Characteristic Features of Neutral Cyclopropenylium-Like Compounds: Synthesis, Structure, and Chemical Behavior of a Cyclopropenylioborate Betaine

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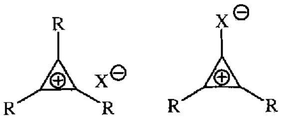
Bis(propynyl)zirconocene was treated with $B(C_6F_5)_3$ and then with two equivalents of *tert*-butyl isocyanide to yield the organometallic three-membered ring product **8**. Subsequent hydrolysis gives the substituted (2-iminioethylidene)cyclopropeneborate betaine system **9** that exhibits a pronounced cyclopropenylioborate betaine character. This follows from its characteristic structural features (X-ray crystal-structure analysis of the isomer *cis*-**9**) and its chemical features. Complex **9** undergoes a very facile *cis/trans* isomerization by formal rotation around the exocyclic partial CC-double bond ($\Delta G^{\ddagger}_{\text{rearr}} \approx 17$ kcal mol^{-1}). Compound **9** reacts cleanly in methanol solution with *tert*-butyl isocyanide by insertion and ring enlargement to form the four-membered ring system **12**. Compound **12** was also characterized by X-ray diffraction.

Introduction

Cyclopropenylium cations **1** are very interesting substrates as they constitute the smallest aromatic ring systems[1]. Of course, their chemistry is dominated to some extent by their positive charge. Therefore, it would be advantageous to have a variety of systems available to study their non-benzenoid aromatic character that exhibit cyclopropenylium character but are not ionic. With some limitations such features can be approached with the chemistry of e.g. the cyclopropenones[2] or the calicenes[3]. It would, however, be even more favourable to construct a cyclopropenylium system, such as **2**, that has the necessary counterion covalently bonded. Such a system would be a neutral, albeit polar molecule, that might exhibit a variety of the typical features of an aromatic carbocyclic three-membered ring system without actually having the chemical influences of a charged species.



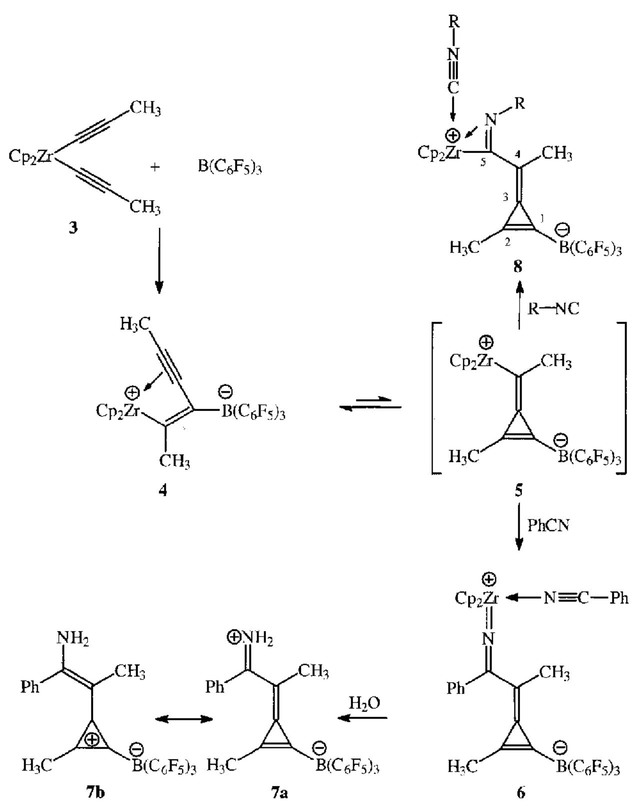
1 **2**

We have recently found a simple synthetic entry to a system that may bear some of the characteristics that are expected of a cyclopropenylium betaine system such as **2**. We had treated bis(propynyl)zirconocene (**3**)[4] with the organometallic Lewis acid tris(pentafluorophenyl)borane[5]. This led to coupling of the propynyl ligands and addition of the $B(C_6F_5)_3$ group to yield **4**[6]. This product appears to be in an (endothermic) equilibrium with a highly reactive metallated methylenecyclopropene system (**5**) by means of an intramolecular alkyne insertion into the zirconium carbon σ-bond, although **5** cannot be observed directly due to its high energy content. However, subsequent treatment with suitable insertion reagents traps **5** selectively from the equilibrium. Thus, the addition of e.g. phenylcyanide yields **6**[7], whose hydrolysis leads to the formation of the compound **7**, for which we have shown a structural participation of a cyclopropenylioborate betaine form (see Scheme 1)[8]. Similarly, treatment of the **4** ⇌ **5** equilibrium system with an isonitrile CN–R leads to the formation of the analogous (η^2-iminoacyl)zirconium-substituted methylenecyclopropene systems **8**, two examples of which [R = *tert*-butyl (**8a**)[9], R = 2,6-dimethylphenyl (**8b**)][6] were characterized by X-ray diffraction. We have now carried out the hydrolytic demetallation reaction of **8a** and obtained a *N*-substituted analogue of **7** that exhibits some typical structural and chemical features that would be expected from a neutral betaine system exhibiting a rather pronounced cyclopropenylium character. Details of this study are presented in this article.

