of complete experimental details concerning the synthesis and characterization of complexes **1**, **2**, **3a**, **3b**, and **3c** and ORTEP diagrams and tables of data acquisition and refinement details, fractional coordinates, selected intramolecular distances and angles, anisotropic thermal parameters, and isotropic or equivalent isotropic thermal parameters for **1**, **2**, and **3a** (24 pages); listings of structure factors for **1**, **2**, and **3a** (65 pages). Ordering information is given on any current masthead page.

Double-Insertion Reaction of Alkynes with $[Cp'_2ZrMe]^+$: Formation of an Unusual Distorted η^5-Pentadienyl Ligand

Andrew D. Horton*

Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research BV), Postbus 3003,
1003 AA Amsterdam, The Netherlands

A. Guy Orpen

School of Chemistry, University of Bristol, Bristol BS8 1TS, U.K.

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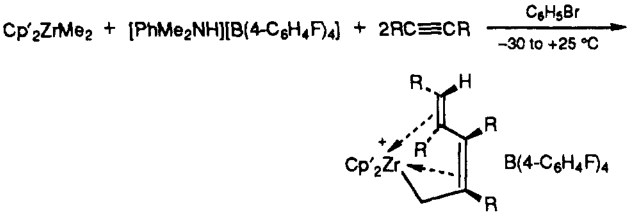
Summary: Reaction of $[Cp'_2ZrMe(NMe_2Ph)][X]$ (**1**; Cp′ = C_5H_5 (**a**), $(Me_3Si)C_5H_4$ (**b**), $(Me_3C)C_5H_4$ (**c**), *rac*-C_2H_4(indenyl)$_2$ (**d**); $[X]^- = [B(4\text{-}C_6H_4F)_4]^-$) with excess 2-butyne gives $[Cp'_2Zr(\eta^5\text{-}CH_2C(Me){=}C(Me)C(Me){=}CHMe)][X]$ (**2a–d**); an X-ray structure analysis of **2c** shows that novel pentadienyl coordination occurs via a σ-bond and two weak unconjugated η^2-interactions with the double bonds. The reaction proceeds via observable, but unstable, alkenyl and 1,3-alkadienyl complexes, followed by a 1,5-hydrogen shift. Double alkyne insertion is unfavorable for crowded $(C_5Me_5)_2ZrMe(X)$, which instead gives $[(C_5Me_5)_2Zr(\eta^3\text{-}CH_2C{\equiv}CMe)][X]$ via a σ-bond metathesis reaction.

In contrast to the high polymerization reactivity of electrophilic d^0 complexes, $[Cp'_2MR]^{n+}$ (n = 0,[1] 1[2]), with alkenes, *multiple* alkyne insertion into such M–alkyl bonds has not previously been reported. Either single alkyne insertion (into the M–R bond[3] or an M–H bond formed on β-hydrogen elimination)[4] to give alkenyl complexes or σ-bond metathesis to give 1-alkynyl (HC≡CR′)[3c,5] or 2-alkynyl (MeC≡CR′)[6] complexes (followed by further reaction) takes place. Our recent isolation of cationic *Lewis-base-free* alkenyl complexes, $[Cp'_2ZrC(R^1){=}C(R^2)Me]^+$,[7] from the reaction of highly electrophilic cations with $Me_3SiC{\equiv}CMe$ or $PhC{\equiv}CPh$, led us to believe that with more reactive alkynes novel multiple-insertion products, of relevance to alkyne oligomerization and polymerization,[8] could be obtained. We now report that double insertion of 2-butyne occurs for all but the most sterically crowded methylzirconocene cations studied, to give remarkable η^5-pentadienyl compounds via ligand isomerization.

Scheme I



Cp′	R = Me	R = Et
C_5H_5	**2a**	**3a**
$(Me_3Si)C_5H_4$	**2b**	
$(Me_3C)C_5H_4$	**2c**	**3c**
rac-C_2H_4(indenyl)$_2$	**2d**	

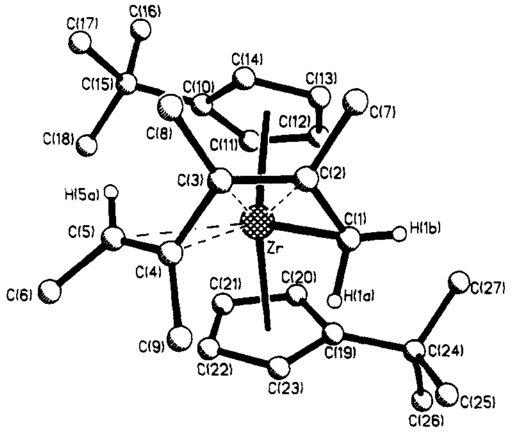


Figure 1. Molecular geometry of **2c**. Hydrogen atoms, except for those on C(1) and C(5), have been omitted for clarity.

