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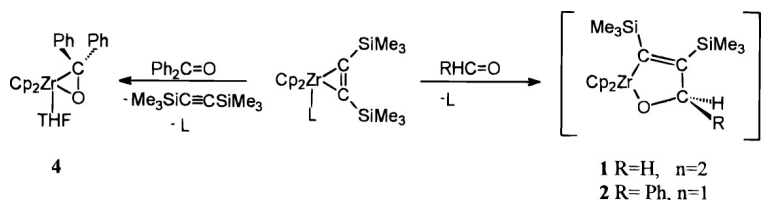
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Reactions of the Zirconocene Complexes of Bis(trimethylsilyl)acetylene with Formaldehyde, Benzaldehyde, and Benzophenone

N. Peulecke, A. Ohff, A. Tillack, W. Baumann, R. Kempe, V. V. Burlakov,[†] and U. Rosenthal^{*,‡}

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In reactions of the zirconocene derivative $\text{Cp}_2\text{ZrC}(\text{SiMe}_3)=\text{C}(\text{SiMe}_3)(\text{THF})$ with ketones and aldehydes the influence of the various substituents of the carbonyl compounds upon the formation of different products was investigated. Formaldehyde reacts by an insertion of the carbonyl unit into a Zr–C bond to give a metallacycle which is additionally stabilized by the formation of a coordination dimer $[\text{Cp}_2\text{ZrOCH}_2\text{C}(\text{SiMe}_3)=\text{C}(\text{SiMe}_3)]_2$ (**1**). Benzaldehyde yields a monomeric metallacycle $\text{Cp}_2\text{ZrOCHPhC}(\text{SiMe}_3)=\text{C}(\text{SiMe}_3)$ (**2**). Complex **2** is less stable than **1**, and at higher temperatures it loses half of its moiety $\text{Me}_3\text{SiC}_2\text{SiMe}_3$, leaving $\{[\text{Cp}_2\text{ZrOCHPhC}(\text{SiMe}_3)=\text{C}(\text{SiMe}_3)][\text{Cp}_2\text{Zr}(\eta^2\text{-O}=\text{CHPh})]\}$ (**3**). Benzophenone gives no insertion, and the monomeric η^2 -ketone complex $\text{Cp}_2\text{Zr}(\text{THF})(\eta^2\text{-O}=\text{CPh}_2)$ (**4**) was obtained.

Introduction

Zirconocene complexes of ketones or aldehydes^{1,2} are of great interest for carbon–carbon bond formation reactions with unsaturated compounds.² The classical example of such complexes, $\text{Cp}_2\text{Zr}(\eta^2\text{-O}=\text{CPh}_2)$, was obtained in the carbonylation of diphenylzirconocene, Cp_2ZrPh_2 , by Erker.^{3–5} X-ray structural analysis of the monomeric compound was not reported. The solid-state structural characterization indicated a dimeric structure $[\text{Cp}_2\text{Zr}(\eta^2\text{-O}=\text{CPh}_2)]_2$.² The first structurally characterized monomeric η^2 -ketone complex of a group 4 metal was $(\text{Ar}'\text{O})_2\text{Ti}(\text{PMe}_3)(\eta^2\text{-O}=\text{CPh}_2)$ ($\text{Ar}'\text{O} = 2,6$ -diphenylphenoxide),⁶ but metallocene analogues are unknown so far. The zirconocene-induced coupling reaction of alkynes with carbonyl compounds to give zirconadihydofurans is known,^{1,2,7} but detailed investigations concerning the influence of the substituents of the alkynes and carbonyl compounds on the nature of the products have not been reported.

Recently, we reported the insertion of acetone into zirconacyclopentene complexes $\text{Cp}_2\text{ZrC}(\text{SiMe}_3)=\text{C}(\text{SiMe}_3)-$

(L), L = THF⁸ or pyridine,⁹ which gave the metallacycle $\text{Cp}_2\text{ZrOCMe}_2\text{C}(\text{SiMe}_3)=\text{C}(\text{SiMe}_3)$.¹⁰ This was rather reactive and underwent acetylene exchange reactions, e.g., with toluene. The resulting complex, $\text{Cp}_2\text{ZrOCMe}_2\text{C}(\text{Ph})=\text{C}(\text{Ph})$, was much more stable and unreactive. The difference in behavior of the two complexes was explained on the basis of electronic and/or steric factors of the alkyne substituents SiMe_3 and Ph .¹⁰ Recently, the regiochemistry of the insertion of acetone into $\text{Cp}_2\text{ZrC}(\text{SiMe}_3)=\text{C}(\text{tBu})(\text{THF})$ was investigated.⁷ At first, the kinetically controlled β -Si-substituted product $\text{Cp}_2\text{ZrOCMe}_2\text{C}(\text{SiMe}_3)=\text{C}(\text{tBu})$ was formed, and after cycloreversion, the thermodynamically more favored α - SiMe_3 product $\text{Cp}_2\text{ZrOCMe}_2\text{C}(\text{tBu})=\text{C}(\text{SiMe}_3)$ was isolated. It seems that in this example the steric factor is responsible for the isomerization. The α -position is less hindered than the β -position, and the SiMe_3 group is slightly larger than the tBu group.

