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Synthesis, Characterization and Reactivity of Formal 20 Electron Zirconocene-Pentafulvene Complexes

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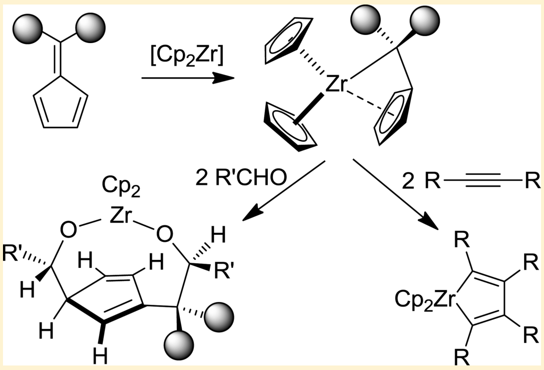
Supporting Information

ABSTRACT: The reaction of low-valent zirconocene reagents formed either from the Negishi reagent $Cp_2Zr(n\text{-butyl})_2$ or from the reduction of Cp_2ZrCl_2 with Mg with various pentafulvenes yielded the first zirconocene−pentafulvene complexes, Cp_2ZrFv (Fv = 6,6-di(aryl), 6,6′-adamantylidene, and 6-*tert*-butylfulvene), which are formal 20-electron complexes. In addition to NMR spectroscopic analysis and DFT calculations, three complexes were characterized by X-ray crystallography, showing a η^5:η^1 dianionic binding mode of the fulvene to the metal. The obtained complexes react with carbonyl compounds (aldehydes and ketones) to unexpectedly afford double-insertion products, as shown by NMR spectroscopy and X-ray studies. In the case of aldehydes these diolate complexes were obtained as single diastereoisomers. The reaction of Cp_2ZrFv with internal alkynes did not result in the formation of insertion products but release of the coordinated fulvene and reductive dimerization of the alkynes to the corresponding zirconacyclopentadienes.



INTRODUCTION

Transition-metal pentafulvene complexes exhibit a wide range of structural and reactivity patterns.[1] With late transition metals bonding to one or two double bonds of the fulvene skeleton has been observed: e.g., complexes **A** and **B** (Figure 1).[2,3] However, most metals bind in a η^6 manner, either with a neutral fulvene fragment bound in a η^2:η^2:η^2 fashion or in a dianion-like η^5:η^1 fashion, as in complexes **C** and **D**, respectively.[4,5] The most widely used synthetic pathway to early-transition-metal and f-element pentafulvene complexes is the heat- or light-induced deprotonation of alkyl-substituted cyclopentadienyl ligands containing protons in the α position.[6] Another method consists of the displacement of neutral ligands from the metal center by the fulvene fragment.[7] In group 4 chemistry, an important breakthrough was achieved when Ti(IV), Zr(IV), and Ti(III) precursors were reduced by sodium or magnesium in the presence of sterically encumbered pentafulvenes (Fv), yielding a range of new mixed Cp/Fv or bis-Fv complexes. These complexes gave rise to numerous transformations, including insertion of electrophiles, small-molecule activation, hydroamination and hydroaminoalkylation reactions, including C−H bond activation reactions.[8]

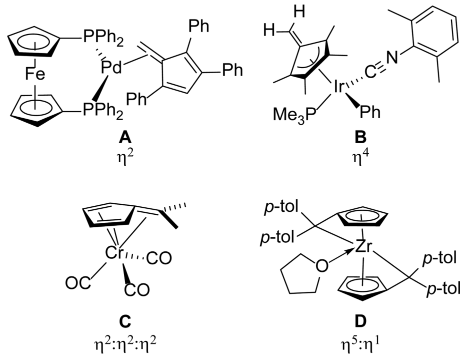


Figure 1. Selected examples of metal−pentafulvene complexes showing different binding modes.

