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Reaction of (σ-alkynyl) Group 4 metallocene cation complexes with alkyl- and arylisocyanides

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Abstract

The cations $[(RCp)_2M(-C\equiv C-CH_3)(THF)^+]$ (**2a**–**d**) $[(RCp)_2M = Cp_2Ti$, Cp_2Zr, $(MeCp)_2Zr$, and $Cp_2Hf]$ were generated in situ by treatment of the respective bis(propynyl) Group 4 metallocenes $(RCp)_2M(-C\equiv C-CH_3)_2$ (**1a**–**d**) with *N*,*N*-dimethylanilinium tetraphenylborate. Addition of excess *tert*-butylisocyanide gave the isonitrile insertion/addition products $[(RCp)_2M(\eta^2\text{-}Me_3C-NC-C\equiv C-CH_3)(\kappa\text{-}C\equiv N-CMe_3)^+]$ (**8a**–**d**). Complex **8b** was characterized by X-ray diffraction. It contains a η^2-iminoacyl ligand with N-inside orientation and there is a κ-*tert*-butylisocyanide coordinated to the cationic metallocene framework. Complex **8b** exhibits the typical structural characteristics of a d°-configurated isonitrile complex (bond lengths 2.350(4) and 1.148(4) Å for the $Zr-C\equiv N-R$ unit). Insertion of 2,6-dimethylphenylisocyanide into the Zr–C(sp) σ-bond of in situ generated $[Cp_2Hf-C\equiv C-CH_3^+]$ cation **2d** leads to the formation of the analogous cationic hafnocene complex **8e**. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Group 4 metallocenes; Isocyanide insertion; Alkynyl metallocene cation; d°-Metal–isocyanide complex.

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1. Introduction

(Alkynyl)metallocene cation complexes (**2**) of the Group 4 transition metals are very reactive species. We have recently shown that the donor–ligand-free systems $[Cp_2M-C\equiv C-R^+]$ **2** can be generated in situ by treatment of the $Cp_2M(-C\equiv C-R)_2$ complexes **1** with trityltetraphenylborate (**4**), but instantaneously react with the starting material **1** to form a dinuclear (μ-hydrocarbyl)bis(zirconocene) cation (**5**) that contains a planar-tetracoordinate carbon atom [1,2] (see Scheme 1). We have also shown that the THF-stabilized cations $[Cp_2M-C\equiv C-CH_3^+\cdot THF]$ (**2**·THF) are formed by treatment of **1** with the Brønsted acid *N*,*N*-dimethylanilinium tetraphenylborate (**3**) in THF solution. The complexes **2**·THF were characterized by NMR spectroscopy in solution, but rapidly decomposed and could not be isolated so far [1].

We have tried to find ways to prepare stable derivatives of the $[Cp_2M-C\equiv C-CH_3^+]$ cations starting from the **2**·THF systems, generated in THF-solution by the protonolysis reaction, but failed to do so in many cases. It appears that any conjugative thermodynamic stabilization of the $[Cp_2M-C\equiv C-CH_3^+]$ cations, if π-conjugation is at all important in these species, does not lead to an increased kinetic stabilization of the system. On the contrary, it appears that the cations **2** and **2**·THF are considerably more reactive and consequently less stable than their well studied $[Cp_2M-CH_3^+]$ or $[Cp_2M-CH_3^+\cdot THF]$ counterparts [3]. This may actually result from a much smaller sterical shielding of the very electrophilic metallocene cation center by the 'lean' linear σ-alkynyl ligand as compared to the spatially more demanding σ-methyl group. Clean insertion reactions of **2** were eventually observed upon treatment with an alkyl- and an arylisocyanide. An interesting type of coordinatively saturated Group 4 metallocene cation addition products have become readily available by this route. Such examples are described in this article.

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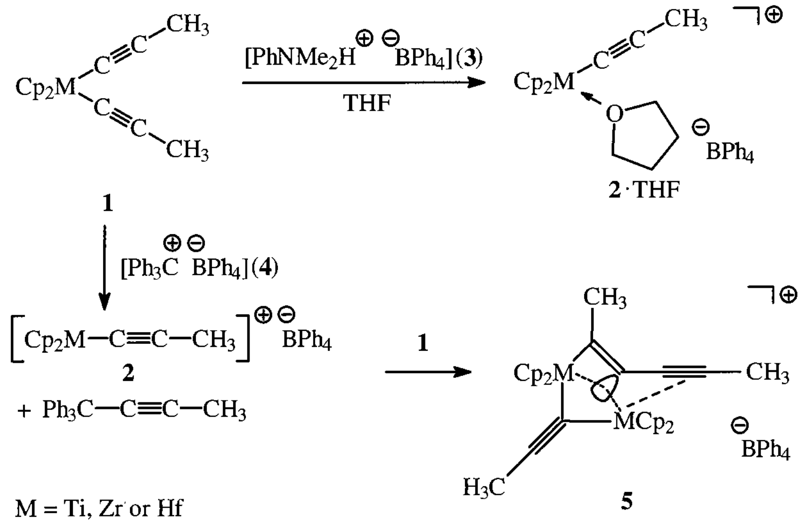


Scheme 1.

