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6-Dimethylaminopentafulvene as a Lewis Base Component in Frustrated Lewis Pairs: Reversible Carbon−Carbon Coupling in FLP Chemistry

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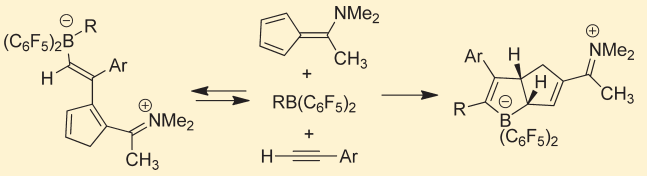
Supporting Information

ABSTRACT: The strongly electrophilic boranes $RB(C_6F_5)_2$ form frustrated Lewis pairs with an aminofulvene derivative. The new C/B FLPs undergo typical cooperative 1,2-addition reactions to alkynes with carbon−carbon bond formation.



Frustrated Lewis pairs (FLPs) are composed of combinations of coexisting Lewis acids and Lewis bases. The usual adduct formation between these components is hindered by steric bulk,[1,2] in some cases supported by specific electronic features.[3] Mostly bulky phosphines or sterically encumbered amines have been employed in combination with strongly electrophilic $RB(C_6F_5)_2$ Lewis acid components.[2,4,5] Utilization of carbon-based Lewis bases is rare. The most prominent examples in this case involve borane combination with bulky N-heterocyclic carbenes, to give FLPs[6] that are able to split dihydrogen heterolytically. Related examples in FLP H_2-activation chemistry comprise $RB(C_6F_5)_2$/imine[7] (or imine-like N-heterocycle[8]) combinations that may lead to direct metal-free FLP hydrogenation of the unsaturated organic component by exposure to dihydrogen at elevated temperatures. Variants of such reactions using catalytic amounts of the electrophilic borane were reported.

Some of the most prominent reactions that FLPs undergo aside from H_2 cleavage is the addition to "small molecules" such as CO_2,[9] N_2O,[10] NO,[11] alkenes,[12] and alkynes.[13] We regard the carbon-Lewis base/$RB(C_6F_5)_2$ Lewis acid derived FLPs as especially interesting for alkene or alkyne addition, since these reactions would represent novel routes of carbon−carbon bond formation and carbon−carbon σ-bond activation, respectively.[8] Therefore, we have studied the chemistry of dimethylaminopentafulvene (**1**)/$RB(C_6F_5)_2$ (**2**) FLPs with 1-alkynes and found a reversible C−C bond formation/C−C bond cleavage behavior.

We first reacted the dimethylaminofulvene (**1**)/$MeB(C_6F_5)_2$ pair (**2a**) with *p*-tolylacetylene (**3a**) in dichloromethane (see Scheme 1). The reaction was carried out in the temperature range of −78 to −35 °C for 12 h, and then the solution was covered with pentane at −35 °C to yield the primary product **4a** as yellow-red crystals (87%). We could not characterize the compound spectroscopically in solution because it was thermally too sensitive (see below), but we were able to determine its molecular structure in the crystal by X-ray diffraction. The X-ray crystal structure analysis revealed that the product **4a** had been formed by carbon−carbon coupling of the acetylene reagent with the fulvene inside the frustrated Lewis pair. The new C−C σ-bond was formed between the fulvene carbon atom C1 and the acetylenic (C_{sp}) center bearing the *p*-tolyl substituent (C1−C12 = 1.480(4) Å). The $MeB(C_6F_5)_2$ Lewis acid is found attached at the former acetylene ≡CH terminus (C11−B1 = 1.621(4) Å). Thus, we note that the aminofulvene/borane pair **1**/**2a** has undergone a regioselective trans-1,2-addition to the added alkyne to yield a typical zwitterionic FLP/acetylene addition product (see Figure 1 and Scheme 1).

