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Reactions of Substituted Zirconocene−Bis(trimethylsilyl)ethyne Complexes with Terminal Alkynes

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The complexes $[Zr(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)(\eta^5\text{-}C_5Me_4R)_2]$ (R = Me (**5**), H (**6**), $SiMe_3$ (**7**)) reacted smoothly with terminal alkynes $HC{\equiv}CR'$ (R′ = CMe_3, $SiMe_3$, ferrocenyl (Fc), Ph) to give the agostic alkenyl−alkynyl complexes $[Zr(\eta^1\text{-}C{\equiv}CR')\{\eta^3\text{-}C(SiMe_3){=}CH(SiMe_3)\}(\eta^5\text{-}C_5Me_4R)_2]$ (R/R′ = Me/CMe_3 (**5a**), Me/$SiMe_3$ (**5b**), H/CMe_3 (**6a**), H/$SiMe_3$ (**6b**), H/Fc (**6c**), H/Ph (**6d**), $SiMe_3$/CMe_3 (**7a**), $SiMe_3$/Fc (**7c**)). Complex **7a**, formed in situ from **7** and $HC{\equiv}CCMe_3$, dimerized *tert*-butylethyne exclusively to give the head-to-tail dimer $Me_3CC{\equiv}CC(CMe_3){=}CH_2$, and when all the terminal alkyne was consumed, **7** was restored. Complex **7** reacted similarly with 1-hexyne, phenylethyne, and (trimethylsilyl)ethyne, affording the respective alkenyl−alkynyl complexes, which also changed back to **7** on evaporation of the reaction solutions; none of these terminal alkynes was dimerized with **5**−**7**. Heating of complex **6** with $LiC{\equiv}CSiMe_3$ in toluene or THF yielded the diamagnetic zirconate complex $Li[Zr(\eta^1\text{-}C{\equiv}CSiMe_3)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)(\eta^5\text{-}C_5HMe_4)_2]$ (**6e**) and its solvatomorph $Li[Zr(\eta^1\text{-}C{\equiv}CSiMe_3)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)(\eta^5\text{-}C_5HMe_4)_2]\cdot C_4H_8O$ (**6f**), respectively. The lithium cation in **6e** and **6f** is placed in a position at the side of the alkynyl triple bond and close to C^β of the $\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3$ ligand, apparently interacting with both moieties. All presented complexes were characterized by the standard spectral methods, and the structures of **5a**, **6a**, **6c**, **6d**, and **6e** were determined by single-crystal X-ray diffraction.

Introduction

Bis(trimethylsilyl)ethyne, $Me_3SiC{\equiv}CSiMe_3$ (btmse), complexes of group 4 transition-metal metallocenes (Ti and Zr) have great synthetic potential.[1] The η^2-coordinated btmse not only stabilizes extremely reactive d^2 titanocenes[2] and zirconocenes by π-back-bonding interactions[3] but also acts as an excellent leaving ligand. Hence, the titanocene complexes $[Ti(\eta^2\text{-btmse})(\eta^5\text{-}C_5H_{5-n}Me_n)_2]$ (n = 0−5; n = 0 (**1**), 5 (**2**))[3c] can be used as synthetic equivalents of the hypothetical titanocenes;[1a,3a] an insertion into the titanium−btmse bond has been so far observed only with **1** and CO_2.[4] In the analogous zirconocene complexes $[Zr(\eta^2\text{-btmse})(\eta^5\text{-}C_5H_{5-n}Me_n)_2]$ (n = 0−5),[5] the compounds having unsubstituted or less methyl-substituted cyclopentadienyl ligands (n = 0−2) can be isolated only after coordination of additional electron donors or in a rearranged form.[3a,b,6] The $[Zr(THF)(\eta^2\text{-btmse})(\eta^5\text{-}C_5H_5)_2]$ (**3**) complex reacts with CO_2, water,[7] and acetone[8] involving btmse in the reaction products, whereas for the reactions with ketimines[9a] or diazadienes[9b] btmse is eliminated. The less Lewis acidic and more sterically congested complex [Zr(*rac*-ebthi)(η^2-btmse)] (**4**; ebthi = 1,2-bis(η^5-tetrahydroindenyl)ethane) does not coordinate electron donors, and the

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btmse ligand can be either liberated or incorporated into the reaction products: e.g., in reactions with alkenyl ketones.[10] The reaction of **4** with $B(C_6F_5)_3$ affords a diamagnetic cationic complex formed via a hydrogen transfer from one of the ebthi cyclopentadienyl rings to btmse to give a 1,2-bis(trimethylsilyl)ethenyl complex possessing an agostic hydrogen atom. This complex, however, eliminates btmse at 100 °C.[11a] A similar hydrogen transfer from the η^5-C_5Me_5 ligand occurred upon reacting $[Zr(\eta^2\text{-}PhC{\equiv}CSiMe_3)(\eta^5\text{-}C_5Me_5)_2]$ with $B(C_6F_5)_3$.[11b]

The reactivity of titanocene and zirconocene btmse complexes toward unsaturated hydrocarbons has been recently reviewed.[12] Differences in the coordination ability of the metals, arising from a larger covalent radius and a higher electropositivity of zirconium as compared to titanium, influence the structures of products and their catalytic potential. The titanocene complex **1** was shown to isomerize double bonds in alkenes to thermodynamically more stable internal positions.[13] The titanocene complexes $[TiL\{\eta^5\text{-}C_5Me_4(SiMe_3)\}_2]$, where L = η^2-btmse and η^2-ethene, are moderately thermally stable,[2b] and one can anticipate that free ethene in excess could effectively compete with btmse for the coordination site in **2**. A further reaction of $[Ti(\eta^2\text{-}CH_2{=}CH_2)\{\eta^5\text{-}C_5Me_4(SiMe_3)\}_2]$ with excess ethene was not observed,[2b] and the titanacyclopentane complex *cyclo*-$[\{(\eta^5\text{-}C_5Me_5)_2Ti\}(CH_2)_4]$ was stable only under an excess of ethene.[14] In contrast, both the sterically defined **4** and coordinatively stabilized **3** react with ethene to give thermally stable zirconacyclopentane complexes.[15] Compound **4** reacts also with the other alkenes: a zirconacyclopentane complex was obtained with styrene,[15] while isoprene gave a zirconacyclopentene product.[10]

Ethyne adds to btmse in **1** at −20 °C, forming titanacyclopentadiene which, at a higher temperature, inserts one of the cyclopentadienyl ligands to give a dihydroindenyl complex.[16a] The latter reaction deactivates the active metal center in ethyne polymerization.[16b] Compound **3** reacts with ethyne to afford a mixture of $[(\mu\text{-}1\eta^1{:}2\eta^1\text{-}C{\equiv}C)\{Zr(C(SiMe_3){=}CH(SiMe_3))(\eta^5\text{-}C_5H_5)_2\}_2]$ and a substituted zirconacyclopentadiene, which thermally decomposes to give paramagnetic products and polyethyne.[16a] Terminal alkynes RC≡CH generally replace btmse in methyl-substituted titanocene−btmse complexes to give the (alken-1-yl)(alkynyl)titanocene complexes $[Ti(\eta^1\text{-}C{\equiv}CR)(\eta^1\text{-}CH{=}CHR)(C_5H_{5-n}Me_n)_2]$ (n = 4, 5).[17] In contrast, zirconocene complex **4** reacted with 2-ethynylpyridine and $[Zr(\eta^2\text{-btmse})(\eta^5\text{-}C_5Me_5)_2]$ (**5**) with phenylethyne by oxidative addition to form an alkynide under a transfer of the proton onto btmse, converting it to a $-C(SiMe_3){=}CH(SiMe_3)$ alkenyl ligand.[16a] Water and methanol reacted with **5** in a similar way, yielding $[ZrX\{C(SiMe_3){=}CH(SiMe_3)\}(\eta^5\text{-}C_5Me_5)_2]$ (X = OH,[7b] OMe[16a]), whereas with **2**, the same protonic acids gave only $[Ti(OH)_2(\eta^5\text{-}C_5Me_5)_2]$[7b] and $[TiH(OMe)(\eta^5\text{-}C_5Me_5)_2]$.[16a]

The above alkenyl−alkynyltitanocene complexes do not react with excess 1-alkynes in the dark; however, they become effective catalysts for head-to-tail dimerization of terminal alkynes when the σ-ligands are photocoupled to give η^2(C≡C)-coordinated head-to-head dimers (reductive elimination).[17b] The activity of these Ti(II) catalysts depends sharply on the structure of the titanocene moiety: the octamethylated $(Ti(\eta^5\text{-}C_5HMe_4)_2)$ catalysts dimerize only *tert*-butylethyne[17b,18a] and the decamethylated $(Ti(\eta^5\text{-}C_5Me_5)_2)$ catalysts dimerize all other common 1-alkynes without electron donor atoms in their substituent.[17b,18b,c] The dimerization of 1-alkynes has been effectively catalyzed also with $[(\eta^5\text{-}C_5Me_5)_2ZrMe][B(4\text{-}C_6H_4F)_4]$ to give head-to-tail dimers for HC≡CR′ with bulky substituents (R′ = CMe_3, Ph, tolyl) and head-to-tail-to-head trimers for smaller substituents (R′ = Me, propyl), whereas $HC{\equiv}CSiMe_3$ was unreactive.[19]

In this contribution we investigate the reactions of $[Zr(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)(\eta^5\text{-}C_5Me_4R)_2]$ (R = Me (**5**), H (**6**), $SiMe_3$ (**7**)) with terminal alkynes HC≡CR′ (R′ = CMe_3, $SiMe_3$, ferrocenyl, Ph), yielding the respective Zr(IV) alkenyl−alkynyl complexes $[Zr(\eta^1\text{-}C{\equiv}CR')\{\eta^3\text{-}C(SiMe_3){=}CH(SiMe_3)\}(\eta^5\text{-}C_5Me_4R)_2]$ stabilized with a $Zr{\cdots}H^\beta{-}C^\beta$ $(C(SiMe_3){=}CH(SiMe_3))$ agostic interaction. We also report the attempted catalytic dimerization of the terminal alkynes with **5**−**7** and the products resulting from the reaction between **6** and $LiC{\equiv}CSiMe_3$.

