Formation of Metallocene-Stabilized Planar-Tetracoordinate Carbon Compounds by a Protonation Route

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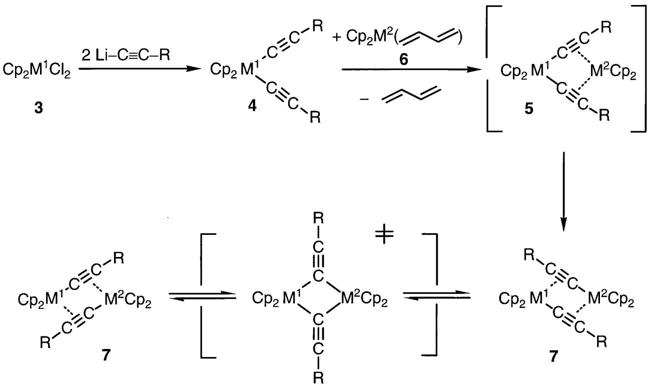
Bis(alkynyl)zirconocene and -hafnocene complexes **4** react with (butadiene)zirconocene or -hafnocene, respectively, to yield the binuclear σ,π-acetylide bridged complexes $[(Cp_2M)_2(\mu\text{-}C{\equiv}C{-}R)_2]$ **7** (M = Zr, Hf; R = CH_3, C_2H_5, or CH_2Ph). The complexes **7** are selectively protonated upon treatment with *N,N*-dimethylanilinium tetraphenylborate or tetrakis(pentafluorophenyl)borate to yield the dinuclear metallocene cation complexes $[(Cp_2M^1)(\mu\text{-}RCC^1{-}H)(\mu\text{-}C{\equiv}C{-}R)M^2Cp_2{}^+]$ **13** ($M^1 = M^2$ = Zr, **a**−**c**; M^1 = Zr, M^2 = Hf, **h**; $M^1 = M^2$ = Hf, **i**) that contain a planar-tetracoordinate carbon atom (C^1-H) bearing a hydrogen substituent. Complex **13a** was characterized by X-ray diffraction. It reveals an agostic interaction of the C^1-H moiety with the M^2Cp_2 unit. The planar-tetracoordinate carbon unit C^1-H of **13a** exhibits $^{13}C/^1H$ NMR chemical shifts of $\delta = 161.0$ and -0.11 and a coupling constant of $^1J_{CH} = 103$ Hz. Selective protonation of (μ-alkynyl)bis(group 4 metallocene) complexes containing other additional bridging ligands provides a rather general synthetic entry to planar-tetracoordinate carbon containing complexes of this type: $[Cp_2M^1(\mu\text{-}C{\equiv}C{-}CH_3)(\mu\text{-}Cl)M^2Cp_2]$ (**10a**−**c**, M^1, M^2 = Zr, Hf) and $[Cp_2M^1(\mu\text{-}C{\equiv}C{-}CH_3)(\mu\text{-}CH_3)M^2Cp_2]$ (**11a**,**b**) selectively add a proton from $[(HNMe_2Ph)^+(BAr_4)^-]$ at carbon atom C^1 of the acetylide ligand to yield the corresponding "anti-van't Hoff/LeBel complexes" $[Cp_2M^1(\mu\text{-}CH_3CC^1{-}H)(\mu\text{-}X)M^2Cp_2{}^+]$ (**13d**−**g** and **k**, X = Cl, CH_3), respectively.

Introduction

Planar-tetracoordinate carbon has an electronic structure that is characterized by an electron-deficient σ-system (six electrons making four bonds) and a doubly occupied p-orbital perpendicular to the σ-plane.[1] Principally, σ-electron donor and π-acceptor substituents should stabilize this "unnatural" carbon coordination geometry.[1][2] We have previously prepared a large number of thermodynamically very stable "anti-van't Hoff/Le Bel" compounds of this general type, where the planar-tetracoordinate carbon atom is part of a C=C double bond and has two metal substituents that share a sp^2-orbital in the carbon σ-plane in a three-center-two-electron bond situation.[3] A very favourable situation arises when the two geminal metal substituents have slightly different σ-donor properties. Typical examples are a combination of Cp_2Zr and AlR_2[4] or Cp_2Zr and Cp_2Zr^+.[5] The complexes **1** and **2** are typical examples out of a large variety of such systems. The stabilization energy of planar-tetracoordinate vs. planar-tricoordinate carbon in these complexes is very high (ca. 35 kcal/mol calculated for **1**, ca. 12 kcal/mol experimentally determined for **2**).[6]

The synthetic routes developed and applied so far have allowed for the preparation of a great variety of examples of the complexes of the type **1** and **2** using various combinations of metal complex fragments, bridging ligands X and of the substituents attached at the carbon atoms C^1 (i.e. the planar-tetracoordinate carbon atom) and C^2, but systems bearing a hydrogen at C^1 were not available by these routes.[7] We have now found a rather simple method to solve this synthetic organometallic problem and have prepared a variety of cationic bis(metallocene) complexes of this general type by a regioselective protonation pathway.



$M^1 = M^2$ = Zr, R = CH_3 (**a**), C_2H_5 (**b**), CH_2Ph (**c**)
M^1 = Zr, M^2 = Hf, R = CH_3 (**d**)
$M^1 = M^2$ = Hf, R = CH_3 (**e**)

Results and Discussion

Synthesis of the Dinuclear Complexes

Dinuclear (μ-alkynyl)zirconocene and -hafnocene complexes were chosen as the starting materials for our new synthesis. We had previously shown that bis(alkynyl)group 4 metallocenes (**4**) react rapidly with in situ generated Cp_2M

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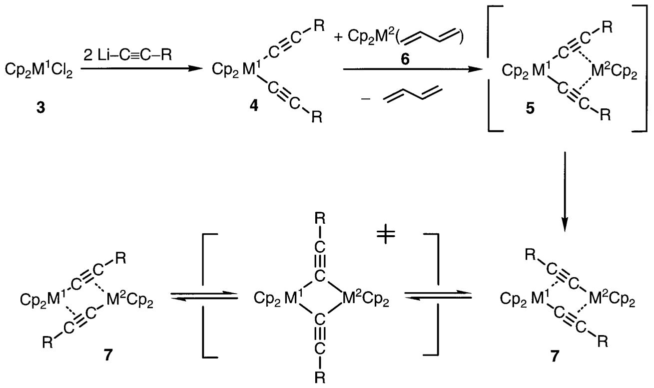
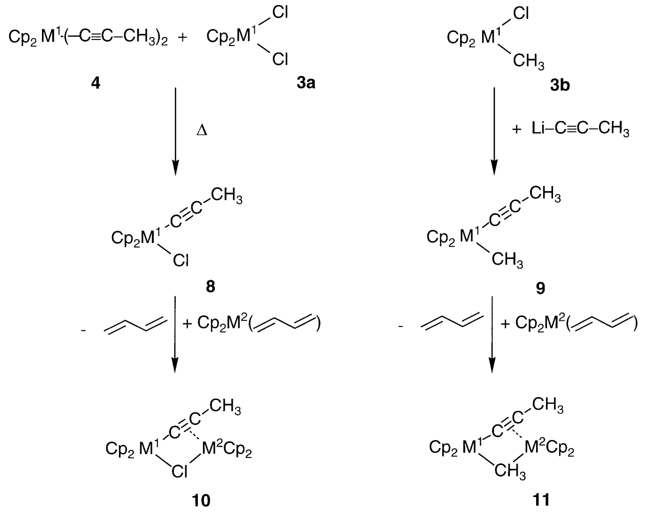
Scheme 1



