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Reaction of Aminodihydropentalenes with $HB(C_6F_5)_2$: The Crucial Role of Dihydrogen Elimination

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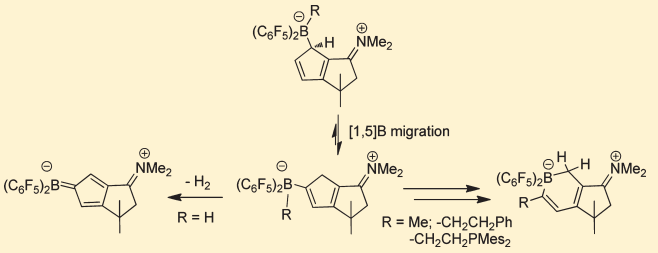
Supporting Information

ABSTRACT: The aminodihydropentalene derivative **1a** reacts with the Lewis acidic $RB(C_6F_5)_2$ boranes (**2a**−**c**) by C−C bond cleavage to yield the formal borylene insertion products **3**. In contrast, **1a**,**b** react with $HB(C_6F_5)_2$ at 55 °C by elimination of dihydrogen to yield the iminium-stabilized zwitterionic heterofulvenes **10a**,**b**. The reaction pathways were studied by preparation of the kinetically controlled intermediates **7a**,**b** and the thermodynamically controlled products **9a**,**b**, monitored by variable-temperature NMR experiments, and supported by DFT calculations. The trapping reactions of **9a** with HCl and PhCHO, respectively, led to the addition products **13** and **14**. Compounds **3c**, **7a**,**b**, **10a**,**b**, **11**, **13**, and **14** were characterized by X-ray diffraction.

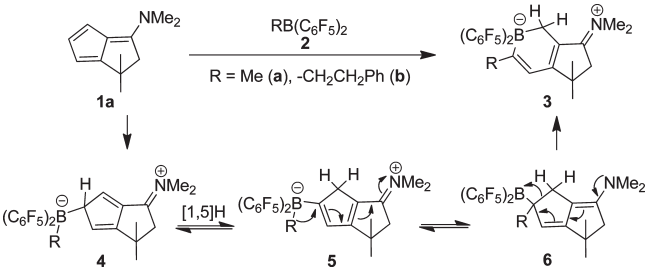


INTRODUCTION

The search for new methods and reagents to attack and activate thermodynamically strong bonds has seen much progress in recent years. The homolytic and heterolytic activation of dihydrogen is a typical example.[1−3] A good number of metal-induced methods are known for H_2 activation,[1] along with their utilization for catalytic hydrogenation reactions.[2,3] In addition, we note some significant recent progress in using metal-free reagents for the heterolytic cleavage of dihydrogen, e.g. by frustrated Lewis pair chemistry.[4] Activation of C−H bonds has almost become an established area.[5−7] Many methods have been developed in recent years that provide useful synthetic protocols for functionalizing organic frameworks by selective C−H bond cleavage.[7] In contrast, C−C bond activation and cleavage of nonactivated C−C bonds are far less developed. In comparison to H−H or C−H activation chemistry, C−C bond activation chemistry can still be regarded to be in its infancy.[8] Of course, there are a small number of "classical" methods available (e.g., ozonolysis[9] or the olefin metathesis reaction[10]), but C−C bond activation is a field where significant development and progress are still needed.

We recently observed a new reaction sequence that resulted in the cleavage of an unactivated C−C bond by treatment of an aminodihydropentalene substrate (**1a**) with the strongly electrophilic borane reagents $RB(C_6F_5)_2$ [R = CH_3 (**2a**), CH_2CH_2Ph (**2b**)] to yield the formal borylene insertion products **3**.[11] This reaction (Scheme 1) results in the overall cleavage of a C−C bond with concomitant formation of a pair of two new carbon−boron bonds, and it requires some additional rearrangement of substituents. A likely reaction sequence was proposed to account for our observation that is initiated by borane addition to generate **4**. Subsequent 1,5-hydrogen shift would lead to **5**, which is electronically set up for intramolecular nucleophilic attack of the [B]−R group at the adjacent electrophilic terminus of an α,β/γ,δ-unsaturated iminium salt to give **6**. Topological reversal of this reaction would then enable the system to undergo ring expansion by alkyl shift with C−C bond rupture to yield the observed final product **3**.

Scheme 1



We have now reacted the aminodihydropentalene **1a** and a derivative (**1b**) with other boranes, notably the intramolecular Lewis pair $Mes_2P-CH_2-CH_2-B(C_6F_5)_2$ (**1c**) and Piers's borane (**2d**),[12] and made some remarkable observations with regard to this general reaction scheme, which may be regarded as a sequence that formally involves an unprecedented variant of the 1,1-carboboration reaction.[13−16]

RESULTS AND DISCUSSION

Reaction of Dimethylaminodihydropentalene (1a) with the Frustrated Lewis Pair $Mes_2P-CH_2-CH_2-B(C_6F_5)_2$ (2c). We recently described the synthesis of the 3-dimethylaminodihydropentalene derivative **1a** by fulvene condensation of the respective doubly methyl-substituted acrylamide.[17] This was

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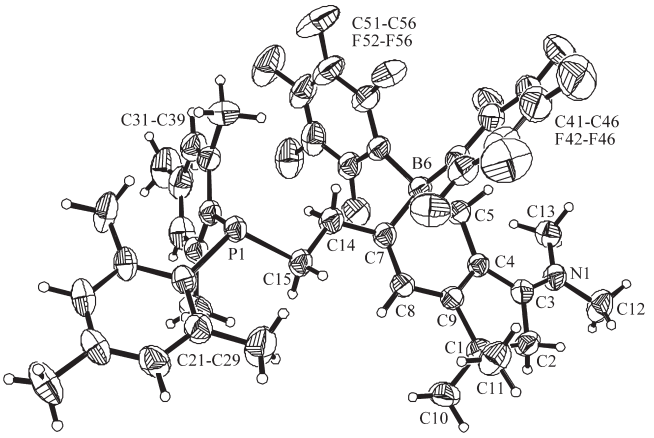
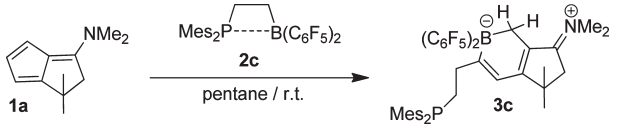


Figure 1. Projection of the molecular geometry of the ring-expanded product **3c**. Selected bond lengths (Å) and angles (deg): C3−N1 1.320(3), C3−C4 1.427(3), C4−C9 1.373(3), C8−C9 1.436(3), C7−C8 1.344(3), C7−B6 1.631(3), C5−B6 1.657(3), C5−B6−C7 109.8(2), C8−C7−B6 121.1(2), C4−C5−B6 112.5(2).

Scheme 2



carried out by dimethylsulfate activation followed by Cp-anion addition and condensation, similar to the method described by Hafner et al. for the synthesis of the parent aminopentafulvenes.[18] The frustrated Lewis pair (FLP) **2c** was in situ generated by $HB(C_6F_5)_2$ hydroboration of dimesitylvinylphosphine.[19] The hydroboration reaction takes place regioselectively with anti-Markovnikov orientation. Addition of **1a** to the FLP in pentane gave a precipitate that was isolated after 24 h at room temperature to furnish the product **3c** in 54% yield as a yellow-red solid. The product was characterized by elemental analysis, spectroscopy, and X-ray diffraction (see Figure 1 and Scheme 2).

The X-ray crystal structure analysis of **3c** shows that the $B(C_6F_5)_2$ unit of the reagent **2c** has formally been inserted into the C═C bond of the substrate **1a**. To make that possible, the $Mes_2P-CH_2-CH_2-$ group had to migrate from boron to carbon. This group is consequently found removed from boron and attached to the adjacent carbon atom C7. In order to make room for the $Mes_2P-CH_2-CH_2-$ migration, the hydrogen substituent at C7 had to move; it is now found at C5. In principle, this is the result of an unusual variant of a 1,1-carboboration sequence.[13−16] The structural characterization shows that **3c** features a zwitterionic conjugated BC_5N unit in the central bicyclic framework. The heterocyclic boratacyclohexadiene moiety shows the typical small deviation from planarity (B6−C7−C8−C9 −1.9(3)°, C5−B6−C7−C8 25.3(3)°). The $Mes_2P-CH_2-CH_2-$ unit that is attached at the ring carbon atom C7 features an antiperiplanar chain conformation (θ C7−C14−C15−P 176.6(2)°). The phosphorus coordination geometry is nonplanar (sum of the C−P−C angles: 316.2°).

In solution (C_6D_6), **3c** shows the ^{1}H NMR resonances of a pair of methyl groups at the iminium nitrogen atom (δ 2.37, 1.54) and the $[P]CH_2CH_2$ methylene resonances at δ 2.94 and 2.81. The newly formed $[B]CH_2$ group inside the boratacyclohexadiene unit shows signals at δ 2.06 (^{1}H) and δ 23.3 (^{13}C, broad). There is a single olefinic ═CH− ^{1}H NMR resonance (δ 6.61). Compound **3c** shows a ^{11}B NMR signal at δ −14.2 and a trio of typical borate $B(C_6F_5)_2$ ^{19}F NMR signals [δ −130.6 (*o*), −162.3 (*p*), −165.2 (*m*)].

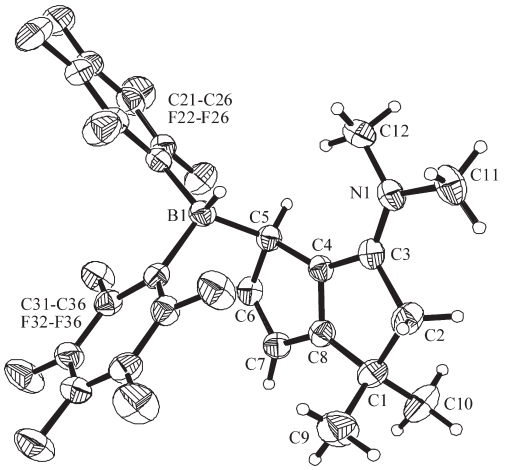


Figure 2. Molecular structure of the kinetic $HB(C_6F_5)_2$ addition product **7a**.

Reactions of the Dimethylaminodihydropentalenes 1 with Piers's Borane. In order to learn more about the reactions of the aminodihydropentalene substrates with reactive C_6F_5-substituted boranes, we treated the substrate **1a** with $HB(C_6F_5)_2$. The borane reacted rapidly with **1a**, even at −40 °C. From the concentrated reaction mixture in dichloromethane, the addition product **7a** was obtained in 63% yield as a colorless solid by crystallization at low temperature (−35 °C). Spectroscopic analysis showed the presence of the $[(C_6F_5)_2BH]$-borate substituent at C5 (^{11}B NMR: doublet at δ −19.4 with $^1J_{BH} \approx 80$ Hz). This was confirmed by X-ray crystal structure analysis of **7a**, which features the boryl substituent at C5 and the presence of a doubly conjugated $\alpha,\beta/\gamma,\delta$-unsaturated iminium ion moiety (see Figure 2 and Tables 1 and 2).

The product **7a** is thermally labile. Warming it from −40 °C to room temperature and keeping it at that temperature overnight resulted in a complete conversion to the isomeric compound **9a**. Compound **9a** was isolated as a yellow-red solid in 90% yield. The product was identified spectroscopically (for details see Table 2 and Experimental Section). It features a typical ^{11}B NMR doublet at δ −22.3 with a $^1J_{BH}$ coupling constant of 87 Hz.