The reaction of the **1**/**2a** FLP with *p*-*tert*-butylacetylene (**3b**) gave the analogous product **4b**. The reaction of *p*-tolylacetylene (**3a**) was also carried out with the Lewis pairs derived from **1** and the borane Lewis acids $[(Z)\text{-}^{n}Pr\text{-}CH{=}C(C_6F_5)]B(C_6F_5)_2$ (**2c**)[14] and $B(C_6F_5)_3$ (**2d**) to yield the corresponding zwitterionic 1-fulvenyl carbon−carbon coupling products **4c** (80%) and **4d** (73%), respectively. Both of these products were isolated as single crystals and characterized by X-ray diffraction. The structure of compound **4c** (see Figure 2) features the alkenyl borane unit[14] attached at the former acetylene terminus C1 (B1−C1 = 1.623(5) Å, C1−C2 = 1.345(4) Å, ∠B1−C1−C2 = 132.5(3)°). The newly formed carbon−carbon linkage was established between the acetylene carbon atom C2 and the fulvene α-carbon atom inside the five-membered ring (C2−C3 = 1.463(4) Å, C3−C4 = 1.369(4) Å). Both the tolyl substituent and the iminium π-system are rotated substantially from the average plane of the central π-system of the zwitterion **4c** (θ(C1−C2−C21−C22) = −115.0(3)°, θ(C3−C4−C8−N1) = 68.4(6)°). The molecular structure of compound **4d** is similar (for details see the Supporting Information).

The compounds **4** are probably formed by cooperative trans-1,2-addition of the aminofulvene/borane FLPs to the acetylenes **3a**,**b** to generate the nonobserved intermediates **5** (see

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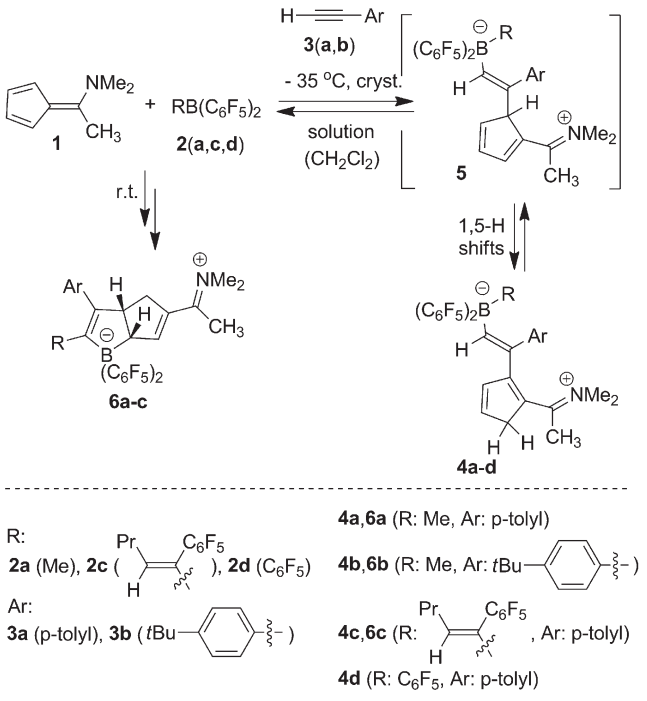
Scheme 1. Cooperative 1,2-Addition of C/B FLPs to Alkynes