2. Results and discussion

The reaction sequence starting from bis(propynyl)zirconocene (**1b**, readily prepared by treatment of Cp_2ZrCl_2 with two molar equivalents of propynyl lithium in tetrahydrofuran [4]) is a typical example. Complex **1b** was treated with *N*,*N*-dimethylanilinium tetraphenylborate (**3**) at 0°C in THF. We had previously shown that under these conditions the THF-stabilized (propynyl)zirconocene cation $[(Cp_2Zr{-}C{\equiv}C{-}CH_3)^+\cdot THF]$ (**2b**) is formed instantaneously. It is generated almost quantitatively, as was shown by NMR spectroscopy and it can be very efficiently trapped, as we have now shown, by a bulky alkyl- or arylisonitrile. We have, therefore, added *tert*-butylisocyanide (ca. 5-fold excess) to the solution at 0°C after a period of a few minutes. The mixture was kept for ca. 2 h at room temperature and then worked up to give a single organometallic product, namely **8b**, that was isolated in $>90\%$ yield.

Analysis of the product showed that two molar equivalents of the isonitrile had reacted with the in situ generated (alkynyl)zirconocene cation **2b**. One of the isonitriles was inserted in the reactive metal to carbon σ-bond to give a η^2-iminoacyl ligand at the bent metallocene unit [5,6]. This is supported by the result of an X-ray crystal structure analysis (see below) and some very typical spectroscopic data of the product **8b** (^{13}C-NMR in THF-d_8: δ 215.5 ppm; IR (KBr): $\tilde{\nu} = 1624$ cm^{-1}). The σ-ligand-derived propynyl substituent exhibits ^{13}C-NMR resonances at δ 133.7 (C2), 74.8 (C3) and 6.23 (3-CH_3). The second *tert*-butylisocyanide moiety was added as such to the electrophilic cationic zirconium center to formally complete the 18-electron valence shell of the transition metal. The isonitrile carbon ^{13}C-NMR resonance appears at δ 121.6 ppm and is characteristic for a situation where metal to carbon π-backbonding is probably completely lacking and the overall bonding situation may be dominated by electrostatic bonding contributions [7]. In such a special situation one would expect that the corresponding IR $\nu(C{\equiv}N{-}R)$ stretching band is not shifted to lower wavenumbers relative to the free isonitrile but to remain unaffected by the d°-metal coordination or even be slightly shifted to *higher* wavenumbers [8]. Such an overall situation is actually observed for the electronically related $[Cp_3Zr{-}C{\equiv}NR^+]$ system which may serve as a reference for this situation [9]. The d°-configurated isonitrile complex $[Cp_3Zr{-}C{\equiv}N{-}CMe_3^+][BPh_4^-]$ exhibits an IR $\nu(C{\equiv}N{-})$ stretching band at 2209 cm^{-1} which is indeed shifted considerably to higher wavenumbers as compared to the free *tert*-butylisocyanide ligand ($\tilde{\nu} = 2140$ cm^{-1}). Complex **8b** shows two sharp IR bands of about equal intensities at 2203 and 2192 cm^{-1} arising inter alia from the C≡C and (M)–C≡N(R) moieties. We cannot clearly make an absolute assignment between these two triple bond vibrations in this specific case, but it seems that the $[Cp_2Zr(\eta^2\text{-iminoacyl})(C{\equiv}NR)^+]$ cation behaves in the typical way of an electrostatically dominated d°-metal–isonitrile complex.