With very few exceptions,[8c,9] the reactive part of early-transition-metal−pentafulvene complexes is the bond between the metal and the exocyclic fulvene carbon (C6). Many insertion reactions have been described using carbonyl groups, nitriles, isonitriles, alkynes, or sulfur-containing compounds as electrophiles to gain access to new metallocene complexes.[6,8,10] With

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boranes cationic metal complexes could be obtained through carbon−boron bond formation.[11]

To date, all metal−pentafulvene complexes contain either one or no cyclopentadienyl-type ligand. To the best of our knowledge, no metallocene−pentafulvene complex has been described. In the case of group 4 metals, η^6 coordination of a fulvene moiety to the 14-electron metallocene part would lead to formal 20-electron complexes, a class of compounds which has attracted considerable interest of both experimental and theoretical chemists.[12] For example, Cp_3MX complexes (X = H, Me, Cl, Cp) show different binding modes in the triad Ti, Zr, Hf: i.e., Ti and Hf mainly bind the Cp ligands in a $2\eta^5{:}1\eta^1$ fashion, whereas Zr generally adopts a $3\eta^5$ mode. The analysis of the electronic configuration in such 20-electron complexes revealed the presence of one ligand-centered molecular orbital which does not interact with the metal, hence reducing the formal 20 electrons down to 18 electrons.[12c,e]

We herein report the synthesis and characterization of the first zirconocene−pentafulvene complexes and their unexpected reaction behavior toward carbonyl compounds and alkynes.

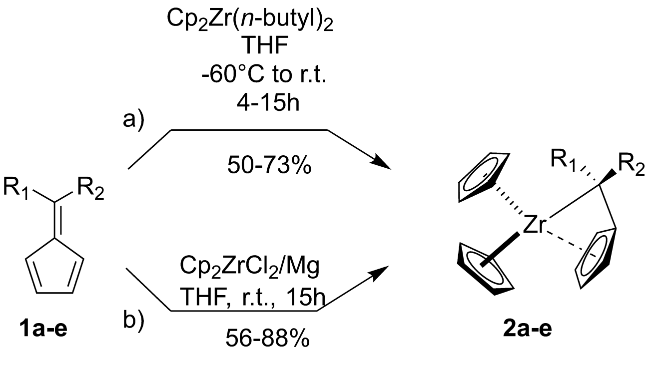
■ RESULTS AND DISCUSSION

Synthesis of Zirconocene−Pentafulvene Complexes.

Negishi Reagent. Low-valent zirconocene(II) equivalents are known to bind well to alkenes, alkynes, and dienes.[13] It was therefore anticipated that the unsaturated fulvene system may readily coordinate onto the metallocene(II) species. The Negishi reagent was chosen for this purpose, as the Zr-bound alkene moiety formed during the warming of $Cp_2Zr(n\text{-butyl})_2$ to room temperature is readily displaced by dienes or alkynes.[14] Indeed, warming this complex from −60 °C to room temperature in the presence of differently substituted pentafulvenes **1a−c** led to the formation of the first zirconocene−pentafulvene complexes Cp_2ZrFv (**2a−c**), which were isolated in good to moderate yields after workup (Scheme 1a). It should be noted that with fulvenes **1a,c** the reaction was complete after 6 h, whereas the bulky adamantylidene fulvene **1b** required 15 h reaction time.

Bimetallic Approach. Alternatively, we also investigated the reduction of Cp_2ZrCl_2 with Mg in the presence of pentafulvenes **1b−e**, in analogy to previous reports on Ti and Zr fulvene complexes.[5,8] These reactions were carried out at room temperature in THF for 15 h and afforded the corresponding Cp_2ZrFv complexes **2b−e** in good to very good isolated yields (Scheme 1b). This approach was successfully employed on a multigram scale.

Scheme 1. Synthesis of Zirconocene−Pentafulvene Complexes $Cp_2Zr(Fv)$ (2a−e)



1a, 2a : R_1= H, R_2 = *t*-butyl
1b, 2b : R_1,R_2 = adamantylidene
1c, 2c : R_1= R_2 = *p*-tolyl
1d, 2d : R_1= R_2 = phenyl
1e, 2e : R_1= R_2 = *p*-F-phenyl

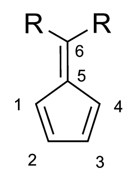
Characterization of Zirconocene−Pentafulvene Complexes.

The obtained yellow to orange solids **2a−e** are stable under an inert atmosphere for weeks at room temperature but decompose quickly upon heating above 100 °C. They are well soluble in ethereal and aromatic solvents, show poor solubility in alkanes, and decompose in chlorinated solvents. The complexes were fully characterized by multinuclear NMR spectroscopy, single-crystal X-ray diffraction studies, and electron-impact mass spectrometry. Correct elemental analysis could only be obtained in the case of **2e**; in all other cases the analyses showed systematically low values for carbon.

