Chemical Behavior of a Pair of (COD)CpRh and −Ir Complexes with Pendant Peripheral $-B(C_6F_5)_2$ Groups†

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Received March 2, 2008

Hydroboration of (COD)Rh(η^5-C_5H_4-allyl) (**7**) with the strongly electrophilic reagent $HB(C_6F_5)_2$ yields (COD)Rh[η^5-C_5H_4-$(CH_2)_3B(C_6F_5)_2$] (**8**). Nucleophilic *N*-heterocyclic reagents (1-methylimidazole or 1-methylbenzimidazole) add to the boron atom of the bifunctional complex to yield the respective adducts (**9a**, **9b**). Both were characterized by X-ray diffraction. Addition of $HB(C_6F_5)_2$ to the corresponding (COD)Ir(η^5-C_5H_4-allyl) complex (**10**) eventually results in the formation and isolation of the cycloborylated zwitterionic (COD)(η^5-C_5H_3-*cyclo*-$(CH_2)_3B(C_6F_5)_2$]IrH product (**13**) (also characterized by X-ray crystal structure analysis). However, **13** seems to thermally equilibrate in a reverse electrophilic aromatic substitution reaction with the thermodynamically disfavored open-chain (COD)Ir[η^5-C_5H_4-$(CH_2)_3B(C_6F_5)_2$] isomer (**11**). This follows from reactions of **13** with 1-methylimidazole or 1-methylbenzimidazole, which rapidly yield the corresponding open-chain adducts **14a** and **14b** at room temperature (both characterized by X-ray diffraction). In a slow reaction complex **13** even eventually reacts with pyrrole by ring opening to yield the open-chain product **15**, which features the 2*H*-pyrrole isomer coordinated to the strong $-B(C_6F_5)_2$ Lewis acid at the end of the trimethylene tether. Complex **15** was also characterized by an X-ray crystal structure analysis.

Introduction

Metal complexes with pendant very electrophilic boryl groups attached to their periphery represent bifunctional transition metal/main group element systems of considerable interest.[1–3] The transition metal component can potentially act as a catalyst precursor. The main group electrophile can bind nucleophilic organic substrates and can potentially act as an intramolecular catalyst activator. However, a limited number of these systems have shown some unusual chemical behavior initiated by attack of the boron electrophile at a π-ligand,[4] most notably at the Cp ligand to which it is bonded by a tether. The [Zr/B] system **1** is a typical example.[5] Within hours after being generated by hydroboration of its respective alkenyl precursor, the complete conversion to the "Cp-cycloborate" system (**2**) was observed. We have recently reported a similar reaction in an iridium system (**3** → **4**) (see Scheme 1).[6]

We have now prepared a pair of group 9 (COD)MCp-X complexes (M = Rh, Ir) that each carry a pendant $-(CH_2)_3B(C_6F_5)_2$ substituent at the cyclopentadienyl ring. We have found some remarkable differences in chemical behavior between the rhodium and iridium examples. This will be described and discussed in this article.

† Dedicated to Professor Ernst-Ulrich Würthwein on the occasion of his 60th birthday.

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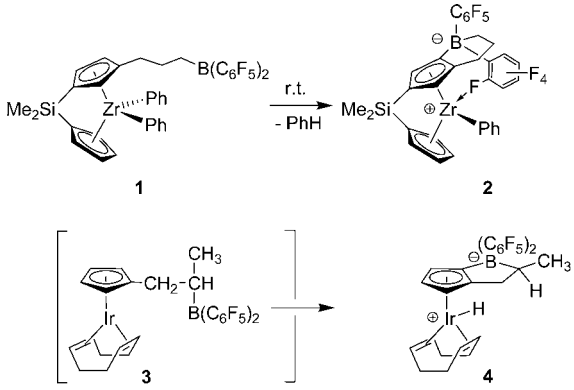
10.1021/om800195d CCC: $40.75
Publication on Web 04/15/2008

Scheme 1

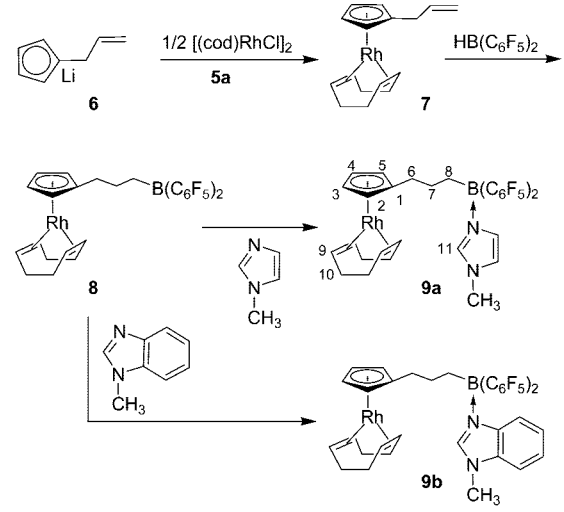


Results and Discussion

We started this study with the synthesis of the respective rhodium systems. For this purpose we reacted the η^4-cyclooctadienyl rhodium chloride dimer $[(COD)RhCl]_2$ (**5a**) with the (allyl-Cp)lithium reagent (**6**)[7] to yield the corresponding allyl-functionalized CpRh(I) complex (**7**) (see Scheme 2). The pendant alkenyl functionality was then subjected to the hydroboration reaction[8] using the $HB(C_6F_5)_2$ reagent[9,10] to yield the anticipated bifunctional [Rh/B] system **8**.

The hydroboration product **8** in our hands proved to be too sensitive for isolation as a clean neat substance. Therefore, it was generated in situ for spectroscopic characterization (see below) and for carrying out subsequent reactions. Analysis of the typical spectra of compound **8** in situ generated in d_2-dichloromethane (alternatively in d_6-benzene) showed that a regioselective $H-B(C_6F_5)_2$ addition to the pendant $-CH_2-CH=$

Scheme 2



CH_2 vinylic moiety had taken place with the usual "anti-Markovnikov" orientation. The ^{19}F NMR features are very typical for the presence of tricoordinated boron[11] in **8** [δ −129.8 (*o*), −147.4 (*p*), −160.9 (*m*)], as is the characteristic ^{11}B NMR resonance at δ 72.6. The $B(C_6F_5)_2$ unit is connected to the adjacent η^5-C_5H_4 ring [^{13}C NMR: δ 106.3 (*ipso*), and 86.9 (C2, C5), 85.7 (C3, C4) all three as doublets with $^1J_{RhC} = 3.8$ Hz] by a saturated trimethylene tether [^{13}C NMR: δ 32.5 (br, CH_2-[B]), 27.4, 30.9]. The η^4-1,5-COD ligand at Rh features a very characteristic set of three ^1H NMR resonances at δ 3.72 (br m, 4H, −CH=CH−) and δ 2.12, 1.89 (m, total of 8H, $-CH_2-CH_2-$) with a pair of corresponding ^{13}C NMR resonances at δ 64.3 ($^1J_{RhC} = 14.2$ Hz, −CH=) and δ 32.7 ($-CH_2-$).

Complex **8** rapidly adds *N*-heterocyclic donors to the boron center as expected.[12,13] We have prepared the respective 1-methylimidazole and 1-methylbenzimidazole adducts (**9a**, **9b**) by simply adding the respective heterocyclic reagents to a solution of **8** generated in situ in toluene solvent. Both systems were isolated and characterized spectroscopically (see Table 1), by elemental analysis, and by X-ray diffraction.

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Table 1. Selected NMR Data of the Complexes 9 and 14[a]

cmpd	M	lig	^{13}C9	^{13}C10	^{13}C/^{1}H11	^{1}H2/5	^{1}H3/4	^{19}F: *o,p,m*-B(C_6F_5)$_2$			^{11}B
9a[b]	Rh	im	63.7	32.4	136.0/7.69	5.09	4.91	−133.3	−159.9	−164.3	−6.1
9b[c]	Rh	bim	64.4	32.9	141.3/7.53	5.13	4.77	−133.1	−158.8	−164.1	−6.4
14a[c]	Ir	im	47.3	34.5	135.7/7.00	5.00	4.72	−133.4	−159.0	−164.1	−5.5
14b[c]	Ir	bim	47.4	34.4	141.2/7.55	5.00	4.71	−132.9	−158.3	−163.8	−5.9

[a] im = 1-methylimidazole, bim = 1-methylbenzimidazole, atom numbering see Scheme 2. [b] NMR spectra recorded in $CDCl_3$. [c] NMR spectra recorded in d_6-benzene.