This is supported by the results of the X-ray crystal structure analysis of complex **8b**. Suitable single crystals were obtained by slow diffusion of pentane into a THF-solution of **8b**. A projection of the molecular structure of the cation of **8b** is shown in Fig. 1. In the crystal the $[Cp_2Zr(\eta^2\text{-}Me_3C{-}NC{-}C{\equiv}C{-}CH_3)(\kappa\text{-}C{\equiv}N{-}CMe_3)^+]$ cation and the $[BPh_4^-]$ anion are well separated. The cation contains a Group 4 bent metallocene unit with an averaged C(Cp)–Zr bond length of 2.501(4) Å. The Cp(centroid)–Zr–Cp(centroid) angle is 130.4°. Both the η^2-iminoacyl ligand and the κ-*tert*-

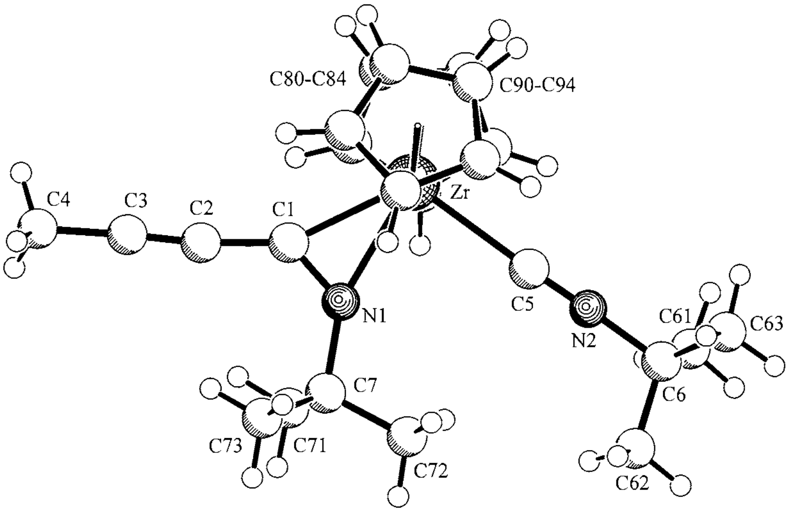


Fig. 1. A view of the molecular geometry of **8b** (cation only) with atom numbering scheme. Selected bond lengths (Å) and angles (°): Zr–C1 2.194(3), Zr–N1 2.229(3), Zr–C5 2.350(4), Zr–C_{Cp} 2.501(4), C1–N1 1.264(4), C1–C2 1.412(5), C2–C3 1.191(5), C3–C4 1.453(5), N1–C7 1.499(4), C5–N2 1.148(4), N2–C6 1.464(4); C1–Zr–C5 117.36(12), C1–Zr–N1 33.20(11), N1–Zr–C5 84.17(11), Zr–C1–N1 74.9(2), Zr–C1–C2 153.7(3), Zr–N1–C1 71.9(2), Zr–N1–C7 158.8(2), Zr–C5–N2 177.3(3), C1–C2–C3 173.0(4), C2–C3–C4 177.2(4), C2–C1–N1 131.3(3), C1–N1–C7 129.0(3), C5–N2–C6 176.1(4).

butylisocyanide ligand are bonded in the σ-ligand plane at the front side of the bent metallocene wedge [10]. This gives the cation of **8b** a formal 18 electron count. In this arrangement of ligands two regioisomers could be possible which are distinguished by the relative positioning of the zirconium bonded iminoacyl nitrogen atom in the σ-ligand plane. The η^2-iminoacyl group could be oriented either in the 'N-inside' or the 'N-outside' fashion [5,6]. Of these only the former orientation is realized in the complex **8b**. The crystal contains a single regioisomer that is characterized by coordination of the η^2-iminoacyl nitrogen center in the central position in the σ-ligand plane of the bent metallocene complex, separating the Zr–C1 and Zr–C5 vectors (see Fig. 1). The Zr–C1 bond length is rather short at 2.194(3) Å, it is at the short end of the range of typical Zr–C(sp^2) bonds. The propynyl substituent is attached at carbon atom C1 (d C2–C3 1.191(5) Å). The C1–N1 distance is 1.264(4) Å, which is in the imino C=N double bond range, as it is typically observed for η^2-iminoacyl zirconium complexes [11]. The corresponding Zr–N1 distance is 2.229(3) Å; it is only slightly longer than the adjacent Zr–C1 distance (see above).