Results and Discussion

The turquoise $Zr(\eta^2\text{-btmse})$ complexes **5**−**7** reacted in hexane solution with terminal alkynes HC≡CR′ (R′ = CMe_3, $SiMe_3$, ferrocenyl (Fc), Ph) to give colorless or pale yellow (intense yellow-orange for ferrocene derivatives) agostic zirconocene η^1-alkynide η^3-1,2-bis(trimethylsilyl)ethenyl complexes[20] (Scheme 1), resulting from a rapid oxidative addition of the alkynes to the zirconocene−btmse complexes with a concurrent hydrogen transfer to the btmse ligand. The complexes $[Zr(\eta^1\text{-}C{\equiv}CCMe_3)\{\eta^3\text{-}C(SiMe_3){=}CH(SiMe_3)\}(\eta^5\text{-}C_5Me_5)_2]$ (**5a**), $[Zr(\eta^1\text{-}C{\equiv}CSiMe_3)\{\eta^3\text{-}C(SiMe_3){=}CH(SiMe_3)\}(\eta^5\text{-}C_5Me_5)_2]$

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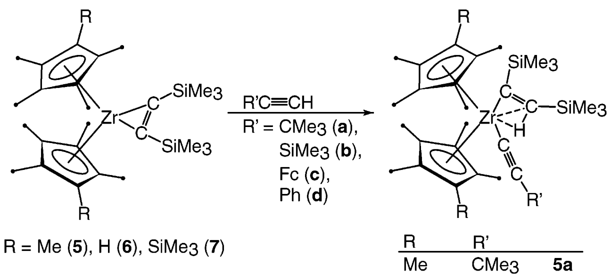
Scheme 1



R	R'	
Me	CMe3	**5a**
	SiMe3	**5b**
H	CMe3	**6a**
	SiMe3	**6b**
	Fc	**6c**
	Ph	**6d**
SiMe3	CMe3	**7a**
	Fc	**7c**

(**5b**), [Zr(η^1-C≡CCMe$_3$){η^3-C(SiMe$_3$)═CH(SiMe$_3$)}(η^5-C$_5$HMe$_4$)$_2$] (**6a**), [Zr(η^1-C≡CSiMe$_3$){η^3-C(SiMe$_3$)═CH(SiMe$_3$)}(η^5-C$_5$HMe$_4$)$_2$] (**6b**), [Zr(η^1-C≡CFc){η^3-C(SiMe$_3$)═CH(SiMe$_3$)}(η^5-C$_5$HMe$_4$)$_2$] (**6c**), [Zr(η^1-C≡CPh){η^3-C(SiMe$_3$)═CH(SiMe$_3$)}(η^5-C$_5$HMe$_4$)$_2$] (**6d**), and [Zr(η^1-C≡CFc){(η^3-C(SiMe$_3$)═CH(SiMe$_3$)}{η^5-C$_5$Me$_4$(SiMe$_3$)}$_2$] (**7c**) were isolated, and characterized by multinuclear NMR, IR, and EI MS spectroscopy. The solid-state structures of **5a**, **6a**, **6c**, and **6d** were further confirmed by X-ray crystallography.

The complex [Zr(η^1-C≡CCMe$_3$){(η^3-C(SiMe$_3$)═CH(SiMe$_3$)}{η^5-C$_5$Me$_4$(SiMe$_3$)}$_2$] (**7a**) catalyzed the linear dimerization of HC≡CCMe$_3$ exclusively to give the head-to-tail dimer Me$_3$C(═CH$_2$)CC≡CCMe$_3$, and in the absence of free HC≡CCMe$_3$ (when all alkyne was consumed), it underwent an effective retro-addition reaction to quantitatively regenerate **7** (see below). Hence, compound **7a** could be characterized only in a mixture formed by reacting **7** with excess *tert*-butylethyne, which contained, according to ^{1}H and ^{13}C NMR spectra, only **7a**, *tert*-butylethyne, and its head-to-tail dimer.

Notable features in the NMR spectra (Table 1) of the complexes are the proton resonances of the agostic hydrogen atom Zr{η^3-C(SiMe$_3$)═C*H*(SiMe$_3$)}, which appear between δ_H 6.83 (**5b**) and 7.35 (**6c**, **6d**). In proton-coupled ^{13}C NMR spectra, the two carbon atoms of the agostic alkenyl ligand exhibit signals at δ_C 109.9−111.3 with typical reduced coupling constants ($^1J_{CH}$ = 95−100 Hz) for the protonated carbon atoms and a singlet at δ_C ca. 224 for the nonprotonated carbon atoms. In addition, the spectra show resonances of the η^1-alkynyl group whose position varies with R′: a doublet due to C$^\alpha$ ($^2J_{CH}$ = 8 Hz) and a singlet due to C$^\beta$. This assignment is in agreement with that reported for [Zr{C(SiMe$_3$)═CHPh}(σ-X)(η^5-C$_5$H$_5$)$_2$] (X = Cl, Br, I),[21] and for compounds featuring the Zr{C(SiMe$_3$)═CH(SiMe$_3$)} moiety,[6a,7a] particularly [Zr(η^1-C≡CPh){η^3-C(SiMe$_3$)═CH(SiMe$_3$)}(η^5-C$_5$Me$_5$)$_2$] (**5d**) and [Zr(η^1-C≡C(py)){η^3-C(SiMe$_3$)═CH(SiMe$_3$)}(*rac*-ebthi)] (**8**; py = 2-pyridyl).[16a]

The presence of η^1-alkynide ligands was independently confirmed by an absorption band of the $\nu_{C≡C}$ vibrations observed in the range 2012−2077 cm^{-1}, its position and intensity depending on the nature of the substituent R′. When R′ = CMe$_3$, low-intensity bands are observed at 2073 and 2077 cm^{-1} for **5a** and **6a**, respectively. In contrast, when R′ = SiMe$_3$, high-intensity bands are found at 2021 and 2013 cm^{-1} for **5b** and **6b**, respectively, whereas for R = Ph, a medium-intensity band appears at 2067 cm^{-1} for **6d**. In contrast, the absorption band of this vibration was missing in IR spectra of ferrocenylethynyl complexes **6c** and **7c**. The absorption band due to the $\nu_{C═C}$ vibration in the agostic ligand was not observed above 1550 cm^{-1} and could not be identified due to either low intensity or overlapping with strong bands of C−H deformation vibrations. Mass spectra of the alkenyl−alkynyl complexes did not show the molecular ions and the [M − (C≡CR′)]$^+$ ions were observed in **6a** and **6d** with only very low abundance (<3%). The [Zr(C$_5$Me$_4$R)$_2$]$^+$ ions were always highly abundant, and the presence of btmse was in all cases indicated by its molecular ion (*m/z* 170) and [btmse − Me]$^+$ fragment (*m/z* 155). Elemental analyses and single-crystal X-ray diffraction analyses confirmed the composition and molecular structure.

Crystal Structures of 5a, 6a, 6c, and 6d. All the molecules display similar structures and, hence, will be discussed jointly. The representative molecular structures of **5a** and **6c** are shown in Figures 1 and 2, respectively (for views of the molecular structures of **6a** and **6d**, see the Supporting Information), the selected geometric parameters are listed in Table 2, and crystallographic data and details of the data collection are given in Table 3.

The tetravalent zirconium atom is π-bonded to two cyclopentadienyl rings and σ-bonded to substituted alkynide and to the 1,2-bis(trimethylsilyl)ethenyl group. The [Zr(η^5-C$_5$Me$_5$)$_2$] moiety in **5a** differs from the [Zr(η^5-C$_5$HMe$_4$)$_2$] moiety in **6a**, **6c**, and **6d** by a larger Cg1−Zr−Cg2 angle and a smaller bite angle φ_1, the differences being in the range of 3−5°. This is caused by the steric hindrance between the methyl groups in hinge positions of the staggered pentamethylcyclopentadienyl ligands. The methyl carbon atoms in **5a** are displaced from the least-squares plane of the cyclopentadienyl ring by as much as 0.365(3) Å. In the more open [Zr(η^5-C$_5$HMe$_4$)$_2$] moiety, the hinge positions are occupied by the hydrogen atoms. The zirconium−alkynyl group in **5a** is practically linear; the most bent arrangement was observed for **6d** (Zr−C$_\gamma$−C$_\delta$ = 169.8(2)°). The alkynyl C$^\gamma$−C$^\delta$ distance was shortest in **6a** (1.201(7) Å**)** and longest in **5a** (1.233(3) Å), and the maximum deviation of alkynyl carbon atoms C$^\delta$ from the plane defined by C$^\alpha$, C$^\gamma$, and Zr atoms did not exceed 0.1 Å. The Zr−σ-C bond lengths Zr−C$^\alpha$ and Zr−C$^\gamma$ were close to each other, falling in the range 2.263(3)−2.298(2) Å.

The geometry of the 1,2-bis(trimethylsilyl)ethenyl group was also rather uniform: the length of the double bond (C$^\alpha$−C$^\beta$) varied from 1.324(7) Å (**6a**) to 1.387(3) Å (**6d**). Rather small differences in the angles Zr−C$^\alpha$−C$^\beta$ (83.9(1)−85.8(3)°), Si$^\alpha$−C$^\alpha$−C$^\beta$ (124.0(1)−126.8(4)°), C$^\alpha$−C$^\beta$−Si$^\beta$ (140.5(1)−142.4(2)°), and C$^\alpha$−C$^\beta$−H$^\beta$ (113(3)−122(3)°) do not allow us to correlate them with properties of the R/R′ groups. In general, however, acute Zr−C$^\alpha$−C$^\beta$ angles and opened C$^\alpha$−C$^\beta$−Si$^\beta$ angles indicate a distortion from sp^2 hybridization at both carbon atoms, induced by the agostic interaction of the C$^\beta$−H$^\beta$ bond with the zirconium atom. The C$^\beta$ carbon atom is more

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Table 1. Selected NMR Parameters for the C(SiMe$_3$)=CH(SiMe$_3$) Alkenyl and Alkynyl Ligands in Zirconocene Complexes (δ, C_6D_6)[a]

	5a	**5b**	**6a**	**6b**	**6c**	**6d**	**7a**	**7c**	**5d**[b]	**8**[b]
					^{1}H NMR					
ZrCH^{β}	7.04	6.83	7.27	7.35	7.12	7.35	7.36	7.50	7.09	7.69
					^{13}C NMR					
C$^{\alpha}$	223.7	224.7	224.1	223.0	223.9	223.7	225.4	224.9	223.1	227.6
C^{β}H	111.3	110.2	111.2	109.8	110.4	109.9	110.7	109.6	110.1	114.5
$^1J_{\mathrm{CH}}$	95	95	100	97	100	96	nd	nd	nd	nd
C$^{\gamma}$	122.6[c]	165.9	121.9	164.8	135.5	140.2	126.6[c]	133.3	nd	nd
C$^{\delta}$	nd	125.9	127.6	125.1	116.8	128.9	n.d.	120.4	nd	nd
					^{29}Si NMR					
Si$^{\alpha}$	−9.0	−8.7	−8.5	−8.2	−8.4	−8.2	n.d.	−9.8	−12.0	−12.8
Si$^{\beta}$	−2.6	−1.3	−3.0	−1.7	−3.2	−3.3	n.d.	−4.4	−9.6	−10.1

[a] See Figure 1 for definitions; nd = not determined. [b] Data from ref 16a. [c] Tentative assignment.

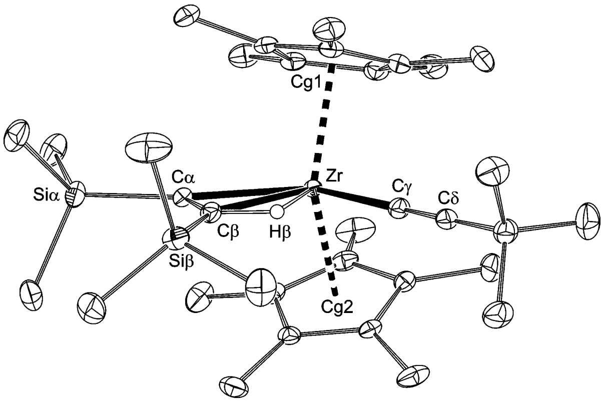

Figure 1. Molecular structure of **5a**.