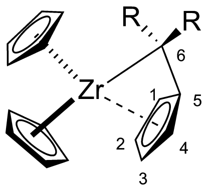
NMR Spectroscopy. The ^1H NMR spectra of the 6,6-disubstituted complexes **2b−e** are very similar (some selected data are summarized in Table 1). They show one signal for the Cp protons between 5.03 and 5.23 ppm and two signals in the ranges 3.85−4.50 and 5.44−5.52 ppm for the fulvene ring protons. In comparison to the free fulvenes, this corresponds to a significant high-field shift, especially for the protons in the 1,4-positions. These signals indicate a symmetrical arrangement of the complex, which is in good agreement with a dianionic η^6 coordination of the fulvene to the metal. For the monosubstituted complex **2a** two signals for the Cp ligand and four signals for the fulvene ring protons are observed. Interestingly, the exocyclic proton in **2a** is shifted upfield to 3.14 ppm with respect to the free fulvene (6.18 ppm): however, at considerably lower field than the corresponding proton in the Cp*(6-*tert*-butylfulvene)TiCl complex (1.68 ppm).[8a] The ^{13}C NMR spectra of **2a−e** indicate a high-field shift for all carbons of the fulvene skeleton with respect to the free fulvenes. Especially, the signals for C6 are shifted up to 60 ppm, confirming important electron donation from the metal to the carbon center. The signals for the fulvene ring are in the vicinity of the Cp signals, in agreement with the formation of a Cp-type ligand upon coordination. The ^1H and ^{13}C spectra of **2c** correspond well to the previously reported spectra for complex D.[5]

X-ray Diffraction Studies. Complexes **2c−e** were further characterized by single-crystal X-ray diffraction studies. Selected bond lengths and angles of these complexes and of free fulvene **1c** for comparison reasons are summarized in Table 2, and the structures are shown in Figure 2. The structures confirm the $\eta^5{:}\eta^1$ coordination of the fulvene moiety to zirconium. As in other metal−pentafulvene complexes, this coordination leads to a bending of the exocyclic C5−C6 bond out of the fulvene plane toward the metal by 28.4−29.2°, slightly more than in complex **D**. The zirconium is in a distorted-trigonal-pyramidal coordination environment, as indicated by the sum of angles around Zr, close to 360°. The metal lies just above the plane defined by the three centroids of the Cp and fulvene ligands (0.20 Å for **2c**, 0.18 Å for **2d,e**) as in other Cp_3ZrX complexes, e.g. 0.20 Å in Cp_3ZrH.[12d] In the fulvene moiety, the coordination to the metallocene fragment leads to the loss of the alternating single-bond-double bond pattern of the free fulvene as shown by the narrow range of the C−C bond lengths (1.390−1.442 Å). The most significant change occurs in the exocyclic bond which is, for example, elongated by 0.08 Å in **2c** compared to **1c**. A slight influence of the para-substituents on the phenyl groups of the fulvene can be observed on the Zr−C6 and the C5−C6 bond

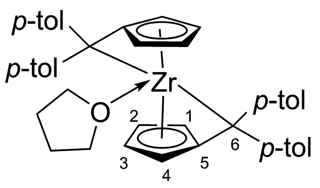
Table 1. Selected ^1H and ^{13}C NMR Data of Fulvenes **1a−c**, Complexes **2a−c**, and Complex **D** in C_6D_6 at Room Temperature



1a-c



2a-c

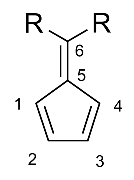


D

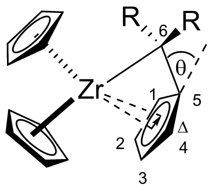
	1a	1b	1c	2a	2b	2c	D[a]
H1	6.18	6.62	6.58	3.58	3.85	4.50	4.17
H2	6.39	6.67	6.66	5.52	5.52	5.49	4.39
H3	6.57	6.67	6.66	5.45	5.52	5.49	5.72
H4	6.69	6.62	6.58	4.25	3.85	4.50	6.43
H6	6.18			3.14			
H(Cp)				5.21, 5.39	5.23	5.13	
C1	120.2	120.5	124.8	111.4	108.2	109.8	92.2
C2	134.5	131.6	132.4	105.1	106.2	108.8	99.1
C3	129.0	131.6	132.4	111.8	106.2	108.8	102.6
C4	129.0	120.5	124.8	111.9	108.2	109.8	114.7
C5	143.4	137.1	144.3	114.9	117.7	117.6	129.2
C6	152.8	167.3	152.1	94.6	106.5	103.8	103.4
C(Cp)				106.4, 106.5	106.7	109.1	

[a] See ref 5.

