co-workers[17,19,20] showed that sterically encumbered phosphines and boranes or alanes, can effect inter- and intramolecular additions affording zwitterionic phosphonium borates. DFT studies have suggested that such additions to olefins occur via an antarafacial asynchronous concerted addition.[25,27,28] For the reactions of alkynes, the *trans*-olefinic products suggest nucleophilic attack on a Lewis acid activated alkyne. Employing more basic phosphines, C–H activation of terminal alkynes affords phosphonium alkynyl borate salts. Recently, the Erker group[29] has shown that the linked phosphine borane $(C_6H_2Me_3)_2PCH_2CH_2B(C_6F_5)_2$, reacts with pentyne to give a related C–H activation product. However, this P/B species also reacts with a vinyl ether and norbornene to give the cyclized zwitterionic phosphonium borates. In a very recent example of similar reactivity, Erker and co-workers[30] have also described the addition of an amine to an intramolecular olefinic residue in the presence of $B(C_6F_5)_3$, which affords a thermally unstable zwitterionic ferrocene ammonium borate derivative. Herein, we describe reactions of sterically encumbered amines with intramolecular olefin or acetylene fragments in the presence of a Lewis acid. The resulting five- and six-membered heterocyclic ammonium borate species demonstrate that FLP reactivity provides a facile route to *intramolecular* cyclizations.

$B(C_6F_5)_3$ was added to a solution of *o*-(2-propenyl)-*N*,*N*-dimethylaniline in CH_2Cl_2 and the mixture was stored at −32 °C for 48 h. Subsequent solvent removal from the supernatant gave a white powder (**1**) in 87 % yield. The ^{11}B NMR spectrum of **1** showed a single resonance at $\delta = -14.3$ ppm. The corresponding ^{19}F NMR resonances were observed at $\delta = -132.0$, -162.2 and -166.0 ppm. These data are consistent with the quaternization of B and thus a borate anion.[31–35] The ^1H NMR spectrum reveals inequivalent methyl resonances at $\delta = 3.25$ and 3.00 ppm in addition to broad resonances attributable to methylene protons at $\delta =$ 2.25 and 1.91 ppm. The latter are consistent with B–C bond formation. These data together with ^{13}C, $^1H/^1H$-COSY, $^1H/^{13}C$-HSQC, and $^1H/^{13}C$-HMBC data were consistent with the formulation of the product as a reduced indole derivative $C_6H_4(NMe_2)(CH_2CH(CH_2B(C_6F_5)_3)$ (Figure 1). This zwitterionic formulation of **1**, comprising a five-membered, cyclic ammonium fragment with a pendant methylene borate group, was subsequently confirmed by X-ray crystallography.[36] The metric parameters were unexceptional.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200903483.

