Syntheses and Insertion Reactions of (η^2-Aldehyde)zirconocene-Supported (Hydrido)zirconocene Cation Systems

Ulrich Blaschke,[a] Frederik Menges,[a] Gerhard Erker,*[a] and Roland Fröhlich[a]

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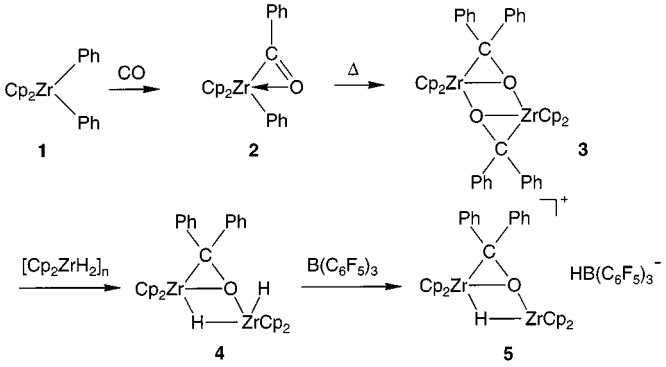
Treatment of the $[Cp_2Zr(\eta^2\text{-acetaldehyde})/H(CH_3)ZrCp_2]$ adduct **8** with $B(C_6F_5)_3$ yields the dimetallabicyclic salt $[Cp_2Zr(\mu\text{-}\eta^1\text{-}O{:}\eta^2\text{-}C,O\text{-}OCHMe)(\mu\text{-}H)(ZrCp_2)]^+[CH_3B(C_6F_5)_3]^-$ **18b**. Similarly, hydride abstraction from the related neutral dimetallabicyclic $[Cp_2Zr(OCHR)/H_2ZrCp_2]$ adducts **11** (R = CH_3) or **14** (R = C_2H_5) with $B(C_6F_5)_3$ yields the systems $[Cp_2Zr(\mu\text{-}\eta^1\text{-}O{:}\eta^2\text{-}C,O\text{-}OCHR)(\mu\text{-}H)(ZrCp_2)]^+[HB(C_6F_5)_3]^-$ (**18a**, **c**) and the reaction of $B(C_6F_5)_3$ with $[Cp_2Zr(OCHCH_2Ph)/H(PhCH_2)ZrCp_2)]^+$ **17** gives $[Cp_2Zr(\mu\text{-}\eta^1\text{-}O{:}\eta^2\text{-}C,O\text{-}(OCHCH_2Ph)(\mu\text{-}H)ZrCp_2]^+[PhCH_2B(C_6F_5)_3]^-$ **18d**. A variety of nitriles $R^2\text{–}C{\equiv}N$ (R = CH_3, CMe_3, *p*-tolyl, or ethyl) cleanly reacts with the cations **18** by addition of the $Zr_2(\mu\text{-}H)$ moiety to the nitrile functionality to yield the respective aldiminium-bridged cations $[Cp_2Zr(\mu\text{-}\eta^1\text{-}O{:}\eta^2\text{-}C,O\text{-}(OCHR^1)(\mu\text{-}N{=}CHR^2)\text{-}ZrCp_2]^+$ (**21**–**24**). Complex **24d** (R^1 = $PhCH_2$, R^2 = C_2H_5) was characterized by an X-ray crystal structure analysis. Similarly, treatment of the systems **18a**–**d** with isocyanates RN=C=O (R = CMe_3, $SiMe_3$, *p*-tolyl, or adamantyl) gave the related μ-formamidato complexes **27**–**30**.

Introduction

It has been shown that (η^2-ketone)- and (η^2-aldehyde)zirconocene complexes structurally and chemically behave as metallaoxiranes.[1] The three-membered metallacycles have a tendency of binding a variety of reactive organometallic species in a specific way by using the nucleophilic character of the metallaoxirane oxygen atom and the strongly electrophilic group 4 metal center in combination. In this way the metallaoxirane template may behave like a molecular metal-oxide model.[2] It has, for instance, been used to bind and stabilize the Cp_2ZrH_2 moiety,[3] that is not persistent as a monomer in solution.[4] The reactivity of the metallaoxirane-template stabilized zirconocene dihydride towards carbon monoxide has been used to devise molecular Fischer–Tropsch models.[5]

Recently we have succeeded in generating a (hydrido)zirconocene cation at a (η^2-diarylketone)zirconocene template.[6] The monomeric $[Cp_2ZrH]^+$ cation is probably an elusive species in solution; but stabilized at this specific metallaoxirane matrix it can readily be generated, characterized and handled. The $[Cp_2Zr(OCPh_2)/(Cp_2Zr{-}H)]^+$ adduct (see Scheme 1) even reacts with ethene to form polyethylene.[6][7]

Unfortunately, we have not been able to experimentally observe and characterize any intermediate insertion products starting from the system **5** so far. Therefore, we have begun to prepare a variety of similarly structured (hydrido)-zirconocene cation systems that are bonded to and stabilized by similar metallaoxirane template frameworks that bear less bulky and sterically demanding substituents at the organometallic three-membered ring. We have succeeded to obtain a number of such systems derived from differently substituted (η^2-aldehyde)zirconocene complexes, and in these cases it was possible to form stable monomeric insertion products by treatment with nitriles and with isocyanates. A series of examples is described in this article.



Scheme 1

Results and Discussion

Preparation of the (η^2-Aldehyde)zirconocene-Stabilized (Hydrido)zirconocene Cation Systems

Starting materials for the preparation of the $[(\eta^2\text{-aldehyde})ZrCp_2/Cp_2ZrH]^+$ complexes investigated in the course of this study were several neutral metallaoxirane adducts of Cp_2ZrH_2 and of $Cp_2Zr(H)R$ complexes. Three different metallaoxirane templates were used, namely (η^2-acetaldehyde)-, (η^2-propionaldehyde)-, and (η^2-phenylacetaldehyde)zirconocene. The starting materials for the preparation of the dinuclear $[(\mu\text{-}\eta^1\text{-}O{:}\eta^2\text{-}C,O\text{-aldehyde})(\mu\text{-}H)(ZrCp_2)_2]^+$ cations were synthesized as follows (see also Scheme 2).

[a] Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40, D-48149 Münster, Germany
Fax: (internat.) + 49(0)251/8336503
E-mail: erker@uni-muenster.de

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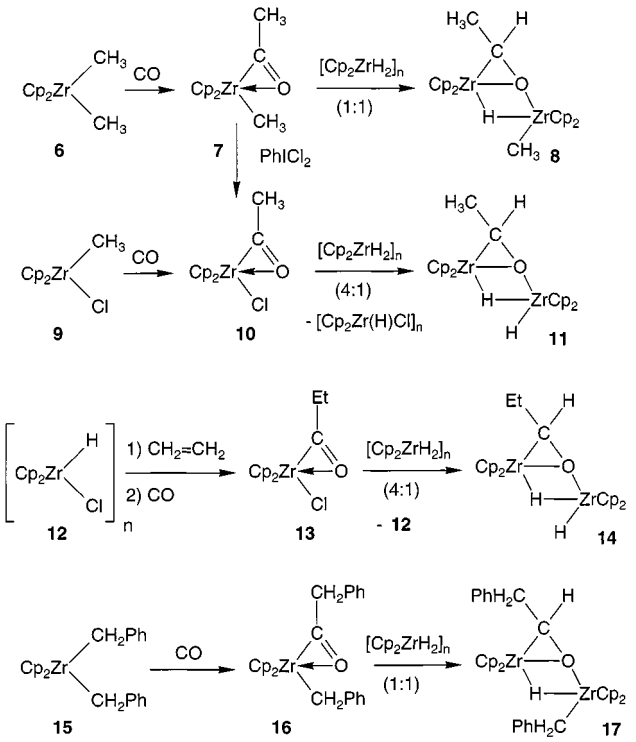


Scheme 2

As previously described by us,[8] the $[Cp_2Zr(OCHMe)/Cp_2Zr(H)Me]$ adduct **8** was prepared by Cp_2ZrH_2 addition to (η^2-acetyl)methyl zirconocene (**7**). The corresponding $[Cp_2Zr(OCHMe)/Cp_2ZrH_2]$ adduct (**11**) was prepared by treatment of (η^2-acetyl)zirconocene chloride (**10**) with excess $[Cp_2ZrH_2]_n$ (4:1 ratio). Under these optimized literature conditions[8] hydride addition to the (η^2-acyl)metallocene moiety is observed and a subsequent chloride vs. hydride exchange reaction is effectively achieved (for details see the Experimental Section). The $[Cp_2Zr(OCHEt)/Cp_2ZrH_2]$ adduct (**14**) was prepared analogously. We have used as an additional starting material the [Cp_2Zr(OCH-benzyl)/Cp_2Zr(H)benzyl] adduct (**17**) that to our knowledge was prepared here for the first time. The reaction sequence employed started from dibenzylzirconocene (**15**). Carbonylation yields the (η^2-phenylacetyl)benzylzirconocene complex **16**. Addition of a stoichiometric quantity of dihydridozirconocene (employed as the oligomeric $[Cp_2ZrH_2]_n$ reagent[4]) then furnished the dinuclear (μ-hydrido)bis(zirconocene) complex **17**.

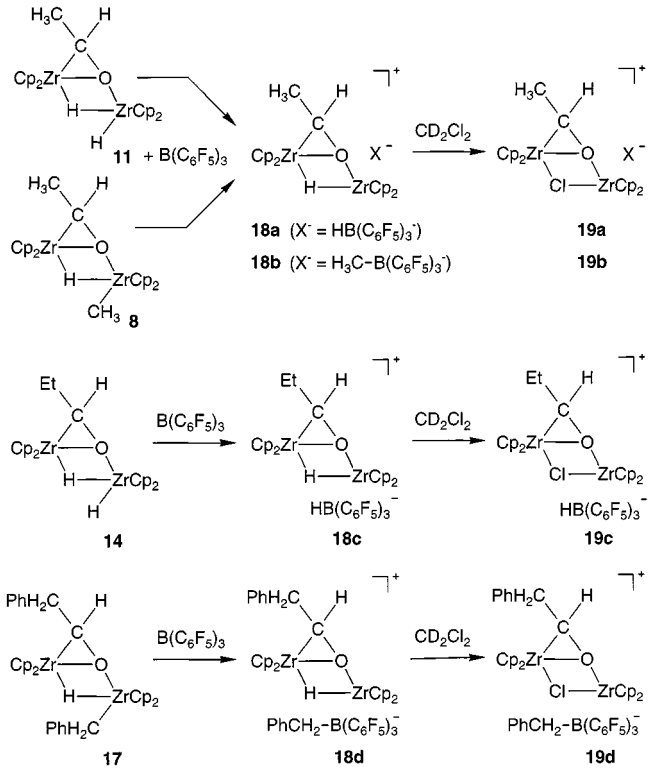
Complex **11** was treated with the organometallic Lewis acid tris(pentafluorophenyl)borane[9] in toluene solution. The reaction between the zirconium hydride and $B(C_6F_5)_3$ takes place instantaneously under these conditions at ambient temperature. The product separates from the solution as a dark colored oil. It dissolves in a [D_8]THF/[D_6]benzene mixture and can thus be characterized spectroscopically. The reaction between **11** and $B(C_6F_5)_3$ has led to abstraction[10] of the terminal hydride ligand at zirconium with formation of the adduct salt $[Cp_2Zr(OCHMe)/Cp_2ZrH]^+[HB(C_6F_5)_3]^-$ (**18a**). The borohydride anion is characterized by its ^{11}B-NMR doublet at δ −24.6 ($^1J_{BH}$ = 82 Hz). The ^{1}H-NMR spectrum of the cation of **18a** shows only a single residual hydride resonance (at δ −1.79) that is very typical of a hydride ligand bridging between two zirconium atoms[11] [see for a comparison: ^{1}H NMR of the bis(zirconocene)dihydride complex **11**: δ 4.32 (terminal Zr−H), δ −1.51 (μ-H), $^2J_{HH}$ = 13.9 Hz].[8] In the complex **18a** the metallaoxirane framework is still intact [^{1}H-NMR signals at δ 3.69 (q, 1 H), 1.48 (d, 3 H, $^3J_{HH}$ = 6.3 Hz); ^{13}C-NMR signals at δ 90.1 (C^1H) and 23.7 (C^1-CH_3)], and both bent metallocene units show diastereotopic splitting of their pairs of Cp-resonances (^{13}C NMR: δ 112.4, 112.1, 106.7, 106.6) due to the adjacent metallaoxirane chirality center (C^1HMeO[Zr]). These NMR features indicate that the chiral dimetallabicyclic framework has remained intact upon treatment of **11** with $B(C_6F_5)_3$. We conclude that this reaction has cleanly resulted in abstraction of the terminal hydride ligand at zirconium by the boron Lewis acid with formation of the dimetallic (η^2-acetaldehyde)zirconocene-template stabilized (hydrido)zirconocene cation complex **18a** (see Scheme 3). Complex **18a** can be dissolved in a halogenated solvent such as [D_2]dichloromethane at low temperature. Its NMR spectra could be recorded at 243 K, but a rather selective reaction with this solvent took place at temperatures above 255 K to replace the μ-hydride ligand by chloride from the solvent to generate **19a**. Surprisingly, dideuteromethane (CD_2H_2) was the only organic product that was detected ^{1}H-NMR spectroscopically (quintett at δ 0.17). The mechanism of this apparently selective double chloride vs. hydride exchange remains to be clarified. An analogous series of reactions was observed upon treatment of the [(η^2-propanal)$ZrCp_2$/H_2ZrCp_2] adduct **14** with $B(C_6F_5)_3$ to yield the cations **18c** and **19c**, subsequently (see Scheme 3).