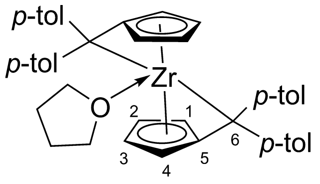
Table 2. Selected X-ray Data of Fulvene **1c**, Complexes **2c−e**, and Complex **D**[a]



1c



2c,d,e



D

	1c[b]	2c	2d	2e	D[c]
C1−C2	1.340(3)	1.390(9)	1.409(3)	1.402(3)	1.412(2), 1.414(2)
C2−C3	1.445(3)	1.419(9)	1.397(4)	1.400(3)	1.401(3), 1.403(2)
C3−C4	1.344(3)	1.402(8)	1.398(4)	1.397(3)	1.415(3), 1.407(2)
C4−C5	1.458(3)	1.434(7)	1.442(3)	1.428(3)	1.443(2), 1.443(2)
C5−C1	1.465(2)	1.432(8)	1.439(3)	1.436(3)	1.446(2), 1.444(2)
C5−C6	1.359(2)	1.440(7)	1.455(3)	1.462(2)	1.443(2), 1.450(2)
Zr−C1		2.474(5)	2.485(2)	2.4907(18)	2.4109(16), 2.4316(16)
Zr−C2		2.597(6)	2.636(4)	2.631(2)	2.5278(17), 2.5273(17)
Zr−C3		2.623(5)	2.617(2)	2.637(2)	2.5322(17), 2.5637(17)
Zr−C4		2.464(5)	2.473(2)	2.4840(19)	2.4058(17), 2.3867(16)
Zr−C5		2.332(5)	2.330(2)	2.3321(17)	2.3266(16), 2.3266(16)
Zr−C6		2.602(6)	2.574(2)	2.5623(17)	2.7084(17), 2.7007(16)
Ct(Fv)−Zr		2.191	2.203	2.213	2.121, 2.129
Ct(Cp)−Zr		2.304, 2.325	2.336, 2.319	2.315, 2.332	
Ct(Cp)−Zr−Ct(Cp)		117.8	117.6	117.7	133.9
Ct(Fv)−Zr−Ct		121.4, 118.5	121.9, 118.4	120.8, 119.6	
∑(angles around Zr)		357.7	357.7	358.1	
θ		28.4	29.2	29.2	26.9
Δ		0.310	0.335	0.340	0.236, 0.262

[a] Bond lengths are given in Å and angles in deg. [b] See ref 8b. [c] See ref 5.

lengths, which are shorter/longer in the case of the hydrogen or fluorine substituents in **2d,e** compared to the methyl group in **2c**.

EI Mass Spectrometry. For all complexes **2a-e,** the molecular ion peak corresponding to Cp_2ZrFv was observed by EI-MS, albeit in low intensity. Furthermore, relevant fragments of the complexes were clearly identified, namely CpZrFv, Cp_2Zr and the free fulvenes.

DFT Calculations. In order to obtain further insights into the bonding situation of the new complexes, DFT calculations were carried out. Complexes **2a−c** were optimized in the gas phase,