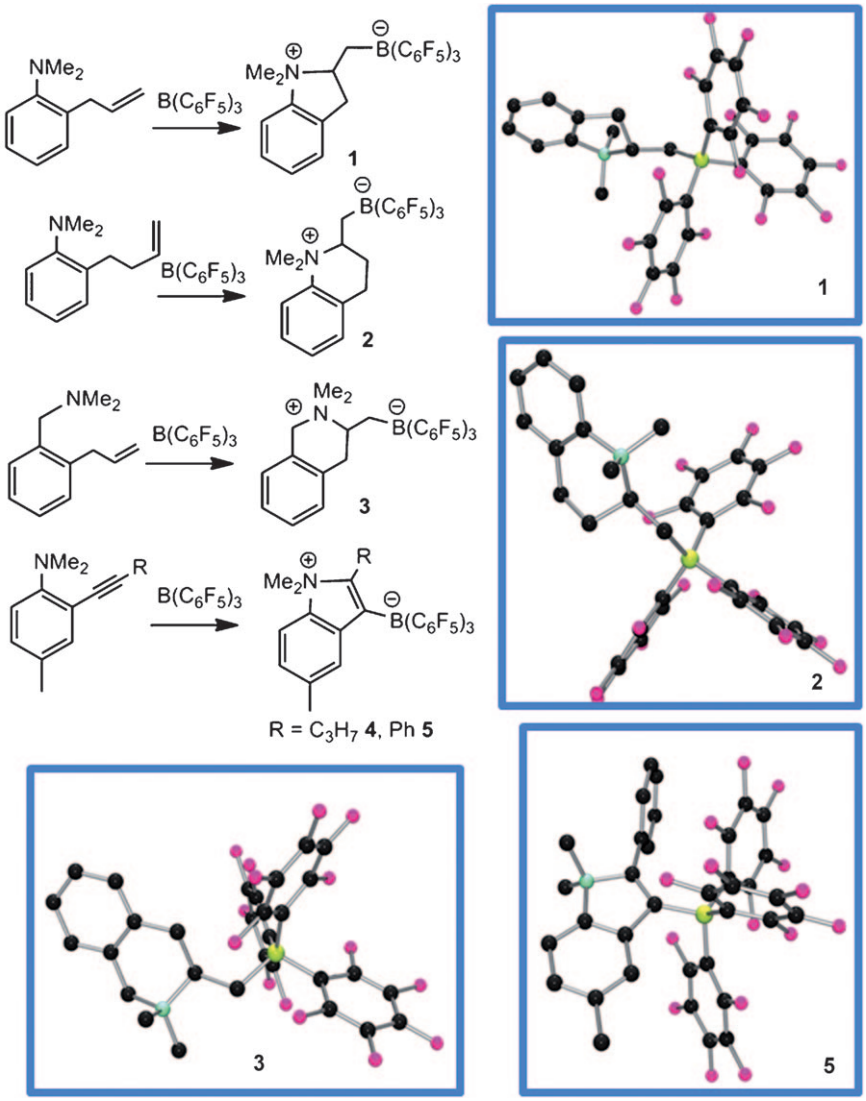

Figure 1. Synthesis of **1**–**5** and POV-ray depictions of **1**, **2**, **3**, and **5** (hydrogen atoms are omitted for clarity). C: black, F: pink, B: yellow-green, N: aquamarine.

In a similar fashion, *o*-(3-butenyl)-*N*,*N*-dimethylaniline reacts with $B(C_6F_5)_3$ to give the new species **2** in 90% isolated yield. The spectroscopic data, in particular the ^{11}B and ^{19}F NMR data were similar to those described for **1**. The $^{1}H/^{13}C$ 1D and 2D NMR spectral data infer that **2** is formulated as the zwitterionic product $C_6H_4(NMe_2)(CH_2CH_2CH(CH_2B(C_6F_5)_3)$ containing a six-membered-ring ammonium fragment again with a pendant methylene borate unit. The structure of **2** was also confirmed by X-ray crystallography[36] (Figure 1).

A structural isomer of **2** was accessible by reaction of *o*-(2-propenyl)-*N*,*N*-dimethylbenzylamine with $B(C_6F_5)_3$. The product **3** was isolated in 70% yield and spectroscopic characterization revealed data similar to that described above for **2**. A notable difference is the observation of the benzylic protons at $\delta = 4.35$ and 4.26 ppm, leading to the formulation of **3** as $C_6H_4(CH_2NMe_2)(CH_2CH(CH_2B(C_6F_5)_3)$. X-ray data[36] were consistent with the connectivity and the formation of the six-membered ammonium ring with the N atom positioned *beta* to the arene ring together with the methylene borate unit on the adjacent carbon (Figure 1).