The salt **18b** was prepared by treatment of **8** with $B(C_6F_5)_3$. In this case, the terminal methyl ligand at the "south-east" zirconocene moiety is selectively removed. The same cation (i.e. $[Cp_2Zr(OCHMe)/Cp_2ZrH]^+$) is obtained from the reaction of **11** with $B(C_6F_5)_3$, only that **18b** contains the $[CH_3B(C_6F_5)_3]^-$ counteranion. Its formation is evident from the respective ^{1}H-NMR (δ 1.03, CH_3B) and ^{11}B-NMR signals (singlet at δ −14.5). The remaining signals of **18a** and **18b** must be considered equivalent, taking into account the pronounced sensitivity of the actual NMR chemical shifts of this charged metallocene system to small changes in solvent polarity (for details see the Experimental Section).

Similarly, treatment of the dinuclear benzyl-substituted metallocene hydride complex **17** with $B(C_6F_5)_3$ results in selective transfer of the σ-benzylligand from zirconium to boron to yield **18d**. Exposure to CD_2Cl_2 at 265 K also leads to H^- vs. Cl^- exchange to generate **19d** and CD_2H_2 (see Scheme 3).

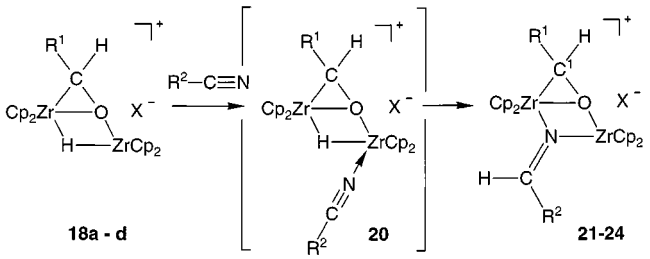
Reaction of the $[Cp_2Zr(OCHR)/Cp_2ZrH]^+$ Cations with Nitriles

The [(μ-acetaldehyde)(μ-hydrido)bis(zirconocene)]$^+$ cation [**18a**, with $HB(C_6F_5)_3^-$ anion] reacts readily with added



Scheme 3

acetonitrile.[12][13] Usually the reaction was carried out by treating a suspension of e.g. **18a** in toluene with $CH_3-C\equiv N$. The addition reaction takes place very rapidly in the two-phase system. After ca. five minutes the oil, that remains separated from the toluene solution, is collected and is shown to consist of the product **21a**. The $HB(C_6F_5)_3^-$ anion is not affected by the treatment with acetonitrile. The cation of **18a** has added its hydride to the acetonitrile $-C\equiv N$ carbon atom with formation of a dimetallated acetaldiminium moiety.[14] In **21a** the iminium nitrogen atom bridges between the two zirconium centers. This leads to the formation of a dimetallabicyclic framework, part of which is the intact (μ-η^1-O:η^2-C,O-acetaldehyde)metallocene template. Consequently, complex **21a** exhibits the typical NMR signals of the metallaoxirane moiety [^{1}H NMR in a [D_8]THF/[D_6]benzene mixture: δ 3.65 (q, 1 H), 1.52 (d, 3 H), $^3J_{HH}$ = 6.1 Hz; ^{13}C NMR: δ 88.5 (C^1-H), 23.9 (C^1-CH_3)]. The presence of the chiral center (C^1) inside the metallaoxirane ring systems results in the observation of the NMR signals of two pairs of diastereotopic Cp ligands at the zirconium centers in complex **21a** (^{13}C NMR in [D_8]THF/[D_6]benzene: δ 113.6, 113.5, 108.8, 108.7). The bridging acetaldiminium moiety shows very typical NMR features; the *H*(Me)*C*=N ^{1}H-/^{13}C-NMR resonances are located at δ 8.67 (^{1}H; q, $^3J_{HH}$ = 4.7 Hz) and δ 187.2 (^{13}C). At such a structural framework two geometrical isomers could in principle be formed that are characterized by having the aldiminium alkyl substituent oriented (*Z*) or (*E*) relative to the metallaoxirane zirconium center. Treatment of **18a** with acetonitrile yielded only a single isomer. In view of an X-ray crystal structure of a related example (see below) we tentatively assign to it the structure of the (*E*)-isomer (see Scheme 4).



R^1	X^-	R^2	CH_3	CMe_3	p-tolyl	Et
CH_3	$HB(C_6F_5)_3^-$	**21**	**a**	**b**	**c**	-
CH_3	$MeB(C_6F_5)_3^-$	**22**	**a**	**b**	**c**	**d**
Et	$HB(C_6F_5)_3^-$	**23**	**a**	**b**	**c**	-
$PhCH_2$	$PhCH_2B(C_6F_5)_3^-$	**24**	**a**	**b**	**c**	**d**

Scheme 4

We have treated most of the complexes **18a−d** (see Scheme 3) with the nitrile reagents R−C≡N with R groups being methyl, ethyl, *tert*-butyl, or *p*-tolyl. In each case a clean 1:1 addition reaction with formation of the respective [(μ-aldiminium)bis(zirconocene)]$^+$ cation complexes (**21−24**) was observed. In each of these cases single isomerically pure products were obtained, that always contained the intact respective metallaoxirane moieties as a part of the dimetallabicyclic framework. Single crystals were obtained of the propionitrile addition product to **18d**. The [(μ-phenylacetaldehyde)(μ-propionaldiminium)bis(zirconocene)]$^+$ cation complex **24d** was characterized by X-ray diffraction. In the crystal there is an enantiomeric disorder at C1 (for details see the Experimental Section). The X-ray crystal structure analysis of complex **24d** shows the presence of a planar dimetallabicyclic framework of the cation. Both zirconium atoms, the C−O part of the μ-aldehyde ligand and the N=CH(R) core are located in the central molecular plane. The (η^2-aldehyde)zirconocene moiety exhibits a very pronounced σ-complex character.[1a,15] Both the Zr1−C1 [2.228(20) Å] and the Zr1−O [2.26(10) Å] linkages are in the σ-bond range. The bond angles inside the Zr1−O−C1 three-membered ring are 71.8(9)° (O−C1−Zr1), 36.2(5)° (C1−Zr1−O) and 72.0(9)° (C1−O−Zr1) (see Figure 1). The C1−O bond length is 1.384(18) Å. The adjacent Zr2−O linkage is very short at 2.007(8) Å. The C1−O−Zr2 angle amounts to 168.7(13)° and Zr1−O−Zr2 angle is at a very typical value of 107.4(5)°. The aldiminium nitrogen bridges between the two zirconium centers [bond lengths Zr2−N 2.187(12) Å, Zr1−N 2.377(11) Å, angle Zr1−N−Zr2 96.7(5)°]. The coordination geometry around the iminium nitrogen atom is trigonally planar. The N−C41 double bond [1.235(19) Å][16] is almost symmetrically arranged in the σ-ligand plane between Zr1 and Zr2 [angles Zr2−N−C41 137.9(11)°, Zr1−N−C41 125.3(12)°], taking into account the rather different coordination environments at Zr2 [angle

O−Zr2−N: 82.2(4)°] and Zr1 [angle O−Zr1−N: 73.6(4)°].[14] Again, there is only a single geometric aldiminium isomer observed in the crystal. It is characterized by having the ethyl substituent ($C^{42}H_2-C^{43}H_3$) at the aldiminium N=C^{41} double bond placed in the (*E*)-orientation relative to the metallaoxirane zirconium center Zr1.

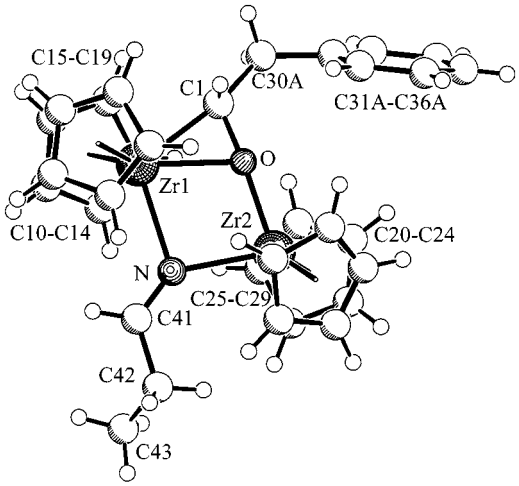
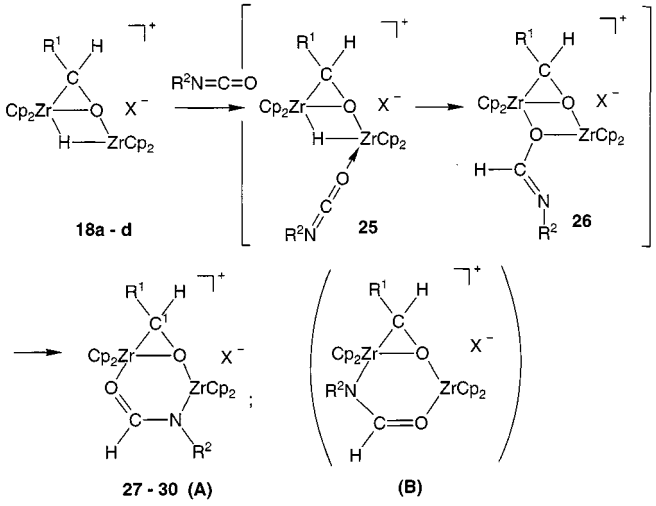


Figure 1. Molecular geometry of complex **24d** (only the cation part is depicted) with selected bond lengths [Å] and angles [°]: Zr1−O 2.26(10), Zr2−O 2.007(8), Zr1−N 2.377(11), Zr2−N 2.187(12), Zr1−C1 2.228(20), O−C1 1.384(18), C1−C30A 1.425(15), C1−C30B 1.423(15), N−C41 1.235(19), C41−C42 1.50(2), C42−C43 1.50(3); Zr1−O−Zr2 107.4(5), Zr1−N−Zr2 96.7(5), Zr1−O−C1 72.0(9), Zr1−C1−O 71.8(9), Zr2−O−C1 168.7(13), C1−Zr1−O 36.2(5), C1−Zr1−N 109.3(5), O−Zr1−N 73.6(4), O−Zr2−N 82.2(4), Zr1−N−C41 125.3(10), Zr2−N−C41 137.9(11), N−C41−C42 127.5(15), C41−C42−C43 113.1(16).

Reactions with Isocyanates

It is mechanistically feasible that an incoming unsaturated reagent may first coordinate to one of the zirconium atoms in the [(μ-aldehyde)(μ-hydride)bis zirconocene]$^+$ cations (**18**) to form an adduct. We assume that coordination probably occurs preferentially at the four-coordinate zirconium and not the five-coordinate zirconium center that is part of the metallaoxirane ring system. Thus, alkyl- or arylnitrile coordination to **18** would be expected to preferentially lead to the reactive intermediate **20** (see Scheme 4). Subsequent hydride shift to the nitrile carbon atom of the activated R−C≡N reagent would in this case directly result in the formation of the (*E*)-stereoisomeric insertion product type that is actually only observed experimentally. It is expected that other unsaturated reagents may follow a similar course when treated with the dinuclear group 4 metallocene hydrido cations **18**. This was in fact observed when the complexes **18** were treated with a series of alkyl or aryl isocyanates RN=C=O (with R being *tert*-butyl, trimethylsilyl, *p*-tolyl, or adamantyl). In each case a single reaction product is formed that was isolated in high yield.

The reaction of **18a** with *tert*-butylisocyanate is a typical example. A single product (**27a**) is obtained, that was isolated as a pale yellow solid in 75% yield. The NMR spectra show that the metallaoxirane moiety inside the dimetallabicyclic framework is retained [^{1}H NMR: δ 3.41 (q, 1 H, C^1-H), 1.53 (d, 3 H, C^1-CH_3), $^3J_{HH}$ = 6.3 Hz; ^{13}C NMR: δ 85.8(C^1), 23.8 (C^1-CH_3)]. Consequently, the signals of two pairs of diastereotopic cyclopentadienyl ligands are registered (^{13}C NMR: δ 114.2, 114.0, 110.0, 109.5 in [D_8]THF/[D_6]benzene solution). The added isocyanate has selectively reacted with the zirconium hydride of the starting material to form a formamidate ligand [^{1}H/^{13}C NMR: δ 7.45/165.1 (O=CH−)].