To study the influence of the substituents of the carbonyl compounds in detail we investigated the reaction of $\text{Cp}_2\text{ZrC}(\text{SiMe}_3)=\text{C}(\text{SiMe}_3)(\text{THF})$ with differently substituted carbonyl compounds ($\text{CH}_2=\text{O}$, $\text{PhCH}=\text{O}$, and $\text{Ph}_2\text{C}=\text{O}$).

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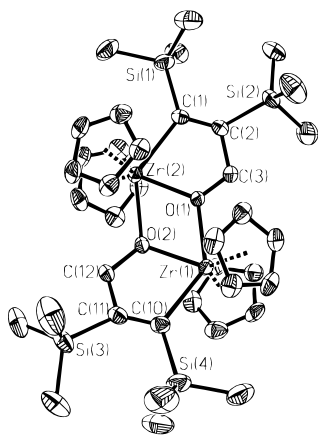
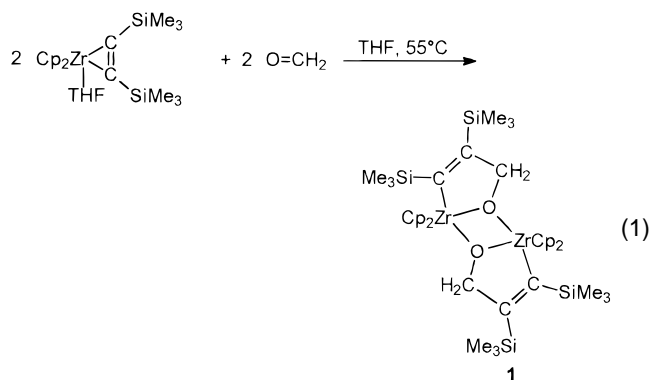


Figure 1. Molecular structure of complex **1**, shown by an ORTEP plot at the 50% probability level.

Results and Discussion

The reaction of $\text{Cp}_2\text{ZrC}(\text{SiMe}_3)=\text{C}(\text{SiMe}_3)(\text{THF})$ with formaldehyde yields, comparable to the reaction with acetone, by an insertion of the carbonyl compound into a Zr–C bond, a metallacyclic product, which is additionally stabilized by the formation of the coordination dimer **1** (eq 1).



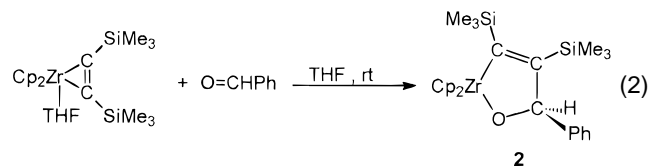
Complex **1** is a colorless, crystalline substance, which is kinetically more stable than the acetone insertion product $\text{Cp}_2\text{ZrOCMe}_2\text{C}(\text{SiMe}_3)=\text{C}(\text{SiMe}_3)$. Thus, **1** does not react with water and carbon dioxide nor with other alkynes such as tolane. A possible reason for this lower reactivity could be the dimeric structure, which prevents the attack of substrates. A similar coupling product of tolane and formaldehyde was obtained by Erker et al.¹¹ in the reaction of the trimeric formaldehyde–zirconocene complex with tolane at 200 °C, for which a monomeric structure $\text{Cp}_2\text{ZrOCH}_2\text{C}(\text{Ph})=\text{C}(\text{Ph})$ was assumed.

The ^1H -NMR spectrum of **1** displays only one signal for the Cp (5.85 ppm), one signal for the CH_2 group (4.72 ppm), and two signals for SiMe_3 units (0.40, 0.41 ppm). Figure 1 shows the X-ray structure of complex **1**.