In each of these cases, the addition of amine and borane to the olefinic fragment occurs with the borane adding to the terminal carbon and N substituting at the secondary carbon atom. The geometry of addition is similar to that seen for the inter- and intramolecular additions of sterically encumbered phosphines and boranes to olefins.[17]

Such Lewis acid mediated addition reactions were extended to involve alkyne fragments. Reaction of *o*-(pentynyl)-*N*,*N*-dimethyl toluidine with $B(C_6F_5)_3$ results in a reaction on standing at room temperature for 24 h. The product **4**, which was isolated in 90% yield, exhibited a ^{11}B NMR signal at $\delta = -16.2$ ppm. The ^{19}F NMR spectrum comprised 15 resonances assigned by $^{19}F/^{19}F$-COSY to three C_6F_5 units. These data suggest the formation of a borate species, in which inhibited rotation of the C_6F_5 rings results in nonequivalent fluorine environments. The ^{1}H NMR spectral data reveal nonequivalent N-methyl groups. The observation of the two ^{13}C NMR signals at $\delta = 150.7$ ppm and at $\delta = 142.2$ ppm [q(1:1:1:1), $^{1}J_{CB} \sim 55$ Hz] suggest the formation of a borato-substituted olefinic fragment. Collectively these data support the formulation of **4** as 4-methyl-*N*,*N*-dimethyl-2-propyl-3-tris(pentafluorophenyl)boratoindolium, $C_6H_3Me(NMe_2)(C(B(C_6F_5)_3)CPr$. In an analogous reaction of *o*-(phenylethynyl)-*N*,*N*-dimethyl toluidine with $B(C_6F_5)_3$, the analogous product **5** was isolated in 93% yield. The spectral data were analogous to those observed for **4**, notably with the ^{13}C NMR resonances at $\delta = 147.8$ ppm and $\delta = 143.7$ ppm [q(1:1:1:1), $^{1}J_{CB} \sim 54$ Hz] attributable to the borato-substituted olefinic subunit. The corresponding formulation of **5** as the indole derivative $C_6H_3Me(NMe_2)(C(B(C_6F_5)_3)CPh$ with a newly formed five-membered ring was confirmed by X-ray crystallography[36] (Figure 1).

The formation of **4** and **5** illustrate the intramolecular addition of an amino group and borane to the alkynyl fragment of the precursors. In contrast to previously reported

intermolecular additions of sterically encumbered phosphines and $B(C_6F_5)_3$ to acetylenes,[19] the present examples demonstrate intramolecular addition to internal acetylenes, affording a *trans*-disposition of these addenda.

The formation of **1–5** proceeds because the classical Lewis acid–base interaction of the amino function with the Lewis acid $B(C_6F_5)_3$ is sterically inhibited. This presumably allows the interaction of the Lewis acid with the π-bond of the olefin or acetylene fragment, activating it for intramolecular nucleophilic attack by the amine, which results in the cyclization. These findings illustrate the utility of the FLP strategy in the formation of such heterocycles. It is noteworthy that related intramolecular phosphino-borane additions to alkynes have been elegantly exploited by Yamaguchi and co-workers[37] to effect the formation of heterocyclic zwitterionic phosphonium borate species, which have applications as electronic materials.

In conclusion, herein we have demonstrated that FLP reactivity can be exploited to effect intramolecular cyclizations of amines with olefinic and acetylenic residues. While the present examples afford five- and six-membered heterocyclic derivatives, the potential for application to a wider variety of systems is evident. We continue to explore a variety of avenues for the exploitation of the concept of "frustrated Lewis pairs" in organic chemistry, small molecule activation, and catalysis.

Experimental Section

General: All syntheses were done under an atmosphere of dry, O_2-free N_2 (Toronto) or argon (Münster) using Schlenk-type glassware and a glovebox. Solvents (including deuterated solvents used for NMR spectroscopy) were dried and distilled under protective gas prior to use. ^1H, ^{13}C, ^{11}B, and ^{19}F NMR spectra and the respective 2D NMR experiments were recorded on 600 or 400 MHz Varian, 400 MHz or 300 MHz Bruker spectrometers. The spectra were referenced relative to $SiMe_4$ using residual solvent signals (^1H and ^{13}C NMR) or an external standard (^{11}B: $(Et_2O)BF_3$, ^{19}F: $CFCl_3$). Chemical shifts are reported in ppm. The *o*-alkenyl-substituted aniline derivatives, *o*-allyldimethylbenzylamine,[38] and the *N*-dialkyl-2-(1-alkynyl)toluidines[39,40] were synthesized according to literature procedures.