R^1	X^-	R^2	CMe_3	$SiMe_3$	p-tolyl	1-adamantyl
CH_3	$HB(C_6F_5)_3^-$	**27**	**a**	**b**	**c**	-
CH_3	$MeB(C_6F_5)_3^-$	**28**	**a**	**b**	**c**	**d**
Et	$HB(C_6F_5)_3^-$	**29**	**a**	**b**	**c**	-
$PhCH_2$	$PhCH_2B(C_6F_5)_3^-$	**30**	**a**	**b**	**c**	-

Scheme 5

It is likely that the zirconium hydride addition reaction to the heterocumulene is also initiated by pre-coordination to the more electrophilic four-coordinate zirconium center in **18** (see Scheme 5). The *tert*-butylisocyanate addition to zirconium probably takes place preferentially by means of the heterocumulene oxygen (to generate **25**). Subsequent hydride addition to the sp-carbon atom of the activated RN=C=O reagent then may lead to the formation of the intermediate **26**. In view of the preferred 1,3-κ^2-bonding mode of many related mononuclear amidate or amidinate ligands at the group 4 metallocenes[18] subsequent stabilizing rearrangement of **26** to yield the final [(μ-amidate)bis(zirconocene)]$^+$ cation systems **27**−**30** must be assumed. Unfortunately, we have not been able to characterize any of the RN=C=O reaction products of **18** by X-ray diffraction. Therefore, we cannot definitively decide whether the isomers **27**−**30A** or **B** were formed in the reactions. In each of the examples listed in Scheme 5 a single differently substituted regioisomer of **27**−**30** was formed selectively. From the mechanistic course, preferred formation of the isomers **27**−**30A** would be expected, if the observed reactions are kinetically controlled.

Conclusions

Our study has shown that (η^2-aldehyde)zirconocene moieties are very well suited to serve as templates to accommodate the elusive Cp_2Zr-H^+ cation reagent. Selective σ-ligand abstraction from the readily available dinuclear $[Cp_2Zr(OCHR^1)/Cp_2Zr(H)R^2]$ (R^2 = alkyl or hydride) precursors provides a reliable synthetic entry to the $[Cp_2Zr(OCHR^1)/Cp_2ZrH]^+$ cation systems. The metallaoxirane template seems ideally suited to accommodate the (hydrido)zirconocene cation species since it contains both a strongly electrophilic zirconocene unit and a pronouncedly nucleophilic metallaoxirane oxygen center. This bifunctional characteristic probably results from the pronounced three-membered ring σ-complex properties of the (η^2-aldehyde)$ZrCp_2$ unit, which makes oxygen to zirconium π-backbonding extremely unfavorable.[19] What remains is the inductive effect of the group 16 element that serves to further decrease the electron deficiency at the formally 16 electron metallocene center of the metallaoxirane subunit.

Formal addition of the $[Cp_2Zr-H]^+$ unit to the bifunctional metallaoxirane 1,2-chelate serves to stabilize both the nucleophilic hydride and the electrophilic metallocene of the formally 14-electron cationic reagent. However, binding the (hydrido)metallocene cation to the bifunctional template preserves the principal reactivity pattern of the $[Cp_2Zr-H]^+$ reagent, only in a moderated form. This becomes evident from the course taken in the polar RC≡N or RN=C=O addition reactions, that still follow the typical reaction pattern expected for cationic zirconocene-hydride addition.[12][13] It is remarkable that the 1:1 addition reactions at the template adducts are taking place with very high regioselectivities. Although it is well known that (η^2-aldehyde)$ZrCp_2$ complexes can insert a variety of polar reagents into their zirconium-carbon σ-bond,[17][20] the reactions of the $[Cp_2Zr(OCHR)/Cp_2ZrH^+]$ template adducts selectively involve only the 1,2-coordinated zirconium hydride under the conditions applied in this study. Thus it seems that (η^2-ketone)- and (η^2-aldehyde)zirconocenes serve as very suitable templates for studying otherwise extremely reactive, or even elusive organometallic species, such as the $[Cp_2Zr-H]^+$ cation, stabilized by attachment to the metallaoxirane matrix and moderated in their reactivity, but not completely changed with regard to their typical reactivity pattern. We are hopeful that the favorable template effect of the group 4 metallaoxiranes can be used for accommodating and investigating the typical properties of a variety of other highly reactive organometallic species as well.

Experimental Section

General Information: All reactions were carried out under argon using Schlenk-type glassware or in a glovebox. Solvents, including deuterated solvents, were dried and distilled under argon prior to use. − The following instruments were used for spectroscopic and physical characterization of the compounds: Bruker AC 200P (^{1}H: 200.13, ^{13}C: 50.3 MHz, ^{11}B: 64.2 MHz), Bruker ARX 300 (^{19}F: 282.4 MHz), and Varian Unity Plus (^{1}H: 599.9, ^{13}C: 150.8 MHz) NMR spectrometers (assignments in the ^{1}H- and ^{13}C-NMR spectra were in some example cases confirmed through GCOSY, GHSQC, and GHMBC spectra[21]); Nicolet 5 DXC FT-IR spectrometer; melting points: DSC 2910 (Thermo Analysis/DuPont); elemental analyses: Foss-Heraeus CHN-Rapid. − Tris(pentafluorophenyl)-borane[9], $[Cp_2ZrH_2]_n$[4], $Cp_2ZrMeCl$ **8**[22], bis(η^5-cyclopentadienyl)(η^2-phenylacetyl)benzylzirconium **16**[23], μ-(η^1-O:η^2-C,O-acetaldehyde)-μ-hydrido[bis(η^5-cyclopentadienyl)hydridozirconium][bis(η^5-cyclopentadienyl)zirconium] **11**, μ-(η^1-O:η^2-C,O-acetaldehyde)-μ-hydrido[bis(η^5-cyclopentadienyl)methylzirconium][bis(η^5-cyclopentadienyl)zirconium] **8**, and μ-(η^1-O:η^2-C,O-propionaldehyde)-μ-hydrido[bis(η^5-cyclopentadienyl)hydridozirconium][bis(η^5-cyclopentadienyl)zirconium] **14**[8] were prepared according to literature procedures. In addition, $Cp_2Zr(COMe)Cl$ (**10**) used for the preparation of **8**, was synthesized according to the procedure reported below.

Preparation of Bis(η^5-cyclopentadienyl)(η^2-acetyl)zirconiumchloride (10): 3.15 g (11.6 mmol) of $Cp_2ZrMeCl$ **9** was loaded into a Schlenk tube and dissolved in 60 mL of toluene. Argon was removed by shortly evaporating the Schlenk tube and then the solution was exposed to carbon monoxide under rapid stirring at 0 °C. After two hours the yellow precipitate was isolated by filtration, twice washed with 10 mL of pentane and dried in vacuo, yield 2.60 g (75%).

Preparation of μ-(η^1-O:η^2-C,O-Phenylacetaldehyde)-μ-hydrido-[bis(η^5-cyclopentadienyl)benzylzirconium][bis(η^5-cyclopentadienyl)zirconium] (17): 1.77 g (4.10 mmol) of **16** and 0.90 g (4.03 mmol) of dihydridozirconocene were weighed in a Schlenk vessel, 100 mL of toluene was added and the suspension was stirred for 5 days at room temperature. From the resulting clear yellow solution all volatiles were removed in vacuo. The remaining yellow powder was suspended in 60 mL of a 5:1 mixture of pentane/toluene, the precipitate collected by filtration and washed three times with 20 mL of pentane. After drying in vacuo, **17** was obtained as a slightly yellow solid, yield 1.20 g (46%), mp 146 °C (DSC, decomp.). − $C_{35}H_{36}OZr_2$ (655.1): calcd. C 64.17, H 5.54, found C 62.51, H 5.49. − ^{1}H NMR (599.9 MHz, [D$_6$]benzene): δ = 7.39 (m, 4 H, *o, m*), 7.06 (pst, 1 H, *p*-Zr-CH_2Ph), 7.31 (pst, 2 H, *m*), 7.26 (psd, 2 H, *o*), 7.20 (pst, 1 H, *p*-$CHCH_2$Ph), 5.40, 5.38, 5.37, 5.26 (each s, each 5 H, Cp), 3.11 (dd, 1 H, $^2J_{HH}$ = 14.9 Hz, $^3J_{HH}$ = 3.4 Hz, CHCH_2), 2.83 (dd, 1 H, $^3J_{HH}$ = 9.9 Hz, $^3J_{HH}$ = 3.4 Hz, 1-H), 2.60 (d, 1 H, $^2J_{HH}$ = 9.7 Hz, Zr-CH_2), 2.41 (dd, 1 H, $^2J_{HH}$ = 14.9 Hz, $^3J_{HH}$ = 9.9 Hz, CHCH_2), 2.18 (d, 1 H, $^2J_{HH}$ = 9.7 Hz, Zr-CH_2), −0.61 (br., 1 H, μ-H). − ^{13}C NMR (150.8 MHz, [D$_6$]benzene): δ = 145.0, 128.8, 128.6, 126.0 (*ipso*, *m*, *o*, *p*-$CHCH_2$Ph), 155.2, 127.7, 127.6, 120.7 (*ipso*, *o*, *m*, *p*-Zr-CH_2Ph), 110.5, 110.4, 104.1, 104.1 (each Cp), 82.8 (C1), 45.8 (Zr-CH_2), 44.6 (CHCH_2) .

Generation of the Hydrido Zirconocene Cations 18a−d: General Procedure: A solution of 210 mg (410 μmol) of tris(pentafluorophenyl)borane in 2 mL of toluene was added to a Schlenk flask containing a solution of 293 μmol dimetallic hydride **11**, **8**, **14**, or **17** in 2 mL of toluene. A dark brown oil precipitated immediately. The reaction mixture was stirred for one minute, the oil allowed to settle and then the toluene phase was decanted. The oil was washed with 2 mL of toluene, followed by 2 mL of pentane and then solidified by stirring with 3 mL of pentane. After decanting the solvent and drying the solid in vacuo, the hydrido zirconocene cations were isolated as red-brown powders. Reported below are the quantities of reagents used and yields of products obtained.

Reaction of 11 with Tris(pentafluorophenyl)borane, Preparation of 18a: 200 mg (410 μmol) of **11** was treated with 210 mg (410 μmol) of $B(C_6F_5)_3$ to yield 341 mg (83%) of **18a**, mp 147°C (DSC, decomp.). − $C_{40}H_{26}BF_{15}OZr_2$ (1000.9): calcd. C 48.00, H 2.62, found C 48.46, H 2.74. − ^{1}H NMR (200.1 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 5.78, 5.77, 5.54, 5.46 (each s, each 5 H, Cp), 3.58 (q, 1 H, $^3J_{HH}$ = 6.3 Hz, 1-H), 1.33 (d, 3 H, $^3J_{HH}$ = 6.3 Hz, CHC*H*$_3$), −1.98 (s, 1 H, μ-H), B-*H* resonance not observed. − ^{13}C NMR (50.3 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 149.0, 138.0, 137.1 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-$B(C_6F_5)_3$], 112.4, 112.1, 106.7, 106.6 (each Cp), 90.1 (C1), 23.7 (CH*C*H$_3$), *ipso*-$B(C_6F_5)_3$ resonance not located. − ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −24.6 (d, $^1J_{BH}$ = 82 Hz). − ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −132.0, −163.5, −166.3 [each m, *o*, *p*, *m*-$B(C_6F_5)_3$].

Reaction of 8 with Tris(pentafluorophenyl)borane, Preparation of 18b: 206 mg (410 μmol) of **8** was treated with 210 mg (410 μmol) of $B(C_6F_5)_3$ to yield 320 mg (77%) of **18b**, mp 140°C (DSC, decomp.). − $C_{41}H_{28}BF_{15}OZr_2$ (1014.9): calcd. C 48.52, H 2.78, found C 48.42, H 2.92. − ^{1}H NMR (200.1 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 5.87, 5.85, 5.62, 5.53 (each s, each 5 H, Cp), 3.65 (q, 1 H, $^3J_{HH}$ = 6.2 Hz, 1-H), 1.37 (d, 3 H, $^3J_{HH}$ = 6.2 Hz, CHC*H*$_3$), 1.03 (br, 3 H, B-C*H*$_3$), −1.92 (s, 1 H, μ-H) . − ^{13}C NMR (50.3 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 149.0, 138.0, 137.1 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-$B(C_6F_5)_3$], 113.0, 112.8, 107.1, 107.0 (each Cp), 90.2 (C1), 23.8 (CH*C*H$_3$) , *ipso*-$B(C_6F_5)_3$ and B-*C*H$_3$ resonances not located. − ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −14.5. − ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −132.0, −163.5, −166.3 [each m, *o*, *p*, *m*-$B(C_6F_5)_3$].

Reaction of 14 with Tris(pentafluorophenyl)borane, Preparation of 18c: 206 mg (410 μmol) of **14** was treated with 210 mg (410 μmol) of $B(C_6F_5)_3$ to yield 350 mg (84%) of **18c**, mp 130°C (DSC, decomp.). − $C_{41}H_{28}BF_{15}OZr_2$ (1014.9): calcd. C 48.52, H 2.78, found C 48.27, H 3.01. − ^{1}H NMR (200.1 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 5.87 (double intensity), 5.58, 5.51 (each s, each 5 H, Cp), 3.41 (pst, 1 H, 1-H), 1.75, 1.45 (each m, each 1 H, C*H*$_2$), 0.98 (pst, 3 H, CH$_2$C*H*$_3$), −1.58 (s, 1 H, μ-H), B-*H* resonance not observed. − ^{13}C NMR (50.3 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 149.0, 138.1, 137.2 (each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-$B(C_6F_5)_3$), 112.8, 112.6, 106.3 (double intensity) (each Cp), 97.2 (C1), 31.1 (*C*H$_2$), 12.7 (CH$_2$*C*H$_3$), *ipso*-$B(C_6F_5)_3$ resonance not located. − ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −24.6 (d, $^1J_{BH}$ = 82 Hz). − ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −132.0, −164.3, −166.9 [each m, *o*, *p*, *m*-$B(C_6F_5)_3$].