$M^1 = M^2 = Zr$, $R = CH_3$ (**a**), C_2H_5 (**b**), CH_2Ph (**c**)
$M^1 = Zr$, $M^2 = Hf$, $R = CH_3$ (**d**)
$M^1 = M^2 = Hf$, $R = CH_3$ (**e**)

Scheme 2



$M^1 = M^2 = Zr$ (**a**)
$M^1 = Hf$, $M^2 = Zr$ (**b**)
$M^1 = M^2 = Hf$ (**c**)

$M^1 = M^2 = Zr$ (**a**)
$M^1 = Hf$, $M^2 = Zr$ (**b**)

(M = Zr, Hf) reagents to cleanly form the [(μ-η^1:η^2-alkynyl)$_2$(MCp$_2$)$_2$] type complexes. There is evidence that the C_{2v}-symmetric species **5** are formed first, that subsequently rearrange to the C_{2h}-complexes **6** that are eventually isolated from the reaction.[8]

We have thus treated bis(propynyl)zirconocene **4a** (M^1 = Zr, R = CH_3) with (butadiene)zirconocene (**6a**, M^2 = Zr)[9] in benzene at ambient temperature (18 h) and obtained the dinuclear complex **7a** in 70% yield. Complex **7a**, like many examples of this type of complexes, is dynamic and undergoes an intramolecular exchange of the two μ-η^1:η^2-alkynyl ligands within the dinuclear metal complex framework that is rapid on the NMR time scale.[8][10]

Complexes **7b** and **7c** were prepared analogously by treatment of the respective bis(alkynyl)zirconocenes **4b** and **4c** with the (butadiene)zirconocene reagent. Treatment of bis(propynyl)hafnocene (**4a′**) with (butadiene)zirconocene cleanly gave the mixed-metal complex **7d**, and treatment of **4a′** with (butadiene)hafnocene furnished the bis(μ-η^1:η^2-propynyl)bis(hafnocene) complex **7e**. The latter reaction required more drastical reaction conditions (2 d at 60 °C) to liberate Cp_2Hf in situ.

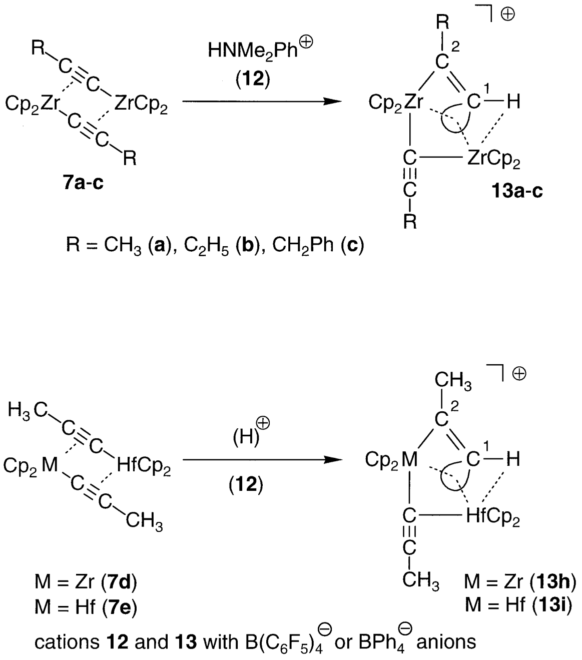
Thermally induced ligand exchange was used to prepare the (propynyl)metallocene chlorides **8**.[8] Subsequent treatment with the (butadiene)metallocenes then gave the (μ-η^1:η^2-propynyl)(μ-chloro)bis(metallocenes) **10a–c** (see Scheme 2). Treatment of **3b** with propynyllithium (to give **9**), followed by treatment with (butadiene)$ZrCp_2$, gave the (μ-η^1:η^2-propynyl)(μ-methyl)bis(metallocenes) **11a**, **b**.

In the synthesis of the μ-methyl bridged systems, only (butadiene)zirconocene was employed as the source for the in situ metallocene generation. Attempts to use the corresponding hafnocene reagent required higher temperatures that led to massive σ-ligand scrambling of the starting materials and precluded a clean product formation.

We then treated the dinuclear (μ-alkynyl)bis(metallocene) complexes **7**, **10**, and **11** with a suitable proton source. As reagents for the proton transfer reaction we choose the *N*,*N*-dimethylanilinium salts [$HNMe_2Ph^+$][$B(C_6F_5)_4^-$] (**12a**) or [$HNMe_2Ph^+$][BPh_4^-] (**12b**), respectively. Both reagents had previously been used for the synthesis of donor-ligand stabilized zirconocene derived cations, such as e.g. [$Cp_2ZrCH_3^+$] (from $Cp_2Zr(CH_3)_2$).[11] Thus, the here selected anions had shown to be of a sufficiently low nucleophilicity to not interfere with the formation of very electrophilic group 4 metallocene-based cation systems.