The system **9a** contains a conjugated *N*,*N*-dimethyliminium ion unit with a boron hydride nucleophile attached at its terminus C6. Therefore, it was tempting to see whether H-transfer would occur upon heating to open a pathway analogous to that depicted in Scheme 1 (see above) that would eventually lead to cleavage of the C6−C5 bond. We heated **9a** to 55 °C overnight and isolated the product **10a** as a red solid from the reaction mixture in 54% yield. Structural analysis (see Scheme 3, Tables 1 and 2, and Figure 3) revealed that here a different reaction pathway is preferred, determined by the facile elimination of dihydrogen. It is likely that the intermediate **8a** is involved in the formation of **9a** from **7a**. Therefore, it may be assumed that **9a** and **8a** can also be interconverted by a reversible, thermally induced 1,5-hydrogen shift and that subsequent loss of H_2 may take place from the intermediate **8a** upon warming (see Scheme 3) to eventually

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Table 1. Selected Structural Data of the Aminodihydropentalene/$HB(C_6F_5)_2$ Reaction Products[a]

	1a	7a	*anti*-7b[b]	10a	10b	11	13	14[c]
C3−N1	1.316(3)	1.308(3)	1.304(4)	1.307(2)	1.308(4)	1.310(3)	1.297(5)	1.309(7)
C3−C4	1.392(3)	1.420(3)	1.417(4)	1.399(2)	1.410(4)	1.426(3)	1.435(5)	1.436(7)
C4−C5	1.434(3)	1.489(3)	1.488(4)	1.385(2)	1.399(4)	1.500(3)	1.501(5)	1.509(7)
C4−C8	1.423(3)	1.372(3)	1.364(4)	1.432(2)	1.437(4)	1.374(3)	1.345(5)	1.344(7)
C7−C8	1.359(3)	1.427(3)	1.423(4)	1.345(2)	1.355(4)	1.418(4)	1.482(5)	1.491(7)
C6−C7	1.434(4)	1.356(3)	1.351(4)	1.452(2)	1.461(4)	1.349(3)	1.559(5)	1.547(7)
C5−C6	1.374(4)	1.480(3)	1.480(4)	1.405(2)	1.420(4)	1.480(3)	1.566(5)	1.565(7)
C5−B1	−	1.712(3)	1.720(4)	−	−	1.741(3)	−	−
C6−B1	−	−	−	1.473(3)	1.489(4)	−	1.612(5)	1.632(8)
C5(C6)−B1−^{i}Ph(F)[a]	−	113.6(2)	109.3(2)	121.1(2)	121.9(3)	111.0(2)	108.3(3)	111.9(4)
C5(C6)−B1− ^{i}Ph(F)[b]	−	110.2(2)	113.4(2)	122.2(2)	123.0(3)	104.4(2)	119.6(3)	115.8(4)
^{i}Ph(F)[a]−B1− ^{i}Ph(F)[b]	−	112.1(2)	112.7(2)	116.7(2)	115.1(3)	112.0(2)	107.8(3)	108.3(4)

[a] Bond distances in angstroms and bond angles in degrees. See Figures 2−8 for the atom (non-systematic) numbering scheme used. [b] Values taken from the major product. [c] Values taken from molecule A.

Table 2. Selected NMR Data of the Aminodihydropentalene/$HB(C_6F_5)_2$ Addition Products[a]

	1a[b]	7a[c]	7b[c,g]	9a[d]	9b[d]	10a[d]	10b[d]	11[e]	13[f]	14[f,g]
					^{1}H NMR					
NMe_2	3.26, 3.13	3.71, 3.32	3.71, 3.34	3.35, 3.25	3.36, 3.28	3.40 3.29	3.41 3.31	3.37, 3.20	3.53, 3.37	3.42, 3.27
2-H_2	2.98	2.98	3.39, 2.66	3.08	3.49, 2.80	3.09	3.49, 2.77	2.92, 2.85	3.14, 3.12	2.91, 2.64
5-H	6.01	4.30	4.32	3.54	3.53	6.77	6.80	4.69	2.92, 2.79	2.65, 2.59
6-H	6.47	7.97	7.97	−	−	−	−	7.73	2.93	3.50
7-H	5.74	6.15	6.17	6.43	6.45	6.10	6.13	6.11	2.74, 2.55	3.54
					^{11}B NMR					
[B]	−	−19.4	−19.3	−22.3	−22.3	51.0	50.4	n.o.	−1.4	1.3
					^{13}C NMR					
C3	161.6	174.3	175.2	170.5	171.6	170.8	171.7	174.0	182.5	181.7
C6	128.7	169.3	169.0	212.8	212.4	146.2	n.o.	169.0	37.8	51.3
C7	105.1	120.5	121.7	128.7	129.9	113.0	114.3	119.3	34.5	56.4
C8	157.7	193.1	189.3	205.2	202.0	158.0	154.0	192.7	208.6	211.7
C4	120.6	142.6	144.5	135.3	137.4	126.5	127.5	139.4	140.8	143.8
					^{19}F NMR					
o-	−	−133.3	−133.2	−132.3	−132.3	−131.6	−131.6	−127.1	−132.1	−133.1
		−134.2	−134.2			−131.8	−131.7	−130.7		−133.7
								−136.6		
								−137.5		
p-	−	−162.4	−162.4	−163.4	−163.4	−155.3	−155.3	−164.0	−164.4	−164.8
		−163.2	−163.2			−155.9	−155.8	−164.7		−165.4
m-	−	−166.1	−166.1	−166.6	−166.6	−163.7	−163.7	−167.0	−167.8	−167.7
		−166.3	−166.3					−167.4		−168.0
								−168.1		
								−168.7		

[a] See Figures 2−8 for the (non-systematic) atom numbering scheme used. [b] CD_2Cl_2 at 298 K (see ref 17 for C_6D_6). [c] CD_2Cl_2 at 233 K. [d] CD_2Cl_2 at 298 K. [e] CD_2Cl_2 at 193 K. [f] [D_8]THF at 298 K. [g] Major isomer.

form **10a**. We checked for the potential reversibility of the **9a** → **10a** + H_2 conversion. However, under our applied reaction conditions, **10a** did not react with H_2 (2.5 or 60 bar) at room temperature.

Compound **10a** was characterized by X-ray diffraction. In the crystal, the substituted dihydropentalene framework shows the typical small out-of-plane torsion inside the "right" five-membered ring system to avoid eclipsed substituent interaction along the C1−C2 vector (C1−C2 1.546(3) Å, see Figure 3). The remaining parts of the framework are arranged close to coplanar. In principle, system **10a** could be described by the isomeric resonance forms [**A**]−[**C**] depicted in Scheme 3. X-ray crystal structure analysis revealed that the actual structure comes close to the iminium-stabilized zwitterionic heterofulvene

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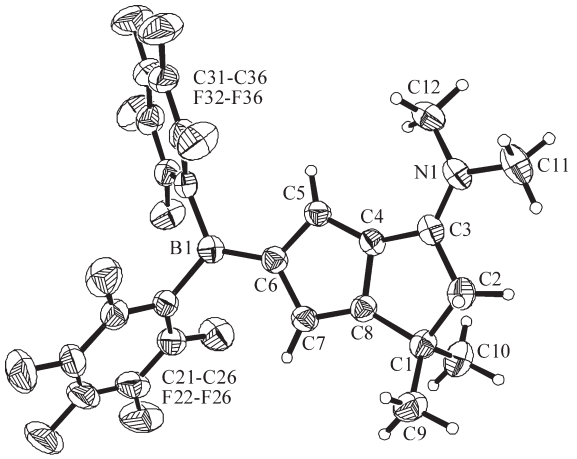


Figure 3. Molecular structure of **10a**.

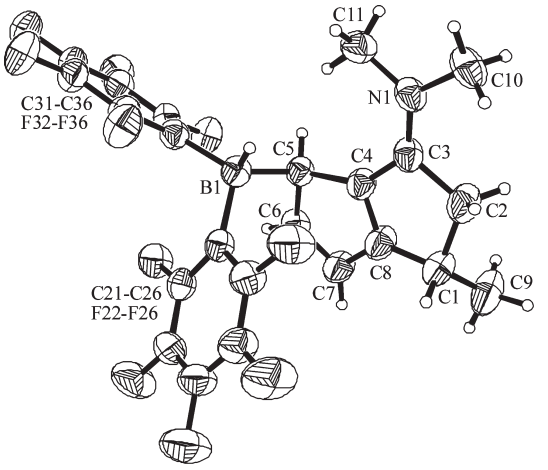
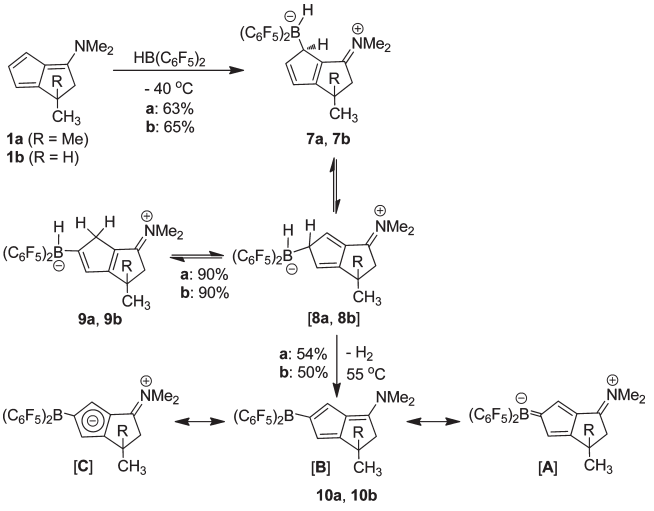


Figure 4. Molecular structure of *anti*-**7b**.

Scheme 3



description [**A**]. The C3−N bond length in **10a** (1.307(2) Å) is in the typical iminium range. The connected five-membered carbocycle exhibits characteristic alternating C−C bond lengths, with long C5−C6 (1.405(2) Å), C6−C7 (1.452(2) Å), and C4−C8 (1.432(2) Å) bonds (C1−C8 1.495(2) Å) and short C7−C8 (1.345(2) Å) and C4−C5 (1.385(2) Å) bonds. The short B1−C6 bond, at 1.473(3) Å, is more than 0.1 Å shorter than the adjacent B−C_6F_5 connections (B1−C21 1.584(3) Å, B1−C31 1.583(3) Å). The boron center in **10a** is planar tricoordinated (sum of C−B−C bond angles: 360.0°), and the $(C_6F_5)_2B$= unit is oriented coplanar with the adjacent unsaturated five-membered ring of the dihydropentalene unit (dihedral angles C7−C6−B1−C21 2.6(3)°, C7−C6−B1−C31 −177.3(2)°).

In solution, **10a** features ^{1}H NMR signals of the olefinic hydrogens 5-H (δ 6.77) and 7-H (δ 6.10). We monitor a ^{11}B NMR resonance at δ 51.0, which indicates some transfer of π-electron density to boron.[20] The ^{19}F NMR spectrum shows a separation of the *p*- and *m*-fluorine resonances of the C_6F_5 ring ($\Delta\delta$ 8.4 and 7.8), which presents an average value between tricoordinated and tetracoordinated boron centers.[21] Consequently, the rotation of the $(C_6F_5)_2B$=C unit around the B−C vector is "frozen" on the NMR time scale in solution even at 298 K, which results in the observation of two sets of *o*-, *p*-, and *m*-F resonances for the pair of *E*- and *Z*-C_6F_5 substituents.

We carried out the analogous reaction starting from the monomethyl-substituted dimethylaminodihydropentalene substrate **1b**. Its treatment with Piers's borane $[HB(C_6F_5)_2]$[12] gave similar products under comparable reaction conditions (see Scheme 3 and Tables 1 and 2). The primary $HB(C_6F_5)_2$ addition product **7b** in this series contains a pair of chirality centers. The chiral center C1 was brought in from the (racemic) starting material **1b**. Addition of the $HB(C_6F_5)_2$ electrophile to the "left" cyclopentadienyl ring has created a new chirality center at C5 (see Scheme 3). Consequently, we observed the formation of a pair of diastereoisomers (*anti*-**7b**, *syn*-**7b**) in a ratio of ca. 2:1. Low-temperature crystallization from dichloromethane/pentane by the diffusion method eventually gave single crystals of one isomer that was characterized by X-ray diffraction.

X-ray crystal structure analysis reveals the presence of *anti*-**7b** (Figure 4). It has the single methyl substitutent at carbon atom C1 and the $[(C_6F_5)_2BH]^-$ substituent at C5 oriented *trans* to each other at the connecting central bicyclic dihydropentalene framework. The remaining structural parameters of *anti*-**7b** are similar to those found for **7a** (see above and Table 1).

Storing **7b** in dichloromethane at room temperature overnight resulted in a clean formation of the single product **9b**. It was isolated as a yellow-red solid in 90% yield and characterized spectroscopically. It features a ^{11}B NMR doublet at δ −22.3 with a typical $^1J_{BH}$ coupling constant of ca. 87 Hz and the 1-H ^{1}H NMR resonance at δ 3.29. Thermolysis of the solution of **9b** in dichloromethane (55 °C overnight) eventually generated a reaction mixture from which crystals of **10b** were obtained. The compound was identified by X-ray crystal structure analysis (see Figure 5 and Scheme 3; for further details see the Experimental Section and the Supporting Information).