Results and Discussion

The starting material used in this study was synthesized as previously described by us in detail. Treatment of zirconocene dichloride with two molar equivalents of propynyllithium gave the complex bis(propynyl)zirconocene (**3**) that was subsequently treated with one molar equivalent of $B(C_6F_5)_3$ to yield **4**. This then in turn was reacted with an excess of *tert*-butyl isocyanide to yield the product **8a** (R = CMe_3, see Scheme 1). Compound **8a** was unequivocally

Scheme 1

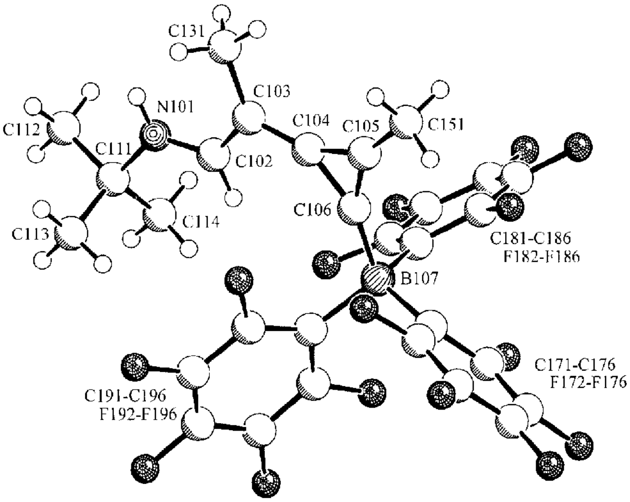


identified and characterized by an X-ray crystal structure analysis[9]. It contains a central methylenecyclopropene unit[10] that exhibits a slight tendency towards a cyclopropenylium-type structure inside the overall organometallic metallocene–μ-organyl–borate betaine arrangement [characteristic bond lengths are C1–C2 1.326(10), C2–C3 1.392(10), C1–C3 1.417(10), C3–C4 1.389(10), and C4–C5 1.426(10) Å]. The X-ray crystal structure analysis clearly shows the presence of a single isomer, that is characterized by an (*E*) arrangement of the pair of methyl groups at the planar central methylenecyclopropene unit (CH_3 groups bonded to C2 and C4, respectively, atom numbering scheme as used in Scheme 2). The iminoacyl functional group is η^2-coordinated to zirconium and there is an additional stabilizing *tert*-butyl isocyanide ligand coordinated to the electrophilic metal center[9,11].

We have now employed this material **8a** in a demetallation reaction. For this purpose the complex **8a** was suspended in toluene and treated with a large excess of methanol at 50–70°C for several minutes. This leads to a clean cleavage of the zirconium-to-carbon bond of **8a**, presumably with concomitant generation of dimethoxyzirconocene, and the formation of **9**. The product **9** was isolated in ca. 60% yield. An aliquot of the thus obtained material was dissolved in toluene, and pentane was allowed to slowly diffuse onto this solution in a closed system of connected Schlenk-flasks over a period of 3 days at ambient temperature. This gave single crystals that were suited for an X-ray crystal structure analysis.

There are two independent molecules of **9** in the crystal that are practically identical with regard to their structural features. Thus, in the text averaged bond angles and bond lengths are provided, whereas the legend of Figure 1 provides the values of the individual molecules 1 (numbers 101–) and 2 (numbers 201–). The crystal structure analysis shows that treatment of **8a** with methanol has resulted in a clean removal of the zirconocene moiety. The $B(C_6F_5)_3$ substituent is retained, however. The $B-C_6F_5$ structural features are unexceptional, they are as found in many other tris(pentafluorophenyl)borate units[12]. The B07–C06 bond length is 1.611(6) Å.