The protonation reactions in all cases led to the formation of the same cationic systems irrespective whether [BPh_4^-] or [$B(C_6F_5)_4^-$] was used as the counteranion. Thus, the bis(μ-η^1:η^2-propynyl)bis(zirconocene) complex **7a** was treated with one molar equivalent of the ammonium salt **12b** at −50 °C in dichloromethane. After workup at room temperature a single cationic product was isolated in close to 60% yield that was identified as **13a** spectroscopically and by an X-ray crystal structure analysis (see below). The product exhibits a pair of $^1H/^{13}C$-NMR Cp signals at δ = 6.03, 5.71 / 109.7, 108.4 (in [D$_2$]dichloromethane) and methyl group resonances at δ = 2.83, 2.44 / 25.1, 10.2. Noteworthy is the [Zr]-σ-alkenyl C^2 ^{13}C-NMR resonance at δ = 217.6 and the $^1H/^{13}C$-NMR resonances of the planar-tetracoordinate carbon C^1-H group at δ = −0.11 (broad singlet) / 161.0 ($^1J_{CH}$ = 103 Hz). Thus, the planar-tetracoordinate carbon atom exhibits a chemical shift in the olefinic region, as it is expected for sp^2-hybridized carbon, but its $^1J_{CH}$ coupling constant is quite unusual at a very low value of close to 100 Hz. As we shall see, this is a very typical feature of the planar-tetracoordinate carbon compounds that bear a hydrogen substituent at C^1. It is probably the close vicinity of the C^1-H hydrogen to its adjacent zirconium center Zr^2 that results in such a marked decrease of the $^1J_{CH}$ value of this (sp^2)C-H moiety. According to the X-ray crystal structure analysis of **13a** (see below) an α-agostic interaction[12] between C^1-H and Zr^2 must be assumed.

Scheme 3



R = CH$_3$ (**a**), C$_2$H$_5$ (**b**), CH$_2$Ph (**c**)

M = Zr (**7d**)
M = Hf (**7e**)

cations **12** and **13** with $B(C_6F_5)_4^{\ominus}$ or $BPh_4^{\ominus}$ anions

The protonation reactions of the related complexes **7b** and **7c** proceed analogously to yield the corresponding planar-tetracoordinate carbon complexes **13b** and **13c**, respectively. Some of their typical spectroscopic parameters are listed in Table 1. Protonation of the bis(μ-η^1:η^2-propynyl)bis(hafnocene) complex **7e** also proceeds cleanly to yield **13i**. Noteworthy is here that the C^1-*H* ^{1}H-NMR resonance is shifted markedly to a larger δ-value (+0.42) as compared to the zirconium-containing examples **10a–c** (see Table 1), whereas the $^1J_{C^1\text{-}H}$ coupling constant is still very low at 99 Hz. It thus may be that the ^{1}H-NMR C^1-*H* chemical shift is sensitive to the very nature of its closely adjacent metal center. This specific feature turned out to be of some diagnostic value in the protonation reactions of the heterodimetallic precursors.

Protonation of the bis(μ-η^1:η^2-propynyl)(HfCp$_2$)(ZrCp$_2$) complex **7d** could in principle lead to the formation of two regioisomeric products arising from H$^+$-addition to either the CH$_3$−C≡C−HfCp$_2$ or the CH$_3$−C=C−ZrCp$_2$ unit. The reaction of the heterodimetallic complex **7d** with **12b** resulted in the formation of a single organometallic product (**13h**) that was isolated in ca. 50% yield. The product exhibits ^{1}H/^{13}C-NMR pairs of Cp resonances at δ 5.94, 5.72 / 108.6, 108.1, and ^{13}C/^{1}H-NMR signals of the C^1-H unit at δ 162.5 ($^1J_{CH}$ = 100 Hz) and +0.38. The latter value is in the typical range expected of an α-agostic C^1-H moiety at HfCp$_2$. We therefore propose that protonation has occured regioselectively at the CH$_3$−C≡C−HfCp$_2$ part of the starting material **4e**, leading to the heterodinuclear planar-tetracoordinate carbon compound **13h**.

A very similar situation was found when the μ-chloro- and μ-methyl-bridged metallocene complexes were protonated. Treatment of (μ-η^1:η^2-propynyl)(μ-Cl)(ZrCp$_2$)$_2$ **10a**

Scheme 4

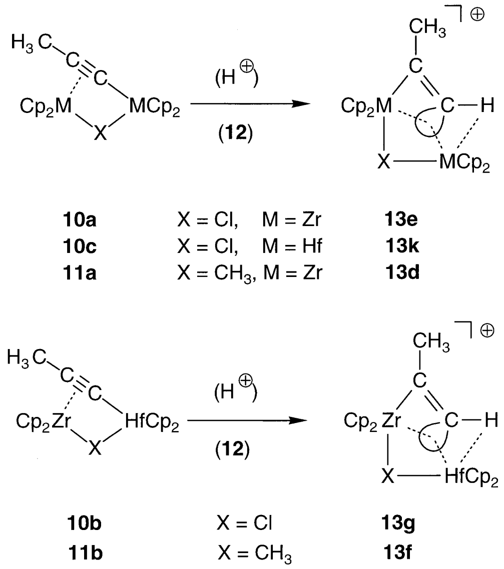


Table 1. Selected NMR data of the planar-tetracoordinate carbon complexes **13** and related reference compounds

Compd.	prepd. from	R	X	anion	M	δ C^2	δ C^1-H[d]		$^1J_{C^1\text{-}H}$ [Hz]
13a	**7a**	CH$_3$	[a]	[b]	Zr,Zr	217.6	161.0	−0.11	103
13b	**7b**	C$_2$H$_5$	[a]	[b][c]	Zr,Zr	227.6	160.4	−0.16	103
13c	**7c**	CH$_2$Ph	[a]	[b]	Zr,Zr	225.2	165.3	−0.47	[m]
13d	**11a**	CH$_3$	CH$_3$	[b][c]	Zr,Zr	229.8	159.3	0.83	108
13e	**10a**	CH$_3$	Cl	[b]	Zr,Zr	273.7	157.7	0.51	103
13f	**11b**	CH$_3$	CH$_3$	[c]	Zr,Hf	233.7	160.1	1.47	106
13g	**10b**	CH$_3$	Cl	[b]	Zr,Hf	227.1	156.4	1.12	99
13h	**7d**	CH$_3$	[a]	[b]	Zr,Hf	[e]	162.5	0.38	100
13i	**7e**	CH$_3$	[a]	[b]	Hf,Hf	225.1	167.4	0.42	99
13k	**10c**	CH$_3$	Cl	[b]	Hf,Hf	228.6	160.8	1.05	97
2a	–	CH$_3$	[a]	[c]	Zr,Zr	210.4	127.7[f]	[g][h]	–
2b	–	CH$_3$	[a]	[c]	Zr,Hf	217.1	129.5[f]	[g][h]	–
2c	–	n-C$_3$H$_7$	Cl	[c]	Zr,Zr	224.9	125.3	[g][h]	–
1a	–	CH$_3$	CCPh	–	Zr,Al	208.6	144.2[f]	[i][k]	–
1b	–	CH$_3$	CC−C$_6$H$_{11}$	–	Zr,Al	197.7	152.0[f]	[k][l]	–