The **7**→**9** transformation formally can be described as a 1,5-borane shift along the π-perimeter of the "left" five-membered dihydropentalene ring. However, it remained to be determined whether this isomerization reaction takes place intra- or intermolecularly. Having the pair of $HB(C_6F_5)_2$ addition products **7a**, **b** available, we could perform the necessary experiments with ease. Thus, in a typical experiment, we mixed the primary addition product **7a**, obtained by treatment of $HB(C_6F_5)_2$ with the 1,1-dimethyl-3-dimethylamino-1,2-dihydropentalene substrate

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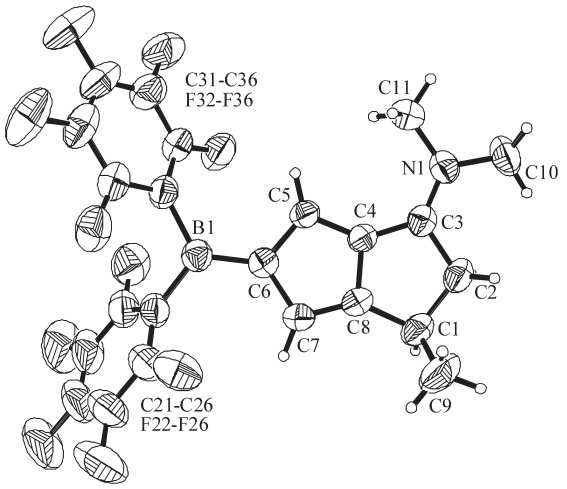
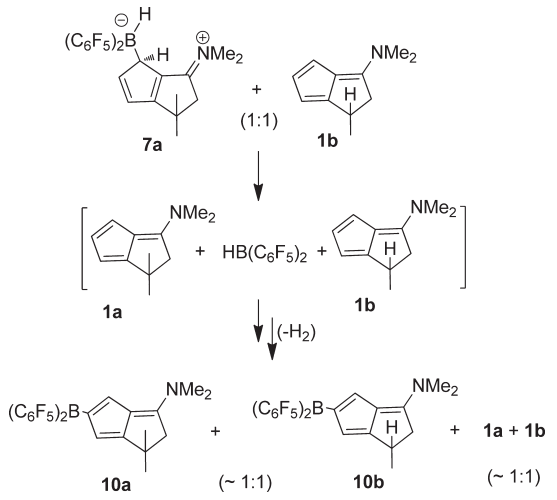


Figure 5. Molecular structure of **10b**.

Scheme 4



(**1a**) with 1 molar equivalent of 1-methyl-3-dimethylamino-1,2-dihydropentalene (**1b**) at −40 °C. Slowly warming the mixture to 25 °C and keeping it at that temperature eventually resulted in the observation of a ca. 1:1 mixture of the dehydrogenation products **10a**,**b**, along with ca. 50% of a ca. 1:1 mixture of the free aminodihydropentalenes **1a**,**b** (see Scheme 4; for further details, including the intermediate observation of **7a**,**b** and **9a**,**b**, see the Supporting Information). The outcome of this and related experiments indicated that the **7a**→**9a** (and conversely the **7b**→**9b**) isomerization takes place by an intermolecular route involving reversal of the $HB(C_6F_5)_2$-to-aminodihydropentalene addition. Apparently, here intramolecular 1,5-$HB(C_6F_5)_2$ migration along the π-system is not a facile process.[22,23] This is a surprising result. We tried to find some explanation for this unexpected behavior by DFT analysis of the underlying 1,5-BX_3 migration in the related substituted cyclopentadiene system. Unfortunately, calculation of the B−C bond dissociation process in the respective $[R_3BCp]^-$ anion systems met with some difficulties. However, the theoretical description of the intramolecular 1,5-boron shifts was possible. This gave a remarkable result.

The 1,5-shift of various functional groups (R = Me, BH_3, SiH_3, $B(C_6F_5)_3$) in the model R-C_5H_5 anions was investigated by

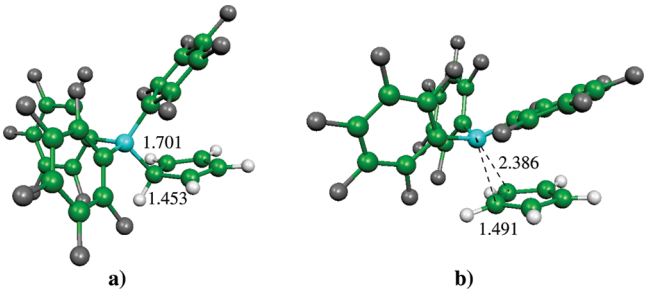


Figure 6. Optimized structures (TPSS-D3/def2-TZVP) of the minimum (a) and TS (b) for R = $B(C_6F_5)_3$. The bond lengths are given in angstroms.

Table 3. Reaction Barriers and Activation Enthalpies (in Parentheses, All Values in kcal/mol) at the TPSS-D3/def2-TZVP and B2PLYP-D3/def2-TZVP Levels for the 1,5-Shift in Monosubstituted Cyclopentadienes

R	TPSS	B2PLYP
BF_3	16.4	17.7 (17.1)
BH_3	12.2	13.1 (12.8)
$B(C_6F_5)_3$	22.9	25.8 (24.1)
CH_3	38.1	42.5 (41.7)
SiH_3	10.4	13.2 (12.5)

quantum chemical calculations based on Kohn−Sham density functional theory (DFT[24,25]). These were carried out using the TURBOMOLE quantum chemical program system.[26] For the corresponding minima and transition states (TSs), we performed full structural optimizations assuming C_s symmetry for the TS. Large triple-ζ Gaussian AO basis sets (def2-TZVP[27]), which yielded almost convergent results for the investigated properties, and the RI integral approximation[28] were employed. As density functional, the almost nonempirical meta-GGA (TPSS[29]) constructions were used for the geometry optimizations. In all DFT treatments, we used the now well-established correction for long-range London dispersion effects,[30] in its third revised version (DFT-D3 method[31]), that have more or less been absent in all previous standard density functionals. Intramolecular dispersion effects are of particular importance for large molecules when bulky substituents (C_6F_5 in one of our cases) spatially come close together (for a recent example, see ref 32). Single-point calculations were also performed using the B2PLYP double-hybrid functional,[33] which yields more accurate thermodynamic properties and reaction barriers. The stationary points were properly characterized as either minima or TSs by computation of harmonic vibration frequencies at the LDA/SV(P) level (which yields structures similar to those obtained with TPSS-D3/def2-TZVP).

The structures for R = $B(C_6F_5)_3$ as an example, as obtained at the DFT level, are show in Figure 6. The C−B bond length of about 1.7 Å in the equilibrium structure increases to a typical value of about 2.4 Å in the TS. The formal single C−C bonds in the cyclopentadiene ring decrease by about 0.04 Å to a value of 1.45 Å, which indicates some π-delocalization in the TS. The two hydrogen atoms bound to the carbon atoms above which the group R moves are only slightly tilted out of the ring plane. The cyclopentadiene ring in the TS is at least in part structurally similar to the (planar) cyclopentadienyl anion. The Wiberg bond

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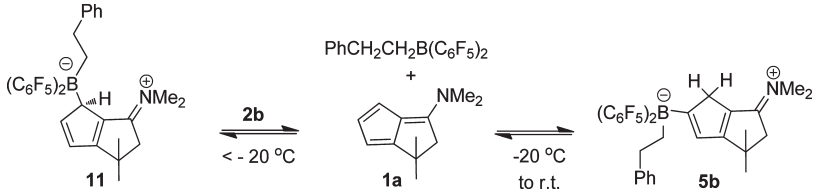
Scheme 5



order for the formed/broken C−B bonds in the TS is 0.32, which is a rather typical value for a concerted reaction and should be compared to the value for the formal C−B single bond in the minimum structure of 0.87.[34] This means that the loss of covalent bonding contribution of the broken C−B bond is, to a significant degree, compensated by the forming bond.

Similar structures were obtained for the other considered substituents. In addition to the experimentally investigated $B(C_6F_5)_3$ group, we conducted calculations for other boron-containing groups (BH_3 and BF_3) and, for comparison, also for methyl and silyl substituents.

As can be seen from the compilation of the obtained data (Table 3), the calculated barriers are very strongly substituent dependent, ranging from about 13 kcal/mol (for BH_3 and SiH_3) to 42.5 kcal/mol (CH_3). As expected, the values are slightly underestimated by the semilocal TPSS density functional compared to the more reliable B2PLYP results (which are discussed in the following). The thermal and zero-point vibrational corrections are also small (cf. values in parentheses). The value for the experimentally studied $B(C_6F_5)_3$ substituent, 25.8 kcal/mol, is intermediate in our series but 8−12 kcal/mol larger than those calculated for other boron-containing groups. This once again shows how important it is to employ "real" substituents in accurate quantum chemical studies. The computed activation enthalpy of 24.1 kcal/mol is apparently too large for a sufficiently fast chemical reaction at ambient temperatures to compete with the observed alternative reaction pathway. This behavior marks a pronounced substituent effect of the large C_6F_5 groups at boron.

Coming Back to the Carbon−Carbon Bond Activation Scheme. Since we had shown that $HB(C_6F_5)_2$ added to the carbon atom C5 of the aminodihydropentalene substrates **1** under kinetic control to give the adducts **7** (see Scheme 3), it was tempting to speculate that the alkyl-$B(C_6F_5)_2$ reagents **2** might behave similarly. That was indeed the case. We showed that the reagent $PhCH_2CH_2B(C_6F_5)_2$ (**2b**) reacted with substrate **1a** in dichloromethane at −80 °C to give the primary addition product **11** (see Scheme 5). Compound **11** features the 5-H ^{1}H NMR signal at δ 4.69 as a broad singlet. It shows olefinic resonances at δ 7.73 and 6.11 (6-H and 7-H).

Compound **11** was also characterized by X-ray diffraction (see Figure 7). It shows the bulky $PhCH_2CH_2B(C_6F_5)_2$-borane moiety attached at carbon atom C5 of the dihydropentalene core (B1−C13 1.644(3) Å, dihedral angle B1−C13−C14−C15 175.2(2)°). The iminium ion (C3−N1 1.310(3) Å) is doubly conjugated to the diene unit inside the "left" cyclopentadiene ring of the aminodihydropentalene system (C3−C4 1.426(3) Å, C4−C8 1.374(3) Å, C8−C7 1.418(4) Å, C7−C6 1.349(3) Å).

Warming a sample of **11** in dichloromethane to room temperature allowed us to observe the formation of the "rearrangement" product **5b** (see Schemes 1 and 5) before it eventually reacted further by C−C bond cleavage to yield **3b** (see Scheme 1).

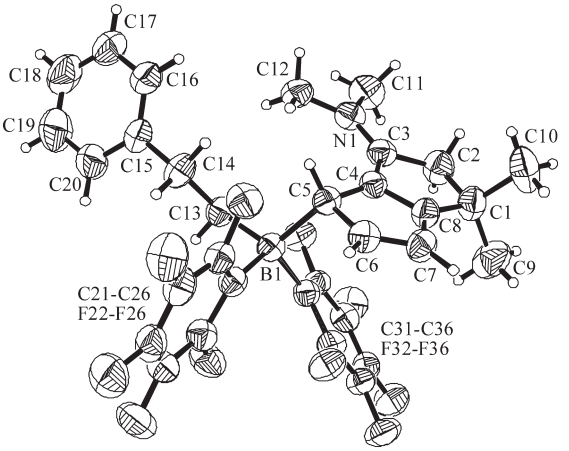


Figure 7. Molecular structure of **11**.

The intermediate **5b** was characterized spectroscopically [^{1}H NMR δ 6.77 (7-H), 2.26/1.30 (CH_2-CH_2-[B]), 3.45 (5-H_2), 3.32/3.20 (NMe_2); ^{13}C δ 212.4 (br, =CB), 170.7 (C=NMe_2), 127.8 (C7), 204.3 (C8), 135.1 (C4); ^{19}F $\Delta\delta(p,m)$ = 2.4].[11]

In view of the course taken in the related reactions of **1a**,**b** with $HB(C_6F_5)_2$, we assume that the **11**→**5b** conversion may also involve an intermolecular mechanism for the formal 1,5-borane shift. We conclude that the observation of the preformation of the addition product **11** under kinetic control leads to an extension of the overall reaction scheme of the C−C bond activation/cleavage of substrate **1** by the $RB(C_6F_5)_2$ reagent (see Scheme 1) to include the reaction sequence described in Scheme 5.

In the C−C bond activation scheme (see Scheme 1), we proposed 1,2-alkyl migration from boron to the adjacent conjugated dienyl iminium moiety as an essential step (**5**→**6**). In the related $HB(C_6F_5)_2$-derived series, a similar pathway to C−C bond cleavage, which would be initiated by the **9**→**12** transformation, was apparently not opened (see Scheme 6). Instead, we observed a more favorable H_2 elimination, probably via **9**⇌**8** equilibration (see Scheme 3). The question remained whether the **9**→**12** hydrogen shift was taking place at all or if it was just unproductive in view of the preferred **9**⇌**8**→**10** reaction sequence.

In two experiments, we indirectly found out by trapping reactions that the **9**⇌**12** equilibration can actually take place in the aminodihydropentalene plus $HB(C_6F_5)_2$ system.