Synthesis of 1, 2, and 3: These compounds were prepared in a similar fashion and thus only one preparation is detailed. A solution of *o*-(2-propenyl)-*N*,*N*-dimethylaniline (30 mg, 0.186 mmol) and $B(C_6F_5)_3$ (95.4 mg, 0.186 mmol) in dichloromethane (2 mL) was stored at −32 °C for two days. The supernatant was removed by using a syringe, and the remaining white powder washed with pentane twice. Drying in vacuo yielded the product (109 mg, 0.162 mmol; 87%). Single crystals suitable for X-ray analysis were obtained from a concentrated dichloromethane solution at room temperature after several days. **1**: ^1H NMR (400 MHz, CD_2Cl_2, 298 K): $\delta = 7.46$ (m, 2H, C_6H_4); 7.36 (m, 2H, C_6H_4); 3.80 (m, 1H, NCH); 3.25 (s, 3H, NCH_3); 3.00 (s, 3H, NCH_3); 2.99 (m, 1H, $ArCH_2$); 2.70 (dd, $^2J = 16.8$ Hz, $^3J = 6.8$ Hz, 1H, $ArCH_2$); 2.25 (br, 1H, BCH_2); 1.91 ppm (br, 1H, BCH_2);^{13}C NMR (101 MHz, CD_2Cl_2, 298 K): $\delta = 148.2$ (dm, $^1J_{FC} = 239.6$ Hz, C_6F_5); 146.6 (C_q); 138.3 (dm, $^1J_{FC} = 248.6$ Hz, C_6F_5); 136.7 (dm, $^1J_{FC} = 246.6$ Hz, C_6F_5); 134.1 (C_q); 131.3, 129.2, 127.2, 116.3 (C_6H_4); 86.9 (NCH); 49.4 (NCH_3); 48.6 (NCH_3); 32.4 ($ArCH_2$); 19.7 ppm (br, BCH_2), not assigned (*i*-C_6F_5); ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): $\delta = -132.0$ (m, *o*-C_6F_5); −162.2 (t, $^3J = 22.8$ Hz, *p*-C_6F_5); −166.0 (m, *m*-C_6F_5). ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K) $\delta = -14.3$ ppm (s, $\nu_{1/2} = 28.9$ Hz); **2**: ^1H NMR (400 MHz, CD_2Cl_2, 298 K): $\delta = 7.46$ (m, 1H, C_6H_4); 7.39 (m, 2H, C_6H_4); 7.23 (m, 1H, C_6H_4); 3.31 (s, 3H, NCH_3); 3.29 (s, 