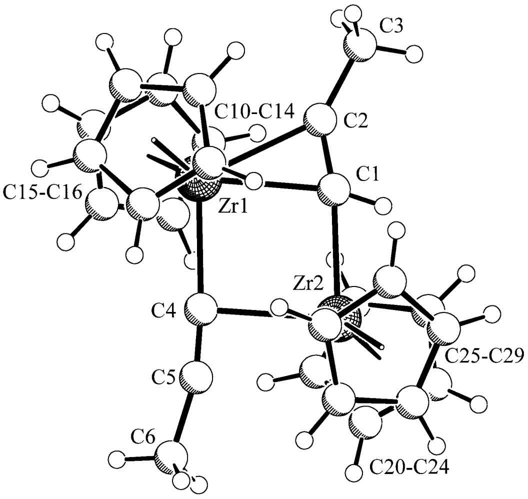
[a] C≡C−R. – [b] $B(C_6F_5)_4^-$. – [c] BPh_4^- . – [d] NMR spectra in CD$_2$Cl$_2$. – [e] Not located. – [f] Tentative assignment. – [g] C^1-CH$_3$. – [h] From ref.[3][5][6]. – [i] C^1-Ph. – [k] From ref.[3][4]. – [l] C^1-cyclohexyl. – [m] Not determined.

with $[HNMe_2Ph^+][B(C_6F_5)_4^-]$ (**12b**) gave rise to the formation of the planar-tetracoordinate carbon compound **13e** ($^1H/^{13}C$ NMR of the C^1-H unit: δ = 0.51/157.7 ($^1J_{CH}$ = 103 Hz). Protonation of the corresponding mixed metal compound **10b** selectively led to a single product (**13g**) whose C^1-*H* ^{1}H-NMR resonance is found shifted to δ 1.12. A similar value was found in the planar-tetracoordinate carbon complex **13k** containing the $(\mu\text{-Cl})(Cp_2Hf)_2$ framework (see Table 1), and a similar trend was observed upon protonation of **11a** and **11b** giving rise to the selective formation of the planar-tetracoordinate carbon compounds **13d** and **13f**, respectively. In all these cases the $HfCp_2$ unit ended up in the "south-east position" of the planar-tetracoordinate carbon containing dimetallic framework, similarly as it was observed for a related series of mixed metal derivatives of the complex type **2** (see above).

X-ray Crystal Structure Analysis of 13a

Single crystals suited for the X-ray crystal structure analysis were obtained by allowing a solution of **13a** [$\cdot B(C_6F_5)_4^-$] in dichloromethane to equilibrate with toluene by gas-phase diffusion in a closed system. The dimetallic cation **13a** and the $B(C_6F_5)_4^-$ anion are independent in the crystal. In the cation the two zirconocene units are well separated from each other (Zr1···Zr2 separation 3.477 Å). The zirconium centers are connected by means of two hydrocarbyl ligands, namely the $H_3C^3C^2C^1H$ unit and the $C^4C^5C^6H_3$ moiety. The special structural features of the former make complex **13a** so noteworthy. It contains the carbon atom C^1 that is planar-tetracoordinate. Carbon atom C^1 is bonded to C^2 [d C^1-C^2 1.255(9) Å], the metal atoms Zr^1 [d Zr^1-C^1 2.377(6) Å] and Zr^2 [d Zr^2-C^1 2.274(7) Å] and a hydrogen atom (crystallographically located, d C^1-H 0.91 Å). The atoms C^1, C^2, H^1, Zr^1, and Zr^2 are oriented coplanar (their neighboring atoms C^3, C^4, C^5, C^6 are located in the same plane, which is the typical σ-ligand plane of the two group 4 bent metallocene subunits).[13] The bonding angles around the planar-tetracoordinate carbon atom C^1 are 96.7(2)° ($Zr^1-C^1-Zr^2$), 74.1(5)° ($Zr^1-C^1-C^2$), 119° ($C^2-C^1-H^1$), and 70° ($Zr^2-C^1-H^1$) (sum of bonding angles at C^1: 359.8°).

Figure 1. A view of the molecular geometry of **13a**[a]



[a] Selected bond lengths [Å] and angles [°]: Zr1−C1 2.377(6), Zr1−C2 2.365(8), Zr1−C4 2.313(6), Zr2−C1 2.274(7), Zr2−C4 2.406(6), Zr2−C5 2.693(8), Zr2−H1 2.14(7), C1−C2 1.255(9), C1−H1 0.91(7), C2−C3 1.492(10), C4−C5 1.199(9), C5−C6 1.468(10), Zr1−C1−Zr2 96.7(2), Zr1−C4−Zr2 94.9(2), Zr1−C1−C2 74.1(5), Zr1−C1−H1 166(4), Zr1−C2−C1 75.2(5), Zr1−C2−C3 144.0(6), Zr2−C1−C2 170.1(6), Zr2−C1−H1 70(4), C1−C2−C3 140.8(8), Zr1−C4−C5 174.4(6), Zr2−C4−C5 90.3(5), C4−C5−C6 166.6(8).

In a comparison with typical planar-tetracoordinate carbon compounds and related complexes of this general structural type (see Table 2) it becomes apparent that the complexes **13** exhibit a few very special bonding parameters. The Zr^1-C^1 bond, the "extra bond" between the acceptor-metallocene Cp_2Zr^1 and the planar-tetracoordinate carbon center, is the shortest found in the overall series of complexes so far. This bond is by ca. 0.12 Å shorter than its equivalent in the related bis(zirconocene) complex **2a** ($M^1 = M^2 = Zr$, $R^1 = R^2 = CH_3$) (see Scheme 5 and Table 2). Only in the μ-N≡C−Ph complex **14** is this metal-to-bridgehead atom bond shorter. We also note that the C^1-C^2 bond in **13a** is rather short. Also the Zr^1-C^2 separation in **13a** [2.365(8) Å] is much larger than this was found in **2a** [2.182(5) Å]. We conclude that the $Cp_2Zr^1(\mu\text{-}\eta^1{:}\eta^2\text{-}H_3C^3-C^2C^1H)(Zr^2Cp_2)$ subunit in **13a** is in its structural details somewhat different from the bonding parameters of the related typical Zr/Zr$^+$ or Zr/Al containing planar-tetracoordinate carbon complexes (**2**, **1**). In some of its structural characteristics this unit in **13a** still resembles its Zr(μ-acetylide)Zr precursor unit. In some respect this unit behaves more as a "protonated alkynyl complex" than a (μ-alkyne)bis(zirconocene) cation [the $C^1≡C^2$ bond length in the $Cp_2Zr-C≡C-Ph$ dimer (**7f**) is 1.261(2) Å, the corresponding Zr^1-C^1 and Zr^1-C^2 distances are 2.431(2) and 2.407(2) Å, the Zr^2-C^1 bond length is 2.188(2) Å,[8] see Scheme 5].