An orange solution of **9a** in dichloromethane was treated with an equimolar amount of HCl (added as HCl solution in ether) at room temperature. The solution became colorless after some time, and after stirring the mixture overnight we isolated product **13** in 73% yield. X-ray crystal structure analysis (see Figure 8 and Table 1) revealed that actually this product must be

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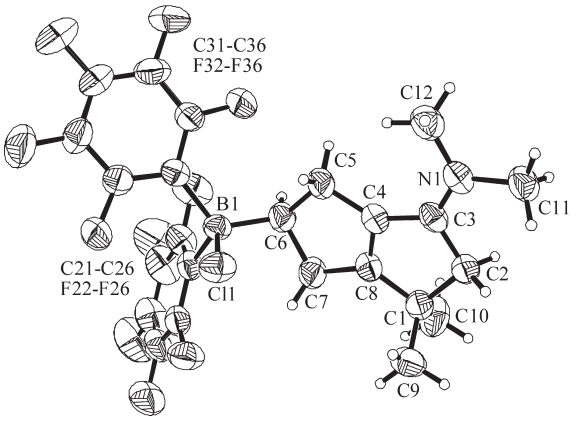
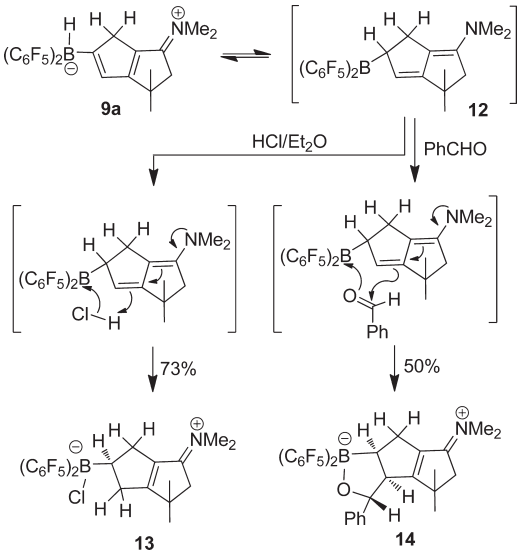


Figure 8. Molecular structure of **13**.

Scheme 6



regarded to have been formed by HCl addition to the H-shifted intermediate **12**. The carbon atom C6 in **13** adjacent to boron is sp^3-hybridized and bears a hydrogen atom. Protonation took place at the former dienamine terminus C7, and the chloride anion was added to the borane. Consequently, **13** contains an α,β-unsaturated iminium functionality (C4−C8 1.345(5) Å, C4−C3 1.435(5) Å, C3−N1 1.297(5) Å).

In solution, **13** features a ^{11}B NMR resonance at δ −1.4 and the ^{1}H NMR signal of the adjacent 6-H at δ 2.93. The 5-H/H′ hydrogens (δ 2.92/2.79) and the 7-H/H′ hydrogen atoms (δ 2.74/2.55) are pairwise diastereotopic (for further spectroscopic details, see Table 2 and the Supporting Information).

The proposed intermediate **12** could also be trapped with benzaldehyde. Treatment of **9a** with 1 molar equivalent of PhCHO in dichloromethane at room temperature gave a colorless precipitate of the addition product **14** (see Scheme 6), which we isolated in ca. 50% yield. Single crystals of **14** were obtained from THF/pentane by the diffusion method. X-ray crystal structure analysis (see Figure 9 and Table 1) revealed that a stereoselective cycloaddition had taken place, leading to a system of three annelated five-membered rings. The AB ring junction is cis. The aldehyde oxygen atom has become attached to the boron

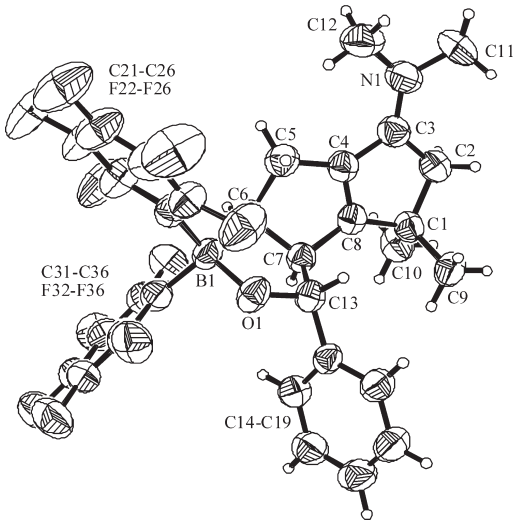


Figure 9. Molecular structure of **14** (molecule A is shown).

center, and the dienamine subunit has added to the aldehyde carbonyl carbon via its nucleophilic sp^2 terminus, forming a new stereogenic center at C13 (see Scheme 6). We found the product that was formed along the sterically least hindered pathway.

In solution, a mixture of two diastereomers in a 1:6 ratio was observed for **14**, which we tentatively assigned as (6*S**,7*S**,13*R**) and (6*S**,7*S**,13*S**), respectively. Consequently, we observed two sets of three ^{19}F NMR resonances for the diastereotopic C_6F_5 groups at boron for each diastereomer. The diastereotopic hydrogens of the methylene carbon atoms C2 and C5 were found in the ^{1}H NMR spectrum at δ 2.91/2.64 (δ^{13}C 53.2) and δ 2.65/2.59 (δ^{13}C 35.5), respectively, and the pair of C1 methyl resonances at δ 1.11 and 0.05 (major isomer; for further details, see the Supporting Information).

CONCLUSIONS

We have found a remarkable reaction system in which addition of a borane of the type $RB(C_6F_5)_2$ to the aminodihydropentalenes **1** (see Scheme 1) results in activation and cleavage of a strong, nonactivated C═C bond inside the "left" five-membered carbocycle. This leads to a formal insertion of a borylene unit [i.e., $B(C_6F_5)_2$] into the C═C bond, with a concomitant series of alkyl and hydrogen migration reactions. The overall reaction sequence can formally be regarded as a unique 1,1-carboboration reaction of an olefin.[35]

The present study has revealed a number of significant mechanistic features of this remarkable reaction sequence. At the same time, we have learned details about the scope and limitations of the use of different boranes in this reaction. There is a marked dependency on the nature of the "active" R-group of the $RB(C_6F_5)_2$ reagents: R = C_6F_5 marks one limiting situation, where apparently the poor migratory aptitude of the electron-poor C_6F_5 group is not sufficient to initiate the overall sequence leading to C═C cleavage.[11] R = H marks another limiting situation, where at the stage of an essential intermediate (**8**, see Scheme 3) a competing reaction pathway, namely facile, thermally induced irreversible elimination of dihydrogen, takes over and determines the overall reaction outcome. With such rather detailed knowledge about this specific example of a potentially important new reaction type, it is temping to search for other and, it is hoped, more generally applicable examples

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of such specific Lewis acid-induced C═C bond activation processes.

EXPERIMENTAL SECTION

General Procedures. Reactions with air- and moisture-sensitive compounds were carried out under argon using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. The aminodihydropentalene derivatives **1a**,**b**,[17] dimesitylvinylphosphine ($Mes_2PCH{=}CH_2$),[19] and bis(2,3,4,5,6-pentafluorophenyl)borane [$HB(C_6F_5)_2$][12] were prepared as described in the literature. Styrene and benzaldehyde were distilled using vacuum transfer prior to use. The following instruments were used for physical characterization of the compounds: elemental analyses, Foss-Heraeus CHNO-Rapid; ESI mass spectra, Bruker Daltonics MicroTOF; NMR spectra, Varian UNITY plus (^{1}H, 599.9 MHz; ^{13}C, 150.8 MHz; ^{19}F, 564.4 MHz; ^{11}B, 192.4 MHz) and Varian 500 MHz INOVA (^{1}H, 499.9 MHz; ^{13}C, 125.7 MHz; ^{19}F, 470.3 MHz; ^{11}B, 160.4 MHz). For ^{1}H and ^{13}C NMR data, chemical shift δ is given relative to TMS and referenced to the solvent signal; for ^{19}F NMR, δ is given relative to $CFCl_3$ (external reference); for ^{11}B NMR, δ is given relative to $BF_3 \cdot Et_2O$ (external reference). Assignments of the resonances were supported by 2D experiments.

X-ray Crystal Structure Analyses. Data sets were collected with a Nonius KappaCCD diffractometer. The following programs were used: data collection, COLLECT (Nonius B.V., 1998); data reduction, Denzo-SMN,[36] absorption correction, Denzo;[37] structure solution, SHELXS-97;[38] structure refinement, SHELXL-97;[39] graphics, XP (BrukerAXS, 2000). Graphics show the thermal ellipsoids at the 50% probability level. *R*-values are given for observed reflections and wR^2-values for all reflections.

Synthesis of Compound 3c. A solution of $Mes_2PCH{=}CH_2$ (100 mg, 0.34 mmol) and $HB(C_6F_5)_2$ (117 mg, 0.34 mmol) in pentane (6 mL) was stirred for 15 min. A solution of **1a** (65 mg, 0.37 mmol) in pentane (3 mL) was then added at room temperature, and after 1 h a yellow-red solid began to precipitate. After the reaction mixture had been stirred for 24 h, the solid was isolated via cannula filtration and washed twice with cold pentane (2.5 mL). Removal of all volatiles in vacuo yielded **3c** (150 mg, 54%) as a red powder. Crystals suitable for X-ray crystal structure analysis were grown from a saturated pentane solution of **3c** at −30 °C. Anal. Calcd for $C_{44}H_{43}BF_{10}NP$: C, 64.64; H, 5.30; N, 1.71. Found: C, 64.51; H, 5.36; N, 1.65. ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ = 6.69 (d, $^4J_{PH}$ = 2.5 Hz, 4H, *m*-Mes), 6.61 (s, 1H, ═CH), 2.94 (m, 2H, $^PCH_2$), 2.81 (m, 2H, $^BCH_2$), 2.41 (s, 12 H, *o*-CH_3^{Mes}), 2.37 (br s, 3H, NMe^Z), 2.11 (s, 6H, *p*-CH_3^{Mes}), 2.06 (br s, 2H, B-CH_2), 1.54 (br s, 3H, NMe^E), 1.49 (br s, 2H, CH_2), 0.89 (s, 6H, Me). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ = 196.2 (br, ═C-B), 189.0 (C9), 181.2 (C═N), 148.7 (dm, $^1J_{FC} \approx$ 237 Hz, C_6F_5), 142.0 (d, $^3J_{PC}$ = 13.3 Hz, *o*-Mes), 138.6 (dm, $^1J_{FC} \approx$ 245 Hz, C_6F_5), 137.4 (*p*-Mes), 137.3 (dm, $^1J_{FC} \approx$ 249 Hz, C_6F_5), 133.7 (d, $^1J_{PC}$ = 22.7 Hz, *i*-Mes), 130.3 (d, J_{PC} = 2.8 Hz, *m*-Mes), 128.9 (C4), 121.0 (C8), 48.7 (C2), 43.2 (NMe^E), 41.6 (C1), 41.2 (NMe^Z), 36.5 (d, $^2J_{PC}$ = 20.9 Hz, $^BCH_2$), 27.0 (d, $^1J_{PC}$ = 16.9 Hz, $^PCH_2$), 26.9 (Me), 23.3 (d, $^3J_{PC}$ = 13.3 Hz, *o*-CH_3^{Mes}), 23.3 (br, B−CH_2), 20.7 (*p*-CH_3^{Mes}). ^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 298 K): δ = −14.2 ($\nu_{1/2}$ = 90 Hz). ^{19}F{^{1}H} NMR (470 MHz, C_6D_6, 298 K): δ = −130.6 (2F, *o*-C_6F_5), −162.3 (1F, *p*-C_6F_5), −165.2 (2F, *m*-C_6F_5). ^{31}P{^{1}H} NMR (202 MHz, 298 K, C_6D_6): δ = −20.6 ($\nu_{1/2}$ = 4 Hz).