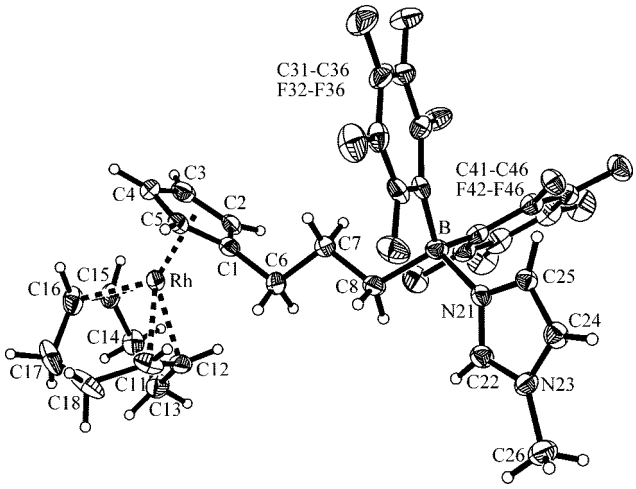


Figure 1. Molecular geometry of the [Rh/B]-1-methylimidazole adduct **9a**.

Table 2. Selected Structural Parameters of the Complexes 9 and 14[a]

	9a	**9b**	**14a**	**14b**
M	Rh	Rh	Ir	Ir
lig[b]	im	bim	im	bim
M−C1	2.211(3)	2.224(4)	2.208(3)	2.211(4)
M−C2	2.247(3)	2.256(4)	2.235(4)	2.260(5)
M−C3	2.239(3)	2.224(5)	2.236(4)	2.263(5)
M−C4	2.274(4)	2.271(5)	2.279(4)	2.210(5)
M−C5	2.266(3)	2.273(5)	2.253(3)	2.229(5)
M−C11	2.105(3)	2.116(4)	2.114(3)	2.108(4)
M−C12	2.106(3)	2.110(4)	2.118(4)	2.104(4)
M−C15	2.121(3)	2.128(4)	2.110(3)	2.111(4)
M−C16	2.132(3)	2.117(4)	2.114(3)	2.108(4)
C11−C12	1.400(5)	1.417(7)	1.430(5)	1.415(7)
C15−C16	1.398(5)	1.409(6)	1.431(6)	1.416(6)
C8−B	1.616(5)	1.622(6)	1.614(5)	1.625(5)
B−N21	1.623(4)	1.604(5)	1.614(4)	1.603(5)
C8−B−N21	106.6(3)	109.3(3)	107.7(3)	108.7(3)
B−N21−C22	125.5(3)	125.9(3)	125.0(3)	126.6(3)
C1−C6−C7−C8	177.1(3)	−72.8(5)	177.1(3)	73.3(5)
C6−C7−C8−B	167.4(3)	160.4(3)	167.2(3)	−160.6(3)
C7−C8−B−N21	169.1(3)	−70.2(4)	168.9(3)	69.7(4)
C2−C1−C6−C7	84.9(4)	90.3(5)	85.9(4)	84.1(5)

[a] Bond lengths in Å, angles and dihedral angles in deg. [b] im = 1-methyl imidazole, bim = 1-methylbenzimidazole.

Single crystals of **9a** were obtained from a d_2-dichloromethane solution. Complex **9a** features the structural parameters of a typical CpRh(COD) moiety. The monosubstituted C_5H_4 ring is uniformly η^5-coordinated to rhodium with Rh−C(Cp) bond lengths ranging from 2.211(3) to 2.274(4) Å (see Figure 1 and Table 2).[14] The bonds of the Rh center to the COD C(sp^2) carbons are shorter, ranging from 2.105(3) to 2.132(3) Å. The trimethylene tether at the Cp ring is found in a fully extended all-antiperiplanar conformation. The boron center at its end is pseudotetrahedrally coordinated to C8, the *ipso* carbon atoms of a pair of $-C_6F_5$ groups (B−C31: 1.636(5) Å, B−C41: 1.647(5) Å), and the 1-methylimidazole nitrogen center [bond angles at B: C8−B−N21: 106.6(3)°, C31−B−C41: 113.5(3)°, C31−B−C8: 108.4(3)°, C31−B−N21: 107.4(3)°, C41−B−N21: 104.3(2)°, C41−B−C8: 115.9(3)°]. The ligand nitrogen center (N21) bonded to boron is planar-tricoordinate (angles B−N21−C25: 127.7(3)°, B−N21−C22: 125.5(3)°, C22−N21−C25: 106.9(3)°). Complex **9a** adopts a conformation in the crystal that has the C1−C6 substituent vector at Cp oriented above the COD C11−C12 double bond.

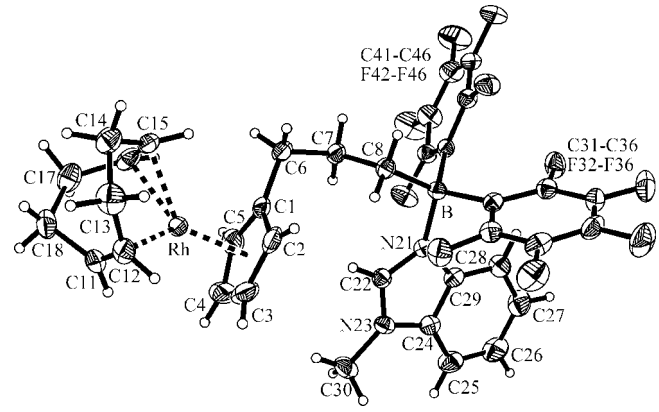
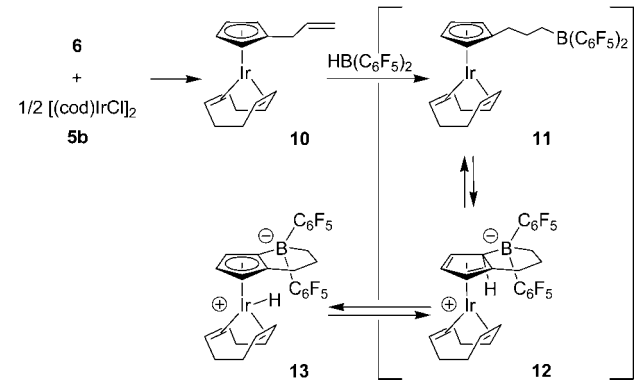


Figure 2. Molecular geometry of the 1-methylbenzimidazole [Rh/B] complex **9b**.

Scheme 3



The 1-methylbenzimidazole [Rh/B] complex **9b** (see Figure 2 and Table 2) shows similar structural features. However, it adopts a different conformation of the trimethylene tether in the crystal as compared to **9a**.

We then set out to study the chemistry of the analogous bifunctional iridium/boron systems but encountered some remarkable differences between these two series. The synthesis was started with the reaction of the (Cp-allyl)lithium reagent (**6**) with the (COD)Ir chloride dimer [(COD)IrCl]$_2$ (**5b**) to give (Cp−CH_2−CH=CH_2)Ir(COD) (**10**) as expected (see Scheme 3). Its subsequent hydroboration reaction with HB(C_6F_5)$_2$ was carried out under similar conditions to those in the Rh series, only that pentane was chosen as the solvent. Addition of HB(C_6F_5)$_2$ to (Cp-allyl)Ir(COD) (**10**) at room temperature gave

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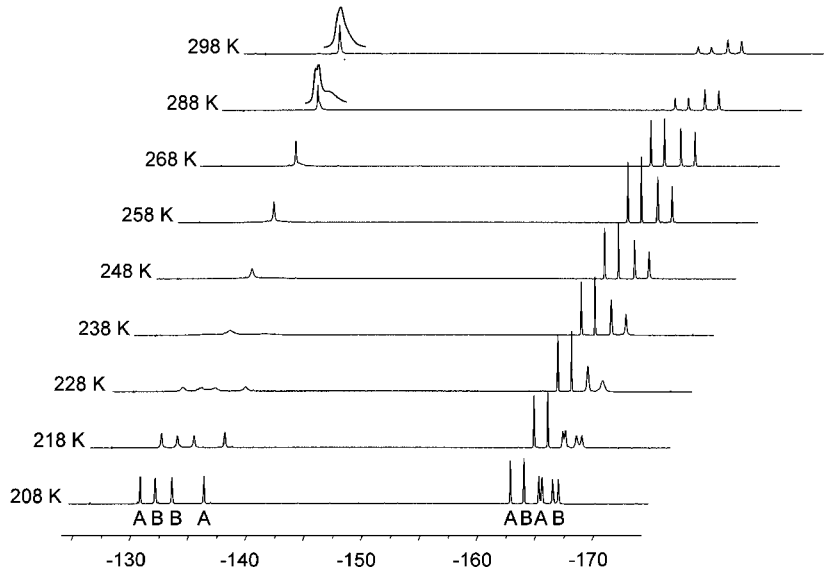

Figure 3. Dynamic ^{19}F NMR spectra of complex **13** (564.2 MHz in CD_2Cl_2).

a bright yellow solution, from which a white solid began to precipitate immediately. After the solution had completely decolorized, the white precipitate was collected and isolated in 85% yield. The subsequent analysis, including an X-ray crystal structure analysis of the product, revealed that we had not isolated the [Ir/B] system (**11**) with an extended $-(CH_2)_3B(C_6F_5)_2$ substituent but rather its ring-closed zwitterionic hydrido-Ir/borate isomer (**13**).