3H, NCH_3); 2.97 (m, 1H, NCH); 2.79 (dm, $^2J = 16.9$ Hz, 1H, $ArCH_2$); 2.60 (br, 1H, BCH_2); 2.45 (m, 1H, $ArCH_2$); 2.25 (dm, $^2J = 16.9$ Hz, 1H, $CHCH_2$); 2.10 (m, 1H, $CHCH_2$); 1.59 ppm (br, 1H, BCH_2); ^{13}C NMR (101 MHz, CD_2Cl_2, 298 K): $\delta = 144.6$ (C_q); 131.5 (C_q); 132.0, 130.5, 128.9, 121.6 (C_6H_4); 81.5 (NCH); 53.9 (NCH_3); 50.8 (NCH_3); 27.7 ($ArCH_2$); 22.6 ($CHCH_2$); 20.6 ppm (br, BCH_2), not assigned (C_6F_5); ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): $\delta = -132.0$ (m, 2F, *o*-C_6F_5); −162.2 (t, $^3J = 20.6$ Hz, 1F, *p*-C_6F_5); −166.0 ppm (m, 2F, *m*-C_6F_5); ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): $\delta = -14.2$ ppm (s, $\nu_{1/2} = 30.0$ Hz); **3**: ^1H NMR (400 MHz, CD_2Cl_2, 298 K): $\delta = 7.30$ (m, 2H, C_6H_4); 7.07 (m, 2H, C_6H_4); 4.35 (d, $^2J = 16.0$ Hz, 1H, NCH_2); 4.26 (d, $^2J = 16.0$ Hz, 1H, NCH_2); 3.14 (m, 1H, $ArCH_2$); 3.03 (s, 3H, NCH_3); 3.01 (m, 2H, $ArCH_2$, NCH); 2.94 (s, 3H, NCH_3); 2.33 (br, 1H, BCH_2); 1.70 ppm (br, 1H, BCH_2); ^{13}C NMR (101 MHz, CD_2Cl_2, 298 K): $\delta = 148.1$ (dm, $^1J = 240.5$ Hz, C_6F_5); 138.7 (dm, $^1J = 237.8$ Hz, C_6F_5); 136.7 (dm, $^1J = 240.6$ Hz, C_6F_5); 131.4 (C_q); 129.6, 127.9, 129.3, 126.8 (C_6H_4); 125.2 (C_q); 77.0 (NCH); 66.5 (NCH_2); 53.1 (NCH_3); 44.0 (NCH_3); 29.7 ($ArCH_2$); 19.3 ppm (br, BCH_2), not assigned (*i*-C_6F_5); ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): $\delta = -131.7$ (m, 2F, *o*-C_6F_5); −162.2 (t, $^3J = 20.4$ Hz, 1F, *p*-C_6F_5); −166.0 ppm (m, 2F, *m*-C_6F_5); ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): $\delta = -14.4$ ppm (s, $\nu_{1/2} = 32.1$ Hz).