X-ray Crystal Structure Analysis of ***3c***. Formula $C_{44}H_{43}BF_{10}NP \cdot {}^1/_2$-$C_5H_{12}$, *M* = 853.65, colorless crystal 0.40 × 0.25 × 0.03 mm, *a* = 10.6333(3), *b* = 11.1091(5), and *c* = 19.3290(11) Å, α = 101.818(6), β = 98.509(2), and γ = 98.229(3)°, *V* = 2174.50(17) Å^3, ρ_{calc} = 1.304 g cm^{-3}, μ = 1.222 mm^{-1}, empirical absorption correction (0.641 ≤ *T* ≤ 0.964), *Z* = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, *T* = 223(2) K, ω and φ scans, 26 347 reflections collected (±*h*,±*k*,±*l*), [(sin θ)/λ] = 0.60 Å^{-1}, 7513 independent (R_{int} = 0.051) and 6425 observed reflections [$I \geq 2\,\sigma(I)$], 546 refined parameters, *R* = 0.052, wR^2 = 0.143, max (min) residual electron density 0.43 (−0.31) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of 7a. Compound **1a** (100.0 mg, 0.57 mmol) and $HB(C_6F_5)_2$ (198.0 mg, 0.57 mmol) were put together in a Schlenk flask and cooled to −40 °C. Precooled dichloromethane (10 mL) was then added. The reaction mixture was stirred at −40 °C for 15 min and concentrated to 5 mL in vacuo. After crystallization at −35 °C, **7a** was obtained as a colorless solid (187.0 mg, 0.36 mmol, 63%). Crystals suitable for X-ray crystal structure analysis were obtained by gas diffusion of pentane into a solution of **7a** in dichloromethane at −35 °C. Anal. Calcd for $C_{24}H_{18}BNF_{10}$: C, 55.31; H, 3.48; N, 2.69. Found: C, 54.85; H, 3.50; N, 3.01. ^{1}H NMR (500 MHz, CD_2Cl_2, 233 K): δ = 7.97 (m, 1H, 6-H), 6.15 (m, 1H, 7-H), 4.30 (br s, 1H, BCH), 3.71 (s, 3H, NMe_2^Z), 3.32 (s, 3H, NMe_2^E), 3.27 (br, 1H, BH), 2.98 (s, 2H, 2-H), 1.23 (s, 3H, Me^b), 0.87 (s, 3H, Me^a). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 233 K): δ = 193.1 (C8), 174.3 (C═N), 169.3 (C6), 142.6 (C4), 120.5 (C7), 53.2 (C2), 53.0 (br, BCH), 44.2 (NMe_2^Z), 42.9 (NMe_2^E), 38.7 (C1), 27.5 (Me^b), 27.0 (Me^a) [C_6F_5 not listed]. ^{11}B NMR (160 MHz, CD_2Cl_2, 233 K): δ = −19.4 ($^1J_{BH} \approx$ 80 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 233 K): δ = −133.3 (br, 2F, *o*-$C_6F_5^a$), −134.2 (br, 2F, *o*-$C_6F_5^b$), −162.4 (1F, *p*-$C_6F_5^a$), −163.2 (1F, *p*-$C_6F_5^b$), −166.1 (2F, *m*-$C_6F_5^b$), −166.3 (2F, *m*-$C_6F_5^a$).

X-ray Crystal Structure Analysis of ***7a***. Formula $C_{24}H_{18}BF_{10}N$, *M* = 521.20, colorless crystal 0.20 × 0.15 × 0.10 mm, *a* = 19.5277(8), *b* = 6.5056(3), and *c* = 18.7809(6) Å, β = 112.021(2)°, *V* = 2211.85(15) Å^3, ρ_{calc} = 1.565 g cm^{-3}, μ = 1.332 mm^{-1}, empirical absorption correction (0.777 ≤ *T* ≤ 0.878), *Z* = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, *T* = 223(2) K, ω and φ scans, 13 524 reflections collected (±*h*,±*k*,±*l*), [(sin θ)/λ] = 0.60 Å^{-1}, 3845 independent (R_{int} = 0.042) and 3319 observed reflections [$I \geq 2\,\sigma(I)$], 329 refined parameters, *R* = 0.045, wR^2 = 0.121, max (min) residual electron density 0.28 (−0.26) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of 7b. Compound **1b** (100 mg, 0.62 mmol) and $HB(C_6F_5)_2$ (216 mg, 0.62 mmol) were put together in a Schlenk flask and cooled to −40 °C. Precooled dichloromethane (10 mL) was then added. The reaction mixture was stirred at −40 °C for 15 min and concentrated to 5 mL in vacuo. After crystallization at −35 °C, **7b** was obtained as a colorless mixture (204 mg, 0.40 mmol, 65%) containing a major isomer (*anti*-**7b**, tentative assignment) and a minor isomer (*syn*-**7b**) in a ratio of 2:1. Crystals of *anti*-**7b** suitable for X-ray crystal structure analysis were obtained by gas diffusion of pentane into a solution of **7b** in dichloromethane at −35 °C. Anal. Calcd for $C_{23}H_{16}BNF_{10}$: C, 54.47; H, 3.18; N, 2.76. Found: C, 54.04; H, 3.16; N, 3.07.

NMR Analysis of the Major Isomer. ^{1}H NMR (500 MHz, CD_2Cl_2, 233 K): δ = 7.97 (d, $^3J_{HH}$ = 3.9 Hz, 1H, 6-H), 6.17 (d, $^3J_{HH}$ = 3.9 Hz, 1H, 7-H), 4.32 (br, 1H, 5-H), 3.71 (s, 3H, NMe_2^Z), 3.39 (dd, $^2J_{HH}$ = 18.2 Hz, $^3J_{HH}$ = 5.6 Hz, 1H, 2-H^b), 3.34 (s, 3H, NMe_2^E), 3.11 (m, 1H, 1-H), 2.66 (d, $^2J_{HH}$ = 18.2 Hz, 1H, 2-H^a), 0.83 (d, $^3J_{HH}$ = 7.2 Hz, 3H, Me). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 233 K): δ = 189.3 (C8), 175.2 (C═N), 169.0 (C6), 144.5 (C4), 121.7 (C7), 53.0 (br, C5), 46.3 (C2), 44.1 (NMe_2^Z), 42.9 (NMe_2^E), 32.7 (C1), 19.0 (Me) [C_6F_5 not listed] . ^{11}B NMR (160 MHz, CD_2Cl_2, 233 K): δ = −19.3 ($^1J_{BH} \approx$ 80 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 233 K): δ = −133.2 (2F, *o*-$C_6F_5^a$), −134.2 (2F, *o*-$C_6F_5^b$), −162.4 (1F, *p*-$C_6F_5^a$), −163.2 (1F, *p*-$C_6F_5^b$), −166.1 (2F, *m*-$C_6F_5^b$), −166.3 (2F, *m*-$C_6F_5^a$).

NMR Analysis of the Minor Isomer. ^{1}H NMR (500 MHz, CD_2Cl_2, 233 K): δ = 7.94 (d, ^3J = 4.9 Hz, 1H, 6-H), 6.14 (d, $^3J_{HH}$ = 4.9 Hz, 1H, 7-H), 4.36 (br, 1H, 5-H), 3.72 (s, 3H, NMe_2^Z), 3.38 (m, 1H, 2-H^b), 3.33 (s, 3H, NMe_2^E), 2.77 (m, 1H, 1-H), 2.70 (d, $^2J_{HH}$ = 18.4 Hz, 1H, 2-H^a), 1.17 (d, $^3J_{HH}$ = 7.2 Hz, 3H, Me). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 233 K): δ = 188.6 (C8), 175.1 (C═N), 168.7 (C6), 144.4 (C4), 121.7 (C7), 53.5 (br, C5), 46.2 (C2), 44.1 (NMe_2^Z), 42.9 (NMe_2^E), 32.5 (C1), 18.8 (Me) [C_6F_5 not listed]. ^{11}B NMR (160 MHz, CD_2Cl_2,

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233 K): δ = −19.3 ($^1J_{BH} \approx 80$ Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 233 K): δ = −133.9 (2F, *o*-$C_6F_5^a$), −134.2 (2F, *o*-$C_6F_5^b$), −162.2 (1F, *p*-$C_6F_5^a$), −163.1 (1F, *p*-$C_6F_5^b$), −166.2 (2F, *m*-$C_6F_5^b$), −166.7 (2F, *m*-$C_6F_5^a$).

*X-ray Crystal Structure Analysis of anti-**7b**.* Formula $C_{23}H_{16}BF_{10}N$, M = 507.18, yellow crystal 0.30 × 0.15 × 0.07 mm, a = 19.0148(12), b = 6.3803(4), and c = 18.4629(10) Å, β = 109.883(4)°, V = 2106.4(2) Å^3, ρ_{calc} = 1.599 g cm^{-3}, μ = 1.381 mm^{-1}, empirical absorption correction (0.682 ≤ T ≤ 0.910), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 16 172 reflections collected (±h,±k,±l), [(sin θ)/λ] = 0.60 Å^{-1}, 3693 independent (R_{int} = 0.047) and 3398 observed reflections [$I \geq 2\sigma(I)$], 330 refined parameters, R = 0.059, wR^2 = 0.140, max (min) residual electron density 0.28 (−0.26) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms, group C2−C1−C9 refined with split positions using geometrical and thermal restraints.

Preparation of 9a. A solution of **7a** (100.0 mg, 0.19 mmol) in 10 mL of dichloromethane was stirred at room temperature overnight. The solvent was removed under vacuum, and the resulting solid was suspended in precooled pentane, filtered, and dried under vacuum. Compound **9a** was obtained as a yellow-red solid (89.0 mg, 0.17 mmol, 90%). ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 6.43 (br, 1H, 7-H), 3.54 (s, 2H, 5-H), 3.35, 3.25 (each s, each 3H, NMe_2), 3.08 (s, 2H, 2-H), 1.35 (s, 6H, Me). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ = 212.8 (br, =CB), 205.2 (C8), 170.5 (C=N), 148.3 (dm, $^1J_{FC} \approx 238$ Hz, C_6F_5), 138.4 (dm, $^1J_{FC} \approx 244$ Hz, C_6F_5), 137.1 (dm, $^1J_{FC} \approx 246$ Hz, C_6F_5), 135.3 (C4), 128.7 (C7), 124.8 (br, *i*-C_6F_5), 53.6 (C2), 44.5 (C5), 42.7, 42.6 (NMe_2), 40.0 (C1), 27.1 (Me). ^{11}B NMR (192 MHz, CD_2Cl_2, 298 K): δ = −22.3 ($^1J_{BH}$ = 87 Hz). ^{19}F NMR (564 MHz, CD_2Cl_2, 298 K): δ = −132.3 (2F, *o*-C_6F_5), −163.4 (1F, *p*-C_6F_5), −166.6 (2F, *m*-C_6F_5).

Preparation of 9b. A solution of **7b** (100 mg, 0.20 mmol) in 10 mL of dichloromethane was stirred at room temperature overnight. The solvent was removed under vacuum, and the resulting solid was suspended in precooled pentane, filtered, and dried under vacuum. Compound **9b** was obtained as a yellow-red solid (90 mg, 0.18 mmol, 90%). ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 6.45 (s, 1H, 7-H), 3.53 (br s, 2H, 5-H), 3.49 (dd, $^2J_{HH}$ = 18.4 Hz, $^3J_{HH}$ = 5.8 Hz, 1H, 2-H^b), 3.36 (s, 3H, NMe_2^Z), 3.29 (m, 1H, 1-H), 3.28 (s, 3H, NMe_2^E), 2.80 (d, $^2J_{HH}$ = 18.4 Hz, 1H, 2-H^a), 1.30 (d, $^3J_{HH}$ = 7.4 Hz, 3H, Me). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ = 212.4 (br, =CB), 202.0 (C8), 171.6 (C=N), 148.3 (dm, $^1J_{FC} \approx 238$ Hz, C_6F_5), 138.5 (dm, $^1J_{FC} \approx 244$ Hz, C_6F_5), 137.4 (C4), 137.0 (dm, $^1J_{FC} \approx 247$ Hz, C_6F_5), 129.9 (C7), 125.0 (br, *i*-C_6F_5), 46.5 (C2), 44.4 (br, C5), 42.7 (br, NMe_2), 33.9 (C1), 18.7 (Me). ^{11}B NMR (192 MHz, CD_2Cl_2, 298 K): δ = −22.3 ($^1J_{BH} \approx 87$ Hz). ^{19}F NMR (564 MHz, CD_2Cl_2, 298 K): δ = −132.3 (2F, *o*-C_6F_5), −163.4 (1F, *p*-C_6F_5), −166.6 (2F, *m*-C_6F_5).

Preparation of 10a. A solution of **9a** (100.0 mg, 0.19 mmol) in dichloromethane was warmed to 55 °C and stirred overnight. The solvent was removed under vacuum, and the resulting solid was suspended in cold pentane, filtered, and dried under vacuum. Compound **10a** was obtained as a red solid (53.0 mg, 0.10 mmol, 54%). Crystals suitable for X-ray crystal structure analysis were obtained by gas diffusion of pentane into a solution of **10a** in benzene at room temperature. HRMS (ESI) exact mass for $[M+H]^+$ ($C_{24}H_{16}BNF_{10}$): calcd m/z 520.1289, found 520.1278. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 6.77 (s, 1H, 5-H), 6.10 (s, 1H, 7-H), 3.40 (s, 3H, NMe_2^Z), 3.29 (s, 3H, NMe_2^E), 3.09 (s, 2H, 2-H), 1.37 (s, 6H, Me). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ = 170.8 (C=N), 158.0 (C8), 146.2 (C6), 128.8 (C5), 126.5 (C4), 116.8 (br, *i*-C_6F_5), 113.0 (C7), 55.5 (C2), 43.5 (NMe_2^Z), 42.9 (NMe_2^E), 37.0 (C1), 30.5 (Me) [C_6F_5 not listed]. ^{11}B NMR (160 MHz, CD_2Cl_2, 298 K): δ = 51.0 ($\nu_{1/2} \approx 700$ Hz). ^{19}F NMR (564 MHz, CD_2Cl_2, 298 K): δ = −131.6, −131.8 (each 2F, *o*-C_6F_5), −155.3, −155.9 (each 1F, *p*-C_6F_5), −163.7 (4F, *m*-C_6F_5).