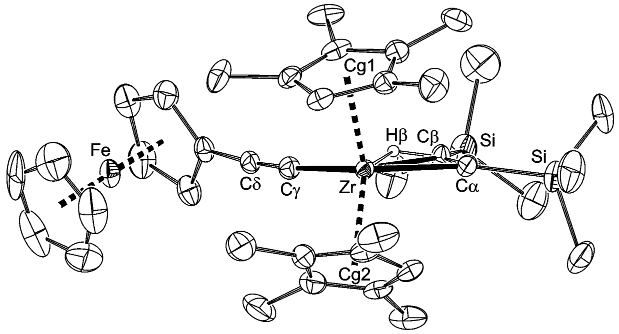

Figure 2. Molecular structure of **6c**.

distant from the zirconium atom (2.527(2)−2.545(6) Å), and according to MO analysis it is mainly the interaction of the $C^{\beta}-H^{\beta}$ bond with the d_{π} MO directed in the axis of the Cg−Zr−Cg angle that stabilizes the agostic complexes.[21b] The alkenyl group is approximately planar but declined from the C$^{\alpha}$, Zr, C$^{\gamma}$ plane as indicated by distances of C$^{\beta}$ and H$^{\beta}$ atoms from this plane (Table 2). The bond lengths $C^{\beta}-H^{\beta}$ range from 1.00(5) Å (**6a**) to 1.14(2) Å (**5a**). The Zr−H$^{\beta}$ distances (2.06(6) Å (**6c**) to 2.21(5) Å (**6a**)) are considerably longer than the usual Zr−H distances in zirconocene hydride derivatives, which are typically close to 1.80 Å,[22,23a−c] but fall within the range observed for bridging distances in dimeric zirconocene dihydrides (1.94−2.40 Å).[23] The whole Zr−alkenyl geometry including Zr−H$^{\beta}$ distances is very similar to the known structures, where strong agostic Zr−H interactions were indicated by NMR spectra.[6a,7a,16a,21] The geometric parameters for complex **8**,[16a] so far the only structurally characterized complex of this type, fall into the ranges for the aforementioned structures.

Dimerization of *tert*-Butylethyne Catalyzed by Complex 7. As mentioned above, the reaction of **7** with excess HC≡CCMe$_3$ gave **7a** quantitatively. However, upon removal of the alkyne under vacuum, the precursor complex **7** was completely regenerated. In the presence of the alkyne, complex **7a** induced its slow dimerization, yielding exclusively head-to-tail dimer 5,5-dimethyl-2-(2-methylprop-2-yl)hex-3-yn-1-ene:[24]

$$2\mathrm{Me_3CC{\equiv}CH} \rightarrow \mathrm{Me_3CC{\equiv}CC(CMe_3){=}CH_2}$$

An estimate of the reaction rate at 70 °C was as low as 4 mol of alkyne/1 mol of **7**/1 h. However, no deactivation was observed with pure alkyne upon following the reaction by electronic absorption spectroscopy (consumption of the terminal alkyne and restoration of **7**) or by NMR spectroscopy (conversion of the alkyne to the dimer and of **7a** to **7**). The NMR spectra did not indicate a complexation of Me$_3$CC≡CC(CMe$_3$)=CH$_2$ with zirconium, as observed in the case of decamethyltitanocene−btmse complexes.[17b] The dimerization reaction proceeded thermally in the dark, and no evidence of rate acceleration was observed when the reaction was carried out in daylight.

Complex **7** in hexane immediately reacted with excess 1-hexyne, phenylethyne, or (trimethylsilyl)ethyne, giving mixtures containing the colorless analogues of **7a** and free alkyne. These mixtures were stable upon heating to 90 °C for 2 weeks, forming no alkyne dimers and regenerating **7** after evaporation of all volatiles under vacuum.

Complex **7** was the only one among the zirconocene−btmse complexes **5**−**7** that catalyzed head-to-tail dimerization. Of all the tested terminal alkynes HC≡CR′ (R′ = CMe$_3$, SiMe$_3$, Ph, *n*-Bu), only *tert*-butylethyne was dimerized. A similar behavior was observed for titanocene−btmse complexes. [Ti(η^2-btmse)(η^5-C$_5$Me$_5$)$_2$] catalyzed head-to-tail dimerization of 1-alkynes not bearing electron donor atoms in their substituent except

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Table 2. Comparison of the Selected Geometric Parameters for 6a, 6d, 6c, 5a, and 6e[a]

	5a	**6a**	**6c**	**6d**	**6e**
			Bond Distances (Å)		
$\mathrm{Zr{-}Cg1}^{b}$	2.272(1)	2.257(2)	2.246(3)	2.249(1)	2.286(2)
$\mathrm{Zr{-}Cg2}^{b}$	2.272(1)	2.257(2)	2.264(2)	2.245(1)	2.271(2)
$\mathrm{Zr{-}C}^{\gamma}$	2.268(2)	2.268(5)	2.263(3)	2.280(2)	2.310(5)
$\mathrm{Zr{-}C}^{\alpha}$	2.298(2)	2.274(4)	2.265(5)	2.265(2)	2.343(8)
$\mathrm{Zr{-}C}^{\beta}$	2.534(2)	2.535(5)	2.545(6)	2.527(2)	2.393(8)
$\mathrm{Zr{-}H}^{\beta c}$	2.09(2)	2.21(5)	2.06(6)	2.11(2)	2.926(8)[d]
$\mathrm{C}^{\alpha}{-}\mathrm{C}^{\beta}$	1.340(3)	1.324(7)	1.336(6)	1.387(3)	1.183(8)
$\mathrm{C}^{\gamma}{-}\mathrm{C}^{\delta}$	1.233(3)	1.201(7)	1.204(6)	1.214(3)	1.220(7)
$\mathrm{C}^{\beta}{-}\mathrm{H}^{\beta}$	1.14(2)	1.00(5)	1.00(4)	1.06(2)	2.179(9)[d]
			Bond Angles (deg)		
Cg1−Zr−Cg2	136.21(3)	132.82(8)	133.75(10)	133.41(4)	133.32(9)
$\mathrm{C}^{\alpha}{-}\mathrm{Zr}{-}\mathrm{C}^{\gamma}$	115.46(7)	113.95(18)	114.26(16)	112.48(8)	112.7(2)
$\mathrm{C}^{\beta}{-}\mathrm{Zr}{-}\mathrm{C}^{\gamma}$	83.74(6)	83.50(18)	82.86(16)	81.59(8)	84.2(2)
$\mathrm{C}^{\alpha}{-}\mathrm{Zr}{-}\mathrm{C}^{\beta}$	31.72(6)	31.36(17)	31.56(14)	31.65(8)	28.9(2)
$\mathrm{Si}^{\alpha}{-}\mathrm{C}^{\alpha}{-}\mathrm{C}^{\beta}$	124.01(14)	126.8(4)	126.2(4)	125.93(17)	133.8(7)
$\mathrm{Si}^{\beta}{-}\mathrm{C}^{\beta}{-}\mathrm{C}^{\alpha}$	140.50(15)	140.9(4)	141.2(3)	142.43(18)	126.7(7)
$\mathrm{C}^{\alpha}{-}\mathrm{C}^{\beta}{-}\mathrm{H}^{\beta}$	119(1)	122(3)	113(3)	117.6(6)	147.7(6)[d]
$\mathrm{Zr}{-}\mathrm{C}^{\alpha}{-}\mathrm{C}^{\beta}$	83.9(1)	85.3(3)	85.8(3)	85.1(1)	77.9(6)
$\mathrm{Zr}{-}\mathrm{C}^{\gamma}{-}\mathrm{C}^{\delta}$	179.2(2)	176.4(4)	175.0(5)	169.8(2)	172.1(5)
$\mathrm{C}^{\gamma}{-}\mathrm{C}^{\delta}{-}\mathrm{C(Si)}^{e}$	177.8(2)	177.3(6)	174.9(6)	177.3(2)	171.5(5)
φ^{f}	44.5(1)	49.7(2)	48.9(3)	49.1(1)	49.4(2)
$\varphi_1{}^{g}$	23.2(1)	29.5(2)	25.4(2)	28.5(1)	28.0(2)
			Distances of Atoms from the Zr, C^{α}, C^{γ} Plane (Å)		
C^{β}	0.009(3)	0.335(7)	0.146(9)	0.305(3)	0.195(9)
H^{β}	0.02(2)	0.63(5)	0.29(5)	0.54(1)	1.09(1)[d]

[a] See Figure 1 for definitions. [b] Cg denotes the centroid of the corresponding cyclopentadienyl ring. [c] Hydrogen atom bonded to the C^{β} carbon atom. [d] Lithium atom instead of H^{β}. [e] Silicon atom in complex **6e**. [f] Dihedral angle between the least-squares planes of the cyclopentadienyl rings. [g] Dihedral angle between the least-squares plane of the cyclopentadienyl ring C(1−5) and the Zr, C^{α}, and C^{γ} plane.

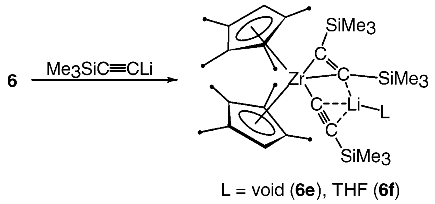
Table 3. Crystallographic Data and Details of the Data Collection and Structure Refinement for 6a, 6d, 6c, 5a, and 6e[a]

	6a	**6d**	**6c**	**5a**	**6e**
formula	$C_{32}H_{54}Si_2Zr$	$C_{34}H_{50}Si_2Zr$	$C_{38}H_{53}FeSi_2Zr$	$C_{34}H_{58}Si_2Zr$	$C_{31}H_{53}LiSi_3Zr$
mol wt	586.15	606.14	713.05	614.20	608.16
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a (Å)	10.5860(3)	14.1290(2)	11.001(3)	9.9670(2)	11.8880(3)
b (Å)	35.8920(11)	15.1560(2)	17.1274(18)	10.8970(2)	27.5590(4)
c (Å)	9.6130(3)	15.9940(2)	20.027(4)	17.7370(3)	11.7600(4)
α (deg)	90.00	90.00	90.00	88.6220(10)	90.00
β (deg)	110.4750(14)	103.4900(8)	100.76(3)	78.3450(11)	113.2130(11)
γ (deg)	90.00	90.00	90.00	68.8160(10)	90.00
V (Å^3); Z	3421.74(18); 4	3330.45(9); 4	3707.1(13); 4	1756.68(6); 2	3540.92(16); 4
D_{calcd} (g cm^{-3})	1.138	1.209	1.278	1.161	1.141
μ (mm^{-1})	0.408	0.422	0.761	0.400	0.428
color; habit	white; prism	yellow; prism	orange; fragment	pale yellow; block	yellow; plate
cryst size (mm^3)	0.5 × 0.7 × 0.8	0.30 × 0.45 × 0.53	0.2 × 0.2 × 0.4	0.20 × 0.38 × 0.63	0.2 × 0.5 × 0.5
T (K)	293(2)	120(2)	293(2)	150(2)	293(2)
θ_{min}; θ_{max} (deg)	3.00; 29.67	3.20; 27.49	1.58; 24.94	3.17; 27.52	2.91; 26.03
range of h	−14 to +14	0−18	0−12	0−12	0−14
range of k	−43 to +48	0−19	−20 to +20	−12 to +14	0−33
range of l	−11 to +12	−20 to +20	0−23	−22 to +23	−14 to +12
no. of diffrns collected	11 133	7623	3136	7949	5540
no. of unique diffrns	5648	6623	2173	7445	4743
F(000)	1256	1288	1500	660	1296
no. of params	345	349	397	566	339
$R(F)$; $R_w(F^2)$ all data (%)	6.05; 12.97	4.61; 9.08	6.32; 6.42	3.59; 7.94	7.63; 14.25
GOF (F^2), all data	1.332	1.049	1.028	1.087	1.107
$R(F)$; $R_w(F^2)$ ($I > 2\sigma(I)$)	5.94; 12.92	3.67; 8.53	2.59; 5.59	3.20; 7.64	6.37; 13.37
$\Delta\rho$ (e Å^{-3})	0.504; −0.750	0.712; −0.685	0.167; −0.150	1.192; −0.530	1.262; −1.089