Synthesis of 4 and 5: These compounds were prepared in a similar fashion and thus only one preparation is detailed. In a glovebox the solution of $B(C_6F_5)_3$ (52 mg, 0.1 mmol) in pentane (5 mL) was added to the solution of alkynyl toluidine (20.1 mg, 0.1 mmol) in pentane (2 mL) in a small glass vial. The mixture was kept at room temperature overnight. The liquid was decanted from a precipitated solid. The solid was washed with pentane (3×1 mL) and dried under vacuum overnight to give the product as a white solid (63 mg, 90%) that was pure enough for analysis. **4**: ^1H NMR (CD_2Cl_2, 298 K): $\delta =$ 7.29 (d, $^3J_{HH} = 8.3$ Hz, 1H, C_6H_3), 7.21 (br, 1H, C_6H_3), 7.17 (dm, $^3J_{HH} = 8.3$ Hz, 1H, C_6H_3), 3.41 (s, 3H, NCH_3), 3.21 (s, 3H, NCH_3), 2.57, 2.47 (each m, each 1H, $^{Pr}CH_2$), 2.26 (s, 3H, $^{Ar}CH_3$), 1.61, 1.46 (each m, each 1H, $^{Pr}CH_2$), 0.79 ppm (t, $^3J_{HH} = 7.2$ Hz, 3H, $^{Pr}CH_3$); $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 298 K): $\delta = 150.7$ (br, NC^{Pr}), 145.4 (NC^{Ar}), 142.2 (q(1:1:1:1), $^1J_{CB}$ ~55 Hz, BC), 141.7 (C_q), 140.1(C_q), 127.8 (C_6H_3), 125.8 (′d′, partial relaxed $^3J_{CB}$ ~6.2 Hz, C_6H_3), 123.3 (br, *i*-C_6F_5), 114.1 (C_6H_3), 54.2 (NCH_3), 51.4 (NCH_3), 28.1 (′d′, partial relaxed $^3J_{CB}$ ~6.2 Hz, $^{Pr}CH_2$), 22.0 ($^{Pr}CH_2$), 21.6 ($^{Ar}CH_3$), 14.9 ppm ($^{Pr}CH_3$), not assigned (C_6F_5); ^{19}F NMR (CD_2Cl_2, 298 K): δ −129.1, −132.8 (*o*), −161.5 (*p*), −164.9, −166.40 (*m*) (each m, 1F, $C_6F_5{}^A$), −130.5, −130.6 (*o*), −161.8 (*p*), −166.43, −166.8 (*m*) (each m, 1F, $C_6F_5{}^B$), −131.2, −131.9 (*o*), −161.9 (*p*), −166.1, −166.9 ppm (*m*) (each m, 1F, $C_6F_5{}^C$); ^{11}B NMR (96 MHz, CD_2Cl_2, 298 K): $\delta = -16.2$ ppm ($\nu_{1/2}$ ~23 Hz). **5**: ^1H NMR (CD_2Cl_2, 298 K): $\delta = 7.54$ (br, 1H, *o*-Ph), 7.48 (br, 1H, *m*-Ph), 7.41 (tt, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 1.1$ Hz, 1H, *p*-Ph), 7.36 (d, $^3J_{HH} = 8.2$ Hz, 1H, C_6H_3), 7.30 (br, m, 1H, *o*′-Ph), 7.28 (br, 1H, C_6H_3), 7.22 (dm, $^3J_{HH} = 8.2$ Hz, 1H, C_6H_3), 7.22 (br, 1H, *m*′-Ph), 3.31 (s, 3H, NCH_3), 3.05 (s, 3H, NCH_3), 2.29 ppm (s, 3H, $^{Ar}CH_3$); $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 298 K): $\delta =$ 147.8 (m, NC^{Ph}), 144.4 (NC^{Ar}), 143.7 (q(1:1:1:1), $^1J_{CB}$ ~54 Hz, BC), 141.9 (C_q), 140.3 (C_q), 133.2 (br, *o*-Ph), 133.1 (′d′, partial relaxed $^3J_{CB}$ ~14 Hz, *o*′-Ph), 130.4 (*p*-Ph), 128.6 (br, *m*′-Ph), 128.4 (C_6H_3), 128.4 (*m*-Ph), 127.2 (*i*-Ph), 126.5 (m, C_6H_3), 123.1 (br, *i*-C_6F_5), 114.9 (C_6H_3), 52.2 (NCH_3), 51.5 (NCH_3), 21.7 ppm ($^{Ar}CH_3$), not assigned (C_6F_5); ^{19}F NMR (564 MHz, CD_2Cl_2, 298 K): $\delta =$ −128.6, −133.3 (*o*), −161.2 (*p*), −166.1, −166.8 (*m*) (each m, each 1F, $C_6F_5{}^A$), −130.3, −132.3 (*o*), −162.1 (*p*), −167.2, −167.3 (*m*) (each m, each 1F, $C_6F_5{}^B$), −123.7, −136.4 (o), −162.7 (p), −165.1, , −166.9 ppm (*m*) (each m, each 1F, $C_6F_5{}^C$); ^{11}B NMR (96 MHz, CD_2Cl_2, 298 K): $\delta = -16.5$ ppm ($\nu_{1/2}$ ~22 Hz).