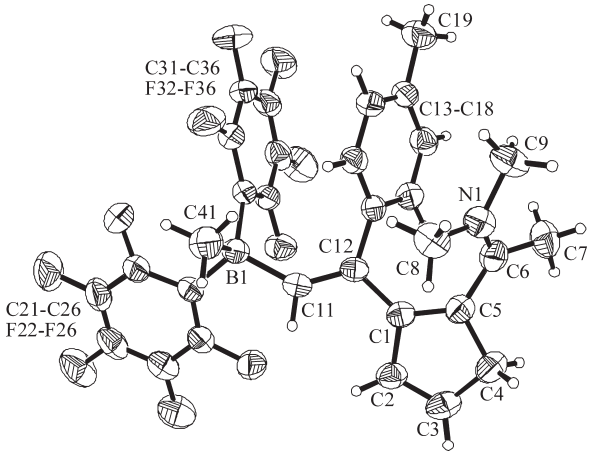


Figure 1. View of the zwitterionic aminofulvene/borane FLP addition product (**4a**) to *p*-tolylacetylene. Selected bond lengths (Å): C11—C12 = 1.352(4), C1—C5 = 1.372(4), C2—C3 = 1.359(4), C5—C6 = 1.454(4), C6—N1 = 1.295(4). Selected dihedral angles (deg): B1—C11—C12—C1 = −179.1(3), C12—C1—C5—C6 = 1.8(5), C1—C5—C6—N1 = 57.6(4)°.

Scheme 1), which are subsequently stabilized by rapid consecutive 1,5-hydrogen migrations to yield the observed carbon—carbon-coupled products. The products **4** are formed under kinetic control. When we dissolved, for example, compound **4a** in dichloromethane and stirred it at room temperature for 6 h, we isolated compound **6a**, the product of thermodynamic control, in good yield (83%).

The X-ray crystal structure analysis of **6a** (see Figure 3) shows a heterobicyclic [3.3.0]borabicyclooctane type framework. It features a cis junction between the two rings (C1—C5 = 1.551(3) Å) and the C═C double bond (C2—C3 = 1.349(4)

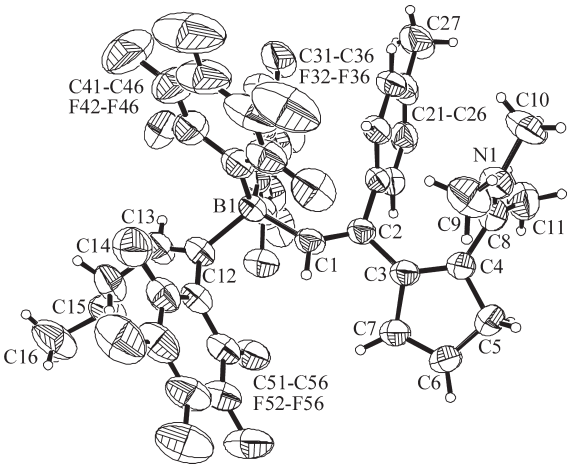


Figure 2. Molecular structure of compound **4c**.

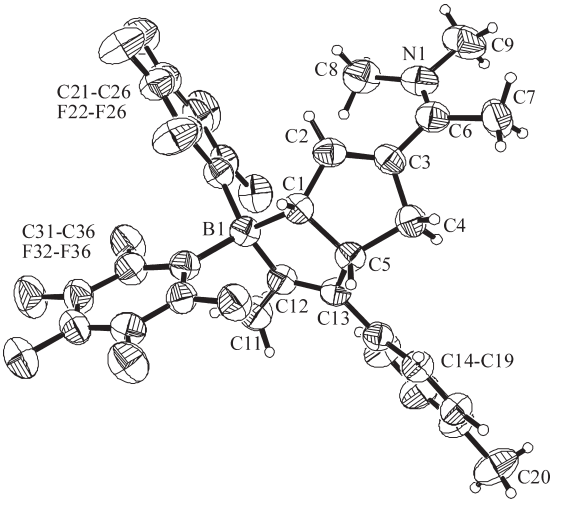


Figure 3. Projection of the molecular structure of compound **6a**.