[a] Definitions: $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w(F^2) = [\sum(w(F_o{}^2 - F_c{}^2)^2)/(\sum w(F_o{}^2)^2)]^{1/2}$, GOF $= [\sum(w(F_o{}^2 - F_c{}^2)^2)/(N_{\mathrm{diffrs}} - N_{\mathrm{params}})]^{1/2}$.

tert-butylethyne, whereas [Ti(η^2-btmse)(η^5-C_5HMe_4)$_2$] induced head-to-tail dimerization of *tert*-butylethyne only.[18] Although several steps of the interaction between the titanocene complexes and 1-alkynes were established, including a photoassisted step, the different behavior of the [Ti(η^2-btmse)(η^5-C_5Me_5)$_2$] and [Ti(η^2-btmse)(η^5-C_5HMe_4)$_2$] catalysts has not yet been clarified.[17b] Tentatively, the Ti(η^5-C_5HMe_4)$_2$ unit offers more space for the dimerization reaction of the sterically hindered triple bond in *tert*-butylethyne than Ti(η^5-C_5Me_5)$_2$ (φ 50.0° versus 41.1°).[3c] In the present case of Zr precursors, the bite angles φ were determined as follows: **5**, 41.0°; **6**, 49.5°;[5] **7**, 41.5°.[22] The dimerization activity of solely **7** for only *tert*-butylethyne indicates

Scheme 2



that the magnitude of coordination space, which increases with increasing φ, does not determine the dimerization activity. With regard to the electronic effects, the first reduction potentials of the highly substituted zirconocene dichlorides (E°: $[ZrCl_2(\eta^5\text{-}C_5Me_5)_2]$, −2.418 V; $[ZrCl_2(\eta^5\text{-}C_5HMe_4)_2]$, −2.438 V; $[ZrCl_2\{\eta^5\text{-}C_5Me_4(SiMe_3)\}(\eta^5\text{-}C_5HMe_4)]$, −2.348 V), which reflect the relative electron density at zirconium, are in addition to electronic effects of the cyclopentadienyl substituents influenced by the magnitude of the bite angle for rotating cyclopentadienyl ligands.[25] Its value should be smaller than that obtained in the solid by X-ray diffraction and is experimentally not accessible in solution.[25] Thus, one can hardly correlate the ability of **7** to dimerize *tert*-butylethyne with the available physicochemical properties. It is likely that a lower thermal stability of **7** as compared to that of **5**[22] determines the observed catalytic activity of **7**. Considering that the dimerization proceeds via the formation of an alkynyl−alkenyl intermediate such as in the decamethyltitanocene case, a low dimerization rate can be brought about by the difficulty in replacing the agostically bonded alkenyl generated from btmse with an alkenyl formed from *tert*-butylethyne, which should *not* be agostically stabilized.[21b]

Reaction of 6 with $LiC{\equiv}CSiMe_3$. Complexes **5**−**7** were reacted with excess alkynides $LiC{\equiv}CSiMe_3$ and $LiC{\equiv}CCMe_3$ in either hexane or THF at elevated temperatures (Scheme 2). The green color of the starting btmse complexes always disappeared, and mixtures of khaki or brown products formed. Only in the case of **6** and $LiC{\equiv}CSiMe_3$ did the crude reaction product obtained after 48 h at 60 °C afford a defined, yellow crystalline product, $Li[Zr(\eta^1\text{-}C{\equiv}CSiMe_3)(\eta^2\text{-btmse})(\eta^5\text{-}C_5HMe_4)_2]$ (**6e**). The molecular structure of **6e** was determined by X-ray diffraction analysis and by spectral methods. In ^1H and ^{13}C NMR spectra, **6e** shows, besides resonances expected for the metallocene unit and three nonequivalent trimethylsilyl groups (also in ^{29}Si NMR spectra), a single signal at δ_C 235.3 due to the η^2-coordinated triple bond carbon atoms (cf. δ_C 259.5 for **6**[22]) and two signals due to the triple bond of the alkynide ligand split into quadruplets by the coordinated lithium cation (^7Li, $I = {}^3/_2$, abundance ca. 97%). In IR spectra, the absorption band of the $C{\equiv}CSiMe_3$ group at 2021 cm^{-1} is shifted to higher energies compared to **6b** (2013 cm^{-1}) and the weak absorption band at 2151 cm^{-1} is ascribed to a weakly and asymmetrically coordinated btmse. The extra high wavenumber of the $\nu_{C\equiv C}$ band in btmse observed for **6e** likely reflects the interaction of the C≡C bond with the Li^+ cation (N.B.: the position of this band is not known for noncoordinated btmse, due to the molecular symmetry).

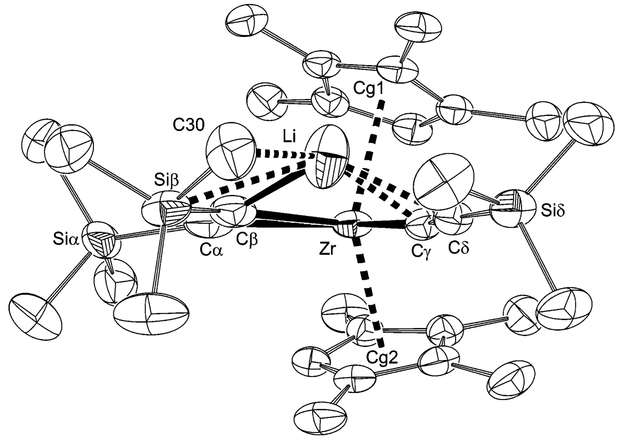


Figure 3. Molecular structure of **6e**.

When a similar reaction was carried out in THF and the product worked up by evaporation of THF and extraction into hexane, the solvatomorph $Li[Zr(\eta^1\text{-}C{\equiv}CSiMe_3)(\eta^2\text{-btmse})(\eta^5\text{-}C_5HMe_4)_2]\cdot C_4H_8O$ (**6f**) was obtained. The ^1H, ^{13}C, ^{29}Si, and ^7Li NMR spectra of **6f** were very similar to that of **6e**, except that additional resonances due to the coordinated THF molecule were clearly discernible. The presence of THF was also confirmed during attempted evaporation of **6f** in the direct inlet of the MS spectrometer (m/z 72, 42).

Crystal Structure of 6e. A view of the molecule of **6e** (Figure 3) resembles those of the above alkynyl−alkenyl complexes in that the carbon atoms of both triple bonds lie in the plane roughly perpendicular to the Cg1−Zr−Cg2 plane. A substantial difference arose from the addition of $[C{\equiv}CSiMe_3]^-$ to zirconium, whereupon btmse remained coordinated as a π-ligand. In comparison with **6**, the formal Zr(II) valency did not change but the coordination number was increased by 1. As a result, the Zr−Cg distances are longer (2.286(2) and 2.271(2) Å vs 2.230(3) Å in **6**), whereas the bite angle φ remains unchanged (49.4(1)°). The Zr−btmse bonds are elongated as well ($Zr{-}C^{\alpha} = 2.343(8)$ Å and $Zr{-}C^{\beta} = 2.393(8)$ Å vs 2.202(2) Å in **6**), while the weaker bonding of the btmse ligand causes its triple bond to remain virtually unaffected by the coordination ($C^{\alpha}{-}C^{\beta} = 1.183(8)$ Å versus 1.316(3) Å in **6**).[22] The (trimethylsilyl)ethynyl group is η^1-bonded to zirconium at a distance slightly longer than in the alkynyl−alkenyl complexes ($Zr{-}C^{\gamma} = 2.310(5)$ Å; cf. Table 2), in the dialkynide $[Zr(\eta^1\text{-}C{\equiv}CSiMe_3)_2(\eta^5\text{-}C_5HMe_4)_2]$ (2.227(4) and 2.223(5) Å), and in the tweezer complex $K[Zr(\eta^1\text{-}C{\equiv}CSiMe_3)_2(\eta^5\text{-}C_5HMe_4)_2]$ (2.264(4) and 2.279(4) Å).[26] The triple-bond length in the alkynide group (1.220(7) Å) falls within the values found in the above alkynyl−alkenyl complexes (1.201(7) Å for **6a** to 1.233(3) Å for **5a**). The Li ion in **6e** is placed in a side position to the alkynide triple bond closer to the inner carbon atom, as is common in Zr(III)[26] and Ti(III) metallocene tweezer complexes with alkali-metal cations.[27] The $Li{-}C^{\gamma}$ (2.033(8) Å) and $Li{-}C^{\delta}$ (2.328(8) Å) distances are shorter than the corresponding distances in $[Li(THF)_2][Ti(\eta^5\text{-}C_5HMe_4)_2(\eta^1\text{-}C{\equiv}CSiMe_3)_2]$ (2.256(9) and 2.510(6) Å)[27b] or $[Li(THF)_2][Ti(\eta^5\text{-}C_5HMe_4)_2(\eta^1C{\equiv}CC{\equiv}CSiMe_3)_2]$ (2.277(7) and 2.541(7) Å);[27c] however, the long distances in the

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latter complexes can be brought about by the coordination of THF. The placement of the alkali-metal cation at some distance from the plane defined by the Zr atom and inner carbon atoms of triple bonds was generally observed in all the above-mentioned alkali-metal tweezers and was caused by the intermolecular interaction of the alkali metal with one of the cyclopentadienyl rings of the neighboring molecule.[27b] In **6e**, the Li^+ ion is 1.09(1) Å above the Zr, C^α, C^γ plane at short distances to one carbon atom of the btmse ligand ($Li-C^\beta = 2.179(9)$ Å) and to one carbon atom of those residing on the Si^β trimethylsilyl group ($Li-C30 = 2.22(1)$ Å). These distances are close to the aforementioned distances to sp carbon atoms of the alkynide group and shorter than, e.g., the Li−C distances in $(LiMe)_4$ (2.28 Å).[28] The implied bonding interaction of Li^+ with C^β and a hydrogen atom residing on C30 is supported by a longer $Zr-C^\beta$ distance compared to $Zr-C^\alpha$ and by a very slightly longer $Si^\beta-C30$ distance compared to the other two $Si^\beta-C$ bonds. Because the nature of these bonding interactions is mainly ionic, one has to suggest that a negative charge supplied by the alkynide anion to **6** is shared by both the alkynide arm and the coordinated btmse ligand. A similar bonding situation apparently occurred in $Li[(\eta^5\text{-}C_5H_5)_2Zr(\eta^1\text{-}C{\equiv}CPh)(\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)]$, where, however, the lithium position was not specified.[29]