The Zr–O distances in the two metallacyclic bridged zirconadihydrofurans (O1–Zr2 2.125(2), O2–Zr1 2.131(2) Å) correspond to that in the trimeric η^2 -formaldehyde–zirconocene complex (2.135(5) Å).¹¹ However, the other bridging Zr–O distances (O1–Zr1 2.274(2), O2–Zr2 2.269(2) Å) are significantly longer compared to the

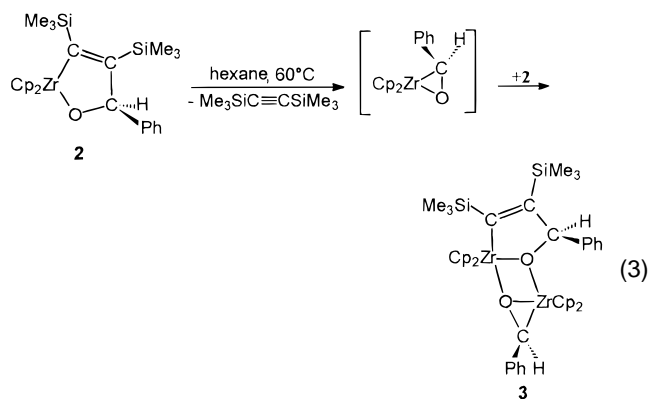
trimeric η^2 -formaldehyde–zirconocene complex (Zr–O 2.179 Å)¹¹ being in the same region as, e.g., in the dimeric structure $[\text{Cp}_2\text{Zr}(\eta^2\text{-O}=\text{CPh}_2)]_2$ (2.287(2) and 2.304(2) Å²). A comparison with other coordination dimers is shown in Table 1.

The reaction of $\text{Cp}_2\text{ZrC}(\text{SiMe}_3)=\text{C}(\text{SiMe}_3)(\text{THF})$ with benzaldehyde yields the orange, crystalline insertion product **2** (eq 2).



When complex **2** is heated above 100 °C, elimination of the alkyne occurs and formation of complex **3** occurs (see below). The ^1H -NMR spectrum of **2** shows in addition to the Ph signals singlets for the nonequivalent SiMe_3 (−0.10, 0.22 ppm) and Cp groups (6.24, 6.38 ppm). The signal of the former aldehyde proton appears at 5.55 ppm. The ^{13}C -NMR spectrum exhibits the typical downfield shift for the α - and β -olefinic carbon atoms at 222.2 and 185.8 ppm (cf. 213.3 and 193.2 ppm in $\text{Cp}_2\text{ZrOCMe}_2\text{C}(\text{SiMe}_3)=\text{C}(\text{SiMe}_3)$).¹⁰

The structure of complex **2** is shown in Figure 2. It is very similar to that of the acetone insertion product $\text{Cp}_2\text{ZrOCMe}_2\text{C}(\text{SiMe}_3)=\text{C}(\text{SiMe}_3)$.¹⁰ The C(1)–C(2) distance of 1.365(4) Å in **2** is in the expected range for a C–C double bond. The C–O distance of 1.423(4) Å is in the C–O single bond range¹²). Compound **2**, in contrast to $\text{Cp}_2\text{ZrOCMe}_2\text{C}(\text{SiMe}_3)=\text{C}(\text{SiMe}_3)$, is unreactive toward carbon dioxide and tolane, but it is thermally less stable than the coordination dimer **1**. Complex **2** decomposes in solution at 60 °C with elimination of the acetylene. In the assumed reaction course the resulting (not isolated) complex “ $\text{Cp}_2\text{Zr}(\eta^2\text{-O}=\text{CHPh})$ ” reacts with a molecule of as yet undecomposed **2** to form a coordination complex, **3**, via the well-known four-membered Zr–O–Zr–O ring (eq 3).



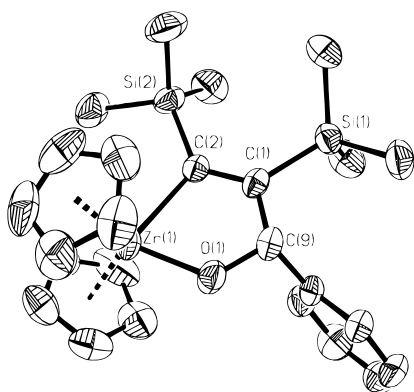
Complex **3** is a pale yellow, crystalline solid. Unfortunately the poor quality of the crystals (and elimination of included solvent during X-ray measurement) did not allow an exact determination of bond lengths and