Å) of an α,β-unsaturated iminium ion (C3—C6 = 1.449(4) Å, C6—N1 = 1.287(3) Å) as part of the carbocyclic component. The heterocyclic zwitterion contains an endocyclic borate moiety (C1—B1 = 1.670(4) Å, B1—C12 = 1.615(4) Å, ∠C12—B1—C1 = 99.9(2)°) and it has the methyl group originating from the $MeB(C_6F_5)_2$ reagent **2a** 1,2-shifted from boron to the adjacent C(sp^2) carbon atom (C12—C11 = 1.518(3) Å, C12—C13 = 1.353(3) Å). Consequently, compound **6a** features corresponding $^1H/^{13}C$ NMR signals of this methyl group at δ 1.59/16.3 ppm and 180.6 resonances of the $-C(CH_3)=NMe_2^+$ iminium moiety at δ 174.5 ppm ($^{13}C\{^1H\}$, C═N) and δ 3.32/3.22 ppm (^1H, $=NMe_2^+$), respectively. The $^{11}B\{^1H\}$ NMR resonance occurs at δ −5.9 ppm ($\nu_{1/2} \approx 50$ Hz), and there are two sets of three ^{19}F NMR resonances of the pair of diastereotopic C_6F_5 groups at boron.

The rearrangement of **4b** at room temperature (24 h) proceeds analogously to give **6b** in good yield (75%). Compound **6b** was also characterized by X-ray diffraction (for details see the Supporting Information), and we obtained the analogous product **6c** by using **4c** (isolated in 72% yield; NMR δ −6.0 ppm ($^{11}B\{^1H\}$), δ 3.34, 3.16 ppm (^1H, NMe_2), δ 180.1 ppm ($^{13}C\{^1H\}$, C═N)) (see Scheme 1).

Apparently, the formation of the compounds **4** (see Scheme 1) is reversible. We must assume that the newly formed strong

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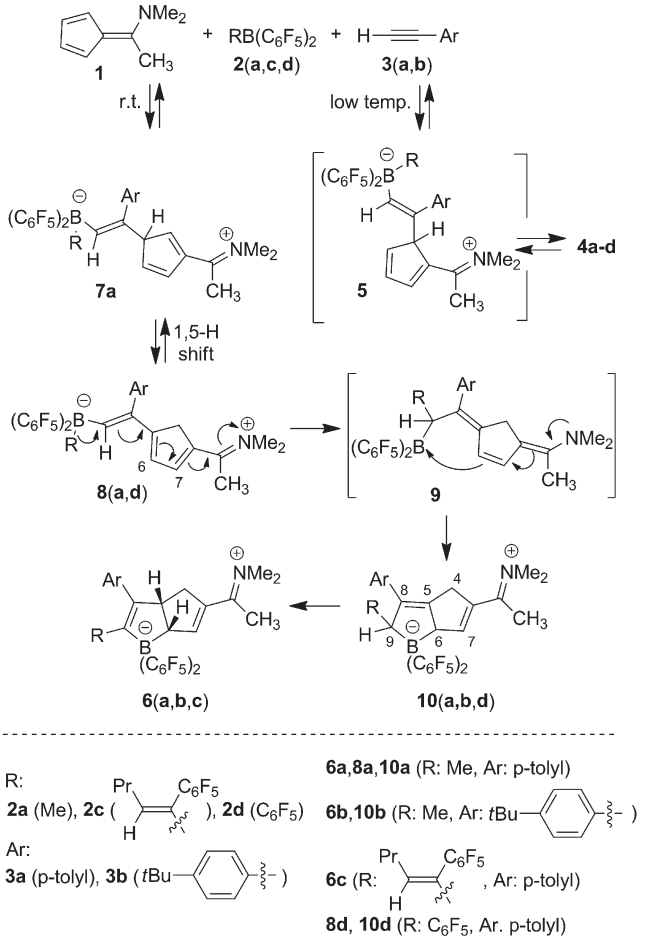
Scheme 2. Mechanistic Scheme of the Reactions of C/B FLPs with Alkynes



C−C bond in the intermediate **5** is easily broken upon warming and the reformed FLP **1**/**2** then adds to the 1-alkynes via the fulvene β-carbon to generate **7**. A subsequent 1,5-hydrogen shift leads to **8**, which is set to have the hydrocarbyl nucleophile R at the borate moiety attack the terminus of the triply conjugated iminium unit to give **9**. This now reacts further by electrophilic borane attack at the adjacent in situ formed dienamine functionality, similar to what we had recently seen happen in related dihydrofulvalene-derived systems,[15] to form **10**. Subsequent isomerization may then take place under the strongly Lewis acidic reaction conditions to eventually yield the observed final stable products **6** (see Scheme 2).