Acknowledgements

G.E. gratefully acknowledges the financial support of the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. D.W.S. gratefully acknowledges the financial support of NSERC of Canada, the award of a Canada Research Chair and a Killam Research Fellowship.

Keywords: alkynes · cyclic ammonium salts · cyclization · frustrated Lewis pairs · heterocycles · olefins

[1] D. W. Stephan, *Dalton Trans.* **2009**, 3129.
[2] D. W. Stephan, *Org. Biomol. Chem.* **2008**, *6*, 1535.
[3] D. W. Stephan, G. Erker, *Angew. Chem.* **2010**, *122*, 50; *Angew. Chem. Int. Ed.* **2010**, *49*, 46.
[4] G. C. Welch, R. R. S. Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124.
[5] G. C. Welch, D. W. Stephan, *J. Am. Chem. Soc.* **2007**, *129*, 1880.
[6] M. Ullrich, A. J. Lough, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 52.
[7] P. Spies, G. Erker, G. Kehr, K. Bergander, R. Fröhlich, S. Grimme, D. W. Stephan, *Chem. Commun.* **2007**, 5072.
[8] P. A. Chase, T. Jurca, D. W. Stephan, *Chem. Commun.* **2008**, 1701.
[9] P. A. Chase, G. C. Welch, T. Jurca, D. W. Stephan, *Angew. Chem.* **2007**, *119*, 8196; *Angew. Chem. Int. Ed.* **2007**, *46*, 8050.
[10] P. Spies, S. Schwendemann, S. Lange, G. Kehr, R. Fröhlich, G. Erker, *Angew. Chem.* **2008**, *120*, 7654; *Angew. Chem. Int. Ed.* **2008**, *47*, 7543.
[11] H. Wang, R. Fröhlich, G. Kehr, G. Erker, *Chem. Commun.* **2008**, 5966.
[12] P. A. Chase, D. W. Stephan, *Angew. Chem.* **2008**, *120*, 7543; *Angew. Chem. Int. Ed.* **2008**, *47*, 7433.
[13] D. Holschumacher, T. Bannenberg, C. G. Hrib, P. G. Jones, M. Tamm, *Angew. Chem.* **2008**, *120*, 7538; *Angew. Chem. Int. Ed.* **2008**, *47*, 7428.
[14] V. Sumerin, F. Schulz, M. Atsumi, C. Wang, M. Nieger, M. Leskela, T. Repo, P. Pyykkö, B. Rieger, *J. Am. Chem. Soc.* **2008**, *130*, 14117.
[15] V. Sumerin, F. Schulz, M. Nieger, M. Leskela, B. Rieger, *Angew. Chem.* **2008**, *120*, 6090; *Angew. Chem. Int. Ed.* **2008**, *47*, 5861.
[16] S. J. Geier, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 3476.
[17] J. S. J. McCahill, G. C. Welch, D. W. Stephan, *Angew. Chem.* **2007**, *119*, 5056; *Angew. Chem. Int. Ed.* **2007**, *46*, 4968.
[18] M. Ullrich, K. S.-H. Seto, A. J. Lough, D. W. Stephan, *Chem. Commun.* **2009**, 2335.
[19] M. A. Dureen, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 8396.
[20] S. J. Geier, M. A. Dureen, E. Y. Ouyang, D. W. Stephan, *Chem. Eur. J.* **2010**, *16*, 988.
[21] M. A. Dureen, A. Lough, T. M. Gilbert, D. W. Stephan, *Chem. Commun.* **2008**, 4303.
[22] M. A. Dureen, G. C. Welch, T. M. Gilbert, D. W. Stephan, *Inorg. Chem.* **2009**, *48*, 9910.
[23] S. Moebs-Sanchez, G. Bouhadir, N. Saffon, L. Maron, D. Bourissou, *Chem. Commun.* **2008**, 3435.