Protonolysis[7] of Cp'_2ZrMe_2 using $[PhMe_2NH][B(4\text{-}C_6H_4F)_4]$ gives unstable electrophilic complexes $[Cp'_2ZrMe(NMe_2Ph)_n][B(4\text{-}C_6H_4F)_4]$ (**1a–e**), in which *N,N*-dimethylaniline (n = 1; **1a–d**) or the anion (Cp′ = C_5Me_5; n = 0; **1e**) is weakly coordinated. In situ reaction

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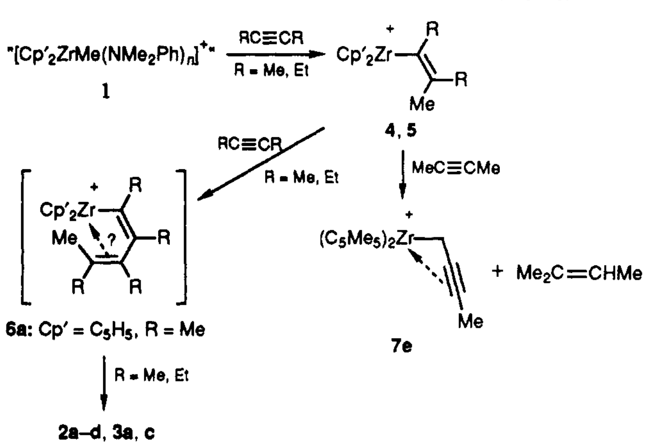
of the less sterically crowded cations **1a–d** with an excess of 2-butyne in bromobenzene gives intensely colored red solutions, which deposit crystalline product on standing or upon addition of hexane. Recrystallization from dichloromethane/hexane solution leads to 50–80% isolated yields of pure complexes **2a–d** (Scheme I). Analogous reactions of **1a** and **1c** with 3-hexyne give related complexes **3a** and **3c**; in contrast to impure **3a**, complex **3c** may be obtained as an analytically pure solid.

NMR spectroscopy,[9-11] and the formation of $CH_2{=}C(Me)CH(Me)C(Me){=}CHMe$ on hydrolysis,[12] confirmed that complexes **2** contain the nine-carbon pentadienyl fragment "$CH_2C(Me)C(Me)C(Me)CHMe$" rather than the expected 1,3-alkadienyl ligand "$C(Me){=}C(Me)C(Me){=}CMe_2$". The observation by ^1H NMR spectroscopy[10] of an AB resonance pattern for the $ZrCH_2$-fragment (**2a–c**, δ 3.4–3.2 and 1.2–0.9 ppm; **2d**, δ 1.84 and −1.30 ppm) and resonances for inequivalent cyclopentadienyl ligands showed the absence of an equatorial plane of symmetry in **2a–d** and therefore ruled out η^1-coordination of the ligand. Further, the upfield location of the $=CHMe$ resonance in **2d** (δ 2.00 ppm), compared to resonances in the range δ 5.3–5.1 ppm for **2a–c**, due to the ring current effect of an *adjacent* indenyl 6-ring, suggested, but did not prove, that at least the terminal double bond is (weakly) coordinated to the metal. However, the observation of two different $^1J_{CH}$ coupling constants[11] for $ZrCH_2$– (δ 76.1–69.7 ppm) of ca. 160 and 135 Hz appeared inconsistent with *normal* σ- ($^1J_{CH}$ ca. 130 Hz) or η^3- or η^5-pentadienyl ($^1J_{CH}$ ca. 160 Hz) bonding.[13]