Product **13** features a set of four different COD $-CH=$ ^{1}H NMR signals (in $CDCl_3$ at 228 K: δ 4.64, 4.49, 3.77, and 3.57). There is a trimethylene unit (^{13}C NMR: δ 23.9, 22.4 20.1) connected to boron. The ^{11}B NMR shift (δ −16.9) is in a typical borate anion range. There are only three Cp (i.e., C_5H_3) ^{1}H NMR resonances (δ 5.80, 5.58, 5.24). Corresponding ^{13}C NMR signals of the CH(Cp) groups were located at δ 87.6, 89.4, and 83.2. One of the former Cp−H hydrogens is now found bonded to the iridium center. The Ir−H ^{1}H NMR resonance was located far "upfield" at δ −11.91.[15]

We thus conclude that **13** contains a borata-six-membered heterocyclic ring anellated with the Cp framework at iridium. Consequently, the $-C_6F_5$ substituents at boron are different, i.e., positioned *cis* or *trans* to iridium. In addition this crowded structural situation has led to an increased rotational barrier around both B−C_6F_5 vectors, so that the ^{19}F NMR spectrum at low temperature (208 K) features two pairs of diastereotopic *o*-fluorine resonances of the pair of $-C_6F_5$ substituents (δ −130.2/−135.7, −131.5/−132.9) in addition to one pair of *p*-F resonances (δ −162.2, −163.4) and two pairs of *m*-F signals (δ −164.7/−164.9, −165.8/−166.3) of the diastereotopic $-C_6F_5$ groups. We note that the small $\Delta(\delta\ m\text{-F})-(\delta\ p\text{-F})$ separation is very typical of a tetraorganylborate-type structure. Increasing the NMR monitoring temperature leads to coalescence of pairs of *o*-F and *m*-F ^{19}F NMR resonances (see Figure 3). As expected the *p*-F NMR signals do not show coalescence behavior. From this temperature-dependent dynamic ^{19}F NMR behavior Gibbs activation energies of $\Delta G^{\ddagger}_{rot}(233\ K) \approx 10.1 \pm 0.2$ kcal mol^{-1} were estimated for the hindered rotation around the *cis*- and *trans*-B−C_6F_5 vectors[16] in complex **13**.

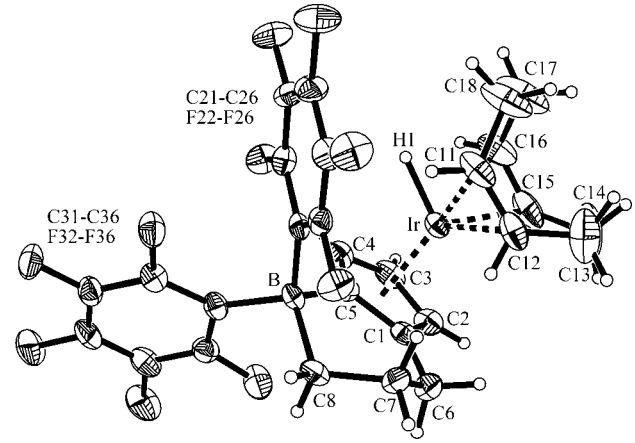

Figure 4. Projection of the molecular structure of complex **13**.

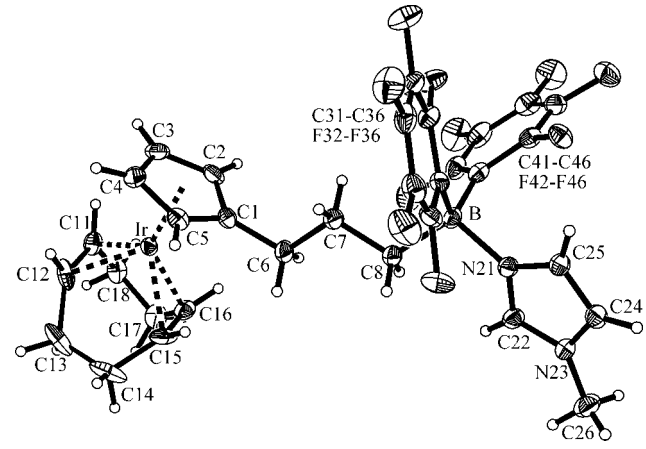

Figure 5. Molecular structure of complex **14a**.

The structural description of compound **13** was confirmed by an X-ray crystal structure analysis (single crystals were

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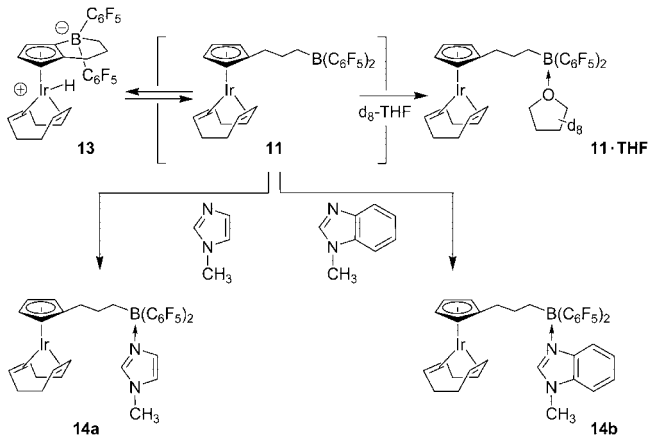
Scheme 4



obtained from a concentrated toluene solution). In complex **13** the iridium atom is coordinated to the pair of CC double bonds of the 1,5-cyclooctadiene ligand (bond lengths Ir1A−C11A: 2.209(5) Å [data of the independent molecule B in square brackets: Ir1B−C11B: 2.218(5) Å], Ir1A−C12A: 2.185(6) Å [2.208(5) Å], C11A−C12A: 1.378(9) Å [1.393(7) Å], Ir1A−C15A: 2.208(5) Å [2.190(5) Å], Ir1A−C16A: 2.216(5) Å [2.200(5) Å], C15A−C16A: 1.393 (9) Å [1.395(8) Å]). It is η^5-bonded to a disubstituted C_5H_3 ligand (Ir−C(Cp) bond lengths within 2.183(5) and 2.288(4) Å [2.183(5) and 2.304(5) Å]), and it is bonded to a hydrogen atom (Ir1A−H1A: 1.51(5) Å, Ir1B−H1B: 1.49(5) Å). A six-membered borata-heterocyclic ring system is anellated with the Cp ring. The C1A−C6A bond length is 1.494(7) Å [1.498(7) Å], and the C5A−B1A bond length amounts to 1.656(7) Å [1.645(7) Å]. The anellated heterocycle features a distorted shallow twist conformation (C1A−C5A: 1.451(7) Å [1.459(7) Å], angles C6A−C1A−C5A: 123.7(4)° [124.6(4)°] and C1A−C5A−B1A: 122.5(4)° [121.3(4)°]). The boron center in complex **13** is four-coordinate (bond angles C5A−B1A−C8A: 104.9(4)° [106.2(4)°], C21A−B1A−C31A: 111.9(4)° [105.0(4)°]).

These results indicate that the hydroboration reaction of **10** with $HB(C_6F_5)_2$ probably initially leads to the regioselective formation of the hydroboration product **11**. This, however, seems to be unstable under the applied reaction conditions with regard to an attack of the strong boron electrophile on its "own" electron-rich adjacent Cp ring. This initial step of an electrophilic aromatic substitution reaction[17] sequence probably generates the reactive intermediate **12**. Complex **12** has two attractive pathways for stabilization with re-formation of the aromatic Cp−π-electron sextet: Rupture of the newly formed C−B bond would lead back to **11**; deprotonation would lead to **13**. This pathway is followed with the iridium atom serving as a metal base[18] to abstract the adjacent proton from the substituted cyclopentadiene ligand in **12** to form the observed zwitterionic iridium hydride complex **13** (see Scheme 3).

There is some evidence that the formation of **13** from **11** via **12** is reversible. Most of this evidence comes from trapping reactions, i.e., the observation of reaction sequences where the addition of a suitable donor ligand to **13** eventually results in the rapid formation of the corresponding adduct of the elusive bifunctional isomer **11**.

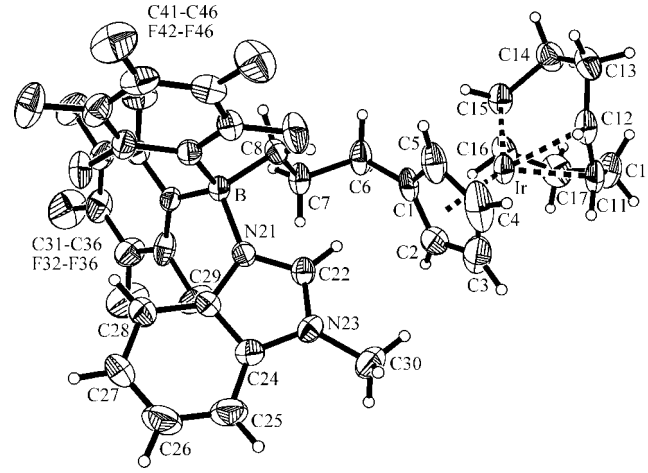


Figure 6. Molecular structure of complex **14b**.