[24] M. W. P. Bebbington, S. Bontemps, G. Bouhadir, D. Bourissou, *Angew. Chem.* **2007**, *119*, 3397; *Angew. Chem. Int. Ed.* **2007**, *46*, 3333.
[25] C. M. Mömming, E. Otten, G. Kehr, R. Fröhlich, S. Grimme, D. W. Stephan, G. Erker, *Angew. Chem.* **2009**, *121*, 6665; *Angew. Chem. Int. Ed.* **2009**, *48*, 6543.
[26] E. Otten, R. Neu, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 9918.
[27] A. Stirling, A. Hamza, T. A. Rokob, I. Papai, *Chem. Commun.* **2008**, 3148.
[28] Y. Guo, S. Li, *Eur. J. Inorg. Chem.* **2008**, 2501.
[29] C. M. Mömming, S. Frömel, G. Kehr, R. Fröhlich, S. Grimme, G. Erker, *J. Am. Chem. Soc.* **2009**, *131*, 12280.
[30] J.-B. Sortais, T. Voss, G. Kehr, R. Fröhlich, G. Erker, *Chem. Commun.* **2009**, 7417.
[31] H. Nöth, B. Wrackmeyer in *NMR Basic Principles and Progress, Vol. 14*, Springer, Berlin, **1978**, p. 461.
[32] B. Wrackmeyer, R. Köster in *Methods in Organic Chemistry, Houben–Weyl, Vol. 13*, **1984**, p. 406.
[33] B. Wrackmeyer, *Annu. Rep. NMR Spectrosc.* **1988**, *20*, 61.
[34] T. Beringhelli, D. Donghi, D. Maggioni, G. D'Alfonso, *Coord. Chem. Rev.* **2008**, *252*, 2292–2313, and references therein.
[35] W. E. Piers, *Adv. Organomet. Chem.* **2004**, *52*, 1.
[36] X-ray data: **1**·0.5(CH_2Cl_2): *C*2/*c*, $a=32.370(3)$, $b=9.1269(8)$, $c=20.8735(18)$ Å, $\beta=115.080(3)°$, $V=5585.4(8)$ mm^3, $Z=8$, data ($>2\sigma$)=6529, variables 438, $R=0.0455$, $R_w=0.0993$, GOF=0.985. **2**: $P2_1/n$, $a=11.2973(8)$ Å, $b=20.4030(15)$ Å, $c=11.6555(8)$ Å, $\beta=101.277(4)°$, $V=2634.7(3)$ mm^3, $Z=4$, data ($>2\sigma$)=7212, variables 426, $R=0.0392$, $R_w=$, 0.0838, GOF=1.004. **3**·0.75(CH_2Cl_2): $P\bar{1}$, $a=9.3247(9)$, $b=15.7303(14)$, $c=21.1553(19)$ Å, $\alpha=98.742(5)$, $\beta=90.647(5)$, $\gamma=92.426(5)°$, $V=3063.8(5)$ mm^3, $Z=4$, data ($>2\sigma$)=12505, variables 877, $R=0.1244$, $R_w=$, 0.3438, GOF 1.339. **5**·1.5(CH_2Cl_2): *C*2/*c*, $a=35.1995(10)$, $b=12.4721(5)$, $c=18.0024(5)$ Å, $\beta=115.529(3)°$, $V=7131.6(4)$ mm^3, $Z=8$, data ($>2\sigma$)=6278, variables 532, $R=0.0633$, $R_w=0.1835$, GOF=1.094. CCDC-764359, CCDC-764360, CCDC-764361, and CCDC-764362 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[37] A. Fukazawa, H. Yamada, S. Yamaguchi, *Angew. Chem.* **2008**, *120*, 5664; *Angew. Chem. Int. Ed.* **2008**, *47*, 5582.
[38] P. A. van de Schaaf, J.-P. Sutter, M. Grellier, G. P. M. van Mier, A. L. Spek, G. van Koten, M. Pfeffer, *J. Am. Chem. Soc.* **1994**, *116*, 5134.
[39] Y. Chen, C.-H. Cho, F. Shi, R. C. Larock, *J. Org. Chem.* **2009**, *74*, 6802.
[40] D. Yue, T. Yao, R. C. Larock, *J. Org. Chem.* **2006**, *71*, 62.

Received: December 18, 2009
Published online: February 8, 2010