An X-ray structural analysis for complex **2c**[14] showed that formal η^5-coordination of the pentadienyl ligand occurs in the solid state, but the bonding is highly distorted. The structure shows one short metal–ligand bond (Zr–C(1) = 2.315 (7) Å; normal for an sp^3 c) and four very long bonds to C(2)–C(5) (Zr–C(2) = 2.705 (6) Å, Zr–C(3) = 2.712 (6) Å, Zr–C(4) = 2.602 (7) Å, Zr–C(5) = 2.759 (7) Å). The alternation in bond lengths along the chain from C(1) to C(5) (1.443 (9), 1.387 (9), 1.492 (9), 1.356 (9) Å) and the large twist about the C(3)–C(4) bond (torsion angle C(8)–C(3)–C(4)–C(9) = −113.8 (7)°) suggest that the metal–ligand bonding is best described as consisting of a σ-bond and two unconjugated η^2-interactions with the C=C double bonds. The weakness of the double-bond coordination is reflected in the long *average* Zr–C(sp^2) bond length of 2.69 Å, compared to an average Zr–C(sp^2) separation of 2.574 Å in a σ,π-coordinated Zr allyl complex,[15] 2.45 Å in a Zr(II) alkene complex,[16] or the Ta–C(sp^2) separation of 2.274 Å in the related Ta(III) pentadienyl complex $(C_5H_5)_2Ta(\sigma,\pi\text{-}CH_2C(Me){=}C(Me)CH{=}CH_2)$.[13a] The average Zr–C($sp^2$) distance is also slightly greater than the Zr–C_{ipso} separations of 2.627 and 2.648 Å in the related cations $[Cp'_2Zr(\eta^2\text{-}CH_2Ph)(NCMe)]^+$.[17] A combination of extreme steric crowding in the equatorial plane, which prevents closer metal–ligand approach, and the absence of back-bonding in d^0 systems is responsible for the unusually weak π-coordination in **2c**. The extended (S) conformation found for the pentadienyl ligand in **2c**, compared to the more normal U-conformation,[13] is required to fit the cleft between the bulky cyclopentadienyl ligands and is related to η^4-*s-trans*-diene[18] coordination in bent-metallocene chemistry.[19] The diastereotopic nature of the methylene group, where H(1a) is bent back out of the C(1)–C(2)–C(3) plane, whereas H(1b) lies in the plane (torsion angles H(1a)–C(1)–C(2)–C(3) = −49 (5)°, H(1b)–C(1)–C(2)–C(3) = −171 (6)°), explains the two different $^1J_{CH}$ coupling constants for $ZrCH_2$. Despite the slightly short Zr···H(1a) separation of 2.60 (9) Å (Zr···H(1b)

Scheme II. Reaction of Cationic Methylzirconocene Complexes with Alkynes (Anion = $[B(4\text{-}C_6H_4F)_4]^-$)



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(9) NMR data for $[B(4\text{-}C_6H_4F)_4]^-$ in 2, 3: ^1H NMR (CD_2Cl_2, 25 °C) δ 7.20 (*o*-C_6H_4F), 6.76 (*m*-C_6H_4F); ^{13}C NMR (CD_2Cl_2, 10 °C) δ 159.5 (d, $^1J_{CF}$ = 240 Hz, *p*-C_6H_4F), 157.5 (q, $^1J_{BC}$ = 50 Hz, ipso C_6H_4F), 135.8 (*o*-C_6H_4F), 111.5 (d, $^2J_{CF}$ = 16 Hz, *m*-C_6H_4F); ^{19}F NMR (CD_2Cl_2, −30 °C) δ −122.0 ($\Delta\nu_{1/2}$ = 24 Hz). Complexes **4** and **5** show anion ^1H and ^{13}C NMR resonances slightly shifted from the "free" anion values due to weak anion–cation interaction; ^{19}F NMR (CD_2Cl_2, −30 °C): **4e**, δ −127.5 ($\Delta\nu_{1/2}$ = 23 Hz); **5e**, δ −126.4 ($\Delta\nu_{1/2}$ = 27 Hz).