Reaction of 17 with Tris(pentafluorophenyl)borane, Preparation of 18d: 269 mg (410 μmol) of **17** was treated with 210 mg (410 μmol) of $B(C_6F_5)_3$ to yield 388 mg (81%) of **18d**, mp 130°C (DSC, decomp.). − $C_{53}H_{36}BF_{15}OZr_2$ (1167.1): calcd. C 54.54, H 3.11, found C 53.89, H 3.18. − ^{1}H NMR (599.9 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 7.26 (pst, 2 H, *m*), 7.19 (pst, 1 H, *p*), 7.09 (psd, 2 H, *o*-CHCH$_2$Ph), 7.16 (psd, 2 H, *o*), 6.98 (pst, 2 H, *m*), 6.85 (pst, 1 H, *p*-B-CH$_2$Ph), 5.76, 5.57, 5.56, 5.46 (each s, each 5 H, Cp), 3.67 (dd, 1 H, $^3J_{HH}$ = 9.1 Hz, $^3J_{HH}$ = 4.0 Hz, 1-H), 3.42 (br, 2 H, B-C*H*$_2$), 2.95 (dd, 1 H, $^2J_{HH}$ = 14.8 Hz, $^3J_{HH}$ = 4.0 Hz, CHC*H*$_2$), 2.46 (dd, 1 H, $^2J_{HH}$ = 14.8 Hz, $^3J_{HH}$ = 9.1 Hz, CHC*H*$_2$), −1.56 (s, 1 H, μ-H). − ^{13}C NMR (150.8 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 149.0, 138.1, 137.2 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-$B(C_6F_5)_3$], 142.9, 128.9, 128.6, 126.7 (*ipso*, *m*, *o*, *p*-CHCH$_2$Ph), 149.2, 129.3, 127.4, 123.1 (*ipso*, *o*, *m*, *p*-B-CH$_2$Ph), 113.0, 112.8, 106.3, 106.2 (each Cp), 95.6 (C1), 44.8 (CH*C*H$_2$), 32.4 (br, B-*C*H$_2$), *ipso*-$B(C_6F_5)_3$ resonance not located. − ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −12.3. − ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −128.1, −164.2, −166.8 [each m, *o*, *p*, *m*-$B(C_6F_5)_3$].

Reaction of 18a−d with [D$_2$]Dichloromethane, Generation of 19a−d. − General Proceedure: 78.1 μmol of dimetallic hydride **11**, **8**, **14**, or **17** and 40 mg (78.1 μmol) of tris(pentafluorophenyl)borane were mixed as solids in a NMR tube, the tube sealed with a septum and cooled to −78°C. Using a syringe, 1 mL of −78°C cold CD_2Cl_2 was added through the septum. The solids slowly dissolved to form a dark red solution which was allowed to warm to room temperature. Above −20°C, gas evolution took place and the color changed to red-orange. NMR spectra were then collected and in all cases CH_2D_2 was observed by ^{1}H NMR at 0.17 (quint.). Reported below are the quantities of reagents used.

Characterization of 19a: 38.1 mg (78.1 μmol) of **11** was treated with 40.0 mg (78.1 μmol) of $B(C_6F_5)_3$ in CD_2Cl_2. − ^{1}H NMR (200.1 MHz, [D$_2$]dichloromethane): δ = 6.47, 6.41, 6.00, 5.96 (each s, each 5 H, Cp), 4.33 (q, 1 H, $^3J_{HH}$ = 6.0 Hz, 1-H), 1.83 (d, 3 H, $^3J_{HH}$ = 6.0 Hz, CHC*H*$_3$), B-*H* resonance not observed. − ^{13}C NMR (50.3 MHz, [D$_2$]dichloromethane): δ = 148.2, 137.9, 136.9 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-$B(C_6F_5)_3$], 116.5, 116.4, 109.7, 109.6 (each Cp), 91.0 (C1), 24.9 (CH*C*H$_3$), *ipso*-$B(C_6F_5)_3$ resonance not located. − ^{11}B NMR (64.2 MHz, [D$_2$]dichloromethane): δ = −25.6 (d, $^1J_{BH}$ = 82 Hz). − ^{19}F NMR (282.4 MHz, [D$_2$]dichloromethane): δ = −130.6, −163.0, −165.4 [each m, *o*, *p*, *m*-$B(C_6F_5)_3$].

Characterization of 19b: 39.2 mg (78.1 μmol) of **8** was treated with 40.0 mg (78.1 μmol) of $B(C_6F_5)_3$ in CD_2Cl_2. − ^{1}H NMR (200.1 MHz, [D$_2$]dichloromethane): δ = 6.50, 6.42, 6.02, 5.98 (each s, each 5 H, Cp), 4.36 (q, 1 H, $^3J_{HH}$ = 6.0 Hz, 1-H), 1.86 (d, 3 H, $^3J_{HH}$ = 6.0 Hz, CHC*H*$_3$), 0.53 (br, 3 H, B-C*H*$_3$). − ^{13}C NMR (50.3 MHz, [D$_2$]dichloromethane): δ = 149.0, 138.0, 137.1 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-$B(C_6F_5)_3$], 116.8, 116.7, 110.0, 109.9 (each Cp), 91.7 (C1), 25.4 (CH*C*H$_3$), *ipso*-$B(C_6F_5)_3$ and B-*C*H$_3$ resonances not located. − ^{11}B NMR (64.2 MHz, [D$_2$]dichloromethane): δ = −15.3. − ^{19}F NMR (282.4 MHz, [D$_2$]dichloromethane): δ = −130.5, −162.7, −165.4 [each m, *o*, *p*, *m*-$B(C_6F_5)_3$].

Characterization of 19c: 39.2 mg (78.1 μmol) of **14** was treated with 40.0 mg (78.1 μmol) of $B(C_6F_5)_3$ in CD_2Cl_2. − ^{1}H NMR (200.1 MHz, [D$_2$]dichloromethane): δ = 6.48, 6.43, 6.03, 5.98 (each s, each 5 H, Cp), 4.08 (dd, 1 H, 1-H), 2.2−1.6 (m, 2 H, C*H*$_2$), 1.10 (pst, 3 H, CH$_2$C*H*$_3$), B-*H* resonance not observed. − ^{13}C NMR (50.3 MHz, [D$_2$]dichloromethane): δ = 148.2, 137.9, 136.9 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-$B(C_6F_5)_3$], 116.7, 116.5, 109.7, 109.5 (each Cp), 98.0 (C1), 32.3 (*C*H$_2$), 13.3 (CH$_2$*C*H$_3$), *ipso*-$B(C_6F_5)_3$ resonance not located. − ^{11}B NMR (64.2 MHz, [D$_2$]dichloromethane): δ = −25.6 (d, $^1J_{BH}$ = 82 Hz). − ^{19}F NMR (282.4 MHz, [D$_2$]dichloromethane): δ = −130.6, −163.0, −165.4 [each m, *o*, *p*, *m*-$B(C_6F_5)_3$].

Characterization of 19d: 51.2 mg (78.1 μmol) of **17** was treated with 40.0 mg (78.1 μmol) of $B(C_6F_5)_3$ in CD_2Cl_2. − ^{1}H NMR (599.9 MHz, [D$_2$]dichloromethane): δ = 7.49 (pst, 2 H, *m*), 7.40 (pst, 1 H, *p*), 7.29 (psd, 2 H, *o*-CH$_2$Ph), 6.88 (pst, 2 H, *m*), 6.80 (pst, 1 H, *p*), 6.76 (psd, 2 H, *o*-B-CH$_2$Ph), 5.76, 5.57, 5.56, 5.46 (Cp), 4.47 (dd, 1 H, $^3J_{HH}$ = 10.6 Hz, $^3J_{HH}$ = 2.8 Hz, 1-H), 3.60 (dd, 1 H, $^2J_{HH}$ = 15.0 Hz, $^3J_{HH}$ = 2.8 Hz, CHC*H*$_2$), 2.92 (dd, 1 H, $^2J_{HH}$ = 15.0 Hz, $^3J_{HH}$ = 10.6 Hz, CHC*H*$_2$), 2.84 (br, 2 H, B-C*H*$_2$). − ^{13}C NMR (150.8 MHz, [D$_2$]dichloromethane): δ = 147.8, 137.5, 135.8 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-$B(C_6F_5)_3$], 140.6, 128.7, 127.7, 126.8 (*ipso*, *m*, *o*, *p*-CH$_2$Ph), 148.3, 128.3, 126.4, 122.1 (*ipso*, *o*, *m*, *p*-B-CH$_2$Ph), 116.4, 115.9, 109.6, 109.2 (each Cp), 94.8 (C1), 44.4 (CH*C*H$_2$), 30.2 (br, B-*C*H$_2$), *ipso*-$B(C_6F_5)_3$ resonance not located.

– ^{11}B NMR (64.2 MHz, [D$_2$]dichloromethane): δ = −12.9. – ^{19}F NMR (282.4 MHz, [D$_2$]dichloromethane): δ = −128.7, −163.8, −165.4 [each m, *o*, *p*, *m*-B(C_6F_5)$_3$].

Reaction of 18a–d with Nitriles and Isocyanates. – General Procedure: Cation **18** was formed in situ by addition of 4 mL of toluene to a Schlenk flask containing 293 μmol of the dimetallic hydride complex **11**, **8**, **14**, or **17** and 210 mg (293 μmol) of B(C_6F_5)$_3$. The two compounds dissolved and within a few seconds, compound **18** precipitated as a dark brown oil. The solution was decanted and the oil washed with 2 mL of toluene. Then 1.1 equiv. of the respective nitrile or isocyanate reagent was added and the reaction mixture was stirred for five minutes. The resulting yellow or orange oil was washed with 2 mL of toluene, followed by 2 mL of pentane, and then solidified by stirring with 3 mL of pentane. After decanting the solvent and drying the solid in vacuo, the insertion products were isolated as yellow or orange powders. Reported below are the quantities of reagents actually used and the yields of products obtained.

Reaction of 18a with Acetonitrile: Preparation of 21a: Reaction of 200 mg (410 μmol) of **11** with 210 mg (410 μmol) of B(C_6F_5)$_3$ and subsequent reaction of the such in situ prepared **18a** with 23.9 μL (18.5 mg, 450 μmol) of acetonitrile gave **21a** as a yellow powder, yield 320 mg (75%), mp 184°C (DSC, 213°C decomp.). – $C_{42}H_{29}BF_{15}NOZr_2$ (1039.0): calcd. C 48.42, H 2.81, N 1.34, found C 48.40, H 3.00, N 1.52. – ^{1}H NMR (200.1 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 8.67 (q, 1 H, $^3J_{HH}$ = 4.7 Hz, N=C*H*), 5.88, 5.81, 5.44, 5.43 (each s, each 5 H, Cp), 3.65 (q, 1 H, $^3J_{HH}$ = 6.1 Hz, 1-H), 1.81 (d, 3 H, $^3J_{HH}$ = 4.7 Hz, N=CHCH_3), 1.52 (d, 3 H, $^3J_{HH}$ = 6.1 Hz, CHCH_3), B-*H* resonance not observed. – ^{13}C NMR (150.8 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 187.2 (N=*C*H) 149.0, 138.0, 136.9 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-B(C_6F_5)$_3$], 113.6, 113.5, 108.8, 108.7 (each Cp), 88.5 (C1), 33.3 (N=CH*C*H$_3$), 23.9 (CH*C*H$_3$), *ipso*-B(C_6F_5)$_3$ resonance not located. – ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −24.6 (d, $^1J_{BH}$ = 82 Hz). – ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −132.0, −163.5, −166.3 [each m, *o*, *p*, *m*-B(C_6F_5)$_3$].

Reaction of 18a with *tert*-Butyl Cyanide: Preparation of 21b: Reaction of 200 mg (410 μmol) of **11** with 210 mg (410 μmol) of B(C_6F_5)$_3$ and subsequent reaction of the in situ prepared **18a** with 49.7 μL (37.4 mg, 450 μmol) *tert*-butyl cyanide gave **21b** as a yellow powder, yield 342 mg (77%), mp 170°C (DSC, decomp.). – $C_{45}H_{35}BF_{15}NOZr_2$ (1084.0): calcd. C 49.86, H 3.25, N 1.29, found C 48.99, H 3.53, N 1.35. – ^{1}H NMR (200.1 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 8.87 (s, 1 H, N=C*H*), 5.91, 5.84, 5.44, 5.43 (each s, each 5 H, Cp), 3.55 (q, 1 H, $^3J_{HH}$ = 6.0 Hz, 1-H), 1.49 (d, 3 H, $^3J_{HH}$ = 6.0 Hz, CHCH_3), 0.85 [s, 9 H, C(CH_3)$_3$], B-*H* resonance not observed. – ^{13}C NMR (50.3 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 197.5 (N=*C*H), 149.0, 138.0, 136.9 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-B(C_6F_5)$_3$], 114.0, 113.8, 109.2 (double intensity) (each Cp), 90.0 (C1), 41.6 [*C*(CH$_3$)$_3$], 25.3 [C(*C*H$_3$)$_3$], 23.4 (CH*C*H$_3$), *ipso*-B(C_6F_5)$_3$ resonance not located. – ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −24.6 (d, $^1J_{BH}$ = 82 Hz). – ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −132.0, −163.5, −166.3 [each m, *o*, *p*, *m*-B(C_6F_5)$_3$].