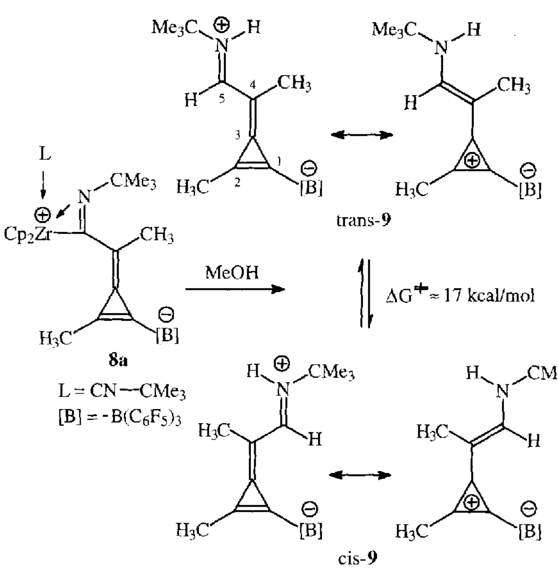
Figure 1. Molecular geometry of **9** with (unsystematic atom numbering scheme, only one of the crystallographically independent but chemically identical molecules is depicted)[a]



[a] Selected bond lengths [Å] and angles [°] of both individual molecules (molecule 1: 101–; molecule 2: 201–): C111–N101 1.484(6), C211–N201 1.477(6), N101–C102 1.316(5), N201–C202 1.326(6), C102–C103 1.382(6), C202–C203 1.370(6), C103–C104 1.387(6), C203–C204 1.395(6), C103–C131 1.501(6), C203–C231 1.510(6), C104–C105 1.383(6), C204–C205 1.373(6), C104–C106 1.415(5), C204–C206 1.399(6), C105–C106 1.350(6), C205–C206 1.356(6), C105–C151 1.471(6), C205–C251 1.481(7), C106–B107 1.611(6), C206–C207 1.610(6), B107–C_{aryl} 1.644(6), B207–C_{aryl} 1.642(6); C111–N101–C102 125.9(4), C211–N201–C202 125.3(4), N101–C102–C103 125.8(4), N201–C202–C203 126.3(4), C102–C103–C104 116.1(4), C202–C203–C204 116.5(4), C103–C104–C105 153.0(4), C203–C204–C205 152.3(4), C103–C104–C106 149.1(4), C203–C204–C206 149.2(4), C105–C104–C106 57.7(3), C205–C204–C206 58.6(3), C104–C105–C106 62.4(3), C204–C205–C206 61.7(3), C104–C106–C105 60.0(3), C204–C206–C205 59.7(3), C104–C106–B107 145.3(4), C204–C206–B207 147.1(4), C105–C106–B107 153.5(4), C205–C206–B207 152.0(4).

The central three-membered ring structure has been retained, but it clearly exhibits a strong tendency towards a cyclopropenylium-type structure[13]. This becomes evident by a comparison of the bond lengths inside the three-membered ring of **9** [C05–C06 1.353(6), C05–C04 1.378(6), C04–C06 1.407(6) Å] with those of **8a** (see above) and **7** [C1–C2 1.341(3), C2–C3 1.372(3), C1–C3 1.399(3) Å]. The equivalent contributions of the cyclopropenylioborate betaine and the (2-iminioethylidene)cyclopropeneborate betaine mesomeric structures of **8a** is further supported by the fact that the C04–C03 [1.391(6) Å] and C03–C02 [1.376(6) Å] bonds are almost identical [as in **7**: C3–C4

Scheme 2



1.396(3), C4–C5 1.383(3) Å]. The adjacent N01–C02 bond length in **9** is 1.321(5) Å.

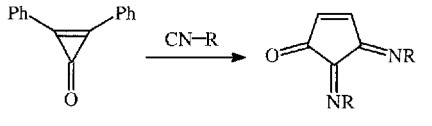
It is most noteworthy that the stereochemistry of the isomer of **9** (i.e. *cis*-**9**) found in the crystal is in two of its characteristic stereochemical descriptors inverted relative to its direct organometallic precursor **8a**. In **9** as in **8a** the substituents at the N–C linkage are oriented coplanarly. In **9** the carbon substituents at the partial N=C bond are *trans*-oriented, whereas in **8a** they are forced into a *cis*-relationship by the organometallic framework at the bent metallocene moiety.

More importantly, in **8a** the methyl substituents at the central methylenecyclopropene moiety are arranged in an (*E*) configuration. In **9**, as it is observed in the crystal, the methyl groups at the central planar methylenecyclopropene-type framework are (*Z*)-oriented. Apparently, the structural skeleton of **9** is electronically set up in such a way that a facile rotation around both the N01–C02 and the C03–C04 vectors is feasible thereby allowing two isomeric equilibrations to occur with a reasonable rate. This allows the system in all its stable isomers to attain the preferred *trans*-aldimine orientation that brings the bulky CMe_3 group at the sp^2-hybridized nitrogen atom and the C02–C03 vector in the energetically favourable *trans*-arrangement. Secondly, the rotation around the C03–C04 vector leads to the formation of *cis*- and *trans*-isomers of **9** (see Scheme 2). These are not expected to be isoenergetic, but they should probably be not too far apart from each other thermodynamically, so that both isomers might become observable in solution. From this equilibrium one isomer could just have been removed by the rather slow crystallization process and thus have become the isomer of **9** that was observed and characterized in the crystal structure analysis.