(10) Selected NMR data for cations **2**. ^1H NMR (CD_2Cl_2, 25 °C): **2a**, δ 6.01, 5.79 (C_5H_5), 5.16 (brq, $=CHMe$), 3.39 (d, $^2J_{HH}$ = 9.0 Hz, $ZrCH_AH_B$), 2.30, 2.17 (Me), 1.94 (d, $^3J_{HH}$ = 6.5 Hz, $=CHMe$), 1.77 (t, $^4J_{HH}$ = 0.5 Hz, $ZrCH_2C(Me){=}$), 0.89 (d, $ZrCH_AH_B$); **2d**, δ 8.0–7.1 (ind-C_6), 6.34, 5.90, 5.73 (ind-C_5), 3.8–3.5 ($-CH_2CH_2-$), 2.04, 2.03 (Me), 2.00 (q, $^3J_{HH}$ = 6.5 Hz, $=CHMe$), 1.84 (d, $^2J_{HH}$ = 10.0 Hz, $ZrCH_AH_B$), 1.61 (d, $=CHMe$), 1.58 ($ZrCH_2C(Me){=}$), −1.30 (d, $ZrCH_AH_B$); **2b,c**, pentadienyl resonances similar to those of **2a**. ^{13}C NMR (CD_2Cl_2, 10 °C): **2a**, δ 148.0, 140.8, 119.1 (*C*Me), 112.1 ($=CHMe$), 110.0, 107.5 (C_5H_5), 71.0 (dd, $^1J_{CH}$ = 161, 136 Hz, $ZrCH_2$), 27.6 ($ZrCH_2C(Me){=}C(Me)$), 24.9 ($ZrCH_2C(Me){=}$), 19.5 ($C(Me){=}CHMe$), 17.6 ($=CHMe$); **2b–d**: pentadienyl resonances similar to those of **2a**.

(11) ^1H NMR: **3a** (assignments confirmed by 2-D COSY NMR), δ 5.97, 5.72 (C_5H_5), 5.04 (t, $^3J_{HH}$ = 7.0 Hz, $=CHEt$), 3.55 (d, $^2J_{HH}$ = 8.5 Hz, $ZrCH_AH_B$), 3.24, 2.69, 2.53 (m, 1, 1, 2, CH_2CH_3), 2.17 (m, $=CH(CH_CH_DCH_3)$), 2.05, 1.93 (m, 1, CH_2CH_3), 1.35, 1.23, 1.17, 1.10 (CH_2CH_3), 0.89 (d, $ZrCH_AH_B$); $=CH(CH_CH_DCH_3)$ resonance obscured; pentadienyl ligand ^1H NMR resonances for **3c** are very similar to those of **3a**, except for $=CHEt$, δ 5.14 (dd, $^3J_{HH}$ = 11.0, 3.5 Hz). ^{13}C NMR: **3a**, δ 151.7, 149.1, 124.0, (*C*Et), 119.4 (d, $^1J_{CH}$ = 147 Hz, $=CHEt$), 110.3, 107.9 (C_5H_5), 70.4 (dd, $^1J_{CH}$ = 162, 133 Hz, $ZrCH_2$), 35.6, 31.9, 27.9, 25.0 (CH_2CH_3), 16.4, 15.7, 14.7, 13.7 (CH_2CH_3).

(12) Reaction of complexes **2** with MeOH or H_2O in CD_2Cl_2, followed by activated alumina filtration, gives $H_2C{=}C(Me)CH(Me)C(Me){=}CHMe$. ^1H NMR: δ 5.29 (m, $=CHMe$), 4.78, 4.72 (s, $H_2C{=}$), 2.70 (q, $^3J_{HH}$ = 7.0 Hz, $CH(Me)$), 1.59 (Me), 1.58 (d, $=CHMe$), 1.46 (m, Me), 1.09 (d, $CH(Me)$). Deuterolysis affords $H_2C{=}C(Me)CD(Me)C(Me){=}CHMe$.

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(14) Crystal data for **2c**: $C_{51}H_{57}BF_4Zr$, M_r = 848.04, monoclinic, space group $P2_1/n$ (No. 14), a = 11.129 (6) Å, b = 16.166 (7) Å, c = 24.128 (11) Å, β = 98.46 (4)°, V = 4293 (4) Å^3, Z = 4, D_{exptl} = 1.31 g cm^{-3}, $F(000)$ = 1776, T = 200 K, graphite-monochromated Mo Kα radiation, λ = 0.71069 Å, μ(Mo Kα) = 3.0 cm^{-1}; R = 0.059, R_w = 0.067, S = 1.56, for 4768 independent absorption-corrected intensities with $I > 2\sigma(I)$ and $2.0 < \theta < 25.0°$.

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= 2.73 (9) Å), a weak α-agostic interaction is unlikely in the formally 18-electron complex.