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Table 1. Comparison of Selected NMR and Structural Data for Monomeric ($n = 1$) and Dimeric ($n = 2$) Zirconacyclic Complexes

	monomeric complexes			coordination dimers		
	5 ($R^1 = R^2 = \text{SiMe}_3$, $R^3 = R^4 = \text{Me}$)	2 ($R^1 = R^2 = \text{SiMe}_3$, $R^3 = \text{H}$, $R^4 = \text{Ph}$)	6 ($R^1 = R^2 = \text{Ph}$, $R^3 = R^4 = \text{Me}$)	1 ($R^1 = R^2 = \text{SiMe}_3$, $R^3 = R^4 = \text{H}$)	8 ($R^1 = R^2 = \text{SiMe}_3$, $R^3, R^4 = \text{O}$)	9 ($R^1 = \text{tBu}$, $R^2 = \text{SiMe}_3$, $R^3, R^4 = \text{O}$)
^{13}C -NMR (δ/ppm)						
C_α (alkyne)	213.3	222.2	185.2	213.6	249.0	<i>a</i>
C_β (alkyne)	193.2	185.8	165.2	158.7	152.9	<i>a</i>
$\Delta\delta$	20.1	36.4	20.0	54.9	96.1	<i>a</i>
angles (deg)						
$\text{R}^1\text{--C}_\alpha\text{--C}_\beta$	128.4(4)	126.8(3)	119.8(2)	119.8(2)	116.8(2)	117.3(4)
$\text{R}^2\text{--C}_\beta\text{--C}_\alpha$	125.6(4)	129.3(3)	123.2(3)	135.2(2)	138.4(3)	139.5(3)
dist (Å)						
M--C_α	2.324(4)	2.324(4)	2.287(3)	2.388(3)	2.376(3)	2.436(4)
$\text{C}_\alpha\text{--C}_\beta$	1.371(7)	1.365(4)	1.348(4)	1.348(4)	1.360(5)	1.354(6)
$\text{C}_\beta\text{--C}_{\beta'} (\text{R}^3\text{R}^4)$	1.544(7)	1.527(5)	1.538(4)	1.514(4)	1.488(5)	1.467(6)
$\text{C}_{\beta'}\text{--O}$	1.426(6)	1.423(4)	1.436(4)	1.416(3)	1.342(4)	1.345(5)
M--O	1.936(3)	1.944(2)	1.932(3)	2.131(2)	2.197(2)	2.163(3)
M--O'				2.274(2)	2.330(2)	2.361(3)

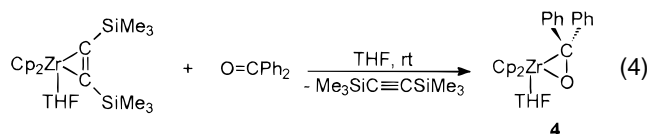
^a No NMR data available (low solubility).**Figure 2.** Molecular structure of complex **2**, shown by an ORTEP plot at the 50% probability level.

angles. Nevertheless, the basic structure has been established.

A similar complex $\{[\text{Cp}_2\text{ZrOCHPhC(Ph)=C(Ph)}][\text{Cp}_2\text{Zr}(\eta^2\text{-O=CH}_2)]\}$ was claimed as a product of the reaction of a mixed dimeric zirconocene complex of benz- and formaldehyde with an excess of toluene, but without a structure determination, by Erker⁵ on the basis of the products of its hydrolysis.

The ^1H -NMR spectrum of **3** exhibits, besides four signals for the nonequivalent Cp protons (5.07, 6.08, 6.21, 6.27 ppm), two signals for the SiMe_3 units (−0.02, 0.41 ppm) and two signals for the former benzaldehyde protons (4.24, 5.94 ppm) of which the first is assigned to the $\mu\text{-}\eta^1\text{:}\eta^2$ and the latter to the inserted benzaldehyde unit (cf. 5.55 ppm in **2**).

The reaction of $\text{Cp}_2\text{ZrC(SiMe}_3\text{)=C(SiMe}_3\text{)(THF)}$ with benzophenone does not yield an insertion product of the carbonyl unit into the zirconacyclopropene ring as found for acetone, formaldehyde, and benzaldehyde but reacts by apparent displacement of the alkyne by the ketone to give complex $\text{Cp}_2\text{Zr(THF)(}\eta^2\text{-O=CPh}_2\text{)}$ (**4**) (eq 4). To our knowledge compound **4** is the first isolated monomeric zirconocene η^2 -ketone complex whose structure has been determined by NMR spectroscopy and X-ray



analysis (Figure 3). Complex **4** was obtained at −30 °C as light yellow crystals, which contain a THF molecule of crystallization in addition to the coordinated THF. At room temperature all THF is lost and a white powder containing the well-known dimers and trimers¹ is formed. The ^1H -NMR spectrum of **4** in $\text{THF-}d_8$ shows, in addition to the Ph multiplets, the signals of THF at 1.78 and 3.62 ppm together with a singlet for the Cp units at 5.54 ppm. The ^{13}C -NMR spectrum in $\text{THF-}d_8$ exhibits together with the signals of THF and Ph units the signals of the Cp groups at 109.9 ppm and of the former carbonyl carbon atom at 94.7 ppm. The structure of **4** is shown in Figure 3.