This situation has turned out to be true. The NMR analysis of the product as it is obtained from the methanolysis reaction (see above) has revealed the presence of a mixture of two isomeric compounds. The same mixture of isomers is obtained when the single crystals, obtained by diffusion method as described above, are dissolved and analyzed by NMR methods in solution. Both isomers have been shown by ^{1}H-NMR NOE measurements to feature the *tert*-butyl group at nitrogen and the aldimine C*H*=NR hydrogen in a *cis* orientation to each other. We thus conclude that both isomers contain (*E*)-configurated aldiminium moieties. They are apparently the expected isomers of **9** [i.e. *cis*-**9** and *trans*-**9**]. Which of the two corresponds to the observed isomer in the crystal has not been established unequivocally; tentatively we would ascribe the major isomer, observed in solution, the *cis* structure. The isomers are clearly distinguished by a number of pairs of ^{1}H-NMR and ^{13}C-NMR signals (for details see the Experimental Section). The mixture, however, only exhibits one set of $B(C_6F_5)_3$ ^{19}F-NMR resonances at $\delta = -133.0$ (*ortho*), -158.9 (*para*), and -164.1 (*meta*-F). Also, a single ^{11}B-NMR signal is observed (in [D$_6$]benzene at δ -18.3). As expected, the two isomers show slightly differentiated N–H bands in the IR spectrum (in KBr at $\tilde{\nu} = 3407$ and 3397 cm^{-1}) but only a single N=C band (1621 cm^{-1}).

The overall observed properties of the betaine **9** with regard to its (*E*/*Z*) isomerization must lead to the assumption that the thermally induced rotation around the C03–C04 vector is taking place rather rapidly in solution. We have consequently searched for indications of this isomerization to be observed in solution and have found some coalescence phenomena pointing to this equilibration becoming rapid on the ^{1}H-NMR time scale at high temperatures. In [D$_5$]bromobenzene solution at 300 K the isomers of **9** show a ca. 20:80 pair of singlets of the C31 methyl group (numbering as in Figure 1) at $\delta = 2.22$ and 2.15. Analogously, the NC(C*H*$_3$)$_3$ resonance is split into two singlets at $\delta = 0.97$ and 0.90 with an equal intensity ratio. Upon raising the temperature of the ^{1}H-NMR spectrometer probe stepwise from 300 to 360 K one observes an (unfortunate) continuous decrease of these two shift differences combined with a coalescence phenomenon that becomes clearly apparent by the fact that both the signals of the major isomer become broad and then sharp again. DNMR5 simulation[14] provided us with an estimate of the rate of this exchange process[15]. From these data an activation energy of this *cis*-**9** $\rightleftharpoons$ *trans*-**9** isomerization of $\Delta G^{\neq}$ (300 K) = 17 ± 1 kcal/mol^{-1} was derived. The *cis*-**9**/*trans*-**9** isomer ratio was determined in a variety of solvents of different solvent polarities by ^{1}H NMR at ambient temperature. There seems to be a tendency that leads to slightly increased amounts of the minor isomer with increasing solvent polarities (*cis*-**9**/*trans*-**9** = 88:12 in [D$_6$]benzene, 85:15 in $CDCl_3$, 82:18 in CD_2Cl_2, 81:19 in [D$_5$]bromobenzene, 81:19 in [D$_8$]toluene/[D$_4$]methanol (3:1), 73:27 in [D$_4$]methanol).

Thus, the rather facile *trans*-**9** $\rightleftharpoons$ *cis*-**9** isomerization supports the interpretation that this neutral betaine compound exhibits a rather pronounced cyclopropenylium character. This is further supported by the observation of a very typical isonitrile insertion reaction that leads to a ring enlarged four-membered product. This reaction (see below) is reminiscent to a variety of typical reactions of carbenium ion type substrates with isonitriles, such as they occur as single steps e.g. in the Passerini or the Ugi reaction[16]. In its characteristics it is related to the ring enlargement of cyclopropenones (e.g. **10**) upon treatment with isonitrile reagents[17].