Thus, we observed the formation of the adduct **11**·THF upon dissolving **13** in d_8-THF. We deduce this from the absence of the Ir−H ^{1}H NMR resonance and the observation of a 2:2 intensity pair (AA′BB′ spin system) of η^5-C_5H_4− ^{1}H NMR signals at δ 5.01, 4.92. Also, the typically increased molecular symmetry gives rise to monitoring only two COD ^{13}C NMR signals [δ 47.2 (C9) and 34.7 (C10)] for **11**·THF.

This seems to be a rather common reaction mode for complex **13**. Treatment with 1 molar equiv of 1-methylimidazole in toluene at room temperature led to the rapid formation of the donor adduct (**14a**) to the electrophilic boron center of the open isomer (**11**). Complex **14a** was isolated in ca. 80% yield from the reaction mixture. It features the typical spectroscopic data of a [(COD)IrCp-$CH_2CH_2CH_2B(C_6F_5)_2$]/1-methylimidazole adduct (see Table 1 and Scheme 4). We observed ^{11}B and ^{19}F NMR shifts characteristic of the B−N-type structure, a 2:2 intensity pair of C_5H_4− ^{1}H NMR resonances (δ 5.00/4.72; corresponding ^{13}C NMR signals at δ 82.3, 80.2; C-*ipso* at δ 103.6) and only one pair of COD ^{13}C NMR resonances (δ 47.3, 34.5, ^{1}H NMR signals at δ 3.74, 2.21/1.97).

Complex **14a** was characterized by X-ray diffraction (single crystals were obtained from d_6-benzene). The molecular structure of the iridium complex **14a** is very similar to that of its rhodium analogue **9a** (see the values listed in Table 2 for a comparison), only that the Ir−C(π) bond lengths seem to be slightly shorter. Even the conformation of the $-(CH_2)_3$-[B] tether is alike for the **14a/9a** pair of complexes. Only some conformational details around the [B]-1-methylimidazole unit seem to be marginally different.

We have also treated complex **13** with 1-methylbenzimidazole and isolated the open [B/N] adduct **14b** (68% yield). It was characterized spectroscopically (see Table 1) and by an X-ray crystal structure analysis (see Figure 6 and Table 2).

Complex **13** even reacts with pyrrole, although this aromatic five-membered heterocycle itself is not a donor ligand. However, its nonaromatic 2*H*-pyrrole isomer[19] is. In order to stabilize the boron center in the open [Ir/B] isomer **11**, isomerization to the "isopyrrole" reagent is required. This has been known to be effected[20,21] by the strong boron Lewis acid $B(C_6F_5)_3$.[22,23] Consequently, the reaction of complex **13** with pyrrole took ca.

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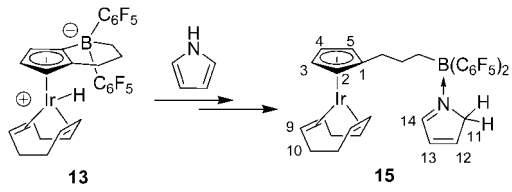
Scheme 5



13 **15**

3 days at room temperature to go to completion. We have isolated the corresponding open [Ir/B]-2*H*-pyrrole adduct **15** in ca. 70% yield (see Scheme 5).

The NMR spectra of product **15** show the presence of a reformed C_5H_4-ring system [^{1}H: δ 4.99 (2-H/5-H), δ 4.75 (3-H/4-H)] and a symmetrically coordinated η^4-COD ligand [^{1}H: δ 3.74 (m, 4H, 9-H), δ 2.21/1.99 (m, 8H, 10-H); ^{13}C: δ 47.3, 34.5]. No IrH resonance was observed. Most noteworthy are the NMR resonances of the 2*H*-pyrrole isomer coordinated to boron [^{1}H: δ 3.49 (2H, CH_2), δ 7.46, 5.37, 6.19 (14-H to 12-H); ^{13}C: δ 168.4 (C14), δ 153.5 (C12), δ 127.2 (C13)]. The ^{13}C NMR signal of the "isopyrrole" CH_2 group occurs at δ 64.8.[20,24]

Single crystals suitable for X-ray crystal structure analysis were obtained from a toluene solution of **15** layered with pentane. Complex **15** features the typical CpIr(COD) framework (see Figure 7) that has a fully extended $-(CH_3-)_3$[B] unit attached at the η^5-C_5H_4 ring [Ir−C(Cp) bond lengths ranging from 2.198(4) to 2.291(4) Å, Ir−C(COD) bond lengths within 2.105(4) to 2.141(4) Å]. The boron center in **15** is tetracoordinated (C8−B9: 1.609(6) Å, B−C31 1.659(6) Å, B−C41: 1.656(6) Å). It has the 2*H*-pyrrole ligand coordinated via its "imine-type" nitrogen atom (B−N10: 1.620(5) Å, angles C8−B9−N10: 107.6(3)°, B9−N10−C11: 126.9(3)°, B9−N10–14: 126.1(3)°, C11−N10−C14: 107.0(4)°). The typical bond lengths within the 2*H*-pyrrole unit[20,24] amount to N10−C14: 1.324(5) Å, C14−C13: 1.459(7) Å, C13−C12: 1.295(7) Å, C12−C11: 1.470(6) Å, and C11−N10: 1.396(5) Å. The bond angle at C11 is 107.4(4)° (N10−C11−C12).

Conclusions

The hydroboration of the (COD)M(Cp-allyl) complexes **7** (M = Rh) and **10** (M = Ir) with the very electrophilic $HB(C_6F_5)_2$ reagent proceeds with the expected "anti-Markovnikov" regioselectivity.[8,10] In both cases we generate a bifunctional group 9 metal/boron system. In the case of the Rh example the formation of the product (**8**) could actually be followed and the obtained compound characterized by NMR spectroscopy, although the system **8** in our hands proved to be too sensitive to be isolated as a pure compound.

Complex **8** contains a strongly electrophilic boron center. The Rh(I) center in **8** on the other hand is electron-rich.

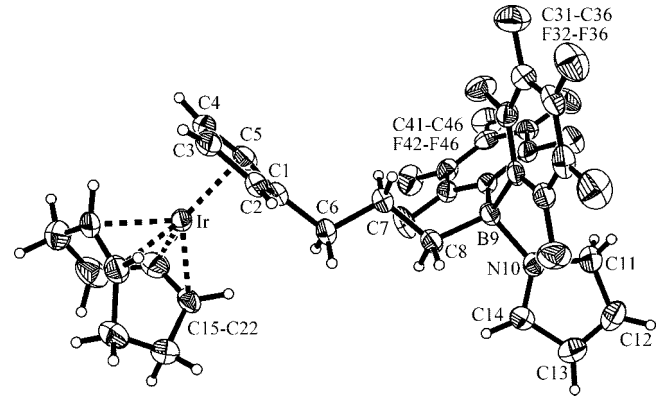


Figure 7. View of the molecular structure of complex **15**.

Therefore, the obtained bifunctional system may potentially be regarded as an intramolecular main group element/transition metal "frustrated" Lewis acid/Lewis base pair,[25] i.e., a pair where Lewis acid/Lewis base adduct formation (and thus quenching of their properties) is prevented by their steric bulk.[26] This does not, however, prevent their single components from reacting with other sterically less congested Lewis or Brønsted acids or bases, which may explain some of the sensitivity of the unique system **8**. Consequently, quenching of one of the reactive sites, here by adding heterocyclic nitrogen donor ligands to boron, results in the formation and isolation of very stable products.

The corresponding iridium system behaves in a more complicated fashion. We must assume that the initial hydroboration product (**11**) is formed as well, but in this case it is unstable with regard to an intramolecular electrophilic aromatic substitution reaction[17,23] at the adjacent Cp−Ir system to yield **13**. Presently it is not completely clear why this apparently very favorable reaction pathway has been observed for the iridium example but not for the closely related rhodium case. It may be that an increased metal basicity[18] of the Ir system might be a decisive factor.

The zwitterionic [Ir/B] system **13** is rather stable, but it is prone to undergo the reverse ring-opening reaction, probably initiated by proton transfer to the respective Cp *ipso*-carbon adjacent to boron. Because of the specific equilibrium position of the **13** ⇄ (**12**) ⇄ **11** system, reversal of the electrophilic aromatic substitution reaction can be observed only in cases where the product (**11**) on the disfavored side is effectively removed from the equilibrium by a suitable scavenger. Imine-type heterocyclic donor ligands serve this purpose very well.

The observation of the formation of **15** does point to the possibility that the very minor equilibrium component (**11**) can be actively involved in catalysis. In view of earlier observations it is likely that in this system the pyrrole → 2*H*-pyrrole tautomerization is catalyzed[20,21,24] by the reactive trivalent boron Lewis acid in **11**, which then subsequently traps the obtained isopyrrole ligand.[27] So it may be envisaged that the pair of isomers in such systems (here **13**/**11**) could serve as specific catalyst or reagents in future chemical transformations. This would give this type of observed

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isomerization reaction a role extended from just a mere protective reaction of a reactive bifunctional main group element/transition metal system.