The η^2 -bound benzophenone in **4** shows some similarities to that in $(\text{Ar}'\text{O})_2\text{Ti(PMe}_3\text{)}(\eta^2\text{-O=CPh}_2)$ ($\text{Ar}'\text{O} = 2,6\text{-diphenylphenoxide}$).⁶ The C–O distances of 1.397(8) Å in ref 6 and 1.389(5) Å in **4** are almost identical and are substantially longer than that in the free ketone of 1.23 Å¹³ but not as long as those in the coordination dimer $[\text{Cp}_2\text{Zr}(\eta^2\text{-O=CPh}_2)]_2$ with values of 1.425(4) and 1.419(4) Å.² The longer metal–ketone distances in **4** of $\text{Zr--C(7)} = 2.301(5)$ and $\text{Zr--O(1)} = 2.041(3)$ Å, compared to the Ti complex of $\text{Ti--C} = 2.150(7)$ and $\text{Ti--O} = 1.849(5)$ Å, result from the larger size of Zr. But the data are in good agreement with analogous averaged bond distances $\text{Zr--C} = 2.384(3)$ and $\text{Zr--O} = 2.111(2)$ Å in the coordination dimer $[\text{Cp}_2\text{Zr}(\eta^2\text{-O=CPh}_2)]_2$,² which are slightly enlarged by additional interactions in the four-membered Zr–O ring. The relatively long Zr–O bond distance of the complexed THF of 2.321(3) Å is a proof of the loose Zr–THF interaction also found in the zirconacyclopropene complex $\text{Cp}_2\text{ZrC(SiMe}_3\text{)=C(SiMe}_3\text{)(THF)}$, 2.390(5) Å.⁸

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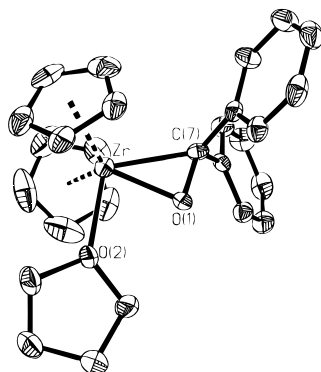


Figure 3. Molecular structure of complex **4**, shown by an ORTEP plot at the 50% probability level.

The NMR spectroscopic and structural data for the obtained monomeric zirconacyclic complexes

$\text{Cp}_2\text{ZrOCR}^3\text{R}^4\text{C(R}^2)=\text{C(R}^1)$, **2** ($\text{R}^1 = \text{R}^2 = \text{SiMe}_3$, $\text{R}^3 = \text{H}$, $\text{R}^4 = \text{Ph}$), **5** ($\text{R}^1 = \text{R}^2 = \text{SiMe}_3$, $\text{R}^3 = \text{R}^4 = \text{Me}^{10}$), and **6** ($\text{R}^1 = \text{R}^2 = \text{Ph}$, $\text{R}^3 = \text{R}^4 = \text{Me}^{10}$), formed by the insertion of ketones or aldehydes into zirconacycloprenes, can be discussed in connection with the observed stability and reactivity. The formaldehyde complex **1** ($\text{R}^1 = \text{R}^2 = \text{SiMe}_3$, $\text{R}^3 = \text{R}^4 = \text{H}$) with a dimeric structure was compared with dimeric zirconafuranone complexes **8** ($\text{R}^1 = \text{R}^2 = \text{SiMe}_3$, $\text{R}^3, \text{R}^4 = \text{O}^{14}$) and **9** ($\text{R}^1 = \text{tBu}$, $\text{R}^2 = \text{SiMe}_3$, $\text{R}^3, \text{R}^4 = \text{O}^7$). Table 1 gives some relevant data.