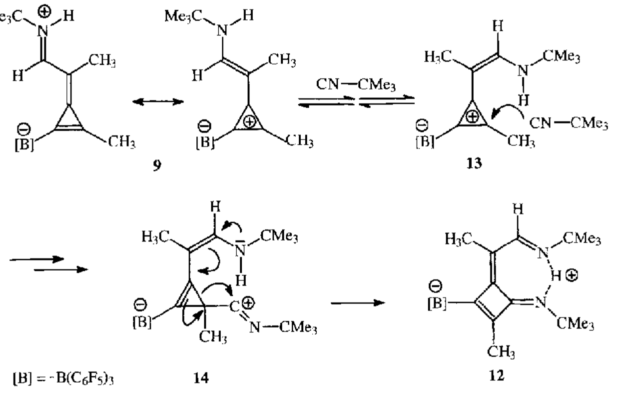
(1)

10 **11**

Complex **9** (*cis*/*trans* mixture) reacts slowly in methanol (or toluene/methanol mixtures), that contains an excess of *tert*-butyl isocyanide, with insertion of one equivalent of the isonitrile reagent into the three-membered ring to form the four-membered insertion product **12** (see Scheme 3). On a preparative scale the product **12** can very conveniently be prepared directly from the organometallic complex **8a** without isolating the intermediate **9** by a prolonged treatment with an excess of *tert*-butyl isonitrile in a toluene/methanol solvent mixture.

Under these conditions the yellow product **12** was obtained on a preparative scale in ca. 75% yield. The product contains a single isomer. It is characterized by ^{1}H-NMR signals (in [D$_8$]THF) at δ = 2.10 and 1.74 (s, each 3H, CH$_3$), 1.44 and 1.35 (s, each 9H, *tert*-butyl), an aldimine N=C*H* singlet at δ = 10.6 and a NH resonance at δ = 10.0.

Scheme 3

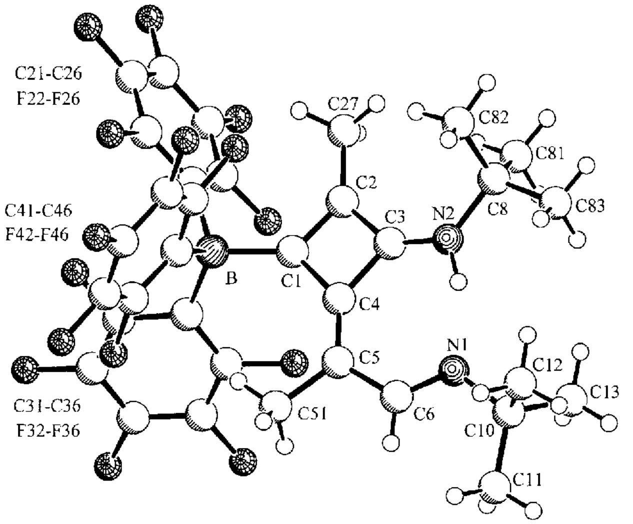


The connectivity of the framework of compound **12** was determined by ^{1}H/^{13}C NMR correlation, and was also secured by an X-ray crystal structure analysis.

Compound **12** exhibits a planar four-membered ring containing sp^2-hybridized carbon atoms. It contains a carbon−carbon double bond [C1−C2 1.383(3) Å] to which the borato substituent [C1−B 1.631(3) Å] and a methyl group are bonded [C2−C27 1.492(3) Å]. On the other hand the cyclobutene-moiety is at the same time part of a conjugated RN=C−C=C−C=NHR$^+$vinylenebiscarbaldiminium system.

The π-system is alternating with typical bond lengths 1.290(3) (N2−C3), 1.481 (3) (C3−C4), 1.340(3) (C4−C5), 1.475(3) (C5−C6), and 1.265(3) Å (C6−N1)[18]. The nitrogen atoms N2 and N1 are connected by means of a hydrogen bridge (N2−H 0.94, H···N1 1.81 Å, angle N2−H···N1 162.2°) that closes the seven-membered heterocyclic substructure of this section of the molecule. The remaining two carbon−carbon bonds inside the central four-membered ring are long, with 1.454(3) Å (C2−C3) and 1.506(3) Å (C1−C4) clearly being in the range of C(sp^2)−C(sp^2) single bonds[19]. Thus, the central structural framework represents a methylenecyclobutenone−imine system.