The structural similarity between the cationic complex **13a** and its precursor, a neutral (acetylide)metallocene di-

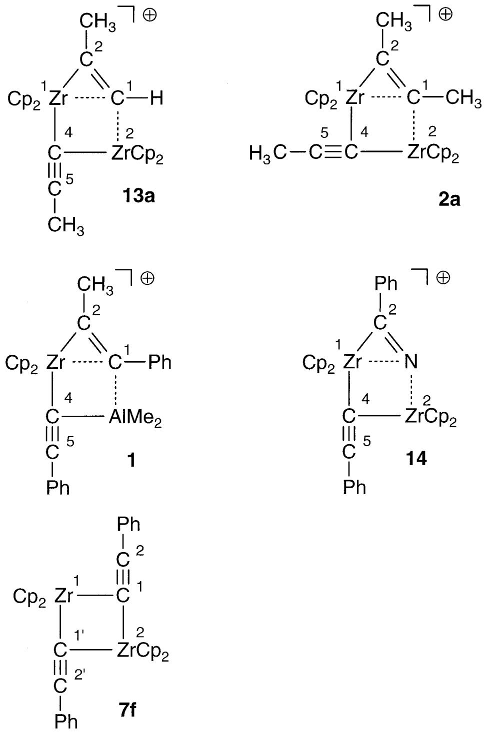
Table 2. A comparison of selected structural parameters of dimetallic planar-tetracoordinate carbon complexes and related systems[a]

Compd.	M^1	M^2	C^1-R	Zr^1-C^1	Zr^1-C^2	C^1-C^2	M^2-C^1	ref.
13a	Cp_2Zr	Cp_2Zr^+	C−H	2.377(6)	2.365(8)	1.255(9)	2.274(7)	[b]
14	Cp_2Zr	Cp_2Zr^+	N	2.338(10)	2.266(14)	1.230(14)[c]	2.075(11)	[14]
1a	Cp_2Zr	$AlMe_2$	C−Ph	2.465(2)	2.163(3)	1.324(4)	2.103(3)	[4]
2a	Cp_2Zr	Cp_2Zr^+	$C-CH_3$	2.509(4)	2.182(5)	1.305(6)	2.324(5)	[5][6]

[a For a schematic representation of the structures of these complexes see Scheme 5 and Figure 1. − [b] This work. − [c] C−N.

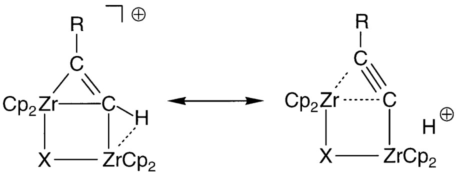
mer (7),[8][10] even is extending to the second bridging hydrocarbyl moiety, the μ-propynyl group.[15] In both planar-tetracoordinate carbon complexes **13** and **2** this bridge is rather unsymmetrically located between the two group 4 metallocene moieties. In **2a** it seems to be strongly σ-bonded to the metal atom Zr^2 [d Zr^2-C^4 2.263(4) Å] and leans over to Zr^1 [d Zr^1-C^4 2.472(4) Å, d Zr^1-C^5 2.814(5) Å][5][6] whereas in the complex **13a** we are encountered with the opposite geometric situation: Zr^1 is linked to C^4 by means of a strong σ-type interaction [d Zr^1-C^4 2.313(6) Å] and the C^4-C^5 triple bond [1.199(9) Å] is η^2-coordinated to Zr^2 [d Zr^2-C^4 2.406(6) Å, d Zr^2-C^5 2.693(7) Å]. The latter structural situation is similar as it is typically found in the related complexes **1** and **14** (see Scheme 5).

Scheme 5



Conclusions

Protonation of dimetallic (μ-η^1:η^2-alkynyl)bis(group 4 metallocene) complexes apparently provides a simple and efficient route to stable and easily isolable cationic planar-tetracoordinate carbon compounds. The X-ray crystal structure analysis of a representative example (**13a**) has shown that four substituents (a carbon atom, two metal centers, and a hydrogen) are oriented coplanar with carbon atom C^1 and are all strongly bonded to it. In addition, there is evidence from the NMR spectra and the X-ray structural analysis that there is some electronic interaction of this hydrogen (C^1)-*H* with the adjacent metal center Zr^2. The $^1J_{C^1\text{-}H}$ coupling constant is rather small, and the C^1-H vector seems to be "leaning over" towards Zr^2 ($Zr^2\cdots H$ separation 2.136 Å). These features may indicate the presence of some α-agostic interaction between Zr^2 and the C^1-H bond, but we must also notice that the Zr^1-C^1 and Zr^1-C^2 separations are almost equal in lengths, and that the C^2-C^1 multiple bond is rather short as is the Zr^1-C^4 linkage. All these features seem to indicate some residual structural resemblance of **13a** with its (acetylide)metallocene dimer precursor. The participation of a hyperconjugative formula (**13′**) could possibly be used to illustrate this specific structural situation.



13 **13'**

Despite these specific structural details the complexes **13** seem to represent additional examples of a large general class of stable easily prepared planar-tetracoordinate carbon compounds. It appears that the thermochemical stabilization of the planar-tetracoordinate carbon center in these dinuclear complexes is so pronounced that protonation routes typically found in other organometallic systems, such as e.g. protolytic cleavage of metal−carbon σ-bonds, become quite disfavored here. The presence of a (probably rather acidic) hydrogen atom at the "square planar" carbon may open up ways of detecting chemical reactions which are typical for this specific bonding situation of the element carbon and for synthesizing novel, potentially functionalized derivatives. We have begun to carry out such investigations in our laboratory.

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Experimental Section

Reactions with organometallic compounds were carried out in an inert atmosphere (argon) using Schlenk type glassware or in a glovebox. Solvents, including deuterated solvents used for NMR spectroscopy, were dried and distilled under argon prior to use. − The following instruments were used for physical characterization of the compounds: Bruker AC 200 P and Varian Unity plus (^{1}H: 600 MHz, ^{13}C: 150 MHz) NMR spectrometers; Nicolet 5 DXC FT-IR spectrometer; elemental analyses were carried out with a Foss-Heraeus CHN-Rapid elemental analyzer, melting points were determined by differential scanning calorimetry (2910 DSC, DuPont/STA Instruments). The spectral assignments were in most cases secured by 2D NMR methods (GHMBC, GHSQC, and GCOSY[16]). The $^1J_{C^1\text{-}H}$ coupling constants were usually determined by means of a selective 1D-GHMBC method. The (alkynyl)metallocene complexes **4** and **7**−**10**, and the (butadiene)metallocenes were prepared according to literature procedures.[8][9]