Two types of intermediate complexes in the formation of the pentadienyl compounds have been identified spectroscopically. ^{1}H NMR monitoring of the reaction of *equimolar* **1a–d** and 2-butyne in C_6D_5Br (−30 to +25 °C) shows the formation of unstable η^1-alkenyl complexes, $[Cp'_2ZrC(Me){=}CMe_2]^+$ (**4a–d**), contaminated by other products (Scheme II).[20] Related pentamethylcyclopentadienyl complexes, $[(C_5Me_5)_2ZrC(R){=}C(R)Me]^+$ (R = Me (**4e**), Et (**5e**)), may, in contrast, be isolated as pure yellow microcrystalline solids on addition of hexane to the reaction mixture of equimolar **1e** and 2-butyne or 3-hexyne, respectively, and have been more fully characterized by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy.[21] The upfield location of the anion ^{19}F NMR resonances at δ −127.5 and −126.4 ppm in **4e** and **5e**, respectively,[9] (free anion: δ −121.8 ppm) suggests that, despite the steric crowding at zirconium, weak and fluxional anion coordination to the cations occurs, presumably via a sterically undemanding Zr–F–R bridge; anion coordination in **4e** and **5e** is related to the formal electron count of 14 for the cations compared to 18 for **2** and **3**, which contain separated cations and anions.[7,9]

The second intermediate in the conversion of **1a** to **2a** may be obtained quantitatively as a microcrystalline precipitate (**6a**·C_6H_5Br) from the low-temperature reaction of **1a** with excess 2-butyne (C_6H_5Br, −30 to 0 °C); recrystallization from dichloromethane/hexane solution at −40 °C affords pure **6a**·CH_2Cl_2. Pale yellow **6a** has been shown by ^{1}H and ^{13}C NMR spectroscopy[22] to be $[(C_5H_5)_2Zr\{C(Me){=}C(Me)C(Me){=}CMe_2\}]^+$, formed on insertion of 2-butyne into the Zr–alkenyl bond of **4a**. Solutions of **6a** are cleanly isomerized to complex **2a** within 1 h at 25 °C.

It is remarkable that related 1,3-alkadienyl intermediates (e.g. **6b–d**) may not be isolated or even detected spectroscopically in the reactions of complexes **1b–d** with a 2-fold excess of 2-butyne (or of **1a** or **1c** with 3-hexyne). The greater stability of complex **6a**, compared to the postulated intermediates in the formation of **2b–d**, **3a**, or **3c**, may be due to more facile coordination of the terminal 1,3-alkadienyl double bond to zirconium in the absence of bulky cyclopentadienyl or 1,3-alkadienyl ligand substituents. The thermodynamic driving force for the formation of **2** and **3** is presumably the change from η^3/η^1-coordination in the intermediate to η^5-coordination. The exact mechanism of the 1,5-hydrogen shift, which likely involves a σ-bond metathesis reaction[3c] between a δ-methyl C–H bond and the Zr–C_α bond, is under investigation at present. However, the formation of complexes **3a** and **3c** suggests that the *Me* group in **1** is the source of both $Zr\mathit{CH_2}$ and $=\!C\mathit{H}R$ in complexes **2** and **3**.

In contrast to the double-insertion reaction found for the less sterically crowded metallocenes, complex **1e** reacts with an excess of 2-butyne (C_6H_5Br, 15 min, 25 °C) to give 2-butynyl complex **7e** and 2-methyl-2-butene (Scheme II). Complex **7e** may be obtained in 60% crude yield by hexane addition to the reaction mixture; subsequent recrystallization from dichloromethane/hexane solution gives pure red product. This propargylic C–H activation has a precedent in the similar reactivity of organolanthanide complexes[6] and presumably proceeds via a σ-bond metathesis reaction between alkenyl complex **4e** and 2-butyne. The high $^1J_{CH}$ coupling constant for the methylene resonance (^{13}C NMR: δ 61.7 ppm, 158 Hz),[23] which is close to the $^1J_{CH}$ value for an sp^2 carbon, together with the free anion ^{19}F NMR resonance (δ −121.9 ppm),[9] suggests that the triple bond is coordinated to the highly electrophilic zirconium center.[6]

That a 1,3-alkadienyl intermediate may be observed for only one of the cyclopentadienyl systems studied (Cp′ = C_5H_5), and that intermolecular C–H activation (of 2-butyne) also occurs in only one case (Cp′ = C_5Me_5), shows the dramatic dependence of the reactivity of cationic metallocenes on the steric and electronic environment at the metal. The increased preference for C–H activation over insertion reactivity under conditions of extreme steric crowding found in this study has been noted previously.[3c] The increased alkyne reactivity of these highly electrophilic complexes, compared to that of related Lewis base adducts, $[Cp'_2ZrR(THF)]^+$,[3a] or neutral[24] isoelectronic complexes such as $(C_5Me_5)_2ScR$,[3c,4] containing a metal of similar ionic radius,[25] illustrates the importance of both a low electron count at the metal and a cationic charge for obtaining such high reactivity.