The *tert*-butylisocyanide ligand is bonded laterally at the zirconocene unit [6,10] adjacent to the Zr–N1 vector. The C1–Zr–C5 angle is rather large at 117.36(12)°, the N1–Zr–C5 angle amounts to 84.17(11)°. The Zr–C5 bond length is 2.350(5) Å. This is a rather long zirconium to carbon distance; it lies at the high end of the zirconium to carbon σ-bond range, and it is drastically different from the short bonds encountered in d^2-configurated Group 4 metallocene isonitrile or carbon monoxide complexes [12]. The long Zr-isonitrile carbon distance observed here seems to be very typical for a d^o-configurated Group 4 metal/C≡NR interaction that is lacking the typical metal to carbon π-interaction that characterize the more electron rich metal–CO or –C≡NR complexes [13]. The electronically closely related reference system [$Cp_3Zr–C≡N–CMe_3^+$] shows a very similar Zr–C(isonitrile) distance of 2.313(3) Å. In this reference cation the C≡N– bond length is 1.145(4) Å, which is identical to that of the free uncoordinated *tert*-butylisocyanide [9]. Consequently, we have found a C5–N2 distance of 1.148(4) Å in **8b**, which again indicates the lack of any significant population of the C≡N-π^*-orbital by metal to ligand π-backbonding. It appears that the d^o-[Zr^+]←C≡NR interaction in **8b** is dominated by the σ-donor properties of the ligand and the σ-acceptor features of the metal center inside the bent metallocene framework. The resulting bonding interaction has probably a pronounced electrostatic (i.e. Coulomb interaction) component [7]. The Zr–C≡N–CMe_3 unit is close to linear (angles Zr–C5–N2 177.3(3)°, C5–N2–C6 176.1(4)°).

We have employed a variety of bis(propynyl)metallocenes (**1**) in the analogous reaction sequence (see Table 1 and Scheme 1). From each of these starting materials the corresponding THF-stabilized (propynyl)metallocene cation (**2**·THF) was generated in situ by treatment with *N*,*N*-dimethylanilinium tetraphenylborate (**3**) in tetrahydrofuran, and then the respective isonitrile reagent was added immediately. In each case effective isonitrile insertion into the metal–C(sp) σ-bond was achieved and the respective (η^2-iminoacyl)metallocene cation complexes (**8**) isolated as their κ-isonitrile adducts (see Scheme 2).

Table 1
Selected spectroscopic features of the $[R^1Cp)_2M(\eta^2\text{-}R^2N{=}C^1(\text{–}C{\equiv}C\text{–}CH_3)(\kappa\text{-}C^5{\equiv}N\text{–}R^2)^+]$ complexes **8**

	M	R^1	R^2	δ C^1 [a]	δ C^5	$\tilde{\nu}$C≡C	C≡NR [b]	N=C
a	Ti	H	CMe_3	202.5 [d]	130.2 [d]	2157	2166	1685
b	Zr	H	CMe_3	215.5	121.6	2192	2203	1624
c	Zr	CH_3	CMe_3	217.1	123.3	2193	2203	1655
d	Hf	H	CMe_3	222.7	121.1	2273	2206	1588
e	Hf	H	$Me_2C_6H_3$ [c]	230.6 [e]	[f]	2189		1618

[a] ^{13}C-NMR spectra in d_8-THF unless otherwise noted.
[b] IR spectra in KBr, tentative relative assignment.
[c] 2,6-Dimethylphenyl.
[d] In $CDCl_3$.
[e] In CD_2Cl_2.
[f] Not observed.

In this way the bis(methylcyclopentadienyl)zirconium derived cation **8c** was generated from $(MeCp)_2Zr(\text{–}C{\equiv}C\text{–}CH_3)_2$ (**1c**) by protonation and treatment with *tert*-butylisocyanide. The characteristic spectroscopic data of **8c** are very similar to those of the parent compound **8b** (see Table 1), only that the presence of a symmetry label at the cyclopentadienyl ligands (Me– at Cp) leads to a diastereotopic differentiation of the C_5H_4Me methine moieties due to the in-plane asymmetry of the σ-ligand framework at this very bent metallocene wedge (*C*H ^{13}C-NMR signals at δ 110.1, 109.7, 107.1, and 106.3 ppm for $C_5H_4CH_3$).

The Coulombic interaction between the *tert*-butylisocyanide ligand and the metal cation seems to be slightly less pronounced in the corresponding titanium system **8a**, that was prepared analogously starting from $Cp_2Ti(\text{–}C{\equiv}C\text{–}CH_3)_2$ (**1a**). There is only a small shift of the C≡N–R IR stretching band to higher wavenumbers observed for **8a** as compared to the related zirconium complexes (see Table 1). The ^{13}C-NMR resonance of the κ-*C*≡NR ligand is observed at δ 130.2 ppm (in $CDCl_3$), and the η^2-iminoacyl carbon ^{13}C-NMR signal is at δ 202.5. In contrast, the corresponding hafnocene complex **8d** exhibits the ^{13}C-NMR iminoacyl carbon resonance at δ 222.7 and a much reduced IR ν(CN) band at 1588 cm^{-1}. In the case of the hafnium system we have also trapped the in situ generated $[Cp_2Hf(\text{–}C{\equiv}C\text{–}CH_3)^+]$ cation by an aromatic isocyanide. Addition of 2,6–dimethylphenylisocyanide resulted in the clean formation of the respective $[Cp_2Hf(\eta^2\text{-}Ar\text{–}NC\text{–}C{\equiv}C\text{–}CH_3)(\kappa\text{-}C{\equiv}NAr)^+]$ cation complex **8e** (again with BPh_4^- anion).