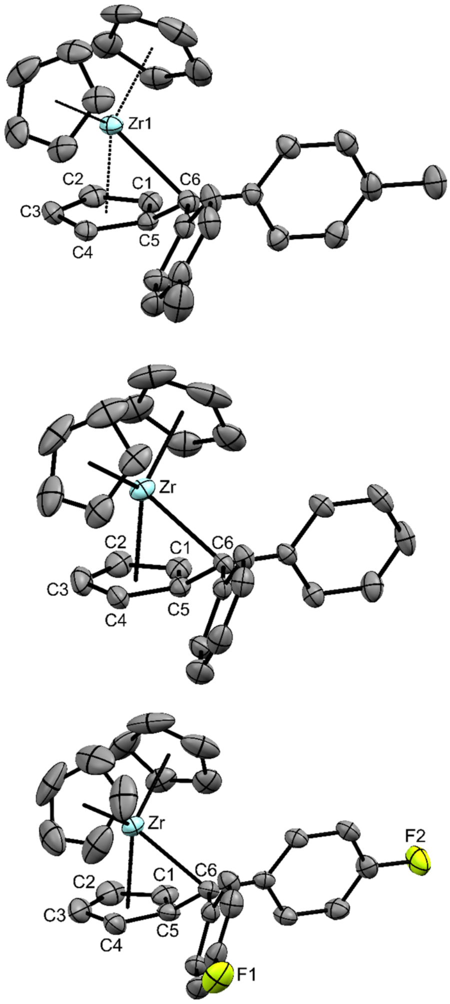


Figure 2. Molecular structures of complexes **2c**−**e**, with 50% probability ellipsoids. Hydrogen atoms and solvent molecules are omitted.

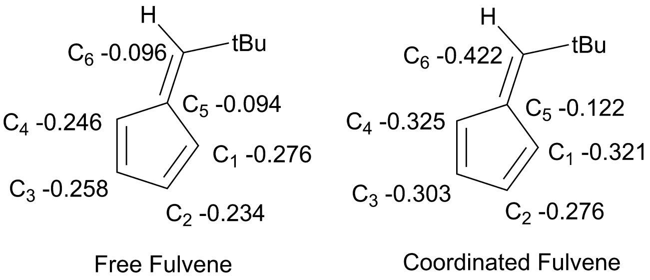


Figure 3. Evolution of NBO charges upon coordination of fulvene **1a** to Cp_2Zr.

with the B3PW91 functional, Def2-QZVP basis set for Zr and 6-31G(d) for all other atoms (see the Supporting Information for details), and the results are shown in Table 3. A good agreement between the crystal structure of **2c** and the optimized calculated structure was obtained. Next, the evolution of NBO charges upon coordination of Zr to the pentafulvene was examined. An important decrease in the charge on the exocyclic carbon is observed, ranging from 0.26 to 0.39 e, which indicates a strong reorganization of the electron density (Figure 3). A comparison of the NICS(0) values between free and coordinated fulvenes shows a strong increase in aromaticity, displaying values of −15.5, −15.6, and −15.1 ppm for **2a**−**c**, respectively, close to that of Cp ligands.[15] Finally, a Mayer bond order analysis performed with the ADF software indicates a clear shift toward a single bond for the C_5−C_6 bond: in the free fulvenes the bond orders are 1.56 for the 6-*tert*-butylfulvene, 1.54 for the 6,6-adamantylidene, and 1.47 for the 6,6-bis-*p*-tolylfulvene, which shift to 1.09, 1.16, and 1.15 for **2a**−**c**, respectively, upon coordination. This analysis further shows an increased interaction in the Zr−C_6 bond (HOMO; see Figure 4) and a similar bond order for Zr−C(Cp) and Zr−C(fulvene ring).

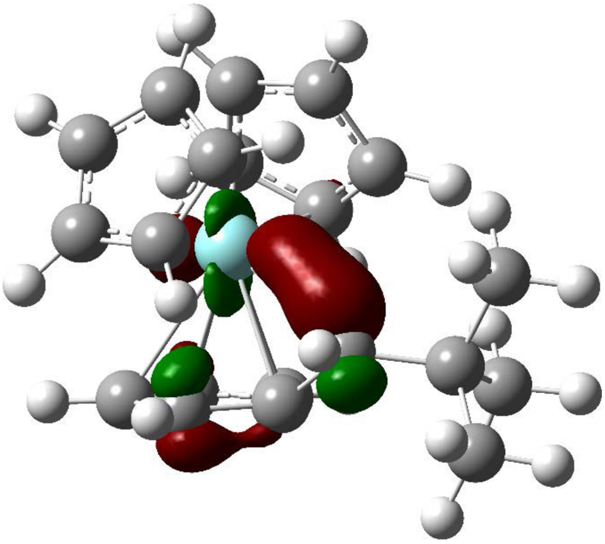


Figure 4. HOMO of complex **2a**.