In both series of complexes the ^{13}C -NMR signals of the C_α and C_β carbon atoms which carry SiMe_3 groups (e.g. **1**, **2**, **5**, and **8**) are shifted more downfield than in **6**. As expected, the signals of the C_α carbon atoms appear more downfield compared to the C_β carbon atoms, but the differences between the chemical shifts of both atoms $\Delta\delta$ seem to be larger for the dimeric complexes, particularly with $\text{R}^3, \text{R}^4 = \text{O}$. The steric restrictions between the substituents at the ring carbons especially at C_β and $\text{C}_{\beta'}$ (carbonyl C) atoms are the explanation for smaller angles $\text{R}^2-\text{C}_\beta-\text{C}_\alpha$ in the monomeric complexes compared to dimeric complexes. In the case of dimeric complexes the C_β substituents can move into the direction of the sterically less demanding groups in $\text{C}_{\beta'}$ (carbonyl C) position. Sterically more demanding groups in this position prevent the dimerization. Compared to the monomeric compounds the dimeric complexes are more stable and do not react with other substrates such as carbon dioxide or alkynes.

Interestingly, in the series of the monomeric complexes there are no significant differences in the $\text{C}_\beta-\text{C}_{\beta'}$ bond distances, but the stability toward dissociation differs markedly in the range $\mathbf{5} < \mathbf{2} < \mathbf{6}$. Therefore, the repulsion of alkyne and carbonyl substituents is assumed to be the reason for the easy dissociation of **5** and **2** (and also the lack of coupling with benzophenone in the formation of **4**), indicating the steric limitations of the coupling reaction of alkynes with ketones and aldehydes by zirconocene complexes.

On the other hand, in the series of products with $\text{H}_2\text{C}=\text{O}$, $\text{PhHC}=\text{O}$, and $\text{Ph}_2\text{C}=\text{O}$ the stability of the products depends on the possibilities to form dimeric

complexes. The formaldehyde insertion product **1** is very stable, because two molecules form a coordination dimer via the $\text{Zr}-\text{O}-\text{Zr}-\text{O}$ bridge. The benzaldehyde complex **2** is stabilized by loss of half of the alkyne and the formation of **3**. The reaction with benzophenone could proceed via a much less stable insertion product (not observed) which eliminates the acetylene very rapidly, and the adduct " $\text{Cp}_2\text{Zr}(\eta^2-\text{O}=\text{CPh}_2)$ " can only be stabilized by an additional solvent molecule (THF) or by oligomerization.

Interestingly, the observed insertion of aldehydes and ketones into zirconacycloprenes are very similar to the analogous reactions of carbonyl compounds with group 14 silacycloprenes found some years ago by Seyferth et al.¹⁵

Experimental Section

All operations were carried out in an inert atmosphere (argon) with standard Schlenk techniques. Solvents were freshly distilled from sodium tetraethylaluminate under argon prior to use. Deuterated solvents were treated with sodium or sodium tetraethylaluminate, distilled, and stored under argon. The following spectrometers were used: NMR, Bruker ARX 400; IR, Nicolet Magna 550 (Nujol mulls using KBr plates); MS, AMD 402. Melting points were measured in sealed capillaries on a Büchi 535 apparatus.

Preparation of $[\text{Cp}_2\text{ZrOCH}_2\text{C}(\text{SiMe}_3)=\text{C}(\text{SiMe}_3)]_2$ (**1**).

An amount of 0.5 g (1.08 mmol) of $\text{Cp}_2\text{ZrC}(\text{SiMe}_3)=\text{C}(\text{SiMe}_3)-(\text{THF})$ was dissolved in 30 mL of THF, and paraformaldehyde (35 mg, 1.1 mmol) was added to the solution. The mixture was stirred for 3 h at 55 °C whereupon the color changed from orange via dark green to pale yellow. After filtration and evaporation to one-half volume an equivalent amount of *n*-hexane was added. On standing at -30 °C for 4 days, colorless crystals deposited, which were washed with cold *n*-hexane and dried in vacuo to give 0.4 g (90%) of **1** (mp 216–218 °C dec). Anal. Calcd for $\text{C}_{38}\text{H}_{60}\text{O}_2\text{Si}_4\text{Zr}_2$ (843.6), monomer 421.8: C, 54.10; H, 7.17. Found: C, 53.50; H, 7.13. IR (Nujol mull): 1245 cm^{-1} ($\delta_s(\text{CH}_3\text{Si})$), 1074 cm^{-1} ($\nu(\text{C}-\text{O}-(\text{Zr}))$). ^1H -NMR (C_6D_6): δ 0.40 (s, 18H, SiMe_3), 0.41 (s, 18H, SiMe_3 , a broad signal indicates a yet uninvestigated dynamic process), 4.72 (s, 4H, CH_2), 5.85 (s, 20H, Cp). ^{13}C -NMR (C_6D_6): δ 3.2, 5.7 (SiMe_3), 91.3 (CH_2), 110.5 (Cp), 213.6 (C_α), 158.6 (C_β). ^{29}Si -NMR (C_6D_6): δ -14.5, -15.9 (SiMe_3). MS (70 eV), m/z : 415 M^+ (monomer) - Me, 390 M^+ - CH_2O , 220 Cp_2Zr^+ , 73 SiMe_3^+ .