Conclusions

Reaction of zirconocene−btmse complexes having highly substituted cyclopentadienyl ligands, $[Zr(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)(\eta^5\text{-}C_5Me_4R)_2]$ (R = Me (**5**), H (**6**), and $SiMe_3$ (**7**)), with terminal alkynes $HC{\equiv}CR'$ (R′ = CMe_3, $SiMe_3$, ferrocenyl, Ph) affords the zirconocene(IV) alkenyl−alkynyl complexes $[Zr(\eta^1\text{-}C{\equiv}CR')\{\eta^3\text{-}C(SiMe_3){=}CH(SiMe_3)\}(\eta^5\text{-}C_5Me_4R)_2]$, stabilized by an agostic interaction of the alkenyl H^β hydrogen atom with the tetravalent zirconium atom. This general reaction was found to be independent of the nature of the cyclopentadienyl and the alkynyl substituents. The zirconocene(IV) alkenyl−alkynyl complexes do not further react with excess alkynes, which is in contrast with the behavior of analogous titanocene−btmse complexes, where two molecules of terminal alkynes promptly replace btmse to give titanocene(IV) alkenyl−alkynyl compounds that, after the necessary photoassisted initiation, catalyze dimerization of some terminal alkynes to head-to-tail dimers.[17b] Solely, the tetramethyl(trimethylsilyl)cyclopentadienyl zirconocene-btmse complex **7**, which is less thermally stable than **5** or **6**,[21] exerted a low dimerization catalytic activity toward *tert*-butylethyne while being totally inactive toward all other tested terminal alkynes. The dimerization rate with **7** is very low, even at the relatively high temperature of 70 °C, apparently because the necessary replacement of btmse in agostically stabilized **7a** by agostically nonstabilized *tert*-butylalkenyl is reversible and the equilibrium is strongly shifted to **7a**. This circumstance does not allow us to investigate the transient species yielding pure head-to-tail dimer.

The partial ionic nature of the alkyne proton and its stabilization by agostic interaction with the zirconium atom provoked the question whether an alkali-metal cation could be stabilized in a similar manner. Although the reaction of zirconocene−btmse complexes with $LiC{\equiv}CSiMe_3$ or $LiC{\equiv}CCMe_3$ was sluggish compared to the reaction of alkynes and resulted in intractable mixtures in most cases, complex **6e**, obtained from **6** and $LiC{\equiv}CSiMe_3$, revealed that addition of the alkali-metal alkynide leads to a new stable, semi-tweezer compound. The structural and spectroscopic data for **6e** indicated that addition of $LiC{\equiv}CSiMe_3$ to **6** leaves the zirconium atom formally divalent, while forming a new σ-$Zr-C{\equiv}C$ bond in an anionic molecular frame and drastically decreasing the strength of coordination of the btmse ligand. The latter moiety shares the negative charge and aids in locating the Li ion embedded in the vicinity of C^β of the btmse ligand and the alkynide triple bond.

Experimental Section

General Considerations. All manipulations, including spectroscopic measurements, were performed under vacuum, using all-sealed glass devices equipped with breakable seals. Ultraviolet−near-infrared (UV−near-IR) spectra were measured on a Varian Cary 17D spectrometer in the 300−2000 nm range using a pair of coupled quartz cuvettes (d = 10.0 and 1.0 mm, Hellma). ^1H (399.95 MHz), ^{13}C (100.58 MHz), ^7Li (155.44 MHz), and ^{29}Si (79.46 MHz) NMR spectra were recorded on a Varian UNITY Inova 400 spectrometer in C_6D_6 solutions at 25 °C. Chemical shifts (δ/ppm) are given relative to the solvent signal (δ_H 7.15, δ_C 128.0), external tetramethylsilane (δ_{Si} 0), and external 1 M aqueous LiCl (δ_{Li} 0). EI-MS spectra were measured on a VG-7070E mass spectrometer at 70 eV. The crystalline samples in sealed capillaries were opened and inserted into the direct inlet under argon. The adjustment of single crystals into capillaries for X-ray analysis and preparation of KBr pellets for infrared measurements were performed under purified nitrogen in a glovebox (mBraun Labmaster 130, O_2 and H_2O concentration lower than 2.0 ppm). IR spectra of KBr pellets were recorded in an air-protected cuvette on a Nicolet Avatar FTIR spectrometer in the range of 400−4000 cm^{-1}.

Chemicals. The solvents THF, hexane, toluene, and benzene-d_6 were dried by refluxing over $LiAlH_4$ and stored as solutions of dimeric titanocene $((\eta^5{:}\eta^5\text{-}C_{10}H_8)(\mu\text{-}H)_2\{Ti(\eta^5\text{-}C_5H_5)\}_2)$.[30] Bis(trimethylsilyl)ethyne (btmse) (Fluka) was degassed, stored as a solution of dimeric titanocene for 4 h, and distributed into ampules by distillation on a vacuum line. (Trimethylsilyl)ethyne (Aldrich, 98%), 3,3-dimethylbut-1-yne (*tert*-butylethyne) (Aldrich, 98%), phenylethyne (Fluka, >97%), and 1-hexyne were degassed, stored as solutions of dimeric titanocene for 4 h, and distributed into ampules by distillation. Ferrocenylethyne[31] was recrystallized from toluene and degassed under vacuum. Lithium (trimethylsilyl)ethynide was obtained by reacting equimolar amounts of $HC{\equiv}CSiMe_3$ and butyllithium in hexane and decanting the solution. A white powder of $LiC{\equiv}CSiMe_3$ was used as such or dissolved in THF. Complexes **5**, **6**,[5] and **7**[21] were prepared as reported previously.

Preparation of $[Zr(\eta^1\text{-}C{\equiv}CCMe_3)\{\eta^3\text{-}C(SiMe_3){=}CH(SiMe_3)\}(\eta^5\text{-}C_5Me_5)_2]$ (5a). Green crystalline **5** (0.531 g, 1.0

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mmol) in hexane (30 mL) and $\mathrm{HC{\equiv}CCMe_3}$ (0.62 mL, 5.0 mmol) were mixed with stirring. The bright green color of **5** disappeared instantly. All volatiles were evaporated under vacuum, and the residue was extracted by hexane. Yellowish crystals of **5a** were obtained from a concentrated solution by cooling to −18 °C. Yield: 0.58 g (95%). Mp: 125 °C. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.41, 0.49 (2 × s, 9 H, $\mathrm{Si}Me_3$), 1.48 (s, 9 H, $\mathrm{C}Me_3$), 1.78 (s, 30 H, $\mathrm{C_5}Me_5$), 7.04 (s, 1 H, $\mathrm{ZrC}H$). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 2.5, 5.4 (2 × q, $^1J_{\mathrm{CH}} = 119$ Hz, $\mathrm{Si}Me_3$), 12.6 (q, $^1J_{\mathrm{CH}} = 126$ Hz, $\mathrm{C_5}Me_5$), 29.3 (s, $C\mathrm{Me_3}$), 32.6 (q, $^1J_{\mathrm{CH}} = 126$ Hz, $\mathrm{C}Me_3$), 111.3 (d, $^1J_{\mathrm{CH}} = 95$ Hz, $C\mathrm{H{=}CSiMe_3}$), 115.7 (s, $C_5\mathrm{Me_5}$), 122.6 (d, $^2J_{\mathrm{CH}} = 8$ Hz, $C\mathrm{{\equiv}CCMe_3}$), 223.7 (s, $\mathrm{Me_3Si}C\mathrm{{=}CHSiMe_3}$). The signal due to $\mathrm{C{\equiv}}C\mathrm{CMe_3}$ was not observed. ^{29}Si NMR ($\mathrm{C_6D_6}$): δ −9.0, −2.6 ($\mathrm{Me_3}Si\mathrm{C{=}CH}Si\mathrm{Me_3}$). IR (KBr, cm^{-1}): 2947 (s), 2886 (s), 2853 (s), 2706 (w), 2073 (w), 1587 (w), 1487 (m), 1440 (vs), 1373 (s), 1353 (m), 1293 (w), 1257 (s), 1240 (vs), 1198 (m), 1060 (w), 1020 (m), 950 (w), 835 (vs), 783 (m), 746 (s), 720 (m), 680 (m), 660 (s), 620 (m), 593 (w), 573 (m), 540 (w), 473 (s), 446 (m), 440 (m). EI-MS (190 °C; *m*/*z* (relative abundance, %)): 365 (7), 364 (21), 363 (9), 362 (32), 361 (33), 360 ([Zr($\mathrm{C_5Me_5}$)$_2$]$^+$; 76), 359 (18), 358 (26), 357 (9), 356 (12), 355 (10), 354 (12), 170 ([btmse]$^+$; 6), 157 (10), 156 (19), 155 ([btmse − Me]$^+$; 100), 136 (11), 135 ([$\mathrm{C_5Me_5}$]$^+$; 5), 121 (14), 119 (15), 105 (11), 73 ([$\mathrm{SiMe_3}$]$^+$, 17), 67 (21), 57 (10), 41 (23). Anal. Calcd for $\mathrm{C_{34}H_{58}Si_2Zr}$ (614.233): C, 66.48; H, 9.52. Found: C, 66.57; H, 9.48.

Preparation of [Zr(η^1-C≡CSiMe$_3$){η^3-C(SiMe$_3$)═CH(SiMe$_3$)}(η^5-C$_5$Me$_5$)$_2$] (5b). The reaction between **5** (1.0 mmol) and $\mathrm{HC{\equiv}CSiMe_3}$ (0.71 mL, 5.0 mmol) was carried out and the product isolated by extraction with hexane as described above for **5a**. The product could not be isolated by crystallization from hexane solution, because the subsequent evaporation of the solution afforded finally a yellowish viscous liquid. Evaporation of the liquid at 90 °C under high vacuum to a trap cooled by liquid nitrogen gave **5b** as a yellowish waxy solid. Yield: 0.60 g (95%). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.40, 0.42, 0.47 (3 × s, 9 H, $\mathrm{Si}Me_3$), 1.76 (s, 30 H, $\mathrm{C_5}Me_5$), 6.83 (s, 1 H, $\mathrm{ZrC}H$). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 1.4, 2.4, 5.3 (3 × q, $^1J_{\mathrm{CH}} = 119$ Hz, $\mathrm{Si}Me_3$), 12.6 (q, $^1J_{\mathrm{CH}} = 126$ Hz, $\mathrm{C_5}Me_5$), 110.2 (d, $^1J_{\mathrm{CH}} = 95$ Hz, $C\mathrm{H{=}CSiMe_3}$), 115.8 (s, $C_5\mathrm{Me_5}$), 125.9 (s, $\mathrm{C{\equiv}}C\mathrm{SiMe_3}$), 165.8 (d, $^2J_{\mathrm{CH}} = 8$ Hz, $C\mathrm{{\equiv}CCSiMe_3}$), 224.7 (s, $\mathrm{Me_3Si}C\mathrm{{=}CH}$). ^{29}Si NMR ($\mathrm{C_6D_6}$): δ −27.0 ($\mathrm{C{\equiv}C}Si\mathrm{Me_3}$), −8.7, −1.3 ($\mathrm{Me_3}Si\mathrm{C{=}CH}Si\mathrm{Me_3}$). IR (KBr, cm^{-1}): 2992 (sh), 2954 (s), 2898 (vs), 2853 (sh), 2720 (vw), 2021 (s), 1493 (w), 1446 (s), 1376 (m), 1245 (vs), 1121 (w), 1100 (w), 1065 (vw), 1023 (w), 839 (vs,b), 787 (w), 754 (m), 692 (s), 657 (m), 717 (w), 620 (vw), 595 (vw), 576 (vw), 474 (w), 445 (w). EI-MS (130 °C; *m*/*z* (relative abundance, %)): 365 (8), 364 (33), 363 (13), 362 (46), 361 (46), 360 ([Zr($\mathrm{C_5Me_5}$)$_2$]$^+$; 100), 359 (23), 358 (30), 357 (13), 356 (16), 355 (12), 354 (14), 353 (10), 352 (9), 223 (8), 155 (19), 83 (35), 73 (20). Anal. Calcd for $\mathrm{C_{33}H_{58}Si_3Zr}$ (630.31): C, 62.88; H, 9.27. Found: C, 63.21; H, 9.16.