Preparation of [(μ-Methyl)(μ-propynyl)($ZrCp_2$)$_2$] **11a**: A solution containing 1.0 g (3.6 mmol) of methyl(propynyl)zirconocene and 1.0 g (3.6 mmol) of (butadiene)zirconocene in 25 ml of benzene was stirred for 24 h at room temperature. Pentane (10 ml) was added to precipitate the product, which was collected by filtration, washed three times with pentane and dried in vacuo to yield 790 mg (44%) of **11a**, m.p. 147°C (decomp.). − ^{1}H NMR (200.1 MHz, 300 K, [D$_6$]benzene): δ = 5.24, 5.17 (each s, each 10 H, Cp-H), 2.64 (s, 3 H, 3-H), −2.77 (s, 3 H, CH$_3$). − ^{13}C NMR (90.6 MHz, 300 K, [D$_6$]benzene): δ = 229.4 (C1), 179.7 (C2), 104.4, 102.5 (Cp), 21.5 (C≡C-CH$_3$), 6.08 (μ-CH$_3$). − $C_{24}H_{26}Zr_2$ (496.91): C 58.01, H 5.27; found C 58.13, H 5.72.

Preparation of [(μ-Methyl)(μ-propynyl)(ZrCp$_2$)(HfCp$_2$)] **11b**: Complex **11b** was prepared analogously as described above from 600 mg (1.66 mmol) of methyl(propynyl)hafnocene and 456 mg (1.66 mmol) of (butadiene)zirconocene in 25 ml of benzene (18 h, ambient temperature). Yield of **11b**: 630 mg (65%), m. p. 159°C (decomp.). ^{1}H NMR (200.1 MHz, 300 K, [D$_6$]benzene): δ = 5.22, 5.16 (each s, each 10 H, Cp-H), 2.65 (s, 3 H, 3-H), −3.09 (s, 3 H, CH$_3$). − ^{13}C NMR (90.6 MHz, 300 K, [D$_6$]benzene): δ = 224.6 (C1), 180.3 (C2), 104.3, 102.4 (Cp), 22.8 (C3), 5.87 (C4). − $C_{24}H_{26}HfZr$ (584.18): C 49.34, H 4.49; found C 47.72, H 4.46.

Protonation of the (μ-Propynyl)zirconocene Dimer **7a**: *Synthesis of* **13a**: A sample of complex **7a** (150 mg, 0.29 mmol) was mixed with solid *N,N*-dimethylanilinium tetrakis(pentafluorophenyl)borate **12a**. Dichloromethane (20 ml) was added at −20°C. The mixture was stirred for 1 h at this temperature and then allowed to warm to ambient temperature. Pentane (5 ml) was added. The precipitated product was collected by filtration, washed with pentane, and dried in vacuo to give 190 mg (59%) of **13a** [with $B(C_6F_5)_4^-$ anion], m.p. 229°C (decomp.). − ^{1}H NMR (599.9 MHz, 300 K, [D$_2$]dichloromethane): δ = 6.02, 5.73 (each s, each 10 H, Cp), 2.83 (d, 3 H, 3-H, $^4J_{HH}$ = 1.8 Hz), 2.44 (s, 3 H, 6-H), −0.11 (br, 1 H, 1-H). − ^{13}C NMR (150.9 MHz, 300 K, [D$_2$]dichloromethane): δ = 217.6 (C2), 161.0 (C1, $^1J_{CH}$ = 103 Hz), 109.7, 108.4 (Cp), 25.1 (C3, $^1J_{CH}$ = 129 Hz), 10.2 (C6, $^1J_{CH}$ = 133 Hz); $B(C_6F_5)_4^-$: 148.5 (*o*-C-F, $^1J_{CF}$ = 242 Hz), 138.5 (*p*-C-F, $^1J_{CF}$ = 245 Hz), 136.7 (*m*-C-F, $^1J_{CF}$ = 244 Hz), 124.2 (br, *i*-C). C4 and C5 not observed. − IR (KBr): ṽ = 3118, 2969, 2919, 2854, 2056 (C≡C), 1645, 1513, 1463, 1262, 1085, 1015, 979, 812 cm^{-1}. − $C_{50}H_{27}BF_{20}Zr_2$ (1200.97): C 50.00, H 2.27; found C 49.26, H 2.58.

X-ray Crystal Structure Analysis of **13a** [· $B(C_6F_5)_4^-$]: Single crystals were obtained by allowing a solution of **13a** in dichloromethane to equilibrate with toluene by diffusion through the gas phase over a period of several days. Formula $C_{50}H_{27}BF_{20}Zr_2$, M = 1200.97, 0.25 × 0.25 × 0.15 mm, a = 15.057(2), b = 16.618(4), c = 18.530(4) Å, β = 99.56(1), V = 4572(2) Å^3, ρ_{calc} = 1.745 g cm^{-3}, μ = 5.75 cm^{-1}, empirical absorption correction via ψ scan data (0.965 ≤ C ≤ 0.999), Z = 4, monoclinic, space group $P2_1/c$ (no. 14), λ = 0.71073 Å, T = 223 K, ω/2θ scans, 9449 reflections collected (±h, +k, −l), [(sinθ)/λ] = 0.62 Å^{-1}, 9156 independent and 5535 observed reflections [$I \geq 2\,\sigma(I)$], 663 refined parameters, R = 0.063, wR^2 = 0.137, max. residual electron density 0.71 (−0.75) e Å^{-3}, hydrogens calculated and riding, hydrogen at C1 found in Difference-Fourier map. Data set was collected with an Enraf Nonius CAD4 diffractometer equipped with a rotating anode FR 591. Programs used: data reduction MolEN, structure solution SHELXS-86, structure refinement SHELXL-93, 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 CCDC-100817. 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].