Preparation of $\text{Cp}_2\text{ZrOCHPhC}(\text{SiMe}_3)=\text{C}(\text{SiMe}_3)$ (**2**).

To an amount of 0.56 g (1.21 mmol) of $\text{Cp}_2\text{ZrC}(\text{SiMe}_3)=\text{C}(\text{SiMe}_3)(\text{THF})$ in 20 mL of THF was added benzaldehyde (122 μL , 1.21 mmol). The solution became light orange in color. It was stirred for 1 h at room temperature. After evaporation to dryness *n*-hexane was added. The solution was filtered, and after 3 days at -30 °C orange crystals were formed. The crystals were washed with cold *n*-hexane and dried in vacuo to give 0.29 g (48%) of **2** (mp 103–105 °C, elimination of alkyne). Anal. Calcd for $\text{C}_{25}\text{H}_{34}\text{OSi}_2\text{Zr}$ (497.9): C, 60.30; H, 6.88. Found: C, 59.30; H, 6.60. IR (Nujol mull): 1246 cm^{-1} ($\delta_s(\text{CH}_3\text{Si})$), 1048 cm^{-1} ($\nu(\text{C}-\text{O}-(\text{Zr}))$), 522 cm^{-1} ($\nu(\text{Zr}-\text{O})$). ^1H -NMR ($\text{THF}-d_6$): δ 0.22 (s, 9H, SiMe_3), -0.10 (s, 9H, SiMe_3), 6.24 (s, 5H, Cp), 6.38 (s, 5H, Cp), 7.2–7.35 (m, 5H, Ph), 5.55 (s, 1H, CH). ^{13}C -NMR ($\text{THF}-d_6$): δ 2.5, 4.9 (SiMe_3), 113.8, 114.3 (Cp), 90.0 (CH), 127.5, 128.5, 129.5, 145.6 (Ph), 222.2 (C_α), 185.8 (C_β). MS (70 eV), m/z : 481 M^+ - Me, 420 M^+ - Ph, 220 Cp_2Zr^+ .

Preparation of $[\text{Cp}_2\text{ZrOCHPhC}(\text{SiMe}_3)=\text{C}(\text{SiMe}_3)][\text{Cp}_2\text{Zr}(\eta^2-\text{O}=\text{CHPh})]$ (3**).** An amount of 0.3 g (0.6 mmol) of **2**

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was dissolved in 20 mL of *n*-hexane and stirred for 2 h at 60 °C. The color of the mixture changed from light orange to pale yellow. After evaporation to dryness, to remove the alkyne, there remained 0.242 g (98%) of **3**. The residue was dissolved in *n*-hexane/THF (3:1) and the solution was kept at -30 °C yielding yellow crystals (mp 160–162 °C dec). Anal. Calcd for C₄₂H₅₀O₂Si₂Zr₂ (822.1): C, 61.30; H, 6.13. Found: C, 60.73; H, 6.14. IR (Nujol mull): 1244 cm⁻¹ (δ_s(CH₃Si)), 1040 cm⁻¹ (ν(C–O–(Zr))). ¹H-NMR (THF-*d*₆): δ -0.02 (s, 9H, SiMe₃), 0.41 (s, 9H, SiMe₃), 4.24 (s, 1H, CH), 5.94 (s, 1H, CH), 5.07, 6.08, 6.21, 6.27 (each s, 5H, Cp), 6.85–7.75 (m, 10H, Ph). ¹³C-NMR (THF-*d*₆): δ 4.0, 6.8 (SiMe₃), 80.1, 102.4 (CH), 109.6, 109.7, 112.4, 112.5 (Cp), 122.3, 122.6, 128.4, 128.6, 129.1, 142.9, 153.4, 165.3 (Ph), 218.7 (C_α), 165.7 (C_β). MS (70 eV), *m/z*: 652 M⁺ – alkyne, 496 M⁺ – Cp₂ZrOCHPh, 220 Cp₂Zr⁺, 73 SiMe₃⁺.