Preparation of [Zr(η^1-C≡CCMe$_3$){η^3-C(SiMe$_3$)═CH(SiMe$_3$)}(η^5-C$_5$HMe$_4$)$_2$] (6a). Green crystalline **6** (0.503 g, 1.0 mmol) was dissolved in hexane (30 mL), and $\mathrm{HC{\equiv}CCMe_3}$ (0.62 mL, 5.0 mmol) was added. The bright green solution of **6** immediately turned pale yellow. All volatiles were evaporated under vacuum, and a crystalline residue was extracted with hexane. Partial evaporation of the extract and cooling to −18 °C overnight gave yellowish crystals of **6a**. Yield: 0.56 g (95%). Mp: at 134 °C turns green (loss of $\mathrm{HC{\equiv}CCMe_3}$) and then melts at 145 °C. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.36, 0.40 (2 × s, 9 H, $\mathrm{Si}Me_3$), 1.42 (s, 9 H, $\mathrm{C}Me_3$), 1.58, 1.64, 1.89, 2.11 (4 × s, 6 H, $\mathrm{C_5}Me_4\mathrm{H}$), 5.09 (s, 2 H, $\mathrm{C_5Me_4}H$), 7.27 (s, 1 H, $\mathrm{ZrC}H$). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 2.2, 3.6 (2 × q, $^1J_{\mathrm{CH}} = 119$ Hz, $\mathrm{Si}Me_3$), 12.4, 13.4 (2 C), 13.9 (4 × q, $^1J_{\mathrm{CH}} = 126$ Hz, $\mathrm{C_5}Me_4\mathrm{H}$), 29.1 (s, $C\mathrm{Me_3}$), 32.7 (q, $^1J_{\mathrm{CH}} = 126$ Hz, $\mathrm{C}Me_3$), 106.1 (d, $^1J_{\mathrm{CH}} = 166$ Hz, $\mathrm{C_5Me_4H}$, CH), 111.2 (d, $^1J_{\mathrm{CH}} = 100$ Hz, $C\mathrm{H{=}CSiMe_3}$), 112.7, 113.8, 117.3 (3H s, $\mathrm{C_5Me_4H}$, C-Me), 121.9 (d, $^2J_{\mathrm{CH}} = 7$ Hz, $C\mathrm{{\equiv}CCMe_3}$), 122.6 (s, $\mathrm{C_5Me_4H}$, C-Me), 127.6 (s, $\mathrm{C{\equiv}}C\mathrm{CMe_3}$), 224.1 (s, $\mathrm{Me_3Si}C\mathrm{{=}CH}$). ^{29}Si NMR ($\mathrm{C_6D_6}$): δ −8.5, −3.0 ($\mathrm{Me_3}Si\mathrm{C{=}CH}Si\mathrm{Me_3}$). IR (KBr, cm^{-1}): 3086 (w), 2953 (s), 2943 (s), 2893 (s), 2857 (m), 2713 (w), 2077 (w), 1447 (m), 1433 (m), 1373 (m), 1353 (m), 1320 (w), 1253 (s), 1240 (vs), 1198 (w), 1143 (w), 1020 (m), 973 (w), 853 (vs), 837 (vs), 820 (vs), 807 (s), 784 (m), 747 (m), 720 (w), 687 (w), 653 (m), 620 (w), 577 (w), 540 (w), 473 (w), 447 (w). EI-MS (180 °C; *m*/*z* (relative abundance, %)): 504 (1), 503 (1), 502 ([M − $\mathrm{C{\equiv}CCMe_3}$]$^+$, 3), 338 (5), 337 (7), 336 (31), 335 (10), 334 (40), 333 (43), 332 ([Zr($\mathrm{C_5HMe_4}$)$_2$]$^+$; 100), 331 (15), 330 (17), 329 (9), 328 (10), 327 (8), 326 (7), 325 (6), 155 ([btmse − Me]$^+$; 21), 73 ([$\mathrm{SiMe_3}$]$^+$; 7), 67 (26), 41 (12), 39 (6). Anal. Calcd for $\mathrm{C_{32}H_{54}Si_2Zr}$ (586.18): C, 65.57; H, 9.29. Found: C, 65.27; H, 9.22.

Preparation of [Zr(η^1-C≡CSiMe$_3$){η^3-C(SiMe$_3$)═CH(SiMe$_3$)}(η^5-C$_5$HMe$_4$)$_2$] (6b). The reaction of **6** (0.503 g, 1.0 mmol) with $\mathrm{HC{\equiv}CSiMe_3}$ (0.71 mL, 5 mmol) and isolation of the product was carried out as for **5b**. A waxy solid of **6b** was obtained by thorough evaporation of the hexane extract. Yield: 0.57 g (95%). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.37, 0.38, 0.38 (3 × s, 9 H, $\mathrm{Si}Me_3$), 1.57, 1.62, 1.89, 2.10 (4 × s, 6 H, $\mathrm{C_5}Me_4\mathrm{H}$), 5.06 (s, 2 H, $\mathrm{C_5Me_4}H$), 7.12 (s, 1 H, $\mathrm{ZrC}H$). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 1.3, 2.2, 3.5 (3 × q, $^1J_{\mathrm{CH}} = 119$ Hz, $\mathrm{Si}Me_3$), 12.3, 13.3, 13.4, 13.9 (4 × q, $^1J_{\mathrm{CH}} = 127$ Hz, $\mathrm{C_5}Me_4\mathrm{H}$), 106.2 (d, $^1J_{\mathrm{CH}} = 167$ Hz, $\mathrm{C_5Me_4}H$), 109.8 (d, $^1J_{\mathrm{CH}} = 97$ Hz, $C\mathrm{H{=}CSiMe_3}$), 113.0, 114.1, 117.3, 122.6 (4 × s, $\mathrm{C_5Me_4H}$, C-Me), 125.1 (s, $\mathrm{C{\equiv}}C\mathrm{SiMe_3}$), 164.8 (d, $^2J_{\mathrm{CH}} = 7$ Hz, $C\mathrm{{\equiv}CCSiMe_3}$), 223.0 (s, $\mathrm{Me_3Si}C\mathrm{{=}CH}$). ^{29}Si NMR ($\mathrm{C_6D_6}$): δ −26.8 (η^1-$\mathrm{C{\equiv}C}Si\mathrm{Me_3}$), −8.2, −1.7 ($\mathrm{Me_3}Si\mathrm{C{=}CH}Si\mathrm{Me_3}$). IR (KBr, cm^{-1}): 2980−2800 (very broad), 2780 (w), 2013 (s), 1617 (w), 1480 (w), 1430 (s), 1367 (s), 1323 (m), 1293 (w), 1240 (s), 1167 (w), 1140 (m), 1104 (s), 1080 (s), 1020 (s), 1000 (m), 970 (m), 887 (w), 835 (vs), 747 (m), 713 (w), 683 (s), 653 (m), 607 (m), 573 (w), 557 (w), 513 (w), 497 (w), 473 (w), 440 (w). EI-MS (direct inlet, 70 eV, 140 °C; *m*/*z* (relative abundance)): 337 (8), 336 (29), 335 (11), 334 (42), 333 (43), 332 ([Zr($\mathrm{C_5HMe_4}$)$_2$]$^+$; 100), 331 (17), 330 (20), 329 (8), 328 (10), 327 (8), 155 ([btmse − Me]$^+$; 18), 83 (32), 73 ([$\mathrm{SiMe_3}$]$^+$; 14). Anal. Calcd for $\mathrm{C_{31}H_{54}Si_3Zr}$ (602.25): C, 61.82; H, 9.04. Found: C, 61.49; H, 8.96.