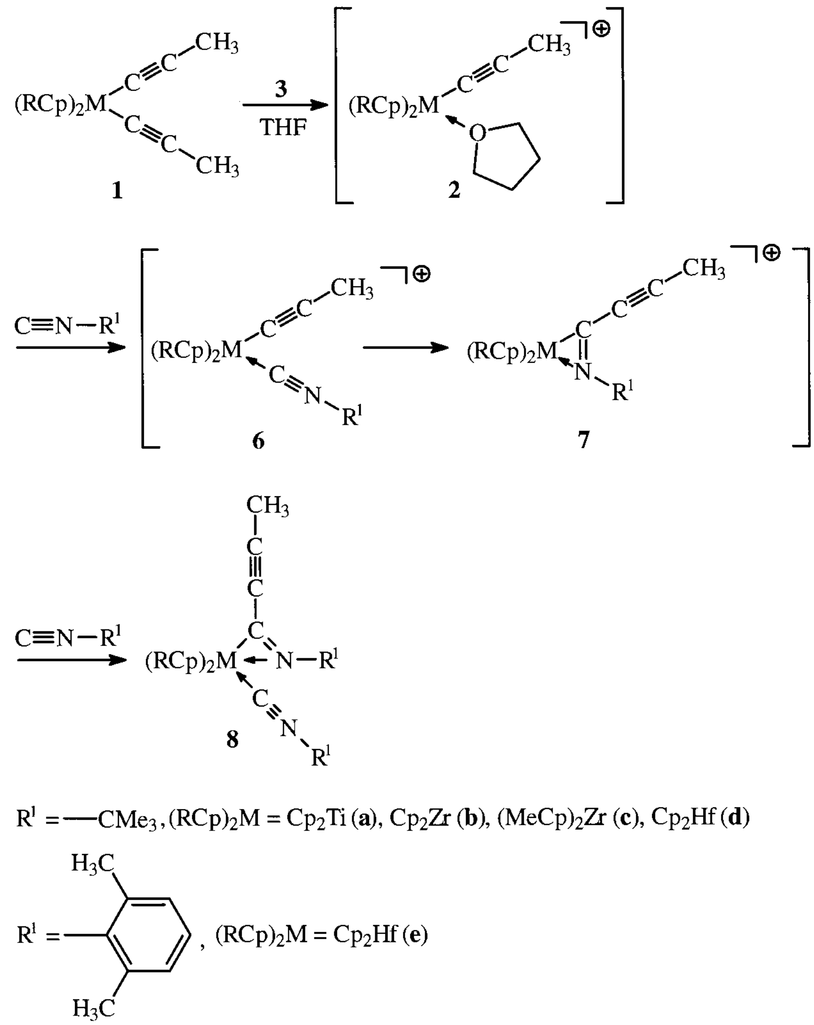
This study shows that σ-alkynyl Group 4 metallocene cation complexes can be generated by a common protonation route in tetrahydrofuran and employed in insertion reactions. It appears that the $[Cp_2M\text{–}C{\equiv}C\text{–}R^+]$ cations are rather sensitive and reactive compounds. This is probably due to the small steric stabilization provided by the linear σ-acetylide ligand and its very limited ability for an electronic stabilization of the adjacent metallocene cation unit. This unfavorable combination of steric and electronic features seems to make the $[Cp_2M\text{–}C{\equiv}C\text{–}R^+]$ cations much more sensitive then e.g. their $[Cp_2M\text{–}CH_3^+]$ relatives. Nevertheless, there is a clean insertion chemistry into the Zr–C(sp) σ-bond observed when sufficiently reactive reagents are used, such as the isonitriles, that lead to the formation of stable sterically and electronically favorable products.

3. Experimental section

All reactions were carried out under an argon atmosphere using Schlenk type glassware or in a glove box. For general information about the experimental conditions, including a list of spectrometers and equipment used for the physical characterization of the compounds, see Refs. [1,3]. The bis(propynyl)metallocene starting materials (**1**) were prepared according to literature procedures [4]. The (σ-propynyl)metallocene cations (**2**) had been spectroscopically characterized in THF-d_8 solution previously [1]. For this study they were in situ generated by treatment with *N*,*N*-dimethylanilinium tetraphenylborate (**3**) in THF solution and employed in the reactions with the respective isonitrile reagents without further characterization. For **8b**–**e** only the NMR data of the cation are listed. The BPh_4^- anion signals are as given for the example of **8a**.