Experimental Section

General Information. All syntheses were performed using dried solvents in an inert gas atmosphere (argon) using Schlenk-type glassware or a glovebox. Solvents were dried and distilled prior to use. The following instruments were used for physical characterization of the compounds: melting points: DSC 2010 (TA-Instruments); elemental analyses: Foss-Heraeus CHNO-Rapid; IR spectra: Varian 3100 FT-IR (Excalibur Series); NMR spectra: Bruker AC 200 P (^{11}B: 64.2 MHz), Bruker AMX400 (^{1}H: 400.1 MHz, ^{13}C: 100.6 MHz), Varian 500 MHz INOVA (^{1}H: 499.8 MHz, ^{13}C: 126 MHz, ^{19}F: 470.2 MHz), and Varian UNITYplus 600 (^{1}H: 599.6 MHz, ^{13}C: 150.8 MHz, ^{19}F: 564.2 MHz). ^{11}B spectra were referenced to an external $Et_2O \cdot BF_3$ sample; ^{19}F spectra were referenced to an external $CFCl_3$ sample. NMR assignments were supported by additional 2D experiments. X-ray diffraction: Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307−326), absorption correction SORTAV (R. H. Blessing, *Acta Crystallogr.* **1995**, *A51*, 33−37; R. H. Blessing, *J. Appl. Crystallogr.* **1997**, *30*, 421−426) and Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr.* **2003**, *A59*, 228−234), structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467−473), structure refinement SHELXL-97 (G. M. Sheldrick, Universität Göttingen, 1997), graphics XP (BrukerAXS, 2000).

(2-Propenyl)cyclopentadienyllithium,[28] bis(pentafluorophenyl)-borane,[9] chloro(1,5-cyclooctadiene)rhodium dimer,[29] and chloro(1,5-cyclooctadiene)iridium dimer[30] were prepared according to literature procedures.

Reaction of [(COD)RhCl]$_2$ (5a) with [allyl-Cp]Li (6); Preparation of 7. At room temperature THF (30 mL) was added carefully to a mixture of compound **5a** (978 mg, 1.98 mmol) and allylcyclopentadienyllithium (**6**) (445 mg, 4.0 mmol). The resulting solution was stirred overnight. The solvent was removed in vacuo and the residue taken up in pentane (100 mL). The suspension was filtered over neutral alumina and washed with pentane (200 mL). The solvent of the combined organic phases was removed in vacuo, and a yellow oil was yielded (849 mg, 67.7%). Anal. Calcd for $C_{16}H_{21}Rh$ (316.2): C, 60.77; H, 6.69. Found: C, 61.42; H, 6.88. ^{1}H NMR (d_6-benzene, 400.1 MHz, 298 K): δ 5.91 (ddt, $^{3}J_{HH}$ = 16.7, 10.0, 6.7 Hz, 1H, 7-H), 5.00 (m, 2H, 8-H), 4.96 (m, 2H, 2,5-H), 4.83 (m, 2H, 3,4-H), 3.84 (m, 4H, 9-H), 2.76 (d, $^{3}J_{HH}$ = 6.7 Hz, 2H, 6-H); 2.24 (m, 4H, 10-H), 1.97 (m, 4H, 10-H′). ^{13}C{^{1}H} NMR (d_6-benzene, 100.6 MHz, 298 K): δ 137.5 (C7), 115.3 (C8), 104.5 (d,$^{1}J_{RhC}$ = 4.0 Hz, C1), 87.1 (d, $^{1}J_{RhC}$ = 3.6 Hz, C2,5), 85.7 (d, $^{1}J_{RhC}$ = 4.0 Hz, C3,4), 64.0 (d, $^{1}J_{RhC}$ = 14.1 Hz, C9), 33.0 (C10), 32.5 (C6). IR (KBr): ν 3077 (m), 2983 (s), 2928 (s), 2872 (s), 2824 (s), 2036 (w), 1970 (w), 1638 (m), 1447 (m), 1425 (m), 1361 (w), 1323 (m), 1238 (m), 1153 (m), 1035 (w), 993 (s), 913 (s), 868 (s), 789 (s), 778 (sh), 566 (m), 486 (m) [cm^{-1}].

Reaction of Complex 7 with HB(C$_6$F$_5$)$_2$; Generation of Compound 8 (NMR-scale experiment). At room temperature a solution of complex **7** (26.1 mg, 0.08 mmol) in deuterated dichloromethane (1.5 mL) (alternatively in d_6-benzene) was added to bis(pentafluorphenyl)borane (28.6 mg, 0.08 mmol). Subsequent NMR measurements showed a complete conversion to **8**. Isolation of the compound could not be achieved. Upon drying in vacuo, a red oil was obtained, which quickly turned brown. **8**: ^{1}H NMR (CD_2Cl_2, 499.8 MHz, 298 K): δ 5.04 (m, 2H, 2,5-H), 4.90 (m, 2H, 3,4-H), 3.72 (br, 4H, 9-H), 2.18 (ps t, 2H, 6-H), 2.12 (m, 6H, 8,10-H), 1.89 (m, 4H, 10-H′), 1.82 (qui, $^{3}J_{HH}$ = 7.4 Hz, 2H, 7-H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 126 MHz, 298 K): δ 147.3 (dm, $^{1}J_{CF}$ = 247 Hz, *o*-C_6F_5), 143.7 (dm, $^{1}J_{CF}$ = 254 Hz, *p*-C_6F_5), 137.9 (dm, $^{1}J_{CF}$ = 251 Hz, *m*-C_6F_5), 114.6 (br, *i*-C_6F_5), 106.3 (d, $^{1}J_{RhC}$ = 3.8 Hz, C1), 86.9 (d, $^{1}J_{RhC}$ = 3.8 Hz, C2,5), 85.7 (d, $^{1}J_{RhC}$ = 3.8 Hz, C3,4), 64.3 (d, $^{1}J_{RhC}$ = 14.2 Hz, C9), 32.7 (C10), 32.5 (br, C8), 30.9 (C6), 27.4 (C7). ^{19}F NMR (d_6-benzene, 282.4 MHz, 298 K): δ −129.8 (m, 4F, *o*-C_6F_5), −147.4 (t, $^{3}J_{FF}$ = 21.0 Hz, 2F, *p*-C_6F_5), −160.9 (m, 4F, *m*-C_6F_5). ^{11}B{^{1}H} NMR (d_6-benzene, 64.2 MHz, 300 K): δ [ppm] 72.6 ($\nu_{1/2}$ = 720 Hz).

Reaction of in Situ-Generated Complex 8 with 1-Methylimidazole; Formation of the Adduct 9a. At room temperature a solution of complex **7** (14.7 mg, 0.05 mmol) in toluene (5 mL) was added to bis(pentafluorophenyl)borane (16.1 mg, 0.05 mmol). The suspension was stirred for several minutes until all solids were dissolved. Then the solution was added to 1-methylimidazole (3.8 mg, 0.05 mmol). Upon addition, the color of the reaction mixture changed from dark red to orange. Subequently the solvent was removed in vacuo and the residue washed with pentane (5 mL). After removing the solvent in vacuo the product was yielded as a pale yellow solid (12.5 mg, 36%). Crystals suitable for X-ray diffraction were obtained from a solution of **9a** in dichloromethane-d_2 in a NMR tube after one week. Mp: 204 °C. Anal. Calcd for $C_{32}H_{28}BF_{10}N_2Rh$ (744.3): C, 51.64; H, 3.79; N, 3.76. Found: C, 52.18; H, 3.88; N 3.78. ^{1}H NMR ($CDCl_3$, 599.6 MHz, 298 K): δ 7.69 (br, 1H, 11-H), 7.16 (br, 1H, 14-H), 6.90 (m, 1H, 13-H), 5.09 (m, 2H, 2,5-H), 4.91 (m, 2H, 3,4-H), 3.77 (s, 3H, 15-H), 3.69 (br, 4H, 9-H), 2.11(m, 4H, 10-H), 2.06 (t, $^{3}J_{HH}$ = 6.3 Hz, 2H, 6-H), 1.86 (m, 4H, 10-H′), 1.22 (m, 2H, 8-H), 1.19 (m, 2H, 7-H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150.8 MHz, 298 K): δ 147.9 (dm, $^{1}J_{CF}$ = 236 Hz, *o*-C_6F_5), 138.9 (dm, $^{1}J_{CF}$ = 248 Hz, *p*-C_6F_5), 137.0 (dm, $^{1}J_{CF}$ = 250 Hz, *m*-C_6F_5), 136.0 (C11), 125.9 (C14), 121.7 (br, *i*-C_6F_5), 121.1 (C13), 107.3 (d, $^{1}J_{RhC}$ = 3.6 Hz, C1), 86.8 (d, $^{1}J_{RhC}$ = 3.4 Hz, C2,5), 84.6 (d, $^{1}J_{RhC}$ = 3.8 Hz, C3,4), 63.7 (d, $^{1}J_{RhC}$ = 13.9 Hz, C9), 35.3 (C15), 32.4 (C10), 31.2 (C6), 27.9 (C7), 23.1 (br, C8). ^{19}F NMR ($CDCl_3$, 564.2 MHz, 298 K): δ −133.3 (m, 4F, *o*-C_6F_5), −159.6 (t, $^{3}J_{FF}$ = 20.5 Hz, 2F, *p*-C_6F_5), −164.3 (m, 4F, *m*-C_6F_5). ^{11}B{^{1}H} NMR ($CDCl_3$, 64.2 MHz, 300 K): δ −6.1 ($\nu_{1/2}$ = 380 Hz). IR (KBr): ν 3184 (w), 3166 (w), 3144 (w), 2990 (m), 2993 (m), 2882 (m), 2853 (m), 2365 (w), 2345 (w), 1643 (m), 1558 (w), 1541 (w), 1517 (s), 1454 (s), 1363 (w), 1281 (m), 1113 (s), 1088 (s), 999 (w), 969 (s), 871 (w), 811 (m), 793 (m), 753 (m), 677 (m), 621 (w) [cm^{-1}].