Preparation of [Zr(η^1-C≡CFc){η^3-C(SiMe$_3$)═CH(SiMe$_3$)}(η^5-C$_5$HMe$_4$)$_2$] (6c). A solution of **6** (0.503 g, 1.0 mmol) in hexane (30 mL) was poured onto $\mathrm{HC{\equiv}CFc}$ (0.210 g, 1.0 mmol), and the mixture was stirred at 40 °C until the green color turned to yellow. All volatiles were evaporated under vacuum and the residue extracted by hexane. Crystallization from a concentrated solution at −5 °C afforded yellow prisms of **6c**. Yield: 0.68 g (95%). Mp: 129 °C. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.39, 0.41 (2 × s, 9 H, $\mathrm{Si}Me_3$), 1.66, 1.66, 1.95, 2.15 (4 × s, 6 H, $\mathrm{C_5}Me_4\mathrm{H}$), 4.03 (apparent t, 3 H, $\mathrm{C_5}H_4\mathrm{Fe}$), 4.28 (s, 5 H, $\mathrm{C_5}H_5\mathrm{Fe}$), 4.47 (apparent t, 3 H, $\mathrm{C_5}H_4\mathrm{Fe}$), 5.12 (s, 2 H, $\mathrm{C_5Me_4}H$), 7.35 (s, 1 H, $\mathrm{ZrC}H$). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 2.1, 3.5 (2H q, $^1J_{\mathrm{CH}} = 119$ Hz, $\mathrm{Si}Me_3$), 12.3, 13.3, 13.4, 13.9 (4H q, $^1J_{\mathrm{CH}} = 126$ Hz, $\mathrm{C_5}Me_4\mathrm{H}$), 67.6 (dm, $^1J_{\mathrm{CH}} = 175$ Hz, $\mathrm{C_5H_4Fe}$, CH), 69.7 (dm, $^1J_{\mathrm{CH}} = 175$ Hz, $C_5\mathrm{H_5Fe}$), 70.7 (dm, $^1J_{\mathrm{CH}} = 175$ Hz, $\mathrm{C_5H_4Fe}$, CH), 72.8 (s, $\mathrm{C_5H_4Fe}$, C_{ipso}), 106.2 (d, $^1J_{\mathrm{CH}} = 167$ Hz, $\mathrm{C_5Me_4H}$, CH), 110.4 (d, $^1J_{\mathrm{CH}} = 100$ Hz, $C\mathrm{H{=}CSiMe_3}$), 112.8, 114.2 (2H s, $\mathrm{C_5Me_4H}$, C-Me); 116.8 (s, $\mathrm{C{\equiv}}C\mathrm{Fc}$), 117.3, 122.9 (2H s, $\mathrm{C_5Me_4H}$, C-Me), 135.5 (d, $^2J_{\mathrm{CH}} = 7$ Hz, $C\mathrm{{\equiv}CFc}$), 223.9 (s, $\mathrm{Me_3Si}C\mathrm{{\equiv}CH}$). ^{29}Si NMR ($\mathrm{C_6D_6}$): δ −8.4, −3.2 ($\mathrm{Me_3}Si\mathrm{C{=}CH}Si\mathrm{Me_3}$). IR (KBr, cm^{-1}): 3090 (m), 3077 (m), 2967 (w), 2944 (s), 2887 (s), 2850 (w), 2713 (w), 1500 (w), 1477 (w), 1440 (vs), 1374 (s), 1327 (w), 1243 (vs), 1226 (m), 1143 (w), 1103 (m), 1034 (w), 1017 (s), 997 (m), 914 (m), 835 (vs), 747 (s), 717 (w), 687 (m), 657 (s), 623 (s), 580 (w), 570 (w), 530 (m), 500 (m), 480 (s), 447 (m). EI-MS (250 °C; *m*/*z* (relative abundance, %)): 336 (8), 334 (13), 333 (13), 332 ([Zr($\mathrm{C_5HMe_4}$)$_2$]$^+$; 29), 331 (15), 330 (28), 329 (12), 328 (14), 327 (9), 326 (11), 325 (7), 324 (7), 210 ([$\mathrm{C{\equiv}CFc}$]$^+$; 7), 170 ([btmse]$^+$; 8), 157 (16), 156 (39), 155 ([btmse − Me]$^+$; 100), 121 (15), 97 (9), 83 (8), 73 ([$\mathrm{SiMe_3}$]$^+$, 48), 70 (35), 56 (11), 45 (24), 43 (22). Anal. Calcd for $\mathrm{C_{38}H_{54}FeSi_2Zr}$ (714.09): C, 63.92; H, 7.62. Found: C, 64.07; H, 7.65.

Preparation of [Zr(η^1-C≡CPh){η^3-C(SiMe$_3$)═CH(SiMe$_3$)}(η^5-C$_5$HMe$_4$)$_2$] (6d). The reaction of **6** (1.0 mmol) with $\mathrm{HC{\equiv}CPh}$ (0.55 mL, 5.0 mmol) and isolation of the product were carried out as for **6a**. Pale yellow crystals of **6d** were obtained and recrystallized from hexane. Yield: 0.58 g (96%). Mp: 128 °C. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.35, 0.40 (2 × s, 9 H, $\mathrm{Si}Me_3$), 1.63, 1.66, 1.94, 2.14 (4 × s, 6 H, $\mathrm{C_5}Me_4\mathrm{H}$), 5.12 (s, 2 H, $\mathrm{C_5Me_4}H$), 7.00−7.06 (m, 1 H, *Ph*), 7.15−7.20 (m, 2 H, *Ph*), 7.35 (s, 1 H, $\mathrm{ZrC}H$), 7.65−7.69 (m, 2 H, *Ph*). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 2.0, 3.5 (2 × q, $^1J_{\mathrm{CH}} = 119$ Hz, $\mathrm{Si}Me_3$), 12.3, 13.2, 13.3, 13.9 (4 × q, $^1J_{\mathrm{CH}} = 127$ Hz, $\mathrm{C_5}Me_4\mathrm{H}$), 106.2 (d, $^1J_{\mathrm{CH}} = 166$ Hz, $\mathrm{C_5Me_4H}$, *C*H), 109.9 (d, $^1J_{\mathrm{CH}} = 96$ Hz, $C\mathrm{H{=}CSiMe_3}$), 112.9, 114.3, 117.4 (3 × s, $\mathrm{C_5Me_4H}$, *C*-Me), 120.8 (t, $^2J_{\mathrm{CH}} = 7$ Hz, Ph, C_{ipso}), 123.1 (s, $\mathrm{C_5Me_4H}$, *C*-Me), 125.7 (dt, $^1J_{\mathrm{CH}} = 161$, $^2J_{\mathrm{CH}} = 8$ Hz, Ph, *C*H), 128.1 (dt, J_{CH} not read due to overlapp with solvent signal, Ph, *C*H), 128.9 (d, $J_{\mathrm{CH}} = 8$ Hz, $\mathrm{Ph}C{\equiv}C$), 131.0 (dt, $^1J_{\mathrm{CH}} = 159$, $^2J_{\mathrm{CH}} = 7$ Hz, Ph, *C*H), 140.2 (d, $J_{\mathrm{CH}} = 8$ Hz, $\mathrm{Ph}C{\equiv}C$), 223.7 (s, $\mathrm{Me_3Si}C{\equiv}\mathrm{CH}$). ^{29}Si NMR ($\mathrm{C_6D_6}$): δ −8.2, −3.3 ($\mathrm{Me_3}Si\mathrm{C{=}CH}Si\mathrm{Me_3}$). IR (KBr, cm^{-1}): 3053 (w), 2960 (w), 2933 (s), 2883 (s), 2843 (w), 2707 (w), 2067 (m), 1587 (m), 1480 (m), 1437 (s), 1367 (m), 1327 (w), 1243 (s), 1199 (m), 1140 (w), 1060 (w), 1020 (m), 835 (vs), 780 (w), 750 (s), 713 (w), 687 (m), 653 (m), 617 (w), 577 (w), 527 (m), 480 (m), 440 (w). EI-MS (140 °C; *m*/*z* (relative abundance, %)): 505 (0.6), 503 (0.6), 502 ([M − C≡CPh]$^+$, 1), 336 (16), 335 (6), 334 (20), 333 (21), 332 ([Zr($\mathrm{C_5HMe_4}$)$_2$]$^+$; 49), 331 (9), 330 (12), 170 ([btmse]$^+$; 6), 157 (9), 156 (18), 155 ([btmse − Me]$^+$; 100), 105 (10), 103 (7), 102 (66), 76 (14), 75 (6), 74 (8), 73 ([$\mathrm{SiMe_3}$]$^+$; 20), 43 (18). Anal. Calcd for $\mathrm{C_{34}H_{50}Si_2Zr}$ (606.17): C, 67.37; H, 8.31. Found: C, 67.42; H, 8.30.

Preparation of [Zr(η^1-C≡CFc){η^3-C($\mathrm{SiMe_3}$)=CH$\mathrm{SiMe_3}$}{η^5-$\mathrm{C_5Me_4(SiMe_3)}$}$_2$] (7c). A solution of **7** (0.646 g, 1.0 mmol) in hexane (30 mL) was poured onto HC≡CFc (0.210 g, 1.0 mmol), and the mixture was stirred at 40 °C until the green color turned to yellow. All volatiles were evaporated under vacuum, and the residue was extracted by hexane. The product did not crystallize from hexane. A subsequent evaporation of the solvent followed by thorough removal of volatiles under high vacuum afforded an ochre sticky wax of **6c**. Yield: 0.68 g (95%). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.45 (s, 18 H, $\mathrm{C_5Me_4Si}Me_3$), 0.49, 0.51 (2H s, 9 H, $\mathrm{{=}CSi}Me_3$), 1.70, 1.79, 1.85, 2.16 (4H s, 6 H, $\mathrm{C_5}Me_4$), 4.06 (apparent t, 2 H, $\mathrm{C_5}H_4\mathrm{Fe}$), 4.33 (s, 5 H, $\mathrm{C_5}H_5\mathrm{Fe}$), 4.49 (apparent t, 2 H, $\mathrm{C_5}H_4\mathrm{Fe}$), 7.50 (s, 1 H, $\mathrm{ZrC}H$). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 3.3 ($\mathrm{{=}CSi}Me_3$), 3.3 ($\mathrm{C_5Me_4Si}Me_3$), 6.3 ($\mathrm{{=}CSi}Me_3$), 12.8, 13.4, 15.9, 16.4 ($\mathrm{C_5}Me_4\mathrm{H}$), 67.5 ($\mathrm{C_5H_4Fe}$, *C*H), 69.6 ($C_5\mathrm{H_5Fe}$), 70.5 ($\mathrm{C_5H_4Fe}$, *C*H), 73.9 ($\mathrm{C_5H_4Fe}$, C_{ipso}), 109.6 ($C\mathrm{H{=}CSiMe_3}$), 115.5, 119.7 ($\mathrm{C_5Me_4H}$, *C*-Si≡*C*-Me), 120.4 (C≡*C*Fc), 122.7, 123.1, 124.8 ($\mathrm{C_5Me_4H}$, *C*-Si≡*C*-Me), 133.3 (*C*≡CFc), 224.9 (s, $\mathrm{Me_3Si}C{\equiv}\mathrm{CH}$). ^{29}Si DEPT ($\mathrm{C_6D_6}$): δ −9.8 ($\mathrm{Me_3SiC{=}CHSiMe_3}$), −7.7 ($\mathrm{C_5Me_4SiMe_3}$), −4.4 ($\mathrm{Me_3SiC{=}CHSiMe_3}$). IR (KBr, cm^{-1}): 3094 (w), 2955 (s), 2899 (s), 2855 (sh), 1482 (w), 1444 (s), 1377 (m), 1338 (m), 1245 (vs), 1127 (m), 1106 (m), 1022 (s), 1000 (m), 912 (m), 838 (vs,b), 755 (s), 687 (m), 656 (m), 630 (m), 569 (w), 530 (w), 496 (m), 470 (m), 449 (m), 418 (m). Anal. Calcd for $\mathrm{C_{44}H_{70}FeSi_4Zr}$ (858.46): C, 61.56; H, 8.22. Found: C, 61.67; H, 8.29.

Dimerization of *tert*-Butylethyne with Complex 7. The dimerization experiments were carried out both in ampules with an attached all-sealed quartz cuvette ($d = 2.0$ mm) and in NMR sample tubes, both under vacuum conditions, and were flame sealed. A glass ampule (30 mL) was charged with a solution of **7** in hexane (10 mL, 0.01 M), and after the electronic absorption spectrum was recorded HC≡C$\mathrm{CMe_3}$ (1.0 mL, 8.0 mmol) was added from a breakable seal. The absorption band due to **7** at 740 nm disappeared, while the band of dissolved alkyne at 1534 nm occurred. After heating in a water bath to 70 °C for 14 h, the latter band disappeared while the band at 740 nm was restored to its initial intensity. The experiment was repeated by adding another 1.0 mL of the alkyne to the reaction mixture, which was consumed after the same period. All volatiles were distilled off under vacuum at 60 °C, and the dimer of *tert*-butylethyne was characterized by GC-MS, IR, and NMR spectra to be the head-to-tail dimer.