3.1. Reaction of the propynyltitanocene cation (*2a*) with tert-butylisocyanide: formation of *8a*

Bis(propynyl)titanocene (**1a**, 200 mg, 781 µmol) and *N*,*N*-dimethylanilinium tetraphenylborate (**3**, 345 mg, 781 µmol) were mixed as solids, and 5 ml of tetrahydrofuran was added at 0°C. The suspension was stirred for 2 min to give a clear solution. One millilitre of *tert*-



Scheme 2.

butylisocyanide was added and the mixture then stirred for 3 days at ambient temperature. Solvent and all volatiles were removed from the dark brown colored solution in vacuo. The residue was treated three times with each pentane and toluene to give the product **8a** as a reasonably clean solid product. Due to some remaining unidentified contaminations the product was only characterized spectroscopically. Yield: 302 mg (55%). ^{1}H-NMR ($CDCl_3$, 360.1 MHz): $\delta = 7.50–7.35$ (m, 8H, *m*-BPh_4), 7.05–7.00 (m, 8H, *o*-BPh_4), 6.90–6.85 (m, 4H, *p*-BPh_4), 5.31 (s, 10H, Cp), 2.35 (s, 3H, CH_3), 1.52 (s, 9H) and 1.25 (s, 9H, $C(CH_3)_3$). ^{13}C-NMR ($CDCl_3$, 90.6 MHz): $\delta = 202.5$ (C1), 164.4 (q, *ipso*-C of BPh_4, $^1J_{CB} = 50$ Hz), 136.4 (*o*-BPh_4), 133.3 (C2), 130.2 (C5), 125.5 (*m*-BPh_4), 121.6 (*p*-BPh_4), 107.0 (Cp), 72.7 (C3), 63.1, 62.3, 29.7 and 28.9 ($C(CH_3)_3$), 6.7 (3-CH_3). IR (KBr): $\tilde{\nu} = 3053$, 3035, 2981, 2930, 2166 and 2157 (C≡C, C≡N), 1685 (C=N), 1580, 1474, 1425, 1370, 1262, 1184, 1016, 819, 732, 704 cm^{-1}. UV/VIS (dichloromethane): $\lambda_{max} = 253$ ($\varepsilon = 33500$), 274 ($\varepsilon = 24700$), 314 ($\varepsilon = 9000$).

3.2. Reaction of the $[Cp_2Zr(-C{\equiv}C-CH_3)^+]$ cation with tert-butylisonitrile: formation of 8b

Ten millilitres of THF was added at 0°C to a mixture of 1.00 g (3.34 mmol) of $Cp_2Zr(-C{\equiv}C-CH_3)_2$ **1b** and 1.48 g (3.36 mmol) of *N*,*N*-dimethylanilinium tetraphenylborate. After 2 min 2 ml of *tert*-butylisocyanide was added. The cooling bath was removed and the mixture stirred for 2 h at ambient temperature. Solvent was removed in vacuo, and the residue washed twice with pentane and toluene to give the product **8b** as a solid. Diffusion of pentane into a THF solution of **8b** gave single crystals suited for the X-ray crystal structure analysis. Yield of **8b**: 2.30 g (93%), m.p. 151°C (decomp). ^{1}H-NMR ($CDCl_3$): $\delta = 5.61$ (s, 10H, Cp), 2.39 (s, 3H, CH_3), 1.51 (s, 9H) and 1.23 (s, 9H, $C(CH_3)_3$). ^{1}H-NMR (THF-d_8, 360.1 MHz): $\delta = 5.82$ (s, 10H, Cp), 2.38 (s, 3H, CH_3), 1.59 (s, 9H) and 1.31 (s, 9H, $C(CH_3)_3$). ^{13}C-NMR (THF-d_8, 90.6 MHz): $\delta = 215.5$ (C1), 133.7 (C2), 121.6 (C5), 108.3 (Cp), 74.8 (C3), 63.6, 61.6, 28.7, 29.5 ($C(CH_3)_3$), 6.2 (3-CH_3).