Reaction of 18a with *p*-Tolunitrile: Preparation of 21c: Reaction of 200 mg (410 μmol) of **11** with 210 mg (410 μmol) of B(C_6F_5)$_3$ and subsequent reaction of the in situ prepared **18a** with 52.7 mg (450 μmol) of *p*-tolunitrile gave **21c** as a yellow powder, yield 325 mg (71%), mp 169°C (DSC, decomp.). – $C_{48}H_{33}BF_{15}NOZr_2$ (1118.0): calcd. C 51.57, H 2.98, N 1.25, found C 51.77, H 3.57, N 1.86. – ^{1}H NMR (200.1 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 9.59 (s, 1 H, N=C*H*), 7.22, 7.15 (each psd, each 2 H, *m*, *o*-PhCH$_3$), 5.92, 5.88, 5.49 (double intensity) (each s, each 5 H, Cp), 3.62 (q, 1 H, $^3J_{HH}$ = 6.1 Hz, 1-H), 2.23 (s, 3 H, PhCH_3), 1.51 (d, 2 H, $^3J_{HH}$ = 6.1 Hz, CHCH_3), B-*H* resonance not observed. – ^{13}C NMR (50.3 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 184.4 (N=*C*H), 149.0, 138.1, 137.2 [each d, each $^1J_{CF}$ = 240 Hz, *o, p, m*-B(C_6F_5)$_3$], 145.7, 134.2, 130.2, 129.7 (*p*, *ipso*, *m*, *o*-PhCH$_3$), 113.7, 113.5, 109.1, 109.0 (each Cp), 89.7 (C1), 23.6 (CH*C*H$_3$), 21.3 (Ph*C*H$_3$), *ipso*-B(C_6F_5)$_3$ resonance not located. – ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −24.6 (d, $^1J_{BH}$ = 82 Hz). – ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −132.0, −164.3, −166.9 [each m, *o*, *p*, *m*-B(C_6F_5)$_3$].

Reaction of 18b with Acetonitrile: Preparation of 22a: Reaction of 206 mg (410 μmol) of **8** with 210 mg (410 μmol) of B(C_6F_5)$_3$ and subsequent reaction of the in situ prepared **18b** with 23.9 μL (18.5 mg, 450 μmol) of acetonitrile gave **22a** as a yellow powder, yield 273 mg (63%), mp 180°C (DSC, 231°C decomp.). – $C_{43}H_{31}BF_{15}NOZr_2$ (1056.0): calcd. C 48.91, H 2.96, N 1.33, found C 48.74, H 3.11, N 1.62. – ^{1}H NMR (200.1 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 8.69 (q, 1 H, $^3J_{HH}$ = 4.8 Hz, N=C*H*), 5.95, 5.88, 5.51, 5.50 (each s, each 5 H, Cp), 3.71 (q, 1 H, $^3J_{HH}$ = 6.0 Hz, 1-H), 1.80 (d, 3 H, $^3J_{HH}$ = 4.8 Hz, N=CHCH_3), 1.53 (d, 3 H, $^3J_{HH}$ = 6.0 Hz, CHCH_3), 1.17 (br, 3 H, B-CH_3). – ^{13}C NMR (150.8 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 186.9 (N=*C*H), 149.0, 138.0, 136.9 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-B(C_6F_5)$_3$], 113.6, 113.4, 108.7, 108.6 (each Cp), 88.4 (C1), 33.2 (N=CH*C*H$_3$), 23.8 (CH*C*H$_3$), *ipso*-B(C_6F_5)$_3$ and B-*C*H$_3$ resonances not located. – ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −14.8. – ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −132.0, −163.5, −166.3 [each m, *o*, *p*, *m*-B(C_6F_5)$_3$].

Reaction of 18b with *tert*-Butyl Cyanide: Preparation of 22b: Reaction of 206 mg (410 μmol) of **8** with 210 mg (410 μmol) of B(C_6F_5)$_3$ and subsequent reaction of the in situ prepared **18b** with 49.7 μL (37.4 mg, 450 μmol) of *tert*-butyl cyanide gave **22b** as a yellow powder, yield 320 mg (71%), mp 169°C (DSC, decomp.). – $C_{46}H_{37}BF_{15}NOZr_2$ (1098.0): calcd. C 50.32, H 3.40, N 1.28, found C 50.58, H 3.69, N 1.44. – ^{1}H NMR (200.1 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 8.84 (s, 1 H, N=C*H*), 5.88, 5.81, 5.42 (double intensity) (each s, each 5 H, Cp), 3.54 (q, 1 H, $^3J_{HH}$ = 6.0 Hz, 1-H), 1.48 (d, 3 H, $^3J_{HH}$ = 6.0 Hz, CHCH_3), 1.17 (br, 3 H, B-CH_3), 0.84 (s, 9 H, C(CH_3)$_3$). – ^{13}C NMR (50.3 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 197.5 (N=*C*H), 149.0, 138.0, 136.9 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-B(C_6F_5)$_3$], 113.9, 113.8, 109.2 (double intensity) (each Cp), 90.0 (C1), 41.6 [*C*(CH$_3$)$_3$], 25.3 [C(*C*H$_3$)$_3$], 23.4 (CH*C*H$_3$), *ipso*-B(C_6F_5)$_3$ and B-*C*H$_3$ resonances not located. – ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −14.8. – ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −132.0, −163.5, −166.3 [each m, *o*, *p*, *m*-B(C_6F_5)$_3$].

Reaction of 18b with *p*-Tolunitrile: Preparation of 22c: Reaction of 206 mg (410 μmol) of **8** with 210 mg (410 μmol) of B(C_6F_5)$_3$ and subsequent reaction of the in situ prepared **18b** with 52.7 mg (450 μmol) of *p*-tolunitrile gave **22c** as a yellow powder, yield 320 mg (68%), mp 188°C (DSC, decomp.). – $C_{49}H_{35}BF_{15}NOZr_2$ (1148.1): C 51.99, H 3.12, N 1.24, found C 52.45, H 3.47, N 1.44. – ^{1}H NMR (200.1 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 9.52 (s, 1 H, N=C*H*), 7.22, 7.15 (each psd, each 2 H, *m*, *o*-PhCH$_3$), 5.84, 5.81, 5.43 (double intensity) (each s, each 5 H, Cp), 3.62 (q, 1 H, $^3J_{HH}$ = 6.1 Hz, 1-H), 2.23 (s, 3 H, PhCH_3), 1.48 (d, 2 H,

$^3J_{HH}$ = 6.1 Hz, CHCH_3), 1.26 (br, 3 H, B-CH_3). − ^{13}C NMR (50.3 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 184.4 (N=*C*H), 149.0, 138.1, 137.2 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-B(C_6F_5)$_3$], 144.3, 134.3, 130.2, 129.7 (*p*, *ipso*, *m*, *o*-PhCH$_3$), 113.7, 113.6, 109.2, 109.1 (each Cp), 89.7 (C1), 23.6 (CH*C*H$_3$), 21.2 (Ph*C*H$_3$), *ipso*-B(C_6F_5)$_3$ and B-*C*H$_3$ resonances not located. − ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −14.4. − ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −132.0, −164.3, −166.9 [each m, *o*, *p*, *m*-B(C_6F_5)$_3$].

Reaction of 18b with Propionitrile: Preparation of 22d: Reaction of 206 mg (410 μmol) of **8** with 210 mg (410 μmol) of B(C_6F_5)$_3$ and subsequent reaction of the in situ prepared **18b** with 32.1 μL (24.7 mg, 450 μmol) of propionitrile gave **22d** as a yellow powder, yield 298 mg (68%), mp 146°C (DSC, 205°C decomp.). − $C_{44}H_{33}BF_{15}NOZr_2$ (1070.0): calcd. C 49.39, H 3.11, N 1.31, found C 48.86, H 3.33, N 1.31. − ^{1}H NMR (200.1 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 8.66 (m, 1 H, N=C*H*), 6.02, 5.96, 5.55 (double intensity) (each s, each 5 H, Cp), 3.75 (q, 1 H, $^3J_{HH}$ = 6.1 Hz, 1-H), 1.95 (m, 2 H, CH_2), 1.54 (d, 3 H, $^3J_{HH}$ = 6.1 Hz, CHCH_3), 1.29 (br, 3 H, B-CH_3), 1.08 (pst, 3 H, CH$_2$CH_3). − ^{13}C NMR (150.8 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 191.8 (N=*C*H), 149.0, 138.0, 136.9 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-B(C_6F_5)$_3$], 113.8, 113.6, 108.9, 108.8 (Cp), 88.6 (C1), 41.1 (*C*H$_2$), 23.8 (CH*C*H$_3$), 8.6 (CH$_2$*C*H$_3$), *ipso*-B(C_6F_5)$_3$ and B-*C*H$_3$ resonances not located. − ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −14.7. − ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −132.0, −163.5, −166.3 [each m, *o*, *p*, *m*-B(C_6F_5)$_3$].

Reaction of 18c with Acetonitrile: Preparation of 23a: Reaction of 206 mg (410 μmol) of **14** with 210 mg (410 μmol) of B(C_6F_5)$_3$ and subsequent reaction of the in situ prepared **18c** with 23.9 μL (18.5 mg, 450 μmol) of acetonitrile gave **23a** as a yellow powder, yield 320 mg (75%), mp 164°C (DSC, 198°C decomp.). − $C_{43}H_{31}BF_{15}NOZr_2$ (1056.0): calcd. C 48.91, H 2.96, N 1.33, found C 48.93, H 3.30, N 1.39. − ^{1}H NMR (200.1 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 8.63 (q, 1 H, $^3J_{HH}$ = 4.7 Hz, N=C*H*), 5.81, 5.76, 5.40, 5.38, (each s, each 5 H, Cp), 3.37 (dd, 1 H, 1-H), 1.76 (d, 3 H, $^3J_{HH}$ = 4.7 Hz, N=CHCH_3), 1.6-1.5 (m, 2 H, CH_2), 0.94 (pst, 3 H, CH$_2$CH_3), B-*H* resonance not observed. − ^{13}C NMR (50.3 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 187.1 (N=*C*H), 149.0 (double intensity), 138.1, 137.2 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-B(C_6F_5)$_3$], 113.6, 108.7, 108.5 (each Cp), 95.5 (C1), 33.3 (NCH*C*H$_3$), 31.6 (*C*H$_2$), 13.2 (CH$_2$*C*H$_3$), *ipso*-B(C_6F_5)$_3$ resonance not located. − ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −24.6 (d, $^1J_{BH}$ = 82 Hz). − ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −132.0, −164.3, −166.9 [each m, *o*, *p*, *m*-B(C_6F_5)$_3$].

Reaction of 18c with *tert*-Butyl Cyanide: Preparation of 23b: Reaction of 206 mg (410 μmol) of **14** with 210 mg (410 μmol) of B(C_6F_5)$_3$ and subsequent reaction of the in situ prepared **18c** with 49.7 μL (37.4 mg, 450 μmol) of *tert*-butyl cyanide gave **23b** as a yellow powder, yield 347 mg (77%), mp 167°C (DSC, decomp.). − $C_{46}H_{37}BF_{15}NOZr_2$ (1098.0): calcd. C 50.32, H 3.40, N 1.28, found C 50.57, H 3.44, N 1.50. − ^{1}H NMR (200.1 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 8.88 (s, 1 H, N=C*H*), 5.89, 5.84, 5.45, 5.43 (each s, each 5 H, Cp), 3.35 (dd, 1 H, 1-H), 1.7-1.4 (m, 2 H, CH_2), 0.96 (pst, 3 H, CH$_2$CH_3), 0.86 [s, 9 H, C(CH_3)$_3$], B-*H* resonance not observed. − ^{13}C NMR (50.3 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 197.6 (N=*C*H), 149.0, 138.1, 137.2 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-B(C_6F_5)$_3$], 114.0 (double intensity), 109.3, 109.1 (each Cp), 97.1 (C1), 41.6 (*C*(CH$_3$)$_3$), 31.3 (*C*H$_2$), 25.3 (C(*C*H$_3$)$_3$), 13.7 (CH$_2$*C*H$_3$), *ipso*-B(C_6F_5)$_3$ resonance not located. − ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −24.6 (d, $^1J_{BH}$ = 82 Hz). − ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −132.0, −164.3, −166.9 [each m, *o*, *p*, *m*-B(C_6F_5)$_3$].