X-ray crystal structure analysis of 9a: formula $C_{32}H_{28}BF_{10}N_2Rh$, M = 744.28, colorless crystal 0.20 × 0.20 × 0.15 mm, a = 10.321(1) Å, b = 10.501(1) Å, c = 14.223(1) Å, α = 74.03(1)°, β = 74.60(1)°, γ = 82.79(1)°, V = 1426.5(2) Å^3, ρ_{calc} = 1.733 g cm^{-3}, μ = 0.692 mm^{-1}, empirical absorption correction (0.874 ≤ T ≤ 0.903), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 198 K, ω and φ scans, 16 516 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.66 Å^{-1}, 6764 independent (R_{int} = 0.072) and 5006 observed reflections [$I \geq 2\sigma(I)$], 416 refined parameters, R = 0.046, wR^2 = 0.112, max. residual electron density 0.74 (−1.07) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Reaction of in Situ-Generated Complex 8 with 1-Methylbenzimidazole; Formation of Adduct 9b. At room temperature a solution of complex **7** (57.9 mg, 0.18 mmol) in toluene (5 mL) was added to bis(pentafluorophenyl)borane (63.3 mg, 0.18 mmol). After stirring until all remaining solids were dissolved 1-methyl-

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benzimidazole (24.2 mg, 0.18 mmol) was added, whereupon the solution turned from a red color to yellow-orange. Then the solvent was removed in vacuo and the residue was washed with pentane (5 mL). After removal of the solvent in vacuo the product was obtained as a yellow powder (116.9 mg, 80.3%). Crystals suitable for X-ray diffraction were obtained from a concentrated solution of **9b** in dichloromethane. Mp: 195 °C. Anal. Calcd for $C_{36}H_{30}BF_{10}N_2Rh \cdot \frac{1}{2}C_7H_8$ (840.4): C, 56.45; H, 4.08; N, 3.33. Found: C, 56.34; H, 4.20; N, 3.71. ^{1}H NMR (d_6-benzene, 499.8 MHz, 298 K): δ 7.77 (dm, $^3J_{HH}$ = 7.9 Hz, 1H, 19-H), 7.53 (br, 1H, 11-H), 6.90 (m, 1H, 18-H), 6.87 (m, 1H, 17-H), 6.48 (dm, $^3J_{HH}$ = 8.2 Hz, 1H, 16-H), 5.13 (m, 2H, 2,5-H), 4.77 (m, 2H, 3,4-H), 3.86 (br, 4H, 9-H), 2.31 (s, 3H, 15-H), 2.26 (m, 4H, 10-H), 2.16 (t, $^3J_{HH}$ = 6.6 Hz, 2H, 6-H), 1.99 (m, 4H, 10-H′), 1.73 (br m, 2H, 8-H), 1.35 (m, 2H, 7-H). ^{13}C{^{1}H} NMR (d_6-benzene, 126 MHz, 298 K): δ 148.9 (dm, $^1J_{CF}$ = 236 Hz, *o*-C_6F_5), 141.3 (C11), 139.6 (dm, $^1J_{CF}$ = 253 Hz, *p*-C_6F_5), 137.4 (dm, $^1J_{CF}$ = 249 Hz, *m*-C_6F_5), 136.5 (C14), 132.9 (C13), 125.6 (C18), 125.3 (C17), 121.8 (br, *i*-C_6F_5), 116.8 (C19), 111.1 (C16), 107.3 (d, $^1J_{RhC}$ = 3.7 Hz, C1), 87.6 (d, $^1J_{RhC}$ = 3.4 Hz, C2,5), 85.5 (d, $^1J_{RhC}$ = 3.9 Hz, C3,4), 64.4 (d, $^1J_{RhC}$ = 14.1 Hz, C9), 32.9 (C10), 31.2 (C6), 30.9 (C15), 28.9 (C7), 21.9 (br, C8). ^{19}F NMR (d_6-benzene, 470.2 MHz, 298 K): δ −133.1 (m, 4F, *o*-C_6F_5), −158.8 (t, $^3J_{FF}$ = 20.6 Hz, 2F, *p*-C_6F_5), −164.1 (m, 4F, *o*-C_6F_5). ^{11}B{^{1}H} NMR (d_6-benzene, 64.2 MHz, 300 K): δ −6.4 ($\nu_{1/2}$ = 530 Hz). IR (KBr): ν 3749 (w), 3129 (w), 2926 (m), 2871 (m), 2826 (m), 2373 (w), 1644 (m), 1554 (m), 1516 (s), 1458 (vs), 1278 (m), 1198 (m), 1091 (s), 967 (s), 869 (w), 777 (w), 746 (m), 688 (w), 500 (w) [cm^{-1}].

X-ray crystal structure analysis of 9b: formula $C_{36}H_{30}BF_{10}N_2Rh \cdot CH_2Cl_2$, M = 879.27, yellow crystal 0.35 × 0.25 × 0.15 mm, a = 9.319(1) Å, b = 11.981(1) Å, c = 17.343(1) Å, α = 109.96(1)°, β = 94.35(1)°, γ = 100.45(1)°, V = 1769.9(3) Å^3, ρ_{calc} = 1.650 g cm^{-3}, μ = 0.718 mm^{-1}, empirical absorption correction (0.787 ≤ T ≤ 0.900), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 198 K, ω and φ scans, 16 583 reflections collected (±h, ± k, ± l), [(sin θ)/λ] = 0.67 Å^{-1}, 8451 independent (R_{int} = 0.064) and 7024 observed reflections [$I \geq 2\sigma(I)$], 479 refined parameters, R = 0.057, wR^2 = 0.158, max. residual electron density 1.07 (−1.76) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Reaction of [(COD)IrCl]$_2$ (5b) with [allyl-Cp]Li (6); Preparation of Complex 10. A solution of allylcyclopentadienyllithium (**6**) (340 mg, 3.03 mmol) in tetrahydrofuran (20 mL) was added to a solution of complex **5b** (980 mg, 1.46 mmol) in tetrahydrofuran (20 mL). The reaction mixture was refluxed for 60 min. Then the solvent was removed in vacuo and the residue was taken up in pentane (100 mL). Short column chromatography over neutral alumina (pentane) yielded the product as a colorless oil after removal of the solvent (969 mg, 82.0%). Anal. Calcd for $C_{16}H_{21}Ir$ (405.6): C, 47.38; H, 5.22. Found: C, 47.84; H, 5.29. ^{1}H NMR (d_6-benzene, 400.1 MHz, 298 K): δ 5.83 (ddt, $^3J_{HH}$ = 16.8, 10.1, 6.8 Hz, 1 H, 7-H), 4.96 (dm, $^3J_{HH}$ = 16.8 Hz, 1 H, 8-H), 4.94 (dm, $^3J_{HH}$ = 10.1 Hz, 1 H, 8-H′), 4.85 (m, 2 H, 2,5-H), 4.76 (m, 2 H, 3,4-H), 3.74 (m, 4 H, 9-H); 2.77 (d, $^3J_{HH}$ = 6.8 Hz, 2 H, 6-H), 2.21 (m, 4 H, 10-H), 1.96 (m, 4 H, 10-H′). ^{13}C{^{1}H} NMR (d_6-benzene, 100.6 MHz, 298 K): δ 137.4 (C7), 115.6 (C8), 100.4 (C1), 82.3 (C2,5), 80.7 (C3,4), 47.3 (C9), 34.5 (C10), 31.9 (C6). IR (KBr): ν 3461 (br), 3076 (w), 2967 (s), 2921 (s), 2872 (s), 2325 (s), 1637 (w), 1429 (w), 1318 (m), 1236 (w), 991 (m), 910 (s), 838 (s), 567 (w), 497 (m) cm^{-1}.