GHMBC-NMR [14] (THF-d_8, 150.8/599.8 MHz): $\delta = 215.46/2.38$ (C1/3-CH$_3$). ^{11}B-NMR (CDCl$_3$): $\delta = -6.7$. IR (KBr): $\tilde{\nu} = 3054$, 3036, 2980, 2967, 2926, 2853, 2203 and 2192 (C≡C, C≡N), 1624 (C=N), 1458, 1262, 1094, 1016, 806, 731, 702, 612 cm^{-1}. UV/VIS (dichloromethane): $\lambda_{max} = 239$ ($\varepsilon = 54400$), 265 ($\varepsilon = 26900$), 273 ($\varepsilon = 20700$). $C_{47}H_{51}N_2BZr \cdot C_4H_8O$ (817.47): calc. C 74.87, H 7.22, N 3.43; found C 74.39, H 7.07, N 3.63%. X-ray crystal structure analysis of **8b**: formula $C_{47}H_{51}BN_2Zr$; $M = 745.93$; $0.50 \times 0.40 \times 0.30$ mm; $a = 13.418(1)$; $b = 18.678(1)$; $c = 16.831(1)$ Å; $\beta = 105.27(1)°$; $V = 4069.3(4)$ Å^3; $\rho_{calc} = 1.218$ g cm^{-3}; $\mu = 3.04$ cm^{-1}; empirical absorption correction via φ scan data ($0.945 \leq C \leq 0.999$); $Z = 4$; monoclinic; space group $P2_1/c$ (No. 14); $\lambda = 0.71073$ Å; $T = 223$ K; $\omega/2\theta$ scans; 8621 reflections collected ($+h$, $+k$, $\pm l$); $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}; 8263 independent and 5308 observed reflections $[I \geq 2\sigma(I)]$; 467 refined parameters; $R = 0.043$; $wR^2 = 0.105$; max residual electron density 0.45 (-0.43) e Å^{-3}; hydrogens calculated and refined as riding atoms. Data set was collected with an Enraf Nonius MACH3 diffractometer. Programs used: data reduction, MolEN; structure solution, SHELXS-86; structure refinement, SHELXL-93; graphics, SCHAKAL-92. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-101212. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

3.3. Reaction of the [(MeCp)$_2$Zr–C≡C–CH$_3^+$] cation with tert-butylisocyanide: formation of ***8c***

(MeCp)$_2$Zr(–C≡C–CH$_3$)$_2$ (**1c**, 200 mg, 611 µmol) was treated with 270 mg (611 µmol) of 3 in 10 ml of THF at 0°C. After 2 min 0.5 ml of *tert*-butylisocyanide was added to the clear solution. Workup carried out analogously as described above gave a slightly contaminated product **8c** that still contained some THF. The product was, therefore, only characterized spectroscopically. Yield of **8c**: 388 mg (75%), m.p. 192°C (decomp). ^{1}H-NMR (CDCl$_3$): $\delta = 5.60$–5.45 (s, 8H, MeCp), 2.40 (s, 3H, CH$_3$), 1.93 (s, 6H, MeCp), 1.51 (s, 9H) and 1.27 (s, 9H, C(C*H*$_3$)$_3$); (THF: 3.49 (m, 4H, CH$_2$), 1.77 (m, 4H, CH$_2$)). ^{1}H-NMR (THF-d_8, 360.1 MHz): $\delta = 5.80$–5.75 (s, 2H, MeCp), 5.75–5.65 (m, 4H, MeCp), 5.60–5.55 (m, 2H, MeCp), 2.40 (s, 3H, 3-CH$_3$), 2.00 (s, 6H, MeCp), 1.60 (s, 9H) and 1.35 (s, 9H, C(C*H*$_3$)$_3$); (THF: 3.64 (m, 4H, CH$_2$), 1.77 (m, 4H, CH$_2$)). ^{13}C-NMR (THF-d_8, 90.6 MHz): $\delta = 217.1$ (C1), 133.7 (C2), 123.3 (C5), 110.1, 109.7, 107.1, 106.3 (MeCp), 74.5 (C3), 64.0, 61.3, 29.6 and 29.1 (*C*(*C*H$_3$)$_3$), 15.2 (MeCp), 6.2 (3-CH$_3$). (THF: 68.2, 26.4). IR (KBr): $\tilde{\nu} = 3054$, 2988, 2203 and 2193 (C≡C, C≡N), 1655 (C=N), 1579, 1479, 1427, 1184, 1032, 817, 743, 733, 704, 612 cm^{-1}. UV/VIS (dichloromethane): $\lambda_{max} = 239$ ($\varepsilon = 29000$), 267 ($\varepsilon = 15100$), 285 ($\varepsilon = 10100$).