Figure 2. Molecular geometry of **12** in the crystal[a]



[a] Selected bond lengths [Å] and angles [°]: B−C$_{aryl}$ 1.653(3), B−C1 1.631(3), C1−C2 1.383(3), C1−C4 1.506(3), C2−C3 1.454(3), C2−C27 1.492(3), C3−N2 1.290(3), C3−C4 1.481(3), N2−C8 1.494(3), C4−C5 1.340(3), C5−C6 1.475(3), C5−C51 1.505(3), C6−N1 1.265(3), N1−C10 1.490(3); B−C1−C2 132.9(2), B−C1−C4 134.6(2), C1−C2−C3 92.2(2), C1−C4−C3 86.4(2), C2−C1−C4 91.5(2), C2−C3−C4 89.8(2), C2−C3−N2 140.6(2), C3−N2−C8 128.3(2), C1−C4−C5 138.3(2), C3−C4−C5 135.2(2), C4−C5−C6 124.4(2), C5−C6−N1 127.1(2), C6−N1−C10 121.3(2).

Conclusion

From its structural parameters, the dynamic features and its chemical behavior one must conclude that compound **9** is not adequately described by a limiting [3-(cyclopropenylidene)-2-butylidene]ammonium-type structure[20]. The substantially reduced π-bond alternation together with the facile *cis* ⇌ *trans* isomerization reactions (see Schemes 1 and 2) clearly indicate that **9** exhibits a rather pronounced cyclopropenylium character. Consequently, this neutral but, of course, polar compound cleanly undergoes a reaction, namely isonitrile insertion with ring enlargement to yield **12**, that is typical of such cyclopropenylium-type compounds (see equation (1) for a comparison[17]). It thus seems that compound **9** and its relatives that are readily available by our organometallic zirconocene template route[6−9] indeed constitute first examples of neutral cyclopropenylioborate betaine compounds, i.e. may be regarded as systems exhibiting the character of cyclopropenylium cations that bear their borate counteranion covalently bonded with them.

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Experimental Section

All reactions with organometallic substrates were carried out in an inert atmosphere (argon) using Schlenk type glassware or in a glovebox. Solvents (including deuterated solvents used for NMR spectroscopic characterization and for performing reactions under a direct NMR control) were dried and distilled under argon prior to use. For additional general information including a list of spectrometers used see ref.[6]. The *tert*-butyl isocyanide insertion product **8a** was prepared as recently described[9].

Hydrolysis of **8a** *and Preparation of* **9**: Complex **8a** (500 mg, 467 μmol) was suspended in 15 ml of toluene. Methanol (5 ml, 3.9 g, 126 mmol) was added and the mixture heated to ca. 50–70°C with stirring (higher temperatures lead to a rapid decomposition). After 5–15 min, a clear solution was obtained. The solution was cooled to room temperature and then stirred overnight. Solvent and all volatile materials were then removed in vacuo. The oily residue was solidified by stirring with pentane. The pentane phase was decanted and discarded. The resulting solid residue was treated with toluene and the organometallic precipitate removed by filtration. Toluene was removed from the clear filtrate in vacuo and the residue solidified by treatment with pentane to give 192 mg (61%) of a mixture of *cis*-**9** and *trans*-**9** (ratio 88:12 to 73:27, depending on the solvent used for the NMR characterization, for details see text), m.p. 150°C. – ^{1}H NMR ([D$_6$]benzene, numbering scheme used as in Scheme 2), major isomer: δ = 7.32 (d, ^3J = 15.3 Hz, 1H, $-CH{=}N$), 4.54 (br. d, ^3J = 15.3 Hz, 1H, NH), 1.76 (s, 3H, 2-CH_3), 1.13 (s, 3H, 4-CH_3), 0.61 (s, 9H, *tert*-butyl); minor isomer: δ = 6.78 (d, ^3J = 15.3 Hz, 1H, $-CH{=}N$), 4.49 (br. d, ^3J = 15 Hz, 1H, NH), 1.72 (s, 3H, 2-CH_3), 1.36 (s, 3H, 4-CH_3), 0.59 (s, 9H, *tert*-butyl). NOE difference spectrum (irradiated signal/resulting signal of enhanced intensity): $C(CH_3)_3$/NH (4%), 5-H (8%); dynamic ^{1}H-NMR spectra (DNMR5 simulation), 300 K: k_{rearr} = 4 s^{-1}/$\Delta G^{+}_{\mathrm{rearr}}$ = 16.7 kcal mol^{-1}, 305 K: 5/16.9; 310 K: 6/17.1; 320 K: 18/16.9, 330 K: 22/17.4; 340 K: 32/17.7; 350 K: 50/17.9; 360 K: 60/18.3, average (all values): $\Delta G^{\ddagger}_{\mathrm{rearr}}$ = 17.4 kcal mol^{-1}. – ^{13}C NMR ([D$_6$]benzene, numbering scheme used as in Scheme 2), major isomer: δ = 175.0 ($^1J_{CB}$ = 54 Hz, C1), 165.2 (C3), 155.7 (C2), 155.5 ($-CH{=}N$), 148.6 ($^1J_{CF}$ = 239 Hz), 139.9 ($^1J_{CF}$ = 250 Hz), 137.7 ($^1J_{CF}$ = 245 Hz, *o*-, *p*-, *m*-CF of C_6F_5), 119.7 (*ipso*-C of C_6F_5), 87.4 (C4), 53.5 (*C*Me$_3$), 28.9 [$C(CH_3)_3$], 11.2 (4-CH_3), 9.6 (2-CH_3); minor isomer: δ = 153.3 ($-CH{=}N$), 89.0 (C4), 29.1 [$C(CH_3)_3$], 10.2 (4-CH_3), remaining signals identical with major isomer. – ^{19}F NMR ([D$_6$]benzene): δ = −133.0, −158.9, −164.1 (*o*-, *p*-, *m*-C_6F_5). – ^{11}B NMR ([D$_6$]benzene): δ = −18.3. – UV/Vis (*c* = 7 mg/100 ml in dichloromethane): $\lambda_{\max}$ = 229 (ε 10350), 305 (ε 27860). – IR (KBr): $\tilde{\nu}$ = 3407, 3397 (NH), 3884, 2935, 1822, 1643, 1621 (C=N, tentative assignment), 1515, 1484, 1465, 1375, 1327, 1313, 1282, 1235, 1199, 1094, 982, 803, 688 cm^{-1}. – MS (EI, 70 eV): *m/z* (%) = 675 (45) [M^+], 660 (41) [$M^+ - CH_3$], 619 (54), 603 (44), 436 (44), 304 (38), 274 (50), 194 (55), 181 (49), 126 (47), 106 (57), 65 (51), 58 (75), 57 (100). – Elemental analysis, calcd. for $C_{29}H_{17}BF_{15}N$ (675.3): C 51.57, H 2.52, N 2.07; found C 51.71, H 2.80, N 2.48.