Reaction of 18c with *p*-Tolunitrile: Preparation of 23c: Reaction of 206 mg (410 μmol) of **14** with 210 mg (410 μmol) of B(C_6F_5)$_3$ and subsequent reaction of the in situ prepared **18c** with 52.7 mg (450 μmol) of *p*-tolunitrile gave **23c** as a yellow powder, yield 344 mg (73%), mp 142°C (DSC, 168°C decomp.). − $C_{49}H_{35}BF_{15}NOZr_2$ (1148.1): calcd. C 51.99, H 3.12, N 1.24, found C 51.76, H 3.46, N 1.15. − ^{1}H NMR (200.1 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 9.65 (s, 1 H, N=C*H*), 7.22, 7.15 (each psd, each 2 H, *m*, *o*-PhCH$_3$), 5.99, 5.98, 5.69, 5.57 (each s, each 5 H, Cp), 3.5 (m, 1 H, 1-H), 2.25 (s, 3 H, PhCH_3), 1.8-1.5 (m, 2 H, CH_2), 1.00 (pst, 3 H, CH$_2$CH_3), B-*H* resonance not observed. − ^{13}C NMR (50.3 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 184.6 (N=*C*H), 149.0, 138.1, 137.2 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-B(C_6F_5)$_3$], 145.7, 134.3, 130.3, 129.7 (*p*, *ipso*, *m*, *o*-PhCH$_3$), 113.8, 113.8, 109.2, 109.0 (each Cp), 96.7 (C1), 31.5 (*C*H$_2$), 21.3 (Ph*C*H$_3$), 13.6 (CH$_2$*C*H$_3$), *ipso*-B(C_6F_5)$_3$ resonance not located. − ^{11}B NMR (64.2 MHz, [D$_6$]benzene[D$_8$]tetrahydrofuran, ca. 4:1): δ = −24.6 (d, $^1J_{BH}$ = 82 Hz). − ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −132.0, −164.3, −166.9 [each m, *o*, *p*, *m*-B(C_6F_5)$_3$].

Reaction of 18d with Acetonitrile: Preparation of 24a: Reaction of 269 mg (410 μmol) of **17** with 210 mg (410 μmol) of B(C_6F_5)$_3$ and subsequent reaction of the in situ prepared **18d** with 23.9 μL (18.5 mg, 450 μmol) of acetonitrile gave **24a** as a yellow powder, yield 376 mg (76%), mp 239°C (DSC, decomp.). − $C_{55}H_{39}BF_{15}NOZr_2$ (1208.2): calcd. C 54.68, H 3.25, N 1.16, found C 54.50, H 3.65, N 1.01. − ^{1}H NMR (599.9 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 8.51 (q, 1 H, $^3J_{HH}$ = 4.7 Hz, N=C*H*), 7.31 (pst, 2 H, *m*), 7.22 (pst, 1 H, *p*), 7.10 (psd, 2 H, *o*-CH$_2$Ph), 7.19 (psd, 2 H, *o*), 6.98 (pst, 2 H, *m*), 6.84 (pst, 1 H, *p*-B-CH$_2$Ph), 5.63, 5.59, 5.45, 5.42 (each s, each 5 H, Cp), 3.82 (dd, 1 H, $^3J_{HH}$ = 10.2 Hz, $^3J_{HH}$ = 3.2 Hz, 1-H), 3.42 (br, 2 H, B-CH_2), 3.14 (dd, 1 H, $^2J_{HH}$ = 15.2 Hz, $^3J_{HH}$ = 3.2 Hz, CHCH_2), 2.58 (dd, 1 H, $^2J_{HH}$ = 15.2 Hz, $^3J_{HH}$ = 10.2 Hz, CHCH_2), 1.67 (d, 3 H, $^3J_{HH}$ = 4.7 Hz, N=CHCH_3). − ^{13}C NMR (150.8 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 186.9 (N=*C*H), 149.0, 138.1, 137.2 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-B(C_6F_5)$_3$], 142.0, 128.9, 128.4, 126.8 (*ipso*, *m*, *o*, *p*-CH$_2$Ph), 149.2, 129.3, 127.4, 123.1 (*ipso*, *o*, *m*, *p*-B-CH$_2$Ph), 113.8, 113.5, 108.9, 108.7 (each Cp), 91.6 (C1), 44.1 (CH*C*H$_2$), 33.2 (N=CH*C*H$_3$), 32.4 (br, B-*C*H$_2$), *ipso*-B(C_6F_5)$_3$ resonance not located. − ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −12.3. − ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −128.1, −164.2, −166.8 [each m, *o*, *p*, *m*-B(C_6F_5)$_3$].

Reaction of 18d with *tert*-Butyl Cyanide: Preparation of 24b: Reaction of 269 mg (410 μmol) of **17** with 210 mg (410 μmol) of B(C_6F_5)$_3$ and subsequent reaction of the in situ prepared **18d** with 49.7 μL (37.4 mg, 450 μmol) of *tert*-butyl cyanide gave **24b** as a yellow powder, yield 364 mg (71%), mp 166°C (DSC, decomp.). − $C_{58}H_{45}BF_{15}NOZr_2$ (1250.2): calcd. C 55.72, H 3.63, N 1.12, found C 55.05, H 4.16, N 1.63. − ^{1}H NMR (599.9 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 8.89 (s, 1 H, N=C*H*), 7.33 (pst, 2 H, *m*), 7.23 (pst, 1 H, *p*), 7.18 (psd, 2 H, *o*-CH$_2$Ph), 7.08 (psd, 2 H, *o*), 6.91 (pst, 2 H, *m*), 6.77 (pst, 1 H, *p*-B-CH$_2$Ph), 5.79, 5.72, 5.58, 5.55 (each s, each 5 H, Cp), 3.87 (dd, 1 H, $^3J_{HH}$ = 10.3 Hz, $^3J_{HH}$ = 3.0 Hz, 1-H), 3.30 (br, 2 H, B-CH_2), 3.18 (dd, 1 H, $^2J_{HH}$ = 15.2 Hz, $^3J_{HH}$ = 3.0 Hz, CHCH_2), 2.67 (dd, 1 H, $^2J_{HH}$ = 15.2 Hz, $^3J_{HH}$ = 10.3 Hz, CHCH_2), 0.87 [s, 9 H, C(CH_3)$_3$]. − ^{13}C NMR

(150.8 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 197.2 (N=*C*H), 149.0, 138.1, 137.2 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-B(C$_6$F$_5$)$_3$], 142.0, 128.5, 128.0, 126.4 (*ipso*, *m*, *o*, *p*-CH$_2$Ph), 148.7, 128.8, 126.7, 122.4 (*ipso*, *o*, *m*, *p*-B-CH$_2$Ph), 113.7, 113.5, 109.1, 108.8 (each Cp), 93.3 (C1), 43.5 (CH*C*H$_2$), 41.2 [*C*(CH$_3$)$_3$], 31.9 (br, B-*C*H$_2$), 24.8 [C(*C*H$_3$)$_3$], *ipso*-B(C$_6$F$_5$)$_3$ resonance not located. − ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −12.3. − ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −128.1, −164.2, −166.8 [each m, *o*, *p*, *m*-B(C$_6$F$_5$)$_3$].

Reaction of 18d with *p*-Tolunitrile: Preparation of 24c: Reaction of 269 mg (410 μmol) of **17** with 210 mg (410 μmol) of B(C$_6$F$_5$)$_3$ and subsequent reaction of the in situ prepared **18d** with 52.7 mg (450 μmol) of *p*-tolunitrile gave **24c** as a yellow powder, yield 347 mg (66%), mp 222°C (DSC, decomp.). − C$_{61}$H$_{43}$BF$_{15}$NOZr$_2$ (1284.3): calcd. C 57.05, H 3.37, N 1.09, found C 56.41, H 3.62, N 1.18. − ^{1}H NMR (599.9 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 9.54 (s, 1 H, N=C*H*), 7.28 (pst, 2 H, *m*), 7.18 (m, 1 H, *p*), 7.14 (psd, 2 H, *o*-CH$_2$Ph), 7.18 (m, 2 H, *m*), 7.07 (psd, 2 H, *o*-PhCH$_3$), 7.02 (psd, 2 H, *o*), 6.84 (pst, 2 H, *m*), 6.70 (pst, 1 H, *p*-B-CH$_2$Ph), 5.77, 5.60, 5.57 (double intensity) (each Cp), 3.88 (dd, 1 H, $^3J_{HH}$ = 10.2 Hz, $^3J_{HH}$ = 2.8 Hz, 1-H), 3.24 (br, 2 H, B-C*H*$_2$), 3.17 (dd, 1 H, $^2J_{HH}$ = 15.0 Hz, $^3J_{HH}$ = 2.8 Hz, CHC*H*$_2$), 2.67 (dd, 1 H, $^2J_{HH}$ = 15.0 Hz, $^3J_{HH}$ = 10.2 Hz, CHC*H*$_2$), 2.19 (s, 3 H, PhC*H*$_3$). − ^{13}C NMR (150.8 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 184.0 (N=*C*H), 149.0, 138.1, 137.2 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-B(C$_6$F$_5$)$_3$], 145.2, 133.9, 129.8, 129.1 (*p*, *ipso*, *m*, *o*-PhCH$_3$), 142.0, 128.5, 128.0, 126.3 (*ipso*, *m*, *o*, *p*-CH$_2$Ph), 148.7, 128.7, 126.8, 122.4 (*ipso*, *o*, *m*, *p*-B-CH$_2$Ph), 113.5, 113.2, 109.0, 108.7 (each Cp), 93.0 (C1), 43.7 (CH*C*H$_2$), 31.9 (br, B-*C*H$_2$), 20.8 (Ph*C*H$_3$), *ipso*-B(C$_6$F$_5$)$_3$ resonance not located. − ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −12.3. − ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −128.1, −164.2, −166.8 [each m, *o*, *p*, *m*-B(C$_6$F$_5$)$_3$].

Reaction of 18d with Propionitrile: Preparation of 24d: Reaction of 269 mg (410 μmol) of **17** with 210 mg (410 μmol) of B(C$_6$F$_5$)$_3$ and subsequent reaction of the in situ prepared **18d** with 32.1 μL (24.7 mg, 450 μmol) of propionitrile gave **24d** as an orange powder, yield 376 mg (75%), mp 195°C (DSC, 259°C decomp.). − C$_{56}$H$_{41}$BF$_{15}$NOZr$_2$ (1222.2): calcd. C 55.03, H 3.38, N 1.15, found C 54.21, H 3.67, N 1.34. − ^{1}H NMR (599.9 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 8.45 (pst, 1 H, N=C*H*), 7.26 (pst, 2 H, *m*), 7.16 (pst, 1 H, *p*), 7.07 (psd, 2 H, *o*-CH$_2$Ph), 7.09 (psd, 2 H, *o*), 6.89 (pst, 2 H, *m*), 6.76 (pst, 1 H, *p*-B-CH$_2$Ph), 5.64, 5.60, 5.46, 5.43 (each s, each 5 H, Cp), 3.80 (dd, 1 H, $^3J_{HH}$ = 10.4 Hz, $^3J_{HH}$ = 3.4 Hz, 1-H), 3.32 (br, 2 H, B-C*H*$_2$), 3.10 (dd, 1 H, $^2J_{HH}$ = 15.4 Hz, $^3J_{HH}$ = 3.4 Hz, CHC*H*$_2$), 2.56 (dd, 1 H, $^2J_{HH}$ = 15.4 Hz, $^3J_{HH}$ = 10.4 Hz, CHC*H*$_2$), 1.75, 1.68 (each m, each 1 H, N=CHC*H*$_2$), 0.96 (pst, 3 H, CH$_2$C*H*$_3$). − ^{13}C NMR (150.8 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 186.9 (N=*C*H), 149.0, 138.1, 137.2 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-B(C$_6$F$_5$)$_3$], 142.0, 128.5, 127.8, 126.3 (*ipso*, *m*, *o*, *p*-CH$_2$Ph), 149.2, 128.8, 126.9, 122.5 (*ipso*, *o*, *m*, *p*-B-CH$_2$Ph), 113.8, 113.5, 108.9, 108.7 (each Cp), 91.6 (C1), 44.1 (CH*C*H$_2$), 33.2 (N=CH*C*H$_2$), 31.5 (br, B-*C*H$_2$), 8.2 (CH$_2$*C*H$_3$), *ipso*-B(C$_6$F$_5$)$_3$ resonance not located. − ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −12.3. − ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −128.1, −164.2, −166.8 [each m, *o*, *p*, *m*-B(C$_6$F$_5$)$_3$].

X-ray Crystal Structure Analysis of 24d: Pentane was allowed to diffuse through the gas phase into a solution of **24d** in a 6:1 mixture of toluene/tetrahydrofuran. After two days a yellow oil precipitated, standing for 1.5 months, single crystals grew out of this oil: formula C$_{56}$H$_{41}$BF$_{15}$NOZr$_2$, M = 1222.15, yellow crystal, 0.30 × 0.20 × 0.10 mm, a = 10.134(1), b = 19.063(1), c = 12.952(2) Å, β = 98.71(1)°, V = 2473.3(5) Å^3, ρ_{calc} = 1.641 g cm^{-3}, F(000) = 1224 e, μ = 5.21 cm^{-1}, empirical absorption correction via φ scan data (0.859 ≤ T ≤ 0.950), Z = 2, monoclinic, space group $P2_1$ (No. 4), λ = 0.71073 Å, T = 223 K, ω/2θ scans, 4757 reflections collected (+h, -k, ±l), [(sinθ)/λ] = 0.59 Å^{-1}, 4492 independent and 2955 observed reflections [$I \geq 2\,\sigma(I)$], 666 refined parameters, R = 0.067, wR^2 = 0.154, max. residual electron density 0.88 (−2.00) e Å^{-3}, Flack parameter 0.05(9), disorder in the benzyl group C30-C36 (55:45(3)%), distances C1−C30(a,b) and C30(a,b)−C31(a,b) refined with restraints, groups C30(a,b)−C36(a,b) refined as rigid groups, hydrogens calculated and refined as riding atoms. The data set was collected with an Enraf Nonius MACH3 diffractometer. Programs used: data reduction MolEN, structure solution SHELXS-86, structure refinement SHELXL-97, graphics SCHAKAL-92. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-106600. 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@ccdc.cam.ac.uk].