All of this information (NBO charges, aromaticity, bond distances, bond orders) points toward the formation of a formal Cp_3ZrX type complex. However, the one-bond link between the Cp moiety and the X ligand in the fulvene prevents a true Cp_3ZrX complex from forming. The Zr−C_6 bond is thus not completely formed, and the C_1−C_6 is not a true single bond but still contains a slight double-bond character. The highest negative charge was found on the exocyclic fulvene carbon in complexes **2a**−**c**, in

Table 3. Selected Structural Parameters, NBO Charges, NICS(0) Values, and Mayer Bond Orders for Cp_2ZrFv complexes[a]

	2a	2b	2c
C_5−C_6 bond (Å)	1.48 (1.35)	1.44 (1.36)	1.45 (1.37)
NBO charge C_6 (e)	−0.42 (−0.10)	−0.18 (0.11)	−0.21 (0.06)
NICS(0) C_1−C_5 ring	−15.5 (−0.9)	−15.6 (−1.7)	−15.1 (−0.7)
Mayer bond order C_5−C_6	1.09 (1.56)	1.16 (1.54)	1.15 (1.47)
av Mayer bond order for Zr−C(Cp)	0.22	0.22	0.24
av Mayer bond order for Zr−C(fulvene ring)	0.27	0.27	0.26

[a] Values for free fulvenes are given in parentheses.

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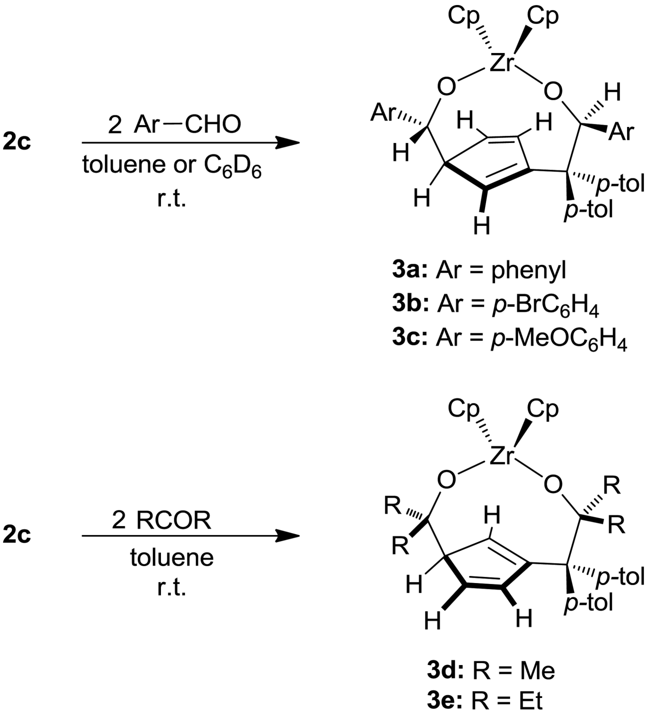
agreement with other early-transition-metal pentafulvene complexes. It was therefore interesting to study the influence of an "excess" of electrons on the reactivity of these complexes.

Reactivity Studies. *Carbonyl Compounds.* It has been well established that the coordination of pentafulvenes to group 4 metals inverts the polarity of the exocyclic carbon atom. This makes insertion of electrophilic reagents into the metal−carbon bond possible. We started our investigations with the addition of 1 equiv of *p*-bromobenzaldehyde to a C_6D_6 solution of **2c**. This led to the transformation of half the amount of **2c** to a new product, while half of the starting material remained, as shown by ^{1}H NMR. Further addition of 1 equiv of *p*-bromobenzaldehyde led to the complete conversion of **2c** to complex **3b** (Scheme 2). The same results were observed in the case of benzaldehyde and *p*-anisaldehyde, resulting in the formation of complexes **3a**,**c**, respectively.

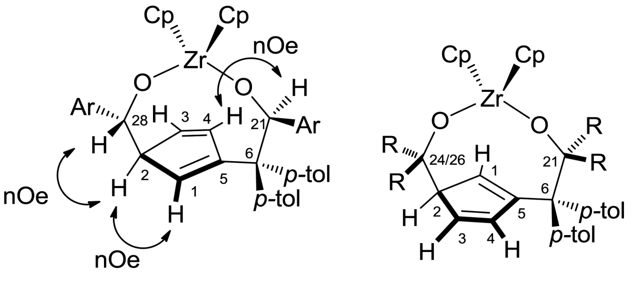
Scheme 2. Reaction of Cp_2ZrFv Complex 2c with Carbonyl Compounds