X-ray Crystal-Structure Analysis of cis-**9**: Single crystals were obtained by the diffusion method starting from a solution of **9** (mixture of isomers) in dichloromethane. Diffusion of pentane into this solution over a period of 3 d at ambient temperature gave the single crystals of *cis*-**9** that were used for the X-ray crystal structure analysis. Formula $C_{29}H_{17}BF_{15}N$, M = 675.25, 0.30 × 0.30 × 0.10 mm, a = 10.160(1), b = 15.870(2), c = 19.207(2) Å, α = 112.04(1), β = 100.85(1), γ = 90.12(1)°, V = 2810.3(5) Å^3, $\rho_{\mathrm{calcd.}}$ = 1.596 g cm^{-3}, μ = 14.66 cm^{-1}, empirical absorption correction via ψ-scan data ($0.928 \leqslant C \leqslant 0.999$), Z = 4, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223 K, $\omega/2\theta$ scans, 11889 reflections collected ($\pm h$, $+k$, $\pm l$), $[\sin\theta/\lambda]_{\max}$ = 0.62 Å^{-1}, 11455 independent and 7188 observed reflections [$I \geqslant 2\sigma(I)$], 846 refined parameters, R = 0.065, wR^2 = 0.184, max. residual electron density 0.37 (−0.31) e Å^{-3}, hydrogens calculated and riding.

Reaction of **9** *with tert-Butyl Isocyanide. – Preparation of* **12**: Compound **12** was prepared by two different protocols either starting from **9** or directly from **8a**, the latter procedure employs **9** generated in situ.

Synthesis Starting from **9**: 100 mg (148 μmol) of **9** (mixture of isomers) was dissolved in a mixture of 3 ml of toluene and 3 ml of methanol. *tert*-Butyl isocyanide (2 ml) was added and the mixture stirred for 3 d at room temperature. Solvent was then removed in vacuo from the intensely yellow colored solution and the residue washed twice with a little pentane to give 81 mg (57%) of **12**.