3.4. Reaction of the [Cp$_2$Hf–C≡C–CH$_3^+$] cation with tert-butylisocyanide: formation of ***8d***

Fifteen millilitres of THF was added to a solid mixture of 1.00 g (2.55 mmol) of bis(propynyl)HfCp$_2$ **1d** and 1.10 g (2.50 mmol) of *N*,*N*-dimethylanilinium tetraphenylborate at 0°C. After 2 min 1 ml of *tert*-butylisocyanide was added to the resulting clear solution. Workup and treatment with toluene and pentane analogously as described above gave 1.08 g (51%) of **8d**, m.p. 141°C (decomp). ^{1}H-NMR (CDCl$_3$): $\delta = 5.55$ (s, 10H, Cp), 2.43 (s, 3H, 3-CH$_3$), 1.54 (s, 9H) and 1.23 (s, 9H, C(C*H*$_3$)$_3$). ^{1}H-NMR (THF-d_8, 360.1 MHz): $\delta = 5.78$ (s, 10H, Cp), 2.42 (s, 3H, 3-CH$_3$), 1.62 (s, 9H) and 1.31 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C-NMR (THF-d_8, 90.6 MHz): $\delta = 222.7$ (C1), 133.1 (C2), 121.1 (C5), 107.0 (Cp), 75.9 (C3), 63.5, 61.3, 29.4 and 28.7 (*C*(*C*H$_3$)$_3$), 6.2 (3-CH$_3$). IR (KBr): $\tilde{\nu} = 3054$, 2984, 2273 and 2206 (C≡C, C≡N), 1588 (C=N), 1480, 1432, 1374, 1012, 817, 746, 705 cm^{-1}. UV/VIS (dichloromethane): $\lambda_{max} = 247$ ($\varepsilon = 8000$), 264 (sh, $\varepsilon = 5800$), 272 (sh, $\varepsilon = 4200$), 288 (sh, $\varepsilon = 1900$), 319 (sh, $\varepsilon = 1200$). Anal. calc. for $C_{47}H_{51}N_2BHf$ (833.24) C, 67.75; H, 6.17; N, 3.36; found C, 67.23; H, 6.11; N, 2.82%.

3.5. Reaction of the [Cp$_2$Hf–C≡C–CH$_3^+$] cation with 2,6-dimethylphenylisocyanide: preparation of ***8e***

Eight millilitres of THF was added to a solid mixture of 500 mg (1.28 mmol) of bis(propynyl)hafnocene (**1d**) and 505 mg (1.25 mmol) of *N*,*N*-dimethylanilinium tetraphenylborate at 0°C. After formation of a clear solution 2.0 g of 2,6-dimethylphenylisocyanide was added. The mixture was stirred for 3 days at ambient temperature, then the solvent was removed in vacuo and the residue was stirred with 20 ml of pentane to give a solid. This was washed twice with 10 ml of pentane and toluene and dried in vacuo to give 865 mg (73%) of **8e**, m.p. 83°C (decomp). ^{1}H-NMR (CDCl$_3$): $\delta = 7.14$ (t, 3H, Ph), 6.98 (t, 3H, Ph), 5.75 (s, 10H, Cp), 2.38 (s, 3H, 3-CH$_3$), 2.08 (s, 6H, Ph*Me*), 1.95 (s, 6H, Ph*Me*), (toluene: 7.46 (m, 5H), 2.32 (s, 3H)). ^{1}H-NMR (dichloromethane-d_2, 360.1 MHz): $\delta = 7.30$–7.10 (m, 6H, Ph), 6.01 (s, 10H, Cp), 2.39 (s, 3H, 3-CH$_3$), 2.17 (s, 6H, Ph*Me*), 2.04 (s, 6H, Ph*Me*). ^{13}C-NMR (dichloromethane-d_2, 90.6 MHz): $\delta = 230.6$ (C1), 144.7, 144.4, 134.67 (*m*-Ph), 132.40 (*p*-Ph), 130.41 (*i*-PhMe), 129.96 (*i*-PhMe), 129.77 (*m*-Ph), 127.52 (*p*-Ph), 107.4 (Cp), 76.6 (C3), 19.2 (PhMe), 18.4 (PhMe), 6.79 (3-CH$_3$), (C5 and C2 not observed). IR (KBr): $\tilde{\nu} = 3053$, 3034, 2982, 2965, 2919, 2852, 2189 (C≡C, C≡N), 1618

(C=N), 1601, 1578, 1440, 1427, 1378, 1262, 1202, 1088, 1031, 810, 774, 733, 703, 610 cm^{-1}. UV/VIS (dichloromethane): $\lambda_{max} = 231$ ($\varepsilon = 78000$), 259 (sh, $\varepsilon = 42600$), 286 (sh, $\varepsilon = 16300$). Anal. calc. for $C_{55}H_{51}N_2BHf$ (929.33) C, 71.08; H, 5.53; found C, 71.57; H, 6.63%.

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