Preparation of **13b**. − a) *With $B(C_6F_5)_4^-$ Anion:* 150 mg (0.27 mmol) of bis(1-butynyl)zirconocene **7b** was treated with 220 mg (0.27 mmol) of the anilinium salt **12a** analogously as described above to give 220 mg (66%) of **13b**(· $B(C_6F_5)_4^-$), m.p. 216°C (decomp.). − ^{1}H NMR (200.1 MHz, 300 K, [D$_2$]dichloromethane): δ = 6.03, 5.71 (each s, each 10 H, Cp), 3.04 (dq, 2 H, 3-H, $^4J_{HH}$ = 1.7 Hz, $^3J_{HH}$ = 7.5 Hz), 2.69 (q, 2 H, 7-H, $^3J_{HH}$ = 7.5 Hz), 1.48 (t, 3 H, 8-H, $^3J_{HH}$ = 7.5 Hz), 1.37 (t, 3 H, 4-H, $^3J_{HH}$ = 7.5 Hz), −0.16 (br, 1 H, 1-H). − ^{13}C NMR (150.9 MHz, 300 K, [D$_2$]dichloromethane), cation only: δ = 227.6 (C2), 160.4 (C1, $^1J_{CH}$ = 103 Hz), 129.5 (C6), 108.5, 107.3 (Cp), 36.1 (C4, $^1J_{CH}$ = 129 Hz), 18.4 (C8, $^1J_{CH}$ = 133 Hz), 15.9 (C5, $^1J_{CH}$ = 125 Hz), 14.6 (C3, $^1J_{CH}$ = 124 Hz); C5 not observed. − IR (KBr): ṽ = 3119, 2962, 2918, 2851, 2054 (C≡C), 1642, 1513, 1463, 1262, 1089, 1020, 980, 812 cm^{-1}. − $C_{52}H_{31}BF_{20}Zr_2$ (1229.03): C 50.82, H 2.54; found C 50.09, H 2.68.

b) *With BPh_4^- Anion:* The preparation was carried out analogously as above. Treatment of 200 mg (0.36 mmol) of **7b** with [HNMe$_2$Ph$^+$][BPh$_4^-$] (**12b**) (150 mg, 0.37 mmol) gave 185 mg (59%) of **13b**(· BPh_4^-), m.p. 193°C (decomp.).

Preparation of **13c**: Treatment of 150 mg (0.22 mmol) of **7c** with 182 mg (0.22 mmol) of **12b** was carried out analogously as described above to yield 260 mg (87%) of **13c** (m. p. 165°C, decomp.), that was characterized spectroscopically. − ^{1}H NMR (599.9 MHz, 300 K, [D$_2$]dichloromethane): δ = 7.65−7.64 (m, 4 H, Ph-H), 7.38−7.37 (m, 4 H, Ph-H), 7.20−7.18 (m, 2 H, Ph-H), 5.86, 5.74 (s, each 10 H, Cp), 4.23 (d, 2 H, 3-H, $^4J_{HH}$ = 1.4 Hz), 4.04 (s, 2 H, 6-H), −0.47 (br, 1 H, 1-H). − ^{13}C NMR (150.9 MHz, 300 K, [D$_2$]dichloromethane), cation only: δ = 225.2 (C2), 165.3 (C1), 140.8, 126.4 (C4, C5), 132.0, 129.5, 126.6, 119.4 (Ph), 110.2, 107.8 (Cp), 46.6 (C3), 30.9 (C6). − IR (KBr): ṽ = 3123, 2960, 2924, 2853, 2050 (C≡C), 1643, 1514, 1462, 1274, 1085, 978, 813 cm^{-1}.

Preparation of **13d**. − a) *With $B(C_6F_5)_4^-$ Anion:* Analogously as described above, treatment of 150 mg (0.30 mmol) of **11a** with 240 mg (0.30 mmol) of **12a** at −50°C in 20 ml of dichloromethane followed by precipitation at room temperature (5 ml of pentane was added) gave **13d** as a yellow oil. Extensive stirring and washing with pentane eventually yielded **13d** as a sticky solid material, 120 mg (34%), m.p. 162°C (decomp.). − ^{1}H NMR (599.9 MHz, 300 K, [D$_2$]dichloromethane): δ = 6.11, 5.83 (s, each 10 H, Cp), 2.69 (d, 3 H, 3-H, $^4J_{HH}$ = 1.9 Hz), 0.84 (br, 1 H, 1-H), −0.79 (s, 3 H, 4-H). − ^{13}C NMR (150.9 MHz, 300 K, [D$_2$]dichloromethane), cation only: δ = 229.8 (C2), 159.3 (C1, $^1J_{CH}$ = 108 Hz), 110.8, 108.6 (Cp), 28.5 (C3), 13.5 (C4, $^1J_{CH}$ = 111 Hz). − IR (KBr): ṽ = 3123, 2961, 2918, 2850, 1644, 1511, 1470, 1275, 1263, 1095, 1018, 973, 810 cm^{-1}.

b) *With BPh_4^- Anion:* A sample of 150 mg (0.30 mmol) of **11a** was treated with 120 mg (0.30 mmol) of **12b** in 20 ml of dichloromethane at −50°C. The mixture was stirred for 30 min at −50°C, then for 1 h at room temperature. 10 ml of toluene was added dropwise with stirring to precipitate the product that was collected by filtration, washed several times with pentane and dried in vacuo to yield 154 mg (63%) of **13d**(· BPh_4^-), m.p. 210°C (decomp.). − $C_{48}H_{47}Zr_2$ (817.15): C 70.55, H 5.80; found C 69.14, H 5.85.

Preparation of **13e**: Treatment of 150 mg (0.30 mmol) of **10a** with 230 mg (0.30 mmol) of **12a** in 20 ml of dichloromethane analogously as described above gave, after precipitation with 5 ml of pentane, 173 mg (48%) of **13e**, m. p. 193°C (decomp.). − ^{1}H NMR (599.9 MHz, 300 K, [D$_2$]dichloromethane): δ = 6.15, 5.79 (s, each 10 H, Cp), 2.79 (d, 3 H, 3-H, $^4J_{HH}$ = 1.8 Hz), 0.50 (br, 1 H, 1-H). − ^{13}C NMR (150.9 MHz, 300 K, [D$_2$]dichloromethane), cation only: δ = 273.7 (C2), 157.7 (C1, $^1J_{CH}$ = 103 Hz), 112.5, 109.4 (Cp), 25.3 (C3, $^1J_{CH}$ = 129 Hz). − IR (KBr): ṽ = 3126, 2966, 2924, 2853, 1644, 1515, 1463, 1276, 1262, 1086, 979, 816 cm^{-1}. − $C_{47}H_{24}BClF_{20}Zr_2$ (1197.37): C 47.15, H 2.02; found C 47.18, H 2.18.