Supplementary Material Available: Full details of the preparation and characterization of the compounds and details of the structure determination and tables of the atomic coordinates, bond distances and angles, anisotropic displacement parameters, and hydrogen atomic parameters of **2c** (18 pages); a listing of observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.

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[20] The ^{1}H NMR spectrum revealed the presence of a major product in each case, showing resonances for equivalent cyclopentadienyl ligands and three alkenyl methyl groups, e.g. **4a**: δ 5.70 ($C_5\mathit{H}_5$), 1.56, 1.24 ($=C\mathit{Me}_2$), 0.44 (ZrC(Me)=). The contaminants were as follows: for **4a**, complex **6a**; for **4b**, **2b**; for **4c**, **2c**; for **4d**, a mixture of **1d** and **2d**.

[21] Although **4e** decomposes within hours in the solid state at 25 °C, **5e** is more stable and a good elemental analysis was obtained; the complex contains 0.25 equiv of CH_2Cl_2 of crystallization. ^{1}H NMR: **4e** ($C_2D_2Cl_4$, −30 °C), δ 1.88 ($C_5\mathit{Me}_5$), 1.82, 1.39 ($=C\mathit{Me}_2$), 0.71 (ZrC(*Me*)=); **5e** ($C_2D_2Cl_4$, 25 °C), δ 2.24 ($C\mathit{H}_2CH_3$), 1.95 ($C_5\mathit{Me}_5$), 1.25 (6, $CH_2C\mathit{H}_3$), 1.18 ($C\mathit{H}_2CH_3$), 1.03 (*Me*). ^{13}C NMR: **4e** ($C_2D_2Cl_4$, −30 °C), δ 189.9 (Zr*C*(Me)=), 139.3 (=*C*Me$_2$), 124.7 (C_5Me_5), 28.4, 25.6 ($=C\mathit{Me}_2$), 14.1 (ZrC(*Me*)=), 12.0 ($C_5\mathit{Me}_5$); **5e** (CD_2Cl_2, −60 °C), δ 193.8 (Zr*C*(Et)=), 141.5 (=*C*(Et)Me), 123.2 (C_5Me_5), 30.5 (=C($\mathit{C}H_2CH_3$)Me), 24.8 (=C(Et)*Me*), 16.2 (ZrC($\mathit{C}H_2CH_3$)=), 14.1, 12.4 ($CH_2\mathit{C}H_3$), 11.0 ($C_5\mathit{Me}_5$).

[22] **6a**: ^{1}H NMR (C_6D_5Br, 25 °C) δ 5.69 (C_5H_5), 1.61 (6, Me), 1.49, 1.35, 1.19 (Me); ^{13}C NMR ($C_2D_2Cl_4$, −30 °C) δ 180.3 (Zr*C*(Me)=), 154.1, 129.2, 119.6 (ZrC(Me)=*C*(Me)*C*(Me)=*C*Me$_2$), 112.6 (C_5H_5), 25.8, 24.1, 22.1, 19.8, 18.0 (Me).

[23] Pure crystalline **7e** decomposes in the solid state at 25 °C, resulting in 0.75% low carbon in the elemental analysis. ^{1}H NMR ($C_2D_2Cl_4$, 25 °C): δ 2.93 (q, $^5J_{HH}$ = 3.0 Hz, $C\mathit{H}_2C{\equiv}CMe$), 1.91 ($C_5\mathit{Me}_5$), 1.56 (t, 3, $CH_2C{\equiv}C\mathit{Me}$). ^{13}C NMR ($C_2D_2Cl_4$, −30 °C): δ 128.4 ($CH_2\mathit{C}{\equiv}CMe$ or $CH_2C{\equiv}\mathit{C}Me$), 126.3 ($\mathit{C}_5Me_5$), 103.5 ($CH_2\mathit{C}{\equiv}CMe$ or $CH_2C{\equiv}\mathit{C}Me$), 61.7 (t, $^1J_{CH}$ = 158 Hz, $\mathit{C}H_2C{\equiv}CMe$), 11.6 ($C_5\mathit{Me}_5$), 9.4 ($CH_2C{\equiv}C\mathit{Me}$).

[24] Crowther, D. J.; Baenziger, N. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 1455.

[25] Ionic radius (6-coordination): Sc^{3+}, 0.75 Å; Zr^{4+}, 0.72 Å. Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.