Preparation of Complex 13. At room temperature a solution of bis(pentafluorophenyl)borane (500 mg, 1.45 mmol) in pentane (15 mL) was added to a solution of complex **10** (587 mg, 1.45 mmol) in pentane (15 mL). The color of the reaction mixture turned a bright yellow, and precipitation of a white powder started. After stirring until the solution was completely decolorized, the precipitate was collected and washed with pentane (20 mL). The pure product was isolated as a white powder (930 mg, 85.0%). Crystals suitable for X-ray diffraction were obtained from a concentrated solution of **13** in toluene. Mp: 152 °C. Anal. Calcd for $C_{28}H_{22}BF_{10}Ir$ (751.5): C, 44.75; H, 2.95. Found: C, 44.36; H, 3.16. ^{1}H NMR ($CDCl_3$, 599.6 MHz, 228 K): δ 5.80 (m, 1H, 2-H), 5.58 (m, 1H, 3-H), 5.24 (m, 1H, 4-H), 4.64 (m, 1H, 14-H), 4.49 (m, 1H, 9-H), 3.77 (m, 1H, 10-H), 3.57 (m, 1H, 13-H), 2.34, 2.26 (each m, each 1H, 11-H), 2.23, 2.08 (each m, each 1H, 15-H), 2.22, 2.09 (each m, each 1H, 16-H), 2.20, 2.16 (each m, each 1H, 12-H), 2.56, 1.84 (each m, each 1H, 6-H), 1.58, 1.26 (each m, each 1H, 7-H), 1.01, 0.83 (each m, each 1H, 8-H), −11.91 (s, 1H, Ir−H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150.8 MHz, 228 K): 110.5 (C1), 89.4 (C3), 87.6 (C2), 83.2 (C4), 69.5 (C9), 68.4 (C10), 65.7 (C14), 65.0 (C13), 33.1 (C15), 32.5 (C16), 31.8 (C12), 31.5 (C11), 23.9 (C6), 22.4 (C7), 20.1 (br, C8), n.o. (C5, C_6F_5). ^{19}F NMR (CD_2Cl_2, 564.2 MHz, 208 K): δ −130.2, −135.7 (each m, each 1 F, *o*-$C_6F_5^A$), −131.5, −132.9 (each m, each 1 F, *o*-$C_6F_5^B$), −162.2 (t, $^3J_{FF}$ = 20.8 Hz, 1F, *p*-$C_6F_5^A$), −163.4 (t, $^3J_{FF}$ = 20.8 Hz, 1F, *p*-$C_6F_5^B$), −164.7, −164.9 (each m, each 1F, *m*-$C_6F_5^A$), −165.8, −166.3 (each m, each 1F, *m*-$C_6F_5^B$). ^{11}B{^{1}H} NMR ($CDCl_3$, 64.2 MHz, 300 K): δ −16.9 ($\nu_{1/2}$ = 94 Hz). IR (KBr): ν 2961 (m), 2923 (m), 2853 (m), 2373 (w), 2157 (w), 1641 (m), 1512 (s), 1457 (vs), 1265 (s), 1082 (s), 964 (s), 804 (m), 768 (m), 643 (w) cm^{-1}.

X-ray crystal structure analysis of 13: formula $C_{28}H_{22}BF_{10}Ir$, M = 751.47, colorless crystal 0.25 × 0.20 × 0.10 mm, a = 11.8637(2) Å, b = 13.7856(2) Å, c = 16.3812(4) Å, α = 105.611(1)°, β = 90.657(1)°, γ = 108.065(1)°, V = 2439.88(8) Å^3, ρ_{calc} = 2.046 g cm^{-3}, μ = 5.567 mm^{-1}, empirical absorption correction (0.337 ≤ T ≤ 0.606), Z = 4, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 198 K, ω and φ scans, 25 816 reflections collected (±h, ± k, ± l), [(sin θ)/λ] = 0.67 Å^{-1}, 11 794 independent (R_{int} = 0.055) and 8702 observed reflections [$I \geq 2\sigma(I)$], 727 refined parameters, R = 0.039, wR^2 = 0.094, max. residual electron density 1.61 (−1.82) e Å^{-3}, two almost identical independent molecules in the asymmetric unit, hydrogen atoms at Ir from difference Fourier calculations, others calculated and refined as riding atoms.

Reaction of Complex 13 with Methylimidazole; Formation of Adduct 14a. After stirring a solution of complex **13** (67.6 mg, 0.09 mmol) and methylimidazole (7.4 mg, 0.09 mmol) in toluene (3 mL) for 10 min, the solvent was removed in vacuo and the residue was washed with pentane (5 mL). The solvent was removed, the residue was dried in vacuo, and the product was isolated as a white powder (61.5 mg, 82.0%). Crystals suitable for X-ray diffraction were obtained from a solution of **14a** in deuterated benzene. Mp: 200 °C. Anal. Calcd for $C_{32}H_{28}BF_{10}N_2Ir$ (833.6): C, 46.11; H, 3.39; N, 3.36. Found: C, 46.22; H, 3.40; N, 3.35. ^{1}H NMR (d_6-benzene, 499.8 MHz, 298 K): δ 7.00 (s, 1H, 11-H), 6.71 (s, 1H, 14-H), 5.44 (m, 1H, 13-H), 5.00 (m, 2H, 2,5-H), 4.72 (m, 2H, 3,4-H), 3.74 (m, 4H, 9-H), 2.35 (t, $^3J_{HH}$ = 7.9 Hz, 2H, 6-H), 2.21 (m, 4H, 10-H), 1.97 (m, 4H, 10-H′), 1.91 (s, 3H, 15-H), 1.50 (m, 2H, 7-H), 1.44 (m, 2H, 8-H). ^{13}C{^{1}H} NMR (d_6-benzene, 126 MHz, 298 K): δ 148.5 (dm, $^1J_{CF}$ = 242 Hz, *o*-C_6F_5), 139.6 (dm, $^1J_{CF}$ = 252 Hz, *p*-C_6F_5), 137.7 (dm, $^1J_{CF}$ = 254 Hz, *m*-C_6F_5), 135.7 (C11), 125.2 (C14), 122.4 (br, *i*-C_6F_5), 120.8 (C13), 103.6 (C1), 82.3 (C2,5), 80.2 (C3,4), 47.3 (C9), 34.5 (C10), 33.4 (C15), 31.4 (C6), 28.5 (C7), 24.4 (br, C8). ^{19}F NMR (d_6-benzene, 564.2 MHz, 298 K): δ −133.4 (m, 4F, *o*-C_6F_5), −159.0 (t, $^3J_{FF}$ = 20.7 Hz, 2F, *p*-C_6F_5), −164.1 (m, 4F, *m*-C_6F_5). ^{11}B{^{1}H} NMR (d_6-benzene, 64.2 MHz, 300 K): δ −5.5 ($\nu_{1/2}$ = 427 Hz). IR (KBr): ν 3446 (br), 3183 (w), 3164 (w), 3096 (w), 2974 (m), 2933 (m), 2917 (m), 2853 (m), 1643 (m), 1557 (w), 1541 (w), 1517 (s), 1455 (s), 1280 (m), 1113 (s), 1088 (s), 959 (s), 810 (m), 779 (w), 751 (m). cm^{-1}.

X-ray crystal structure analysis of 14a: formula $C_{32}H_{28}BF_{10}IrN_2$, M = 833.57, colorless crystal 0.30 × 0.30 × 0.25 mm, a = 10.335(1) Å, b = 10.481(1) Å, c = 14.273(1) Å, α = 74.01(1)°, β = 74.64(1)°, γ = 83.01(1)°, V = 1431.2(2) Å^3, ρ_{calc} = 1.934 g

cm^{-3}, μ= 4.758 mm^{-1}, empirical absorption correction (0.329 ≤ T ≤ 0.383), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 198 K, ω and φ scans, 16 873 reflections collected (±h, ± k, ± l), [(sin θ)/λ] = 0.67 $Å^{-1}$, 6964 independent (R_{int} = 0.043) and 6540 observed reflections [$I \geq 2 \leq (I)$], 416 refined parameters, R = 0.028, wR^2 = 0.070, max. residual electron density 0.75 (−1.97) e $Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.