Preparation of [Cp₂Zr(THF)(η²-O=CPh₂)]·THF (4**).** An amount of 0.48 g (1.03 mmol) of Cp₂ZrC(SiMe₃)=C(SiMe₃)-(THF) in 20 mL of THF was treated with 0.187 g (1.03 mmol) of benzophenone. The solution was stirred for 2 h at room temperature whereupon the color changed from orange to yellow. The solution was then reduced in volume to one-half, and after standing for 2 days at -30 °C, light-yellow crystals were obtained. After washing with cold THF 0.162 g (33%) of **4** was obtained. Anal. Calcd for C₂₇H₂₈O₂Zr·C₄H₈O (546.2): C, 68.11; H, 6.64. Found: C, 66.72; H, 6.48. ¹H-NMR (THF-*d*₆): δ 1.78, 3.62 THF; 5.54 (s, 10H, Cp), 6.83 (m, 2H, *p*-Ph) 7.05–7.65 (m, 8H, *o,m*-Ph). ¹³C-NMR (THF-*d*₆): δ 26.3, 68.1 (THF), 94.7 (C–O), 109.9 (Cp), 122.2, 127.4, 157.4 (Ph, a broadening of the Ph resonances indicates a yet uninvestigated dynamic process). Crystals for the X-ray structural analysis were obtained from a cold solution and contain two additional THF molecules of solvation.

Preparation of [Cp₂ZrOCOC(SiMe₃)=C(SiMe₃)₂] (8**).** This was published in ref 14. ¹³C-NMR (THF-*d*₆): δ 3.8, 5.7 (SiMe₃), 178.6 (CO₂), 249.0 (C_α), 152.9 (C_β) 112.7 (Cp).

X-ray Crystallographic Study of Complexes **1, **2**, and **4**.** Diffraction data were collected on a CAD4 MACH3 diffrac-

tometer using Mo Kα radiation. The structures were solved by direct methods (SHELXS-86: Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, 46, 467) and refined by full-matrix least-squares techniques against *F*² (SHELXL-93: Sheldrick, G. M. University of Göttingen, Germany, 1993). Structural data: (XP, Siemens) are as follows. **1**: space group *P* $\bar{1}$; *a* = 10.659(1), *b* = 14.849(1), *c* = 15.827(1) Å; α = 116.87(1), β = 107.44(1), γ = 93.78(1)°; *V* = 2071.3(3) Å³; crystal dimensions 0.5 × 0.5 × 0.4 mm; *Z* = 2; *D*_c = 1.353 g/cm³; μ = 0.649 mm⁻¹; θ range 2.28–24.97°; number of collected data at 20 °C, 7691; number of unique data, 7265; number of observed data with *I* > 2σ(*I*), 6084; non-hydrogen atoms refined anisotropically; number of variables, 415; *R*₁ = 0.029 (*I* ≥ 2σ(*I*)); *wR*₂ = 0.089 (all data). **2**: space group *P* $\bar{1}$; *a* = 9.4642(8), *b* = 10.843(5), *c* = 14.2391(8) Å; α = 110.563(4), β = 103.296(6), γ = 103.033(6)°; *V* = 1253.97(11) Å³; crystal dimensions 0.2 × 0.2 × 0.15 mm; *Z* = 2; *D*_c = 1.319 g/cm³; μ = 0.547 mm⁻¹; θ range 2.35–25°; number of collected data at 20 °C, 4696; number of unique data, 4405; number of observed data with *I* > 2σ(*I*), 3455; non-hydrogen atoms refined anisotropically; number of variables, 278; *R*₁ = 0.034 (*I* ≥ 2σ(*I*)); *wR*₂ = 0.108 (all data). **4**: space group *P*2₁2₁2₁; *a* = 8.9846(5), *b* = 14.752(1), *c* = 19.768(2) Å; *V* = 2620.1(4) Å³; crystal dimensions 0.3 × 0.3 × 0.3 mm; *Z* = 4; *D*_c = 1.389 g/cm³; μ = 0.45 mm⁻¹; θ range 2.48–24.97°; number of collected data at -80 °C, 2629; number of unique data, 2629; number of observed data with *I* > 2σ(*I*), 2444; non-hydrogen atoms refined anisotropically; number of variables, 311; *R*₁ = 0.035 (*I* ≥ 2σ(*I*)); *wR*₂ = 0.089 (all data).

Supporting Information Available: ORTEP diagrams and tables of X-ray parameters, complete atomic and thermal parameters, anisotropic thermal parameters, and bond distances and angles (28 pages). Ordering information is given on any current masthead page.

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