3a: Ar = phenyl
3b: Ar = *p*-BrC_6H_4
3c: Ar = *p*-$MeOC_6H_4$

3d: R = Me
3e: R = Et

Table 4. Selected ^{1}H and ^{13}C NMR Data of Complexes 3a−e in C_6D_6 at Room Temperature



3a-c **3d,e**

	3a	3b	3c	3d	3e
H1	5.94	5.96	6.03	5.70	5.34
H2	3.52	3.42	3.55	2.84	2.92
H3	6.27	6.17	6.35	6.31	6.31
H4	6.81	6.83	6.84	6.77	7.09
H21	5.50	5.40	5.52		
H28	5.37	5.22	5.40		
H(Cp)	5.97, 6.06	5.95, 6.09	6.03, 6.11	6.00, 6.20	6.05, 6.26
C2	62.0	61.6	62.3	62.7	57.8
C6	63.0	62.7	62.9	64.8	64.3
C21	93.0	92.1	92.4	87.3	92.2
C24/26/28	83.4	82.6	83.1	80.9	86.5

One- and two-dimensional NMR analysis of the newly formed complexes **3a**−**c** revealed their identity, and additional stereochemical information was obtained by NOE experiments (Table 4). The structure of **3b** was further corroborated by X-ray diffraction studies (see below). The ^{1}H NMR spectra of complexes **3a**−**c** show one set of signals, in agreement with a highly diastereoselective reaction. Two peaks are observed for the Cp protons, which are shifted downfield with respect to those for **2c**. The signal for H2 is between 3.42 and 3.55 ppm, in the range of cyclopentadienes, whereas the other protons of the former fulvene ring are found in the alkene region (5.94−6.84 ppm). The ^{13}C NMR spectra reveal a drastic shift for the C2 and C6 carbons, going, for example, from 108.8 and 117.6 ppm in **2c** to 62.0 and 63.0 ppm in **3a**, in good agreement with the loss of the aromatic character of the fulvene moiety.

We next studied the reaction behavior of **2c** toward ketones. The reaction with acetone or 3-pentanone was successful, yielding again the double-insertion products **3d**,**e**, respectively, as shown by NMR analysis and X-ray studies. The generation of two adjacent quaternary carbon centers (C6 and C21) increases the steric crowding of the complexes. This has some influence on the ^{1}H NMR shifts of the cyclopentadiene ring protons, especially H2, and leads to a spreading apart of the signals of the Cp rings (Table 4).

X-ray Diffraction Studies. Complex **3b** was formed as a single diastereoisomer and the solid-state structure confirmed the above description based on NMR spectroscopy (Scheme 2 and Table 4). Some major differences were observed in the solid state structures of **3b** in comparison to **3d**,**e** (Figure 5 and Table 5). First, in the case of **3d**,**e** the nine-membered ring shows considerable strain, as indicated by the long C6−C21 bond lengths (1.634(4) and 1.625(2) Å), which are in contrast only slightly elongated in the case of **3b** (1.595(5) Å). Second, other interesting features are the large Zr−O1−C21 and Zr−O2−C24/C26 angles in **3d**,**e** ranging from 168.42(19) to 171.69(9)°, which are only 151.4(2) and 155.7(3)° in **3b**. A consequence of these angles is that the C24/C26−O2−Zr−O1−C21 system in **3d**,**e** is quasi-planar: e.g. the tilt angles C21−O1−Zr−O2 and O1−Zr−O2−C26 have values of only 1.35 and 3.06°, respectively, in **3e**. In contrast, in **3b** an up-and-down arrangement is observed; here the corresponding tilt angles are 56.5 and 73.0°, respectively. In the literature, two nine-membered zirconocene−diolate complexes have been described. The sterically strained cumulene complex **E** has features between those of complexes **3b** and **3d**,**e**: e.g. Zr−O−C1 and Zr−O−C2 angles of 165.88(10) and 151.12(10)°, respectively.[16] On the other hand, the strain-free phosphonium complex **F** ressembles complex **2b**, with Zr−O−C1 and Zr−O−C2 angles of 142.3(2) and 141.9(2)°, respectively (Figure 6).[17]

Mechanistic Considerations. The diolate complexes **3a**−**e** constitute the first examples of endo- and exocyclic reactivity of metal−fulvene complexes. There is only one other report of a double incorporation of an aldehyde into a metal−fulvene complex, Cp*Fv*Ti; however, in that case both insertions took