*X-ray Crystal Structure Analysis of **10a**.* Formula $C_{24}H_{16}BF_{10}N$, M = 519.19, yellow crystal 0.40 × 0.15 × 0.10 mm, a = 8.4497(1), b = 9.7617(1), and c = 14.2402(2) Å, α = 71.184(1), β = 84.869(1), and γ = 88.108(1)°, V = 1107.34(2) Å^3, ρ_{calc} = 1.557 g cm^{-3}, μ = 1.330 mm^{-1}, empirical absorption correction (0.618 ≤ T ≤ 0.879), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 14 219 reflections collected (±h,±k,±l), [(sin θ)/λ] = 0.60 Å^{-1}, 3939 independent (R_{int} = 0.037) and 3658 observed reflections [$I \geq 2\sigma(I)$], 330 refined parameters, R = 0.048, wR^2 = 0.138, max (min) residual electron density 0.40 (−0.39) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of 10b. A solution of **9b** (100 mg, 0.20 mmol) in dichloromethane was warmed to 55 °C and stirred overnight. The solvent was removed under vacuum, and the resulting solid was suspended in cold pentane, filtered, and dried under vacuum. A mixture of **10b** together with **10b′** was obtained in a ratio of 1.5:1 as a red solid (with traces of **1b**) (50 mg, 0.10 mmol, 50%). Crystals suitable for X-ray crystal structure analysis were obtained by gas diffusion of pentane into a solution of **10b** in benzene at room temperature. HRMS (ESI) exact mass for $[M+H]^+$ ($C_{23}H_{15}BNF_{10}$): calcd m/z 506.1132, found 506.1122. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 6.80 (s, 1H, 5-H), 6.13 (s, 1H, 7-H), 3.49 (dd, $^2J_{HH}$ = 18.4 Hz, $^3J_{HH}$ = 6.8 Hz, 1H, 2-H^b), 3.41 (s, 3H, NMe_2^Z), 3.32 (m, 1H, 1-H), 3.31 (s, 3H, NMe_2^E), 2.77 (ddm, $^2J_{HH}$ = 18.4 Hz, $^3J_{HH}$ = 3.3 Hz, 1H, 2-H^a), 1.31 (d, $^3J_{HH}$ = 7.0 Hz, 3H, Me). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ = 171.7 (C=N), 154.0 (C8), 128.5 (C5), 127.5 (C4), 114.3 (C7), 48.3 (C2), 43.5 (NMe_2^Z), 42.9 (NMe_2^E), 30.7 (C1), 21.8 (Me), n.o. (C6) [C_6F_5 not listed]. ^{11}B NMR (160 MHz, CD_2Cl_2, 298 K): δ = 50.4 ($\nu_{1/2} \approx 700$ Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 298 K): δ = −131.6, −131.7 (br, each 2F, *o*-C_6F_5), −155.3, −155.8 (br, each 1F, *p*-C_6F_5), −163.7 (br, 4F, *m*-C_6F_5).

*X-ray Crystal Structure Analysis of **10b**.* Formula $C_{23}H_{14}BF_{10}N \cdot CH_2Cl_2$, M = 590.09, yellow crystal 0.35 × 0.30 × 0.20 mm, a = 7.9357(4), b = 11.1685(6), and c = 14.6427(9) Å, α = 94.818(2), β = 91.780(3), and γ = 103.119(4)°, V = 1257.76(12) Å^3, ρ_{calc} = 1.558 g cm^{-3}, μ = 3.155 mm^{-1}, empirical absorption correction (0.405 ≤ T ≤ 0.571), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 15 489 reflections collected (±h,±k,±l), [(sin θ)/λ] = 0.60 Å^{-1}, 4330 independent (R_{int} = 0.043) and 3651 observed reflections [$I \geq 2\sigma(I)$], 368 refined parameters, R = 0.067, wR^2 = 0.194, max (min) residual electron density 0.49 (−0.46) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms, solvent molecule refined with split positions using geometrical and thermal restraints.

Preparation of 11 and 5b. Styrene (40 μL, 0.34 mmol) and $HB(C_6F_5)_2$ (117 mg, 0.34 mmol) were dissolved in pentane (6 mL) and stirred for 15 min. A solution of **1a** (65 mg, 0.37 mmol) in pentane (3 mL) was then added at room temperature. Subsequently the reaction mixture was stored at −36 °C. Crystals of **11** suitable for X-ray crystal structure analysis came out overnight. Efforts to isolate **11** failed due to its thermosensitivity.

NMR Scale. An NMR tube containing **1a** (5 mg, 0.03 mmol) and **2b** (13 mg, 0.03 mmol) was cooled to −78 °C. Precooled CD_2Cl_2 (3 mL, −80 °C) was added, and then the NMR tube was sealed under vacuum by using Schlenk techniques. Intermediate **11** was characterized by NMR experiments at −80 °C. Afterward, the NMR sample was stored at −30 °C overnight to give **5b** (ca. 90% NMR yield at −20 °C).

*NMR Analysis of **11**.* ^{1}H NMR (500 MHz, CD_2Cl_2, 193 K): δ = 7.73 (br s, 1H, 6-H), 7.18 (m, 2H, *m*-Ph), 7.07 (m, 2H, *o*-Ph), 7.04 (m, 1H, *p*-Ph), 6.11 (d, 1H, $^3J_{HH}$ = 4.6 Hz, 7-H), 4.69 (br s, 1H, BCH), 3.37 (s, 3H, NMe_2^Z), 3.20 (s, 3H, NMe_2^E), 2.92 (m, 1H, CH_2^b), 2.85 (m, 1H, CH_2^a), 2.17 (m, 2H, $^{Ph}CH_2$), 1.42, 1.14 (each m, each 1H, $^BCH_2$), 1.16 (s, 3H, Me^b), 0.69 (s, 3H, Me^a). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 193 K): δ = 192.7 (C8), 174.0 (N=C), 169.0 (C6), 146.7 (*i*-Ph), 139.4 (C4), 127.6 (*m*-Ph), 127.3 (*o*-Ph), 124.4 (*p*-Ph), 119.3 (C7), 57.4 (br, BCH),

52.7 (CH_2), 44.9 (NMe_2^Z), 42.6 (NMe_2^E), 38.0 (C1), 33.3 ($^{Ph}CH_2$), 29.6 (br, $^{B}CH_2$), 28.0 (Me^b), 25.9 (Me^a) [C_6F_5 not listed]. $^{19}F\{^1H\}$ NMR (470 MHz, CD_2Cl_2, 193 K): δ = −127.1 (1F, *o*-$C_6F_5^a$), −130.7 (1F, *o*-$C_6F_5^b$), −136.6 (1F, *o*-$C_6F_5^b$), −137.5 (1F, *o*-$C_6F_5^a$), −164.0 (1F, *p*-$C_6F_5^a$), −164.7 (1F, *p*-$C_6F_5^b$), −167.0 (1F, *m*-$C_6F_5^b$), −167.4 (1F, *m*-$C_6F_5^b$), −168.1 (1F, *m*-$C_6F_5^a$), −168.7 (1F, *m*-$C_6F_5^a$).

X-ray Crystal Structure Analysis of ***11***. Formula $C_{32}H_{26}BF_{10}N\cdot {}^1/_2C_5H_{12}$, M = 661.42, colorless crystal 0.30 × 0.20 × 0.07 mm, a = 16.5180(8), b = 15.2872(6), and c = 25.8720(11) Å, β = 103.496(4)°, V = 6352.6(5) Å^3, ρ_{calc} = 1.383 g cm^{-3}, μ = 1.047 mm^{-1}, empirical absorption correction (0.744 ≤ T ≤ 0.930), Z = 8, monoclinic, space group $C2/c$ (No. 15), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 24 171 reflections collected (±h,±k,±l), [(sin θ)/λ] = 0.60 Å^{-1}, 5442 independent (R_{int} = 0.052) and 4167 observed reflections [$I \geq 2\,\sigma(I)$], 448 refined parameters, R = 0.052, wR^2 = 0.140, max (min) residual electron density 0.28 (−0.37) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms, solvent molecule refined using geometrical and thermal restraints.

NMR Analysis of ***5b***. ^1H NMR (500 MHz, CD_2Cl_2, 253 K): δ = 7.20 (m, 1H, *m*-Ph), 7.15 (m, 1H, *o*-Ph), 7.06 (m, 1H, *p*-Ph), 6.77 (s, 1H, 7-H), 3.45 (s, 2H, 5-H), 3.32 (s, 3H, NMe_2^Z), 3.20 (s, 3H, NMe_2^E), 3.03 (s, 2H, CH_2), 2.26 (m, 2H, $^{Ph}CH_2$), 1.31 (s, 6H, Me), 1.30 (br, 2H, $^{B}CH_2$). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 253 K): δ = 212.4 (br, C6), 204.3 (C8), 170.7 (C═N), 148.8 (*i*-Ph), 147.9 (dm, $^1J_{FC} \approx$ 239 Hz, C_6F_5), 137.5 (dm, $^1J_{FC} \approx$ 245 Hz, C_6F_5), 136.5 (dm, $^1J_{FC} \approx$ 251 Hz, C_6F_5), 135.1 (C4), 128.1, 128.0 (*o*-, *m*-Ph), 127.8 (C7), 127.3 (br, *i*-C_6F_5), 124.5 (*p*-Ph), 53.0 (C2), 42.6, 42.5 (br, NMe_2), 42.6 (C5), 39.7 (C1), 34.5 ($^{Ph}CH_2$), 28.6 (br, $^{B}CH_2$), 26.8 (Me). $^{19}F\{^1H\}$ NMR (470 MHz, CD_2Cl_2, 253 K): δ = −133.5 (2F, *o*-C_6F_5), −165.5 (1F, *p*-C_6F_5), −167.9 (2F, *m*-C_6F_5).

Preparation of 13. A solution of **9a** (100.0 mg, 0.19 mmol) in dichloromethane (10 mL) was stirred for 5 min. Upon addition of HCl (2 M in Et_2O, 0.1 mL, 0.20 mmol) at room temperature, a colorless solution formed gradually. After the reaction mixture was stirred overnight, the solvent were removed under vacuum. The residue was then washed twice with a mixture (2 mL) of pentane and dichloromethane in a 3:1 ratio. All volatiles were removed in vacuo to yield **13** (77.4 mg, 73%). Crystals suitable for X-ray crystal structure analysis were obtained by gas diffusion of pentane into a solution of **6** in dichloromethane at −30 °C. Anal. Calcd for $C_{24}H_{19}BClF_{10}N$: C, 51.69; H, 3.43; N, 2.51. Found: C, 51.19; H, 4.11; N, 2.11. ^1H NMR (600 MHz, TDF, 298 K): δ = 3.53 (s, 3H, NMe_2^Z), 3.37 (s, 3H, NMe_2^E), 3.14, 3.12 (AB, $^2J_{HH}$ = 19.2 Hz, each 1H, 2-H), 2.93 (m, 1H, BCH), 2.92, 2.79 (each m, each 1H, 5-H), 2.74, 2.55 (each m, each 1H, 7-H), 1.23, 1.24 (each s, each 3H, Me). $^{13}C\{^1H\}$ NMR (151 MHz, TDF, 298 K): δ = 208.6 (C8), 182.5 (C═N), 148.5 (dm, $^1J_{FC} \approx$ 240 Hz, C_6F_5), 140.8 (C4), 139.0 (dm, $^1J_{FC} \approx$ 245 Hz, C_6F_5), 137.3 (dm, $^1J_{FC} \approx$ 246 Hz, C_6F_5), 126.4 (br, *i*-C_6F_5), 53.3 (C2), 43.6 (NMe_2^E), 43.3 (NMe_2^Z), 41.7 (C1), 37.8 (br, C6), 34.7 (C5), 34.5 (C7), 26.14, 26.07 (Me). $^{11}B\{^1H\}$ NMR (192 MHz, TDF, 298 K): δ = −1.4 ($\nu_{1/2} \approx$ 300 Hz). $^{19}F\{^1H\}$ NMR (470 MHz, TDF, 298 K): δ = 132.1 (2F, *o*-C_6F_5), 164.4 (1F, *p*-C_6F_5), 167.8 (2F, *m*-C_6F_5).