This description is supported by the observation of the intermediates **7a**, **8a,d**, and **10a,b,d** by NMR spectroscopy, which were formed from the respective compound **4** or their respective mixtures of starting materials and reagents, in solution under specific reaction conditions (for details see the Supporting Information). In a typical example we dissolved **4d** (see above) at −78 °C in d_2-dichloromethane. Then the sample was warmed and monitored by NMR spectroscopy. At 15 °C **8d** was detected as the major compound (δ −16.2 ppm ($^{11}B\{^1H\}$), δ −131.9 (*o*), −164.1 (*p*), −167.8 (*m*) ppm (^{19}F, $B(C_6F_5)_3$), δ 8.03 (BCH), 7.75/6.00 (7-H/6-H), 4.01 (4-CH_2) ppm (^1H), δ 170.0 (C=N) ppm ($^{13}C\{^1H\}$)). Controlling the sample after 2 weeks at room temperature, we observed **8d** and **10d** in a 1:3 ratio. Similarly, we were able to detect the intermediates **10a,b**, respectively, and the subsequent rearrangement products **6a** (**6b**) (24 h, room temperature) upon dissolving **4a** (**4b**) in d_2-dichloromethane at −60 °C.

As a typical example, compound **10a** was identified spectroscopically ($^{11}B\{^1H\}$ δ −5.0 ppm). The compound features the typical ^{19}F NMR signals of a pair of diastereotopic C_6F_5 groups at boron. It shows typical ^1H NMR resonances at δ 7.62 (7-H), 4.22 (6-H), 3.27 (9-H) ppm, a 9-CH_3 signal at δ 0.67, and δ 3.67, 3.26 (4-CH_2) ppm. The iminium $^{13}C\{^1H\}$ NMR carbon resonance of compound **10a** occurs at δ 177.3 ppm (for further details see the Supporting Information).

This work represents a marked extension of Lewis pair chemistry. We have shown that the aminofulvene **1** can serve very effectively as a carbon-based Lewis base component in frustrated Lewis pair generation and that this can result in a very efficient system for new carbon−carbon bond formation with an added unsaturated substrate. Moreover, the C/B FLP alkyne addition products are able to undergo a remarkably easy cleavage of a strong carbon−carbon σ-bond to enter the observed thermodynamic cycle of product formation. This may eventually open novel pathways for finding and developing new methods of activating strong carbon−carbon σ-bonds.[15,16]

■ ASSOCIATED CONTENT

Supporting Information. Text and figures giving further experimental and spectroscopic details for **4a**−**d**, **6a**−**c**, and the intermediates **7a**, **8a,d**, and **10a,b,d** and CIF files giving crystallographic data for **4a,c,d** and **6a,b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

†X-ray crystal structure analyses.

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■ REFERENCES

(1) (a) Welch, G. C.; Stephan, D. W. *J. Am. Chem. Soc.* **2007**, *129*, 1880–1881. (b) Spies, P.; Erker, G.; Kehr, G.; Bergander, K.; Fröhlich, R.; Grimme, S.; Stephan, D. W. *Chem. Commun.* **2007**, 5072–5074.

(2) Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 46–76. *Angew. Chem.* **2010**, *122*, 50–81.

(3) (a) Stute, A.; Kehr, G.; Fröhlich, R.; Erker, G. *Chem. Commun.* **2011**, *47*, 4288–4290. (b) Rosorius, C.; Kehr, G.; Fröhlich, R.; Grimme, S.; Erker, G. *Organometallics* **2011**, *30*, 4211–4219.