Reaction of 18a with *tert*-Butylisocyanate. − Preparation of 27a: Reaction of 200 mg (410 μmol) of **11** with 210 mg (410 μmol) of B(C$_6$F$_5$)$_3$ and subsequent reaction of the in situ prepared **18a** with 52.8 μL (44.6 mg, 450 μmol) of *tert*-butylisocyanate gave **27a** as a yellow powder, yield 338 mg (75%), mp 205°C (DSC, decomp.). − C$_{45}$H$_{35}$BF$_{15}$NO$_2$Zr$_2$ (1100.0): calcd. C 49.14, H 3.21, N 1.27, found C 49.14, H 3.35, N 1.42. − ^{1}H NMR (200.1 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 7.45 (s, 1 H, O=C*H*), 6.04, 5.95, 5,78, 5.74 (each s, each 5 H, Cp), 3.41 (q, 1 H, $^3J_{HH}$ = 6.3 Hz, 1-H), 1.53 (d, 3 H, $^3J_{HH}$ = 6.3 Hz, CHC*H*$_3$), 1.05 [s, 9 H, C(C*H*$_3$)$_3$], B-*H* resonance not observed. − ^{13}C-NMR (50.3 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 165.1 (O=*C*H), 149.0, 138.0, 136.9 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-B(C$_6$F$_5$)$_3$], 114.2, 114.0, 110.0, 109.5 (each Cp), 85.8 (C1), 56.1 [*C*(CH$_3$)$_3$], 31.0 [C(*C*H$_3$)$_3$], 23.8 (*C*H$_3$), *ipso*-B(C$_6$F$_5$)$_3$ resonance not located. − ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −24.6 (d, $^1J_{BH}$ = 82 Hz). − ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −132.0, −163.5, −166.3 [each m, *o*, *p*, *m*-B(C$_6$F$_5$)$_3$].

Reaction of 18a with Trimethylsilylisocyanate: Preparation of 27b: Reaction of 200 mg (410 μmol) of **11** with 210 mg (410 μmol) of B(C$_6$F$_5$)$_3$ and subsequent reaction of the in situ prepared **18a** with 59.8 μL (51.8 mg, 450 μmol) of trimethylsilylisocyanate gave **27b** as a yellow powder, yield 307 mg (67%), mp 158°C (DSC, decomp.). − C$_{44}$H$_{35}$BF$_{15}$NO$_2$SiZr$_2$ (1116.1): calcd. C 47.35, H 3.16, N 1.25, found C 47.05, H 3.26, N 1.52. − ^{1}H NMR (200.1 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 7.41 (s, 1 H, O=C*H*), 5.91, 5.82, 5,72, 5.68 (each s, each 5 H, Cp), 3.38 (q, 1 H, $^3J_{HH}$ = 6.3 Hz, 1-H), 1.49 (d, 3 H, $^3J_{HH}$ = 6.3 Hz, CHC*H*$_3$), 0.08 [s, 9 H, Si(C*H*$_3$)$_3$], B-*H* resonance not observed. − ^{13}C NMR (50.3 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 170.7 (O=*C*H), 149.0, 138.0, 136.9 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-B(C$_6$F$_5$)$_3$), 114.0, 113.8, 110.0, 109.4 (each Cp), 86.7 (C1), 23.9 (CH*C*H$_3$), −0.1 [Si(*C*H$_3$)$_3$], *ipso*-B(C$_6$F$_5$)$_3$ resonance not located. − ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −24.6 (d, $^1J_{BH}$ = 82 Hz). − ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −132.0, −163.5, −166.3 [each m, *o*, *p*, *m*-B(C$_6$F$_5$)$_3$].

Reaction of 18a with *p*-Tolylisocyanate: Preparation of 27c: Reaction of 200 mg (410 μmol) of **11** with 210 mg (410 μmol) of

$B(C_6F_5)_3$ and subsequent reaction of the in situ prepared **18a** with 56.6 µL (59.9 mg, 450 µmol) of *p*-tolylisocyanate gave **27c** as a yellow powder, yield 335 mg (72%), mp 161°C (DSC, decomp.). – $C_{48}H_{33}BF_{15}NO_2Zr_2$ (1134.0): calcd. C 50.84, H 2.93, N 1.24, found C 51.24, H 3.39, N 1.04. – ^{1}H NMR (200.1 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 7.61 (s, 1 H, O=C*H*), 7.07, 6.72 (m, each 2 H, *m*, *o*-PhCH$_3$), 6.02, 5.79 (double intensity), 5.74 (each s, each 5 H, Cp), 3.47 (q, 1 H, $^3J_{HH}$ = 6.3 Hz, 1-H), 2.19 (s, 3 H, PhC*H*$_3$), 1.50 (d, 3 H, $^3J_{HH}$ = 6.3 Hz, CHC*H*$_3$), B-*H* resonance not observed. – ^{13}C NMR (50.3 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 166.4 (O=*C*H), 149.0, 138.1, 137.2 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-B(C$_6$F$_5$)$_3$], 139.9, 138.0, 130.8, 121.5 (*ipso*, *p*, *m*, *o*-PhCH$_3$), 114.5, 114.1, 110.2, 109.6 (each Cp), 87.9 (C1), 24.1 (CH*C*H$_3$), 20.7 (Ph*C*H$_3$), *ipso*-B(C$_6$F$_5$)$_3$ resonance not located. – ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = –24.6 (d, $^1J_{BH}$ = 82 Hz). – ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = –132.0, –163.5, –166.3 [each m, *o*, *p*, *m*-B(C$_6$F$_5$)$_3$].

Reaction of 18b with *tert*-Butylisocyanate: Preparation of 28a: Reaction of 206 mg (410 µmol) of **8** with 210 mg (410 µmol) of $B(C_6F_5)_3$ and subsequent reaction of the in situ prepared **18b** with 52.8 µL (44.6 mg, 450 µmol) of *tert*-butylisocyanate gave **28a** as a yellow powder, yield 306 mg (67%), mp 203°C (DSC, decomp.). – $C_{46}H_{37}BF_{15}NO_2Zr_2$ (1114.0): calcd. C 49.60, H 3.35, N 1.26, found C 48.61, H 3.38, N 1.10. – ^{1}H NMR (200.1 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 7.31 (s, 1 H, O=C*H*), 5.93, 5.86, 5,70, 5.66 (each s, each 5 H, Cp), 3.36 (q, 1 H, $^3J_{HH}$ = 6.3 Hz, 1-H), 1.50 (d, 3 H, $^3J_{HH}$ = 6.3 Hz, CHC*H*$_3$), 1.18 (br, 3 H, B-C*H*$_3$), 1.00 [s, 9 H, C(C*H*$_3$)$_3$]. – ^{13}C NMR (50.3 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 165.6 (O=*C*H), 149.0, 138.0, 136.9 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-B(C$_6$F$_5$)$_3$], 114.0, 113.8, 109.8, 109.3 (each Cp), 85.9 (C1), 56.0 [*C*(CH$_3$)$_3$], 31.0 [C(*C*H$_3$)$_3$], 23.8 (CH*C*H$_3$), *ipso*-B(C$_6$F$_5$)$_3$ and B-*C*H$_3$ resonances not located. – ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = –14.5. – ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = –132.0, –163.5, –166.3 [each m, *o*, *p*, *m*-B(C$_6$F$_5$)$_3$).

Reaction of 18b with Trimethylsilylisocyanate: Preparation of 28b: Reaction of 206 mg (410 µmol] of **8** with 210 mg (410 µmol) of $B(C_6F_5)_3$ and subsequent reaction of the in situ prepared **18b** with 59.8 µL (51.8 mg, 450 µmol) of trimethylsilylisocyanate gave **28b** as a yellow powder, yield 283 mg (61%), mp 157°C (DSC, decomp.). – $C_{45}H_{37}BF_{15}NO_2SiZr_2$ (1130.1): calcd. C 47.83, H 3.30, N 1.24, found C 47.82, H 3.30, N 1.55. – ^{1}H NMR (200.1 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 7.48 (s, 1 H, O=C*H*), 6.05, 5.97, 5.85, 5.80 (each s, each 5 H, Cp), 3.53 (q, 1 H, $^3J_{HH}$ = 6.3 Hz, 1-H), 1.62 (d, 3 H, $^3J_{HH}$ = 6.3 Hz, CHC*H*$_3$), 1.18 (br, 3 H, B-C*H*$_3$), 0.20 [s, 9 H, Si(C*H*$_3$)$_3$]. – ^{13}C NMR (150.8 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 170.6 (O=*C*H), 149.0, 138.0, 136.9 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-B(C$_6$F$_5$)$_3$], 114.0, 113.8, 110.0, 109.4 (each Cp), 86.7 (C1), 23.9 (CH*C*H$_3$), 11.4 (br, B-*C*H$_3$), 0.1 [Si(*C*H$_3$)$_3$], *ipso*-B(C$_6$F$_5$)$_3$ resonance not located. – ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = –14.6. – ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = –132.0, –163.5, –166.3 [each m, *o*, *p*, *m*-B(C$_6$F$_5$)$_3$].

Reaction of 18b with *p*-Tolylisocyanate: Preparation of 28c: Reaction of 206 mg (410 µmol) of **8** with 210 mg (410 µmol) of $B(C_6F_5)_3$ and subsequent reaction of the in situ prepared **18b** with 56.6 µL (59.9 mg, 450 µmol) of *p*-tolylisocyanate gave **28c** as a yellow powder, yield 334 mg (71%), mp 165°C (DSC, decomp.). – $C_{49}H_{35}BF_{15}NO_2Zr_2$ (1148.1): calcd. C 51.26, H 3.07, N 1.22, found C 52.00, H 3.30, N 1.43. – ^{1}H NMR (200.1 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 7.36 (s, 1 H, O=C*H*), 7.11, 6.69 (m, each 2 H, *m*, *o*-PhCH$_3$) 5.99, 5.78, 5,76, 5.70 (each s, each 5 H, Cp), 3.49 (q, 1 H, $^3J_{HH}$ = 6.3 Hz, 1-H), 2.20 (s, 3 H, PhC*H*$_3$), 1.51 (d, 3 H, $^3J_{HH}$ = 6.3 Hz, CHC*H*$_3$), 1.21 (br, 3 H, B-C*H*$_3$). – ^{13}C NMR (50.3 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 166.0 (O=*C*H), 149.0, 138.1, 137.2 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-B(C$_6$F$_5$)$_3$], 139.8, 138.2, 130.9, 121.5 (*ipso*, *p*, *m*, *o*-PhCH$_3$), 114.5, 114.1, 110.1, 109.5 (each Cp), 88.2 (C1), 24.1 (CH*C*H$_3$), 20.7 (Ph*C*H$_3$), *ipso*-B(C$_6$F$_5$)$_3$ and B-*C*H$_3$ resonances not located. – ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = –14.6. – ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = –132.0, –163.5, –166.3 [each m, *o*, *p*, *m*-B(C$_6$F$_5$)$_3$].

Reaction of 18b with 1-Adamantylisocyanate: Preparation of 28d: Reaction of 206 mg (410 µmol) of **8** with 210 mg (410 µmol) of $B(C_6F_5)_3$ and subsequent reaction of the in situ prepared **18b** with 79.8 mg (450 µmol) of 1-adamantylisocyanate gave **28d** as a yellow powder, yield 354 mg (66%), mp 208°C (DSC, decomp.). – $C_{52}H_{43}BF_{15}NO_2Zr_2$ (1192.2): calcd. C 52.39, H 3.64, N 1.17, found C 51.90, H 4.22, N 1.05, found C 52.69, H 3.91, N 1.93. – ^{1}H NMR (599.9 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 7.36 (s, 1 H, O=C*H*), 5.97, 5.89, 5.73, 5.69 (each s, each 5 H, Cp), 3.37 (q, 1 H, $^3J_{HH}$ = 6.3 Hz, 1-H), 1.96 (br, 3 H, AdC*H*), 1.7-1.4 (m, 18 H, AdC*H*$_2$, CHC*H*$_3$, B-C*H*$_3$). – ^{13}C NMR (150.8 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 165.0 (O=*C*H), 149.0, 138.0, 136.9 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-B(C$_6$F$_5$)$_3$], 114.0, 113.8, 119.9, 109.4 (each Cp), 85.7 (C1), 57.4 (Ad*C*), 44.4, 35.8 (Ad*C*H$_2$), 30.0 (Ad*C*H), 23.8 (CH*C*H$_3$), *ipso*-B(C$_6$F$_5$)$_3$ and B-*C*H$_3$ resonances not located. – ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = –14.6. – ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = –132.0, –163.5, –166.3 [each m, *o*, *p*, *m*-B(C$_6$F$_5$)$_3$].