X-ray Crystal Structure Analysis of ***13***. Formula $C_{24}H_{19}BClF_{10}N\cdot {}^1/_2CH_2Cl_2$, M = 600.13, colorless crystal 0.50 × 0.10 × 0.07 mm, a = 9.4976(5), b = 12.4411(8), and c = 12.8064(8) Å, α = 88.834(4), β = 78.248(3), and γ = 74.602(5)°, V = 1427.40(15) Å^3, ρ_{calc} = 1.396 g cm^{-3}, μ = 2.787 mm^{-1}, empirical absorption correction (0.336 ≤ T ≤ 0.829), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 19 428 reflections collected (±h,±k,±l), [(sin θ)/λ] = 0.60 Å^{-1}, 4792 independent (R_{int} = 0.057) and 3882 observed reflections [$I \geq 2\,\sigma(I)$], 376 refined parameters, R = 0.079, wR^2 = 0.261, max (min) residual electron density 1.14 (−0.24) e Å^{-3} in the region of the disordered solvent molecule, hydrogen atoms calculated and refined as riding atoms, solvent molecule refined with split positions using geometrical and thermal restraints.

Preparation of 14. A solution of **9a** (100.0 mg, 0.19 mmol) in dichloromethane (10 mL) was stirred for 5 min. Upon addition of benzaldehyde (20.0 mg, 0.19 mmol) at room temperature, a white precipitate formed gradually. After the reaction mixture was stirred overnight, the precipitate was isolated via filtration. The residue was then washed twice with a mixture (2 mL) of pentane and dichloromethane (1:1). All volatiles were removed in vacuo to yield minor and major isomers in a ratio of 1:6 (60.0 mg, 50%), which were tentative assignment as **14** and **14′**. Crystals of **14** suitable for X-ray crystal structure analysis were obtained by gas diffusion of pentane into a solution of the isomer mixture in tetrahydrofuran at −30 °C. Anal. Calcd for $C_{31}H_{24}BNOF_{10}\cdot 0.25CH_2Cl_2$: C, 57.87; H, 3.81; N, 2.16. Found: C, 57.97; H, 3.61; N, 2.15. HRMS (ESI) exact mass for $[M+H]^+$ ($C_{38}H_{31}BNO_2F_{10}$): calcd m/z 734.2283, found 734.2297.

NMR Analysis of the Minor Isomer. ^1H NMR (500 MHz, TDF, 298 K): δ = 7.30 (m, 2H, *o*-Ph), 7.14 (m, 2H, *m*-Ph), 7.06 (m, 1H, *p*-Ph), 4.90 (d, $^3J_{HH}$ = 6.0 Hz, 1H, OCH), 3.54 (m, 1H, 7-H), n.o. (BCH), 3.39, 3.31 (each s, each 3H, NMe_2), 3.09, 3.03 (each d, $^2J_{HH}$ = 18.0 Hz, each 1H, 2-H), 2.63, 2.44 (each m, each 1H, 5-H), 1.19, 1.00 (each s, each 3H, Me). $^{13}C\{^1H\}$ NMR (126 MHz, TDF, 298 K): δ = 208.6 (C8), 182.8 (C═N), 148.1 (*i*-Ph), 141.6 (C4), 128.1 (*m*-Ph), 127.9 (*o*-Ph), 126.9 (*p*-Ph), 84.5 (OCH), 58.9 (C7), 53.7 (C2), n.o. (br, BCH), 43.7, 43.3 (NMe_2), 42.5 (C1), 33.8 (C5), 27.0, 26.8 (Me). ^{11}B NMR (160 MHz, TDF, 298 K): δ = 2.4 ($\nu_{1/2} \approx$ 50 Hz). ^{19}F NMR (470 MHz, TDF, 298 K): δ = −133.4 (2F, *o*-$C_6F_5^a$), −135.2 (2F, *o*-$C_6F_5^b$), −165.58 (1F, *p*-$C_6F_5^b$), −165.62 (1F, *p*-$C_6F_5^a$), −168.0 (2F, *m*-$C_6F_5^b$), −168.1 (2F, *m*-$C_6F_5^a$).

NMR Analysis of the Major Isomer. ^1H NMR (500 MHz, TDF, 298 K): δ = 7.32 (m, 2H, *o*-Ph), 7.12 (m, 2H, *m*-Ph), 7.07 (m, 1H, *p*-Ph), 4.85 (d, $^3J_{HH}$ = 8.7 Hz, 1H, OCH), 3.54 (br t, $^3J_{HH} \approx$ 8.5 Hz, 1H, 7-H), 3.50 (br quint, $^3J_{HH} \approx$ 8.5 Hz, 1H, BCH), 3.42, 3.27 (each s, each 3H, NMe_2), 2.91, 2.64 (each d, $^2J_{HH}$ = 18.4 Hz, each 1H, 2-H), 2.65, 2.59 (each dd, $^2J_{HH}$ = 15.2 Hz, $^3J_{HH}$ = 8.5 Hz, each 1H, 5-H), 1.11, 0.05 (each s, each 3H, Me). $^{13}C\{^1H\}$ NMR (126 MHz, TDF, 298 K): δ = 211.7 (C8), 181.7 (C═N), 146.6 (*i*-Ph), 143.8 (C4), 129.1 (*o*-Ph), 128.0 (*m*-Ph), 127.1 (*p*-Ph), 83.9 (OCH), 56.4 (C7), 53.2 (C2), 51.3 (br, BCH), 43.5, 43.4 (NMe_2), 43.1 (C1), 35.5 (C5), 29.0, 24.1 (Me). ^{11}B NMR (160 MHz, TDF, 298 K): δ = 1.3 ($\nu_{1/2} \approx$ 80 Hz). ^{19}F NMR (470 MHz, TDF, 298 K): δ = −133.1 (2F, *o*-$C_6F_5^a$), −133.7 (2F, *o*-$C_6F_5^b$), −164.8 (1F, *p*-$C_6F_5^b$), −165.4 (1F, *p*-$C_6F_5^a$), −167.7 (2F, *m*-$C_6F_5^b$), −168.0 (2F, *m*-$C_6F_5^a$).

X-ray Crystal Structure Analysis of ***14***. Formula $C_{31}H_{24}BF_{10}NO\cdot C_4H_8O$, M = 699.43, colorless crystal 0.12 × 0.10 × 0.10 mm, a = 20.4261(7), b = 10.3146(3), and c = 31.7887(11) Å, β = 103.898(2)°, V = 6501.4(4) Å^3, ρ_{calc} = 1.429 g cm^{-3}, μ = 1.104 mm^{-1}, empirical absorption correction (0.879 ≤ T ≤ 0.898), Z = 8, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 55 470 reflections collected (±h,±k,±l), [(sin θ)/λ] = 0.60 Å^{-1}, 10 652 independent (R_{int} = 0.117) and 5332 observed reflections [$I \geq 2\,\sigma(I)$], 891 refined parameters, R = 0.080, wR^2 = 0.265, max (min) residual electron density 0.69 (−0.46) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms, solvent molecules refined with split positions using geometrical and thermal restraints. Due to crystal quality, the accuracy of the analysis is poor.

■ ASSOCIATED CONTENT

Supporting Information. Text and figures giving further experimental and spectroscopic details and crystallographic data (CIF files) for **3c**, **7a**, **7b**, **10a**, **10b**, **11**, **13**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Review on metal-catalyzed hydrogen activation: (a) DuBois, M. R. *Chem. Rev.* **1989**, *89*, 1–9; See also recent reports: (b) Sweeney, Z. K.; Polse, J. L.; Bergman, R. G.; Andersen, R. A. *Organometallics* **1999**, *18*, 5502–5510; (c) Linck, R. C.; Pafford, R. J.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2001**, *123*, 8856–8857; (d) Kato, H.; Seino, H.; Mizobe, Y.; Hidai, M. *J. Chem. Soc., Dalton Trans.* **2002**, 1494–1499; (e) Sellmann, D.; Prakash, R.; Heinemann, F. W.; Moll, M.; Klimowicz, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 1877–1880; *Angew. Chem.* **2004**, *116*, 1913; (f) Jalón, F. A.; Manzano, B. R.; Caballero, A.; Carrión, M. C.; Santos, L.; Espino, G.; Moreno, M. *J. Am. Chem. Soc.* **2005**, *127*, 15364–15365; (g) Wilson, A. D.; Newell, R. H.; McNevin, M. J.; Muckerman, J. T.; Dubois, M. R.; Dubois, D. L. *J. Am. Chem. Soc.* **2006**, *128*, 358–366; (h) Nagaraja, C. M.; Parameswaran, P.; Jemmis, E. D.; Jagirdar, B. R. *J. Am. Chem. Soc.* **2007**, *129*, 5587–5596; (i) Ogo, S.; Kabe, R.; Uehara, K.; Kure, B.; Nishimura, T.; Menon, S. C.; Harada, R.; Fukuzumi, S.; Higuchi, Y.; Ohhara, T.; Tamada, T.; Kuroki, R. *Science* **2007**, *316*, 585–587; (j) Matsumoto, T.; Nakaya, Y.; Tatsumi, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 1913–1915; *Angew. Chem.* **2008**, *120*, 1939–1941; (k) Adams, R. D.; Captain, B. *Angew. Chem., Int. Ed.* **2008**, *47*, 252–257; *Angew. Chem.* **2008**, *120*, 258–263. (l) Armstrong, F. A.; Fontecilla-Camps, J. C. *Science* **2008**, *321*, 498–499. (m) Misumi, Y.; Seino, H.; Mizobe, Y. *J. Am. Chem. Soc.* **2009**, *131*, 14636–14637.

(2) Selected reviews on metal-catalyzed hydrogenation: (a) Bianchini, C.; Meli, A. *Acc. Chem. Res.* **1998**, *31*, 109–116. (b) Bayón, J. C.; Claver, C.; Masdeu-Bulto, A. M. *Coord. Chem. Rev.* **1999**, *193*−*195*, 73–145. (c) Clapham, S. E.; Hadzovic, A.; Morris, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2201–2237. (d) Cui, X.; Burgess, K. *Chem. Rev.* **2005**, *105*, 3272–3296. (e) Lau, C. P.; Ng, S. M.; Jia, G.; Lin, Z. *Coord. Chem. Rev.* **2007**, *251*, 2223–2237. (f) Minnaard, A. J.; Feringa, B. L.; Lefort, L.; De Vries, J. G. *Acc. Chem. Res.* **2007**, *40*, 1267–1277. (g) Morris, R. H. *Chem. Soc. Rev.* **2009**, *38*, 2282–2291. (h) Gridnev, I. D.; Imamoto, T. *Chem. Commun.* **2009**, 7447–7464. (i) Bartók, M. *Chem. Rev.* **2010**, *110*, 1663–1705.

(3) Some recent reports on metal-catalyzed hydrogenation: (a) Zhu, Y.; Fan, Y.; Burgess, K. *J. Am. Chem. Soc.* **2001**, *132*, 6249–6253. (b) Ito, M.; Hirakawa, M.; Osaku, A.; Ikariya, M. *Organometallics* **2003**, *22*, 4190–4192. (c) Sandoval, C. A.; Ohkuma, T.; Muñiz, K.; Noyori, R. *J. Am. Chem. Soc.* **2003**, *125*, 13490–13503. (d) Bullock, R. M. *Chem. Eur. J.* **2004**, *10*, 2366–2374. (e) Liu, X. Y.; Venkatesan, K.; Schmalle, H. W.; Berke, H. *Organometallics* **2004**, *23*, 3153–3163. (f) Guan, H.; Iimura, M.; Magee, M. P.; Norton, J. R.; Zhu, G. *J. Am. Chem. Soc.* **2005**, *127*, 7805–7814. (g) Casey, C. P.; Bikzhanova, G. A.; Cui, Q.; Guzei, I. A. *J. Am. Chem. Soc.* **2005**, *127*, 14062–14071. (h) Mebi, C. A.; Frost, B. J. *Organometallics* **2005**, *24*, 2339–2346. (i) Ito, M.; Sakaguchi, A.; Kobayashi, C; Ikariya, T. *J. Am. Chem. Soc.* **2007**, *129*, 290–291. (j) Sakamoto, M.; Ohki, Y.; Kehr, G.; Erker, G.; Tatsumi, K. *J. Organomet. Chem.* **2009**, *694*, 2820–2824. (k) Maegawa, T.; Akashi, A.; Yaguchi, K.; Iwasaki, Y.; Shigetsura, M.; Monguchi, Y.; Sajiki, H. *Chem. Eur. J.* **2009**, *15*, 6953–6963. (l) Reguillo, R.; Grellier, M.; Vautravers, N.; Vendier, L.; Sabo-Etienne, S. *J. Am. Chem. Soc.* **2010**, *132*, 7854–7855. (m) Seino, H.; Misumi, Y.; Hojo, Y.; Mizobe, Y. *Dalton Trans.* **2010**, *39*, 3072–3082.