Reaction of Complex 13 with 1-Methylbenzimidazole; Formation of Adduct 14b. After stirring a solution of complex **13** (126.7 mg, 0.17 mmol) and methylbenzimidazole (22.3 mg, 0.17 mmol) in toluene (10 mL) for 10 min the solvent was removed in vacuo. The remaining solid was washed with pentane (10 mL), the solvent was removed, and the residue was dried in vacuo. The product was isolated as a white powder (100.4 mg, 68.0%). Crystals suitable for X-ray diffraction were obtained by gas phase diffusion of pentane into a solution of **14b** in toluene. Mp: 189 °C. Anal. Calcd for $C_{36}H_{30}BF_{10}NIr$ (883.6): C, 48.93; H, 3.42; N, 3.17. Found: C, 48.91; H, 3.52; N, 3.55. ^{1}H NMR (d_6-benzene, 499.8 MHz, 298 K): δ 7.79 (d, $^3J_{HH}$ = 8.3 Hz, 1H, 19-H), 7.55 (s, 1H, 11-H), 6.89 (ddd, $^3J_{HH}$ = 8.3, 7.3 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, 18-H), 6.85 (ddd, $^3J_{HH}$ = 8.3, 7.3 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, 17-H), 6.45 (d, $^3J_{HH}$ = 8.3 Hz, 1H, 16-H), 5.00 (m, 2H, 2,5-H), 4.71 (m, 2H, 3,4-H), 3.72 (m, 4H, 9-H), 2.27 (t, $^3J_{HH}$ = 7.3 Hz, 2H, 6-H), 2.22 (s, 3H, 15-H), 2.20 (m, 4H, 10-H), 1.96 (m, 4H, 10-H′), 1.71 (br t, $^3J_{HH}$ = 8.3 Hz, 2H, 8-H), 1.36 (m, 2H, 7-H). ^{13}C{^{1}H} NMR (d_6-benzene, 126 MHz, 298 K): δ 148.7 (dm, $^1J_{CF}$ = 237 Hz, *o*-C_6F_5), 141.2 (C11), 139.6 (dm, $^1J_{CF}$ = 281 Hz, *p*-C_6F_5), 137.6 (dm, $^1J_{CF}$ = 257 Hz, *m*-C_6F_5), 136.3 (C14), 132.8 (C13), 125.5 (C18), 125.3 (C17), 121.6 (br, *i*-C_6F_5), 117.0 (C19), 111.1 (C16), 103.4 (C1), 82.4 (C2,5), 80.4 (C3,4), 47.4 (C9), 34.4 (C10), 31.0 (C6), 30.8 (C15), 28.7 (C7), 22.7 (br, C8). ^{19}F NMR (d_6-benzene, 470.2 MHz, 298 K): δ −132.9 (m, 4F, *o*-C_6F_5), −158.3 (t, $^3J_{FF}$ = 21 Hz, 2F, *p*-C_6F_5), −163.8 (m, 4F, *m*-C_6F_5). ^{11}B{^{1}H} NMR (d_6-benzene, 64.2 MHz, 300 K): δ −5.9 ($\nu_{1/2}$ = 650 Hz). IR (KBr): ν 3122 (w), 2935 (br), 2874 (m), 2825 (m), 2379 (w), 2313 (w), 1649 (m), 1557 (m), 1517 (s), 1459 (s), 1260 (m), 1093 (m), 971 (m), 803 (w), 751 (w), 691 (w) cm^{-1}.

X-ray crystal structure analysis of 14b. formula $C_{36}H_{30}BF_{10}IrN_2 \cdot ½C_7H_8$, M = 929.70, colorless crystal 0.20 × 0.20 × 0.20 mm, a = 9.378(1) Å, b = 11.921(1) Å, c = 17.189(1) Å, α = 70.04(1)°, β = 79.63(1)°, γ = 79.52(1)°, V = 1761.6(3) $Å^3$, ρ_{calc} = 1.753 g cm^{-3}, μ = 3.876 mm^{-1}, empirical absorption correction (0.511 ≤ T ≤ 0.511), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223 K, ω and φ scans, 19 840 reflections collected (±h, ± k l), [(sin θ)/λ] = 0.67 $Å^{-1}$, 8469 independent (R_{int} = 0.046) and 7102 observed reflections [$I \geq 2\sigma(I)$], 505 refined parameters, R = 0.035, wR^2 = 0.081, max. residual electron density 1.19 (−1.30) e $Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.

Reaction of Complex 13 with Pyrrole; Formation of the 2*H*-Pyrrole Adduct 15. After stirring a solution of complex **13** (48.7 mg, 0.06 mmol) and pyrrole (4.3 mg, 0.06 mmol) in toluene (5 mL) for three days at room temperature, the solvent was removed in vacuo. The residue was washed with pentane (10 mL) and dried in vacuo. The product was obtained as an off-white powder (35 mg, 71.0%). Crystals suitable for X-ray diffraction were obtained by layering a solution of **15** in toluene with pentane. Mp: 142 °C. Anal. Calcd for $C_{32}H_{27}BF_{10}NIr$ (818.6): C, 46.95; H, 3.32; N, 1.71. Found: C, 47.19; H, 3.56; N, 1.56. ^{1}H NMR (d_6-benzene, 599.6 MHz, 298 K): δ 7.46 (s, 1H, 14-H), 6.19 (d, $^3J_{HH}$ = 5.4 Hz, 1H, 12-H), 5.37 (d, $^3J_{HH}$ = 5.4 Hz, 1H, 13-H), 4.99 (m, 2H, 2,5-H), 4.75 (m, 2H, 3,4-H), 3.74 (m, 4H, 9-H), 3.49 (br, 2H, 11-H), 2.30 (t, $^3J_{HH}$ = 7.6 Hz, 2H, 6-H), 2.21 (m, 4H, 10-H), 1.99 (m, 4H, 10-H′), 1.39 (m, 2H, 7-H), 1.19 (m, 2H, 8-H). ^{13}C{^{1}H} NMR (d_6-benzene, 150.8 MHz, 298 K): δ 168.4 (C14), 153.5 (C12), 148.3 (dm, $^1J_{CF}$ = 239 Hz, *o*-C_6F_5), 139.4 (dm, $^1J_{CF}$ = 250 Hz, *p*-C_6F_5), 137.5 (dm, $^1J_{CF}$ = 255 Hz, *m*-C_6F_5), 127.2 (C13), 121.3 (br, *i*-C_6F_5), 103.3 (C1), 82.2 (C2,5), 80.3 (C3,4), 64.8 (C11), 47.3 (C9), 34.5 (C10), 31.4 (C6), 28.4 (C7), 24.5 (br, C8). ^{19}F NMR (d_6-benzene, 564.2 MHz, 298 K): δ −133.4 (m, 4F, *o*-C_6F_5), −158.2 (t, $^3J_{FF}$ = 20.5 Hz, 2F, *p*-C_6F_5), −163.6 (m, 4F, *m*-C_6F_5). ^{11}B{^{1}H} NMR (d_6-benzene, 64.2 MHz, 300 K): δ −5.3 ($\nu_{1/2}$ = 290 Hz). IR (KBr): ν 3446 (br), 2920 (m), 2866 (w), 1644 (m), 1517 (m), 1456 (s), 1380 (w), 1277 (w), 1089 (s), 1013 (m), 1277 (w), 1118 (m), 1089 (s), 1013 (w), 963 (s), 909 (w), 813 (m), 699 (w) cm^{-1}.

X-ray crystal structure analysis of 15: formula $C_{32}H_{27}BF_{10}IrN$, M = 818.56, light yellow crystal 0.15 × 0.10 × 0.03 mm, a = 10.2691(1) Å, b = 19.2190(2) Å, c = 14.5208(2) Å, β = 96.108(1)°, V = 2849.58(6) $Å^3$, ρ_{calc} = 1.908 g cm^{-3}, μ = 4.776 mm^{-1}, empirical absorption correction (0.534 ≤ T ≤ 0.870), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223 K, ω and φ scans, 18 649 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.66 $Å^{-1}$, 6795 independent (R_{int} = 0.051) and 5072 observed reflections [$I \geq 2\sigma(I)$], 406 refined parameters, R = 0.033, wR^2 = 0.072, max. residual electron density 1.14 (−1.22) e $Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.

Reaction of Complex 13 with THF; Formation of Adduct 11 · THF (NMR-scale experiment). A solution of complex **13** (24 mg, 0.03 mmol) in deuterated tetrahydrofuran was characterized by ^{1}H, ^{13}C, ^{11}B, and ^{19}F experiments. ^{1}H NMR (d_8-THF, 499.8 MHz, 298 K): δ 5.01 (m, 2H, 2,5-H), 4.92 (m, 2H, 3,4-H), 3.49 (m, 4H, 9-H), 2.15 (m, 2H, 6-H), 1.94 (m, 4H, 10-H), 1.74 (m, 4H, 10-H′), 1.22 (m, 4H, 7,8-H). ^{13}C{^{1}H} NMR (d_8-THF, 126 MHz, 298 K): δ 149.0 (dm, $^1J_{CF}$ = 243 Hz, *o*-C_6F_5), 140.5 (dm, $^1J_{CF}$ = 250 Hz, *p*-C_6F_5), 137.9 (dm, $^1J_{CF}$ = 251 Hz, *m*-C_6F_5), 119.0 (br, *i*-C_6F_5), 104.1 (C1), 82.7 (C2,5), 80.6 (C3,4), 47.2 (C9), 34.7 (C10), 31.7 (C6), 28.2 (C7), 24.4 (br, C8). ^{19}F NMR (d_8-THF, 470.2 MHz, 298 K): δ −133.7 (m, 4F, *o*-C_6F_5), −159.9 (t, $^3J_{FF}$ = 20 Hz, 2H, *p*-C_6F_5), −165.4 (m, 4F, *m*-C_6F_5). ^{11}B{^{1}H} NMR (d_8-THF, 64.2 MHz, 300 K): δ 6.6 ($\nu_{1/2}$ = 720 Hz).

Acknowledgment. Financial support from the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Supporting Information Available: CIF files giving details of the X-ray crystal structure analysis (**9a**, **9b**, **13**, **14a**, **14b**, and **15**) and text giving additional information about spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800195D