Preparation of **13f**: 150 mg (0.26 mmol) of **11b** was treated with 114 mg (0.28 mmol) of **12b** in 20 ml of dichloromethane at room temperature (45 min). Precipitation with 10 ml of toluene gave a solid that was washed with pentane and dried in vacuo. Yield of **13f**$(\cdot BPh_4^-)$ 180 mg (77%), m.p. 219°C (decomp.). − ^1H NMR (599.9 MHz, 300 K, [D$_2$]dichloromethane): δ = 5.92, 5.83 (s, each 10 H, Cp), 2.75 (d, 3 H, 3-H, $^4J_{HH}$ = 1.8 Hz), 1.48 (br, 1 H, 1-H), −0.72 (s, 3 H, 4-H); BPh$_4$: 7.41−7.33 (m, 8 H, Ph-H), 7.10−7.07 (m, 8 H, Ph-H), 6.96−6.89 (m, 4 H, Ph-H). − ^{13}C NMR (150.9 MHz, 300 K, [D$_2$]dichloromethane), cation only: δ = 233.7 (C2), 160.1 (C1, $^1J_{CH}$ = 106 Hz), 110.1, 109.2 (Cp), 27.0 (C3), 13.3 (C4, $^1J_{CH}$ = 111 Hz). − IR (KBr): $\tilde{\nu}$ = 3109, 3053, 3029, 2981, 2919, 2893, 1579, 1478, 1426, 1366, 1264, 1015, 816, 741, 705, 607 cm^{-1}. − $C_{48}H_{47}BHfZr$ (904.42): C 63.75, H 5.24; found C 61.28, H 5.20.

Preparation of **13g**: A sample of 150 mg (0.25 mmol) of **10b** was treated with 200 mg (0.25 mmol) of **12a** at −30°C in dichloromethane. After stirring for 30 min at −30°C and 30 min at room temperature the product was precipitated by slowly adding pentane (10 ml) at 0°C. The product was collected by filtration, washed with pentane and dried in vacuo to yield 210 mg (65%) of **13g** $[\cdot B(C_6F_5)_4^-]$, m.p. 147°C (decomp.). − ^1H NMR (599.9 MHz, 300 K, [D$_2$]dichloromethane): δ = 6.13, 5.85 (s, each 10 H, Cp-H), 2.83 (d, 3 H, 3-H, $^4J_{HH}$ = 1.8 Hz), 1.12 (q, 1 H, 1-H, $^4J_{HH}$ = 1.8 Hz). − ^{13}C NMR (150.9 MHz, 300 K, [D$_2$]dichloromethane), cation only: δ = 227.1 (C2), 156.4 (C1, $^1J_{CH}$ = 99 Hz), 111.3, 109.5 (Cp), 26.2 (C3, $^1J_{CH}$ = 129 Hz). − IR (KBr): $\tilde{\nu}$ = 3251, 3121, 2960, 2921, 2871, 1644, 1514, 1463, 1273, 1087, 979, 819, 661 cm^{-1}. − $C_{47}H_{24}BClF_{20}HfZr$ (1284.64): C 43.94, H 1.88; found C 43.14, H 2.38.

Preparation of **13h**: A sample of 160 mg (0.26 mmol) of **7d** was treated with 190 mg (0.26 mmol) of **12a** at −50°C in 30 ml of dichloromethane. The mixture was stirred at −50°C for 1 h and then warmed up to room temperature. Addition of 5 ml of pentane gave a red oil, that was solidified by means of a prolonged treatment with 20 ml of pentane to give 170 mg (51%) of **13h** $[\cdot B(C_6F_5)_4^-]$, m.p. 206°C (decomp.). − ^1H NMR (599.9 MHz, 300 K, [D$_2$]dichloromethane): δ = 5.94, 5.72 (s, each 10 H, Cp), 2.84 (d, 3 H, 3-H, $^4J_{HH}$ = 1.8 Hz), 2.53 (s, 3 H, 6-H), 0.37 (br, 1 H, 1-H). − ^{13}C NMR (150.9 MHz, 300 K, [D$_2$]dichloromethane), cation only: δ = 162.5 (C1, $^1J_{CH}$ = 100 Hz), 108.6, 108.1 (Cp), 25.6 (C3), 10.5 (C6). C2, C4, C5 not found. − IR (KBr): $\tilde{\nu}$ = 3126, 2961, 2923, 2853, 1644, 1514, 1467, 1272, 1087, 980, 813 cm^{-1}. − $C_{50}H_{27}BF_{20}HfZr$ (1288.25): C 46.62, H 2.11; found C 47.13, H 2.60.

Preparation of **13i**: Treatment of 150 mg (0.22 mmol) of **7e** with 173 mg (0.22 mmol) of **12a** at −50°C in 20 ml of dichloromethane analogously as described above, followed by addition of 10 ml of toluene gave a brown oil that was solidified by treatment with pentane. Yield of **13i** $[\cdot B(C_6F_5)_4^-]$: 190 mg (63%), m.p. 224°C (decomp.). − ^1H NMR (599.9 MHz, 300 K, [D$_2$]dichloromethane): δ = 5.97, 5.65 (s, each 10 H, Cp), 2.90 (d, 3 H, 3-H, $^4J_{HH}$ = 1.8 Hz), 2.46 (s, 3 H, 6-H), 0.41 (br, 1 H, 1-H). − ^{13}C NMR (150.9 MHz, 300 K, [D$_2$]dichloromethane), cation only: δ = 225.1 (C2), 167.4 (C1, $^1J_{CH}$ = 99 Hz), 109.0, 107.4 (Cp), 27.5 (C3, $^1J_{CH}$ = 128 Hz), 12.0 (C6). − IR (KBr): $\tilde{\nu}$ = 3117, 2961, 2920, 2855, 1643, 1514, 1463, 1374, 1263, 1086, 1016, 979, 817 cm^{-1}. − $C_{50}H_{27}BF_{20}Hf_2$ (1375.52): C 43.66, H 1.98; found C 42.99, H 2.44.

Preparation of **13k**: A sample of 150 mg (0.22 mmol) of **10c** was treated with 173 mg (0.22 mmol) of **12a** at −30°C in 20 ml of dichloromethane. After stirring for 1 h at −30°C and 1 h at room temperature the product was precipitated by addition of 5 ml of pentane. The resulting oil was washed with toluene and then solidified by prolonged treatment with 20 ml of pentane to yield 110 mg (37%) of **13k** $[\cdot B(C_6F_5)_4^-]$, m.p. 136°C (decomp.). − ^1H NMR (599.9 MHz, 300 K, [D$_2$]dichloromethane): δ = 6.12, 5.80 (s, each 10 H, Cp), 3.43 (d, 3 H, 3-H, $^4J_{HH}$ = 4.8 Hz), 1.04 (q, 1 H, 1-H, $^4J_{HH}$ = 4.8 Hz). − ^{13}C NMR (150.9 MHz, 300 K, [D$_2$]dichloromethane), cation only: δ = 228.6 (C2), 160.8 (C1, $^1J_{CH}$ = 97 Hz), 111.1, 108.4 (Cp), 26.3 (C3, $^1J_{CH}$ = 129 Hz). − IR (KBr): $\tilde{\nu}$ = 3129, 2959, 2925, 2854, 1643, 1514, 1463, 1273, 1088, 979, 822 cm^{-1}.

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