(4) Selected reviews on metal-free reagents for hydrogen activation: (a) Stephan, D. W. *Dalton Trans.* **2009**, 3129–3136; (b) Sumerin, V.; Schulz, F.; Nieger, M.; Atsumi, M.; Wang, C.; Leskelä, M.; Pyykkö, P.; Repo, T.; Rieger, B. *J. Organomet. Chem.* **2009**, *694*, 2654–2660; (c) Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 46–76; *Angew. Chem.* **2010**, *122*, 50–81; See also recent reports: (d) Kenward, A. L.; Piers, W. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 38–41; *Angew. Chem.* **2008**, *120*, 38–42. (e) Li, B.; Xu, Z. *J. Am. Chem. Soc.* **2009**, *131*, 16380–16382. (f) Jiang, C.; Blacque, O.; Berke, H. *Organometallics* **2009**, *28*, 5233–5239. (g) Miller, A. J. M.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2010**, *132*, 3301–3303. (h) Schwendemann, S.; Tumay, T. A.; Axenov, K. V.; Peuser, I.; Kehr, G.; Fröhlich, R.; Erker, G. *Organometallics* **2010**, *29*, 1067–1069.

(5) C−H activation: (a) Goldberg, K. I.; Goldman, A. S. *ACS Symp. Ser.* **2004**, *885*, 440 pp. See also selected recent reviews on C−H activation: (b) Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731–1770; (c) Chen, X.; Engle, K. M.; Wang, D. H.; Yu, J. Q. *Angew. Chem., Int. Ed.* **2009**, *48*, 5094–5115; *Angew. Chem.* **2009**, *121*, 5196–5217. (d) Balcells, D.; Clot, E.; Eisenstein, O. *Chem. Rev.* **2010**, *110*, 749–823. (e) Jazzar, R.; Hitce, J.; Renaudat, A.; Sofack-Kreutzer, J.; Baudoin, O. *Chem. Eur. J.* **2010**, *16*, 2654–2672. (f) Conejero, S.; Paneque, M.; Poveda, M. L.; Santos, L. L.; Carmona, E. *Acc. Chem. Res.* **2010**, *43*, 572–580. (g) Gunay, A.; Theopold, K. H. *Chem. Rev.* **2010**, *110*, 1060–1081.

(6) Some recent reports on C−H activation: (a) Ess, D. H.; Nielsen, R. J.; Goddard, W. A., III; Periana, R. A. *J. Am. Chem. Soc.* **2009**, *131*, 11686–11688. (b) Vetter, A. J.; Rieth, R. D.; Brennessel, W. W.; Jones, W. D. *J. Am. Chem. Soc.* **2009**, *131*, 10742–10752. (c) Häller, L. J. L.; Page, M. J.; Macgregor, S. A.; Mahon, M. F.; Whittlesey, M. K. *J. Am. Chem. Soc.* **2009**, *131*, 4604–4605. (d) Lu, P.; Boorman, T. C.; Slawin, A. M. Z.; Larrosa, I. *J. Am. Chem. Soc.* **2010**, *132*, 5580–5581.

(7) Some recent reports on C−H bond activation/C−C bond formation: (a) Wu, J.; Cui, X.; Chen, L.; Jiang, G.; Wu, Y. *J. Am. Chem. Soc.* **2009**, *131*, 13888–13889; (b) Zhou, H.; Xu, Y. H.; Chung, W. J.; Loh, T. P. *Angew. Chem., Int. Ed.* **2009**, *48*, 5355–5357; *Angew. Chem.* **2009**, *121*, 5459–5461; (c) Nishikata, T.; Abela, A. R.; Huang, S.; Lipshutz, B. H. *J. Am. Chem. Soc.* **2010**, *132*, 4978–4979; (d) Li, Q.; Yu, Z. X. *J. Am. Chem. Soc.* **2010**, *132*, 4542–4543; (e) Nishikata, T.; Abela, A. R.; Lipshutz, B. H. *Angew. Chem., Int. Ed.* **2010**, *49*, 781–784; *Angew. Chem.* **2010**, *122*, 793–796. (f) de Petris, G.; Cartoni, A.; Troiani, A.; Barone, V.; Cimino, P.; Angelini, G.; Ursini, O. *Chem. Eur. J.* **2010**, *16*, 6234–6242.

(8) 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.

(9) Reviews: (a) Murray, R. W. *Acc. Chem. Res.* **1968**, *1*, 313–320. (b) Hilt, G.; Weske, D. F. *Chem. Soc. Rev.* **2009**, *38*, 3082–3091. See also: (c) Criegee, R. *Justus Liebigs Ann. Chem.* **1953**, *583*, 12.

(10) Selected recent reviews: (a) Hoveyda, A. H.; Zhugralin, A. R. *Nature* **2007**, *450*, 243–251; (b) Vougioukalakis, G. C.; Grubbs, R. H. *Chem. Rev.* **2010**, *110*, 1746–1787; (c) Basset, J. M.; Copéret, C.; Soulivong, D.; Taoufik, M.; Cazat, J. T. *Acc. Chem. Soc.* **2010**, *43*, 323–334; See also: (d) Grubbs, R. H. *Angew. Chem., Int. Ed.* **2006**, *45*, 3760–3765; *Angew. Chem.* **2006**, *118*, 3845–3850; (e) Schrock, R. R. *Angew. Chem., Int. Ed.* **2006**, 3748–3759; *Angew. Chem.* **2006**, *118*, 3832–3844.

(11) Xu, B.-H.; Kehr, G.; Fröhlich, R.; Erker, G. *Chem. Eur. J.* **2010**, *16*, 12538–12540.

(12) (a) Parks, D. J.; Spence, R. E. v. H.; Piers, W. E. *Angew. Chem., Int. Ed.* **1995**, *34*, 809–811; *Angew. Chem.* **1995**, *107*, 895–897; (b) Spence, R. E. v. H.; Parks, D. J.; Piers, W. E.; MacDonald, M.-A.; Zaworotko, M. J.; Rettig, S. J. *Angew. Chem., Int. Ed.* **1995**, *34*, 1230–1233; *Angew. Chem.* **1995**, *107*, 1337–1340. (c) Spence, R. E. v. H.; Piers, W. E.; Sun, Y.; Parvez, M.; MacGillivray, L. R.; Zaworotko, M. J. *Organometallics* **1998**, *17*, 2459–2469. (d) Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, *26*, 345–354. (e) Parks, D. J.; Piers, W. E.; Yap, G. P. A. *Organometallics* **1998**, *17*, 5492–5503.

(13) Review: (a) Wrackmeyer, B. *Coord. Chem. Rev.* **1995**, *145*, 125–156. See also: (b) Köster, R.; Seidel, G.; Süss, J.; Wrackmeyer, B. *Chem. Ber.* **1993**, *126*, 1107–1114. (c) Köster, R.; Seidel, G.; Klopp, I.; Krüger, C.; Kehr, G.; Süb, J.; Wrackmeyer, B. *Chem. Ber.* **1993**, *126*, 1385–1396. (d) Wrackmeyer, B.; Maisel, H. E.; Süss, J.; Milius, W. *Z. Naturforsch.*

1996, *51b*, 1320–1324. (e) Wrackmeyer, B.; Bhatti, M. H.; Ali, S.; Tok, O. L.; Bubnov, Y. N. *J. Organomet. Chem.* **2002**, *657*, 146–154. (f) Wrackmeyer, B.; Tok, O. L.; Khan, A.; Badshah, A. *Z. Naturforsch.* **2005**, *60b*, 251–257. (g) Wrackmeyer, B. *Heteroat. Chem.* **2006**, *17*, 188–208.

(14) (a) Meyer, F.; Schmidt, M. U.; Paetzold, P. *Chem. Ber.* **1995**, *128*, 947–951. (b) Paetzold, P.; Leuschner, E. *Z. Anorg. Allg. Chem.* **2002**, *628*, 658–660.

(15) (a) Chen, C.; Fröhlich, R.; Kehr, G.; Erker, G. *Chem. Commun.* **2010**, *46*, 3580–3582. (b) Ugolotti, J.; Kehr, G.; Fröhlich, R.; Erker, G. *Chem. Commun.* **2010**, *46*, 3016–3018. (c) Chen, C.; Kehr, G.; Fröhlich, R.; Erker, G. *J. Am. Chem. Soc.* **2010**, *132*, 13594–13595. (d) 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.

(16) Jiang, C.; Blacque, O.; Berke, H. *Organometallics* **2010**, *29*, 125–133.

(17) Xu, B.-H.; Kehr, G.; Fröhlich, R.; Nauha, E.; Erker, G. *Dalton Trans.* **2010**, *39*, 9973–9981.

(18) Hafner, K.; Vöpel, K. H.; Ploss, G.; König, C. *Org. Synth.* **1967**, *47*, 52–54.

(19) (a) Spies, P.; Erker, G.; Kehr, G.; Bergander, K.; Fröhlich, R.; Grimme, S.; Stephan, D. W. *Chem. Commun.* **2007**, 5072–5074. (b) Spies, P.; Kehr, G.; Bergander, K.; Wibbeling, B.; Fröhlich, R.; Erker, G. *Dalton Trans* **2009**, 1534–1541.

(20) (a) Olmstead, M. M.; Power, P. P.; Weese, K. J. *J. Am. Chem. Soc.* **1987**, *109*, 2541–2542; (b) Herberich, G. H.; Fischer, A. *Organometallics* **1996**, *15*, 58–67; (c) Hoefelmeyer, J. D.; Solé, S.; Gabbaï, F. P. *Dalton Trans.* **2004**, 1254–1258; (d) Chiu, C.-W.; Gabbaï, F. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 6878–6881; *Angew. Chem.* **2007**, *116*, 7002–7005.

(21) (a) Piers, W. E. *Adv. Organomet. Chem.* **2005**, *52*, 1–76. (b) Beringhelli, T.; Donghi, D.; Maggioni, D.; D'Alfonso, G. *Coord. Chem. Rev.* **2008**, *252*, 2292–2313 and references cited therein.

(22) Review: (a) Spangler, C. W. *Chem. Rev.* **1976**, *76*, 187–217; See also: (b) Gurskii, M. E.; Gridnev, I. D.; Il'ichev, Y. V.; Ignatenko, A. V.; Bubnov, Y. N. *Angew. Chem., Int. Ed.* **1992**, *31*, 781–783; *Angew. Chem.* **1992**, *104*, 762–764. (c) Gurskii, M. E.; Gridnev, I. D.; Geiderikh, A. V.; Ignatenko, A. V.; Bubnov, Y. N. *Organometallics* **1992**, *11*, 4056–4061. (d) Bubnov, Y. N.; Gurskii, M. E.; Gridnev, I. D.; Ignatenko, A. V. *J. Organomet. Chem.* **1992**, *424*, 127–132. (e) Gridnev, I. G.; Gurskii, M. E.; Ignatenko, A. V.; Bubnov, Y. N. *Organometallics* **1993**, *12*, 2487–2495. (f) Gurskii, M. E.; Gridnev, I. D.; Buevich, A. V.; Bubnov, Y. N. *Organometallics* **1994**, *13*, 4658–4660. (g) Gridnev, I. D.; Schreiner, P. R.; Gurskii, M. E.; Bubnov, Y. N.; Krasavin, A. O.; Mstislavski, V. I. *Chem. Commun.* **1998**, 2507–2508. (h) Tok, O. L.; Gridnev, I. D.; Korobach, E. M.; Bubnov, Y. N. *Chem. Commun.* **2000**, 311–312.

(23) (a) Gridnev, I. D.; Tok, O. L.; Gurskii, M. E.; Bubnov, Y. N. *Chem. Eur. J.* **1996**, *2*, 1483–1488. (b) Gridnev, I. D.; Tok, O. L.; Gridneva, N. A.; Bubnov, Y. N.; Schreiner, P. R. *J. Am. Chem. Soc.* **1998**, *120*, 1034–1043.

(24) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, UK, 1989.

(25) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*; Wiley-VCH: New York, 2001.

(26) Ahlrichs, R. et al. *TURBOMOLE*, version 5.9; Universität Karlsruhe, 2006; http://www.turbomole.com.

(27) Weigend, F.; Ahlrichs, R. *Phys. Chem., Chem. Phys.* **2005**, *7*, 3297–3305.

(28) Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *240*, 283–289.

(29) Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. *Phys. Rev. Lett.* **2003**, *91*, 146401.

(30) Grimme, S.; Antony, J.; Schwabe, T.; Mück-Lichtenfeld, C. *Org. Biomol. Chem.* **2007**, *5*, 741–758.

(31) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.

(32) Spies, P.; Fröhlich, R.; Kehr, G.; Erker, G.; Grimme, S. *Chem. Eur. J.* **2008**, *14*, 333–343.

(33) Grimme, S. *J. Chem. Phys.* **2006**, *124*, 034108.

(34) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083–1096.

(35) Fan, C.; Piers, W. E.; Parvez, M.; McDonald, R. *Organometallics* **2010**, *29*, 5132–5139.

(36) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 302–326.

(37) Otwinowski, D.; Borek, D.; Majewski, W.; Minor, W. *Acta Crystallogr.* **2003**, *A59*, 228–234.

(38) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467–473.

(39) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.