Reaction of 18c with *tert*-Butylisocyanate: Preparation of 29a: Reaction of 206 mg (410 µmol) of **14** with 210 mg (410 µmol) of $B(C_6F_5)_3$ and subsequent reaction of the in situ prepared **18c** with 52.8 µL (44.6 mg, 450 µmol) of *tert*-butylisocyanate gave **29a** as a yellow orange powder, yield 297 mg (65%), mp 176°C (DSC, decomp.). – $C_{46}H_{37}BF_{15}NO_2Zr_2$ (1114.0): calcd. C 49.60, H 3.35, N 1.26, found C 49.45, H 3.56, N 1.27. – ^{1}H NMR (200.1 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 7.39 (s, 1 H, O=C*H*), 5.95, 5.89, 5.71, 5.69 (each s, each 5 H, Cp), 3.15 (dd, 1 H, 1-H), 1.8–1.4 (m, 2 H, C*H*$_2$), 1.01 [s, 9 H, C(C*H*$_3$)$_3$], 0.89 (pst, 3 H, CH$_2$C*H*$_3$), B-*H* resonance not observed. – ^{13}C NMR (50.3 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 165.8 (N=*C*H), 149.0, 138.1, 137.2 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-B(C$_6$F$_5$)$_3$], 114.1 (double intensity), 119.8, 109.5 (each Cp), 93.2 (C1), 56.1 [*C*(CH$_3$)$_3$], 31.7 (*C*H$_2$), 31.1 [C(*C*H$_3$)$_3$], 14.4 (CH$_2$*C*H$_3$), *ipso*-B(C$_6$F$_5$)$_3$ resonance not located. – ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = –24.6 (d, $^1J_{BH}$ = 82 Hz). – ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = –132.0, –164.3, –166.9 [each m, *o*, *p*, *m*-B(C$_6$F$_5$)$_3$].

Reaction of 18c with Trimethylsilylisocyanate: Preparation of 29b: Reaction of 206 mg (410 µmol) of **14** with 210 mg (410 µmol) of $B(C_6F_5)_3$ and subsequent reaction of the in situ prepared **18c** with 59.8 µL (51.8 mg, 450 µmol) of trimethylsilylisocyanate gave **29b** as a yellow powder, yield 297 mg (64%), mp 185°C (DSC, decomp.). – $C_{45}H_{37}BF_{15}NO_2SiZr_2$ (1130.1): calcd. C 47.83, H 3.30, N 1.24, found C 47.90, H 3.42, N 1.37. – ^{1}H NMR (200.1 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 7.45 (s, 1 H, O=C*H*), 6.00, 5.94, 5.78, 5.76 (each s, each 5 H, Cp), 3.27 (dd, 1 H, 1-H), 1.9-1.7, 1.7-1.4 (each m, each 1 H, C*H*$_2$), 0.90 (pst, 3 H,

CH_2CH_3), 0.13 [s, 9 H, Si(CH_3)$_3$], B-*H* resonance not observed. – ^{13}C NMR (50.3 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 170.7 (O=*C*H), 149.0, 138.1, 137.2 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-B(C_6F_5)$_3$], 114.1 (double intensity), 119.9, 109.5 (each Cp), 93.9 (C1), 31.8 (CH_2), 14.5 (CH_2CH_3), −0.1 [Si(CH_3)$_3$], *ipso*-B(C_6F_5)$_3$ resonance not located. – ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −24.6 (d, $^1J_{BH}$ = 82 Hz). – ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −132.0, −164.3, −166.9 [each m, *o*, *p*, *m*-B(C_6F_5)$_3$].

Reaction of 18c with *p*-Tolylisocyanate: Preparation of 29c: Reaction of 206 mg (410 μmol) of **14** with 210 mg (410 μmol) of B(C_6F_5)$_3$ and subsequent reaction of the in situ prepared **18c** with 56.6 μL (59.9 mg, 450 μmol) of *p*-tolylisocyanate gave **29c** as a yellow powder, yield 353 mg (75%), mp 170°C (DSC, decomp.). – $C_{49}H_{35}BF_{15}NO_2Zr_2$ (1148.1): calcd. C 51.26, H 3.07, N 1.22, found C 50.90, H 3.32, N 1.52. – ^{1}H NMR (200.1 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 7.75 (s, 1 H, O=C*H*), 7.16, 6.78 (each psd, each 2 H, *m*, *o*-PhCH$_3$), 6.16, 5.96, 5.92, 5.90 (each s, each 5 H, Cp), 3.37 (dd, 1 H, 1-H), 2.28 (s, 3 H, PhCH_3), 1.9-1.6 (m, 2 H, CH_2), 0.98 (pst, 3 H, CH_2CH_3), B-*H* resonance not observed. – ^{13}C NMR (50.3 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 166.0 (O=*C*H), 149.0, 138.1, 137.2 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-B(C_6F_5)$_3$], 139.8, 138.0, 130.8, 121.4 (*ipso*, *p*, *m*, *o*-PhCH$_3$), 114.5, 114.3, 110.1, 109.6 (each Cp), 94.7 (C1), 31.9 (CH_2), 24.8 (Ph*C*H$_3$), 14.5 (CH_2CH_3), *ipso*-B(C_6F_5)$_3$ resonance not located. – ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −24.6 (d, $^1J_{BH}$ = 82 Hz). – ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −131.9, −164.3, −166.6 [each m, *o*, *p*, *m*-B(C_6F_5)$_3$].

Reaction of 18d with *tert*-Butylisocyanate: Preparation of 30a: Reaction of 269 mg (410 μmol) of **17** with 210 mg (410 μmol) of B(C_6F_5)$_3$ and subsequent reaction of the in situ prepared **18d** with 52.8 μL (44.6 mg, 450 μmol) of *tert*-butylisocyanate gave **30a** as a yellow powder, yield 358 mg (69%), mp 180°C (DSC, decomp.). – $C_{58}H_{45}BF_{15}NO_2Zr_2$ (1266.3): calcd. C 55.02, H 3.58, N 1.11, found C 55.59, H 3.87, N 1.50. – ^{1}H NMR (599.9 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 7.26 (s, 1 H, O=C*H*), 7.34 (pst, 2 H, *m*), 7.22 (pst, 1 H, *p*), 7.18 (m, 2 H, *o*-CH_2Ph), 6.98 (pst, 2 H, *m*), 6.84 (pst, 1 H, *p*-B-CH_2Ph), 5.85, 5.77, 5.69, 5.52 (each s, each 5 H, Cp), 3.68 (dd, 1 H, $^3J_{HH}$ = 9.9 Hz, $^3J_{HH}$ = 3.1 Hz, 1-H), 3.41 (br, 2 H, B-CH_2), 3.01 (dd, 1 H, $^2J_{HH}$ = 14.7 Hz, $^3J_{HH}$ = 3.1 Hz, CHCH_2), 2.67 (dd, 1 H, $^2J_{HH}$ = 14.7 Hz, $^3J_{HH}$ = 9.9 Hz, CHCH_2), 0.98 (s, 9 H, C(CH_3)$_3$). – ^{13}C NMR (150.8 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 165.3 (O=*C*H), 149.0, 138.1, 137.2 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-B(C_6F_5)$_3$], 143.8, 129.0, 128.7, 126.8 (*ipso*, *m*, *o*, *p*-CH_2Ph), 149.2, 129.3, 127.4, 123.1 (*ipso*, *o*, *m*, *p*-B-CH_2Ph), 114.1, 114.0, 109.8, 109.5 (each Cp), 91.8 (C1), 56.1 [*C*(CH_3)$_3$], 45.0 (CH*C*H$_2$), 32.4 (br, B-*C*H$_2$), 31.0 [C(*C*H$_3$)$_3$], *ipso*-B(C_6F_5)$_3$ resonance not located. – ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −12.3. – ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −128.1, −164.2, −166.8 [each m, *o*, *p*, *m*-B(C_6F_5)$_3$].

Reaction of 18d with Trimethylsilylisocyanate: Preparation of 30b: Reaction of 269 mg (410 μmol) of **17** with 210 mg (410 μmol) of B(C_6F_5)$_3$ and subsequent reaction of the in situ prepared **18d** with 59.8 μL (51.8 mg, 450 μmol) of trimethylsilylisocyanate gave **30b** as a yellow-orange powder, yield 342 mg (65%), mp 167°C (DSC, decomp.). – $C_{57}H_{45}NBF_{15}O_2SiZr_2$ (1282.3): calcd. C 53.39, H 3.54, N 1.09, found C 53.36, H 3.85, N 1.13. – ^{1}H NMR (599.9 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 7.30 (s, 1 H, O=C*H*), 7.28 (pst, 2 H, *m*), 7.17 (pst, 1 H, *p*),7.16 (psd, 2 H, *o*-CH_2Ph), 7.09 (psd, 2 H, *o*), 6.90 (pst, 2 H, *m*), 6.76 (pst, 1 H, *p*-B-CH_2Ph), 5.81, 5.77, 5.68, 5.46 (each s, each 5 H, Cp), 3.71 (dd, 1 H, $^3J_{HH}$ = 9.9 Hz, $^3J_{HH}$ = 3.1 Hz, 1-H), 3.32 (br, 2 H, B-CH_2), 2.98 (dd, 1 H, $^2J_{HH}$ = 14.8 Hz, $^3J_{HH}$ = 3.1 Hz, CHCH_2), 2.64 (dd, 1 H, $^2J_{HH}$ = 14.8 Hz, $^3J_{HH}$ = 9.9 Hz, CHCH_2), 0.01 [s, 9 H, Si(CH_3)$_3$]. – ^{13}C NMR (150.8 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 170.4 (O=*C*H), 149.0, 138.1, 137.2 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-B(C_6F_5)$_3$], 144.0, 129.0, 128.8, 126.8 (*ipso*, *m*, *o*, *p*-CH_2Ph), 149.2, 129.3, 127.3, 123.0 (*ipso*, *o*, *m*, *p*-B-CH_2Ph), 114.1, 114.0, 109.9, 109.6 (each Cp), 92.7 (C1), 45.0 (CH*C*H$_2$), 32.4 (br, B-*C*H$_2$), −0.1 [Si(*C*H$_3$)$_3$], *ipso*-B(C_6F_5)$_3$ resonance not located. – ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −12.3. – ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −128.1, −164.2, −166.8 [each m, *o*, *p*, *m*-B(C_6F_5)$_3$].

Reaction of 18d with *p*-Tolylsilylisocyanate: Preparation of 30c: Reaction of 269 mg (410 μmol) of **17** with 210 mg (410 μmol) of B(C_6F_5)$_3$ and subsequent reaction of the in situ prepared **18d** with 56.6 μL (59.9 mg, 450 μmol) of *p*-tolylisocyanate gave **30c** as a yellow-orange powder, yield 341 mg (64%), mp 168°C (DSC, decomp.). – $C_{61}H_{43}BF_{15}NO_2Zr_2$ (1300.3): calcd. C 56.35, H 3.33, N 1.08, found C 56.08, H 3.46, N 1.44. – ^{1}H NMR (599.9 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 7.27 (s, 1 H, O=C*H*), 7.27 (pst, 2 H, *m*), 7.16 (pst, 1 H, *p*), 7.14 (psd, 2 H, *o*-CH_2Ph), 7.09 (psd, 2 H, *o*), 6.85 (pst, 2 H, *m*), 6.75 (pst, 1 H, *p*-B-CH_2Ph), 7.04, 6.63 (each psd, each 2 H, *m*, *o*-PhCH$_3$), 5.90, 5.81, 5.71, 5.37 (each s, each 5 H, Cp), 3.75 (dd, 1 H, $^3J_{HH}$ = 10.1 Hz, $^3J_{HH}$ = 2.7 Hz, 1-H), 3.31 (br, 2 H, B-CH_2), 2.97 (dd, 1 H, $^2J_{HH}$ = 14.7 Hz, $^3J_{HH}$ = 2.7 Hz, CHCH_2), 2.62 (dd, 1 H, $^2J_{HH}$ = 14.7 Hz, $^3J_{HH}$ = 10.1 Hz, CHCH_2), 2.13 (s, 3 H, PhCH_3). – ^{13}C NMR (150.8 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = 165.6 (O=*C*H), 149.0, 138.1, 137.2 [each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-B(C_6F_5)$_3$], 139.8, 138.3, 130.9, 121.5 (*ipso*, *p*, *m*, *o*-PhCH$_3$), 144.0, 129.0, 128.8, 126.8 (*ipso*, *m*, *o*, *p*-CH_2Ph), 149.2, 129.3, 127.4, 123.0 (*ipso*, *o*, *m*, *p*-B-CH_2Ph), 114.5, 114.3, 110.1, 109.7 (each Cp), 93.7 (C1), 45.1 (CH*C*H$_2$), 31.8 (br, B-*C*H$_2$), 20.7 (Ph*C*H$_3$), *ipso*-B(C_6F_5)$_3$ resonance not located. – ^{11}B NMR (64.2 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −12.3. – ^{19}F NMR (282.4 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, ca. 4:1): δ = −128.1, −164.2, −166.8 [each m, *o*, *p*, *m*-B(C_6F_5)$_3$].

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