Synthesis Starting from **8c**: 400 mg (409 μmol) of the complex **8a** was suspended in toluene. Methanol (1 ml) and *tert*-butyl isocyanide (1 ml) were added and the mixture was then briefly heated to 80°C (5 min). The resulting clear solution was stirred for 12 h at room temperature. Volatiles were removed in vacuo and the residue solified by treatment with pentane. The solid was extracted with toluene to remove the organometallic methanolysis products. After filtration a clear yellow-orange colored solution was obtained. Solvent was removed in vacuo and the residue treated with a small amount of pentane to give 233 mg (75%) of **12** as a bright yellow solid, m.p. 182°C (decomp.). – ^{1}H NMR ($CDCl_3$), numbering scheme used as in Fig. 2: δ = 7.45 (br. s, 1H, $-CH{=}N$), 1.96 (s, 3H, 2-CH_3), 1.78 (s, 3H, 4-CH_3), 1.55 (s, 9H, *tert*-butyl), 1.29 (s, 9H, *tert*-butyl), NH not observed. – ^{11}B NMR (CD_2Cl_2): δ = −17.0. – ^{13}C NMR ([D$_8$]THF, 233 K, 150.8 MHz): δ = 181.2 (C4), 176.1 (C3), 164.3 (C6), 161.7 (C2), 148.3 ($^1J_{CF}$ = 242 Hz), 139.7 ($^1J_{CF}$ = 249 Hz), 137.1 ($^1J_{CF}$ = 240 Hz, *o*-, *p*-, *m*-C_6F_5), 124.0 (*ipso*-C of C_6F_5), 112.4 (C5), 60.0, 54.5 (*C*Me$_3$), 32.1, 28.1 [$C(CH_3)_3$], 17.9 (2-CH_3), 11.0 (4-CH_3), C1 not observed. – GHSQC-NMR[21] ([D$_8$]THF, 233 K, 150.8 MHz/600 MHz): δ = 164.3/10.65 (C6/6-H), 32.1/1.35 (*tert*-butyl), 28.1/1.44 (*tert*-butyl), 17.9/2.10 (2-CH_3/2-CH_3), 11.0/1.75 (4-CH_3/4-CH_3). – GHMBC-NMR[21] ([D$_8$]THF, 233 K, 150.8 MHz/600 MHz): δ = 181.2/1.74 (C4/4-CH_3), 176.1/2.10 (C3/2-CH_3), 164.3/1.74 (C6/4-CH_3), 161.7/2.10 (C2/2-CH_3), 112.4/1.74 (C4/4-CH_3), 59.96/1.44 and 54.46/1.35 (*tert*-butyl); – ^{19}F NMR ($CDCl_3$, 233 K): δ = −131.7, −133.4, −135.1, −136.5, −136.6, −138.1 (*o*-C_6F_5), −163.1, −163.7, −163.9 (*p*-C_6F_5), −167.5, −167.8, −168.8, −169.0, −169.25, −169.29 (*m*-C_6F_5). – UV/Vis (dichloromethane): $\lambda_{\max}$ = 232 (ε = 17700), 258 (shoulder, ε ca. 10000), 300 (ε 11000), 345 (ε 5500). – IR (KBr): $\tilde{\nu}$ = 2979, 2927, 2861, 1701 (C=C), 1634, 1612 and 1598 (C=N, tentative assignments), 1515, 1462, 1370, 1262, 1206, 1093, 979, 805 cm^{-1}. – MS (EI, 70 eV): *m/z* (%) = 758 (3) [M^+], 701 (18), 687 (12), 645 (9), 631 (12), 536 (11), 479 (20), 284 (23), 168 (5), 133 (12), 83 (12), 58 (16), 57 (100). – HRMS, calcd. for $C_{34}H_{26}BF_{15}N_2$: 758.1956, found 758.1981.

X-ray Crystal-Structure Analysis of **12**: Single crystals were obtained from a sample that contained both **9** and **12** in toluene solution. Slow diffusion of pentane into this solution over a period of 1 week at room temperature selectively gave clear yellow crystals of **12** that were used for the structure determination. Formula $C_{34}H_{26}BF_{15}N_2$, M = 758.38, 0.50 × 0.20 × 0.20 mm, a =

12.031(1), b = 12.253(1), c = 12.322(1) Å, α = 103.52(1), β = 92.96(1), γ = 105.11(1)°, V = 1692.8(2) Å^3, $\rho_{\mathrm{calcd.}}$ = 1.488 g cm^{-3}, μ = 1.45 cm^{-1}, empirical absorption correction via ψ-scan data ($0.946 \leqslant C \leqslant 0.999$), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223 K, $\omega/2\theta$ scans, 7154 reflections collected ($\pm h$, $-k$, $\pm l$), $[\sin \theta/\lambda]_{\max}$ = 0.62 Å^{-1}, 6821 independent and 4265 observed reflections [$I \geqslant 2\sigma(I)$], 480 refined parameters, R = 0.041, wR^2 = 0.098, max. residual electron density 0.25 (−0.21) e Å^{-3}, hydrogens calculated and riding. All data sets were collected with an Enraf Nonius CAD4 diffractometer. Programs used: data reduction MolEN, structure solution SHELXS-86, structure refinement SHELXL-93, graphics SCHAKAL-92. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100395. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@chemcrys.cam.ac.uk].

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