In the NMR experiment, crystalline **7** (0.10 g, 0.17 mmol) was dissolved in $\mathrm{C_6D_6}$ (2 mL). HC≡C$\mathrm{CMe_3}$ (0.1 mL, 0.8 mmol) was added, and the mixture was sealed with gentle cooling in an NMR tube. NMR spectra were recorded for this mixture and then repeatedly after heating in a bath kept at 70 °C. The initial sample contained **7a**, HC≡C$\mathrm{CMe_3}$, and traces of the head-to-tail dimer; the final mixture contained only **7** and the dimer.

Analytical data for [Zr(η^1-C≡C$\mathrm{CMe_3}$)(η^3-C($\mathrm{SiMe_3}$)=CH($\mathrm{SiMe_3}$){η^5-$\mathrm{C_5Me_4(SiMe_3)}$}$_2$] (**7a**) are as follows. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.33 (s, 18 H, $\mathrm{C_5Me_4Si}Me_3$), 0.41, 0.47 (2 × s, 9 H, $Me_3\mathrm{SiCH{=}CSi}Me_3$), 1.44 (s, 9 H, $\mathrm{C}Me_3$), 1.70, 1.73, 1.95, 2.13 (4 × s, 6 H, $\mathrm{C_5}Me_4$), 7.36 (s, 1 H, $\mathrm{Me_3SiC}H\mathrm{{=}CSiMe_3}$). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 3.3 ($Me_3\mathrm{SiCH{=}CSi}Me_3$), 3.5 ($\mathrm{C_5Me_4Si}Me_3$), 6.8 ($Me_3\mathrm{SiCH{=}CSi}Me_3$), 13.5, 13.7, 16.5, 17.1 ($\mathrm{C_5}Me_4$), 29.5 ($C\mathrm{Me_3}$), 32.4 ($\mathrm{C}Me_3$), 110.74 ($\mathrm{Me_3Si}C\mathrm{H{=}CSiMe_3}$), 113.3, 121.2, 122.2, 124.2, 126.6 (*C*≡*C*, $\mathrm{C_{ipso}(C_4Me_5)}$), 225.4 ($\mathrm{Me_3SiCH{=}}C\mathrm{SiMe_3}$).

Analytical data for $\mathrm{Me_3CC{\equiv}CH}$ are as follows. NMR ($\mathrm{C_6D_6}$): δ_{H} 1.10 (s, 9 H, $\mathrm{C}Me_3$), 1.88 (s, 1 H, ≡C*H*); δ_{C} 27.4 ($C\mathrm{Me_3}$), 31.1 ($\mathrm{C}Me_3$), 67.3 (≡*C*H), 92.39 (≡*C*).

Analytical data for $\mathrm{Me_3CC{\equiv}CC(CMe_3){=}CH_2}$ are as follows. NMR ($\mathrm{C_6D_6}$): δ_{H} 1.15, 1.19 (2H s, 9 H, $\mathrm{C}Me_3$), 5.10, 5.31 (2H d, $^2J_{\mathrm{HH}} = 1.7$ Hz, 1 H, $\mathrm{{=}C}H_2$); δ_{C} 28.1 ($C\mathrm{Me_3}$), 29.2, 31.2 ($\mathrm{C}Me_3$), 79.6, 99.1 (*C*≡*C*), 116.0 ($\mathrm{{=}}C\mathrm{H_2}$), 142.33 (=*C*).

Attempted Dimerization of 1-Alkynes with Complex 7. Purified (trimethylsilyl)ethyne (0.1 mL, 0.7 mmol), phenylethyne (0.1 mL, 0.9 mmol), or hex-1-yne (0.1 mL, 0.9 mmol) was added to a solution of **7** in hexane (10 mL, 0.01 M) in a cuvette, as described for the dimerization of $\mathrm{Me_3CC{\equiv}CH}$. The green color of **7** always immediately disappeared, and the absorption band due to the alkynes in the region 1534−1543 nm appeared. The cuvette was thermostated at 70 °C, and the intensity of the absorption band of 1-alkynes measured in approximately 8 h intervals. In neither case a significant decrease of the band intensity was observed after 40 h.

Preparation of Li[Zr(η^1-C≡C$\mathrm{SiMe_3}$)(η^2-$\mathrm{Me_3SiC{\equiv}CSiMe_3}$)($\eta^5$-$\mathrm{C_5HMe_4}$)$_2$] (6e). Crystalline **6** (1.0 mmol, 0.503 g) was dissolved in hexane (30 mL), and the solution was mixed with a white suspension of $\mathrm{LiC{\equiv}CSiMe_3}$ (5.0 mmol, 0.52 g) in hexane. The bright green color of the solution turned dark khaki after heating to 60 °C for 2 days. The solution was separated from an excess of white, insoluble $\mathrm{LiC{\equiv}CSiMe_3}$ and concentrated to induce crystallization. A small portion of powdery $\mathrm{LiC{\equiv}CSiMe_3}$ precipitated on the glass walls at −5 °C. A clear solution was separated and crystallized at −18 °C. Yellow crystals of **6e** were separated from the mother liquor and recrystallized from hexane. Yield: 0.27 g (45%). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.25, 0.27, 0.50 (3 × s, 9 H, $\mathrm{Si}Me_3$), 1.48, 1.68, 1.77, 2.15 (4 × s, 6 H, $\mathrm{C_5}Me_4\mathrm{H}$), 5.16 (s, 2 H, $\mathrm{C_5Me_4}H$). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 1.2, 2.8, 4.1 ($\mathrm{Si}Me_3$), 11.8, 13.3, 13.7, 13.9 ($\mathrm{C_5}Me_4\mathrm{H}$), 104.6 ($\mathrm{C_5Me_4H}$, *C*H), 108.8, 109.7, 111.1, 119.1 ($\mathrm{C_5Me_4H}$, *C*-Me), 175.2 (quadruplet, $^1J(^{13}\mathrm{C}^7\mathrm{Li}) = 14$ Hz) and 184.2 (quadruplet, $^1J(^{13}\mathrm{C}^7\mathrm{Li}) = 10$ Hz; η^1-$C{\equiv}C\mathrm{SiMe_3}$), 235.3 ($\eta^2$-$\mathrm{Me_3Si}C{\equiv}C\mathrm{SiMe_3}$). ^{7}Li NMR: δ 3.8. ^{29}Si NMR ($\mathrm{C_6D_6}$): δ −26.4 (η^1-$\mathrm{C{\equiv}C}Si\mathrm{Me_3}$), −12.0, −9.6 ($\eta^2$-$\mathrm{Me_3}Si\mathrm{C{\equiv}C}Si\mathrm{Me_3}$). IR (KBr, cm^{-1}): 2953 (s), 2903 (s), 2862 (w), 2723 (w), 2151 (w), 2021 (s), 1502 (w), 1439 (s), 1379 (m), 1365 (m), 1328 (w), 1245 (vs), 1147 (w), 1025 (m), 977 (w), 936 (m), 835 (vs), 755 (s), 689 (vs), 658 (m), 518 (w), 508 (w), 500 (w), 479 (m), 468 (w), 458 (m), 450 (w), 419 (m), 408 (m). Anal. Calcd for $\mathrm{C_{31}H_{53}LiSi_3Zr}$ (608.18): C, 61.22; H, 8.78. Found: C, 61.09; H, 8.73.

Preparation of Li[Zr(η^1-C≡C$\mathrm{SiMe_3}$)(η^2-$\mathrm{Me_3SiC{\equiv}CSiMe_3}$)($\eta^5$-$\mathrm{C_5HMe_4}$)$_2$]A($\mathrm{C_4H_8O}$) (6f). Crystalline **6** (1.0 mmol, 0.503 g) was dissolved in THF (20 mL), and the solution was poured onto powdery $\mathrm{LiC{\equiv}CSiMe_3}$ (5.0 mmol, 0.52 g; precipitated from hexane). After it was heated for $^1/_2$ day to 60 °C, the originally green solution changed to dark khaki. Then, THF was evaporated and khaki oily product was extracted with hexane. The hexane solution was removed from a white crystalline solid ($\mathrm{LiC{\equiv}CSiMe_3}$) and concentrated to induce crystallization. Yellow crystals of **6f** were separated and recrystallized from hexane. The yield of **6f** was 0.41 g (60%). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.30, 0.35, 0.55 (3 × s, 9 H, $\mathrm{Si}Me_3$); 1.26 (br s, 4 H, THF, $\mathrm{C}H_2$-

CH$_2$O), 1.55, 1.85, 1.86, 2.10 (4 × s, 6 H, C$_5$*Me*$_4$H), 3.49 (br s, 4 H, THF, C*H*$_2$O), 5.07 (s, 2 H, C$_5$Me$_4$*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 1.4, 3.3, 4.8 (Si*Me*$_3$), 12.1, 13.2, 13.8, 14.4 (C$_5$*Me*$_4$H), 25.1 (br, THF, *C*H$_2$CH$_2$O), 104.3 (C$_5$Me$_4$H, *C*H), 108.3, 110.5, 112.3, 118.5 (C$_5$Me$_4$H, *C*-Me), 175.9 (quadruplet, $^1J(^{13}\mathrm{C}^7\mathrm{Li}) = 14$ Hz) and 184.7 (quadruplet, $^1J(^{13}\mathrm{C}^7\mathrm{Li}) = 10$ Hz; η^1-*C*≡*C*SiMe$_3$), 237.9 (η^2-Me$_3$Si*C*≡*C*SiMe$_3$). ^{7}Li NMR: δ 3.0 s. ^{29}Si NMR (C$_6$D$_6$): δ −27.1 (η^1-C≡C*Si*Me$_3$), −12.8, −10.1 (η^2-Me$_3$*Si*C≡C*Si*Me$_3$). Anal. Calcd for C$_{35}$H$_{61}$OLiSi$_3$Zr (680.29): C, 61.79; H, 9.04. Found: C, 61.71; H, 8.97.

X-ray Crystallography. Pale yellow crystals of **5a, 6a**, and **6d**, yellow crystals of **6c**, and **6e** were inserted into Lindemann glass capillaries in a glovebox, and the capillaries were sealed with wax. The diffraction data for all these complexes were collected on a Nonius KappaCCD diffractometer (Mo Kα radiation, $\lambda = 0.710\,73$ Å) and analyzed by the HKL program package.[32] The structures were solved by direct methods (SIR97),[33] followed by consecutive Fourier syntheses, and refined by full-matrix least squares on F^2 (SHELX97).[34] In all cases, the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were treated as follows. For **5a**, all hydrogen atoms were located on difference electron density maps and refined isotropically. For **6a**, hydrogen atoms residing on the cyclopentadienyl rings and the agostic hydrogen (H(5), H(14), and H(26)) were located on difference electron density maps and refined isotropically; all others were fixed and refined in their idealized positions. For **6c** and **6d**, agostic hydrogen atoms (H(32) and H(27)) were located on difference electron density maps and refined isotropically; all others were fixed and refined in their theoretical positions. For **6e**, all hydrogen atoms were fixed and refined in their theoretical positions.

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Supporting Information Available: Tables of crystallographic data, atomic coordinates, thermal parameters, intramolecular distances and angles, and dihedral angles of least-squares planes and packing diagrams for **5a**, **6a**, **6c**, **6d**, and **6e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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