(4) (a) Erös, G.; Mehdi, H.; Pápai, I.; Rokob, T. A.; Király, P.; Tárkányi, G.; Soós, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 6559–6563. *Angew. Chem.* **2010**, *122*, 6709–6713. (b) Xu, B.-H.; Kehr, G.; Fröhlich, R.; Wibbeling, B.; Schirmer, B.; Grimme, S.; Erker, G. *Angew. Chem., Int. Ed.* **2011**, *50*, 7183–7186. *Angew. Chem.* **2011**, *123*, 7321–7324.

(5) For other types of Lewis acid components see: (a) Ménard, G.; Stephan, D. W. *J. Am. Chem. Soc.* **2010**, *132*, 1796–1797. (b) Appelt, C.; Westenberg, H.; Bertini, F.; Ehlers, A. W.; Slootweg, J. C.; Lammertsma, K.; Uhl, W. *Angew. Chem., Int. Ed.* **2011**, *50*, 3925–3928. *Angew. Chem.*

2011, *123*, 4011–4014. (c) Chapman, A. M.; Haddow, M. F.; Wass, D. F. *J. Am. Chem. Soc.* **2011**, *133*, 8826–8829.

(6) (a) Holschumacher, D.; Bannenberg, T.; Hrib, C. G.; Jones, P. G.; Tamm, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 7428–7432. *Angew. Chem.* **2008**, *120*, 7538–7542. (b) Holschumacher, D.; Taouss, C.; Bannenberg, T.; Hrib, C. G.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. *Dalton Trans.* **2009**, 6927–6929. (c) Holschumacher, D.; Bannenberg, T.; Ibrom, K.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. *Dalton Trans.* **2010**, *39*, 10590–10592. (d) Kronig, S.; Theuergarten, E.; Holschumacher, D.; Bannenberg, T.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. *Inorg. Chem.* **2011**, *50*, 7344–7359.

(7) (a) Chase, P. A.; Jurca, T.; Stephan, D. W. *Chem. Commun.* **2008**, 1701–1703. (b) Heiden, Z. M.; Stephan, D. W. *Chem. Commun.* **2011**, *47*, 5729–5731. (c) Axenov, K. V.; Kehr, G.; Fröhlich, R.; Erker, G. *J. Am. Chem. Soc.* **2011**, *131*, 3454–3455.

(8) (a) Geier, S. J.; Chase, P. A.; Stephan, D. W. *Chem. Commun.* **2010**, *46*, 4884–4886. (b) Geier, S. J.; Gille, A. L.; Gilbert, T. M.; Stephan, D. W. *Inorg. Chem.* **2009**, *48*, 1066–10474. See also:(c) Dureen, M. A.; Brown, C. C.; Stephan, D. W. *Organometallics* **2010**, *29*, 6422–6432.

(9) (a) Mömming, C. M.; Otten, E.; Kehr, G.; Fröhlich, R.; Grimme, S.; Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 6643–6646. *Angew. Chem.* **2009**, *121*, 6770–6773. (b) Peuser, I.; Neu, R. C.; Zhao, X.; Ulrich, M.; Schirmer, B.; Tannert, J. A.; Kehr, G.; Fröhlich, R.; Grimme, S.; Erker, G.; Stephan, D. W. *Chem. Eur. J.* **2011**, *17*, 9640–9650.

(10) (a) Otten, E.; Neu, R. C.; Stephan, D. W. *J. Am. Chem. Soc.* **2009**, *131*, 9918–9919. (b) Neu, R. C.; Otten, E.; Lough, A.; Stephan, D. W. *Chem. Sci.* **2011**, *2*, 170–176.

(11) Cardenas, A. J. P.; Culotta, B. J.; Warren, T. H.; Grimme, S.; Stute, A.; Fröhlich, R.; Kehr, G.; Erker, G. *Angew. Chem., Int. Ed.* **2011**, *50*, 7567–7571. *Angew. Chem.* **2011**, *123*, 7709–7713.

(12) (a) Voss, T.; Sortais, J.-B.; Fröhlich, R.; Kehr, G.; Erker, G. *Organometallics* **2011**, *30*, 584–594. (b) Sortais, J.-B.; Voss, T.; Kehr, G.; Fröhlich, R.; Erker, G. *Chem. Commun.* **2009**, 7417–7418. (c) McCahill, J. S. J.; Welch, G. C.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 4968–4971. *Angew. Chem.* **2007**, *119*, 5056–5059. (d) Mömming, C. M.; Kehr, G.; Fröhlich, R.; Grimme, S.; Erker, G. *J. Am. Chem. Soc.* **2009**, *131*, 12280–12289. For theoretical analysis see: (e) Stirling, A.; Hamza, A.; Rokob, T. A.; Papai, I. *Chem. Commun.* **2008**, 3148–3150. (f) Guo, Y.; Li, S. *Eur. J. Inorg. Chem.* **2008**, 2501–2505.

(13) (a) Mömming, C. M.; Kehr, G.; Wibbeling, B.; Fröhlich, R.; Schirmer, B.; Grimme, S.; Erker, G. *Angew. Chem, Int. Ed.* **2010**, *49*, 2414–2417. *Angew. Chem.* **2010**, *122*, 2464–2467. (b) Dureen, M. A.; Brown, C. C.; Stephan, D. W. *Organometallics* **2010**, *29*, 6422–6432. (c) Dureen, M. A.; Brown, C. C.; Stephan, D. W. *Organometallics* **2010**, *29*, 6594–6607. (d) Dureen, M. A.; Stephan, D. W. *J. Am. Chem. Soc.* **2009**, *131*, 8396–8397. (e) Voss, T.; Chen, C.; Kehr, G.; Nauha, E.; Erker, G.; Stephan, D. W. *Chem. Eur. J.* **2010**, *16*, 3005–3008.

(14) Compound **2c** is readily available by a simple 1,1-carboboration of 1-pentyne with $B(C_6F_5)_3$, as recently described by us: (a) Chen, C.; Eweiner, F.; Wibbeling, B.; Fröhlich, R.; Senda, S.; Ohki, Y.; Tatsumi, K.; Grimme, S.; Kehr, G.; Erker, G. *Chem. Asian J.* **2010**, *5*, 2199–2208. (b) Chen, C.; Kehr, G.; Fröhlich, R.; Erker, G. *J. Am. Chem. Soc.* **2010**, *132*, 13594–13595. (c) Chen, C.; Voss, T.; Fröhlich, R.; Kehr, G.; Erker, G. *Org. Lett.* **2011**, *13*, 62–65. For 1,1-carboboration reactions see also: (d) Jiang, C.; Blacque, O.; Berke, H. *Organometallics* **2010**, *29*, 125–133. (e) Chen, C.; Fröhlich, R.; Kehr, G.; Erker, G. *Chem. Commun.* **2010**, *46*, 3580–3582.

(15) (a) Xu, B.-H.; Kehr, G.; Fröhlich, R.; Erker, G. *Chem. Eur. J.* **2010**, *16*, 12538–12540. (b) Xu, B.-H.; Kehr, G.; Fröhlich, R.; Grimme, S.; Erker, G. *J. Am. Chem. Soc.* **2011**, *133*, 3480–3491.

(16) Reviews on C−C bond activation: (a) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245–269. (b) Rybtchinski, B.; Milstein, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 870–883. *Angew. Chem.* **1999**, *111*, 918–932. (c) Jun, C.-H. *Chem. Soc. Rev.* **2004**, *33*, 610–618. (d) Park, Y. J.; Park, J. W.; Jun, C.-H. *Acc. Chem. Res.* **2008**, *41*, 222–234. See also: (e) Li, T.; García, J. J.; Brennessel, W.; Jones, W. D. *Organometallics* **2010**, *29*, 2430–2445. (f) Nakao, Y.; Yada, A.; Hiyama, T. *J. Am. Chem. Soc.* **2010**, *132*, 10024–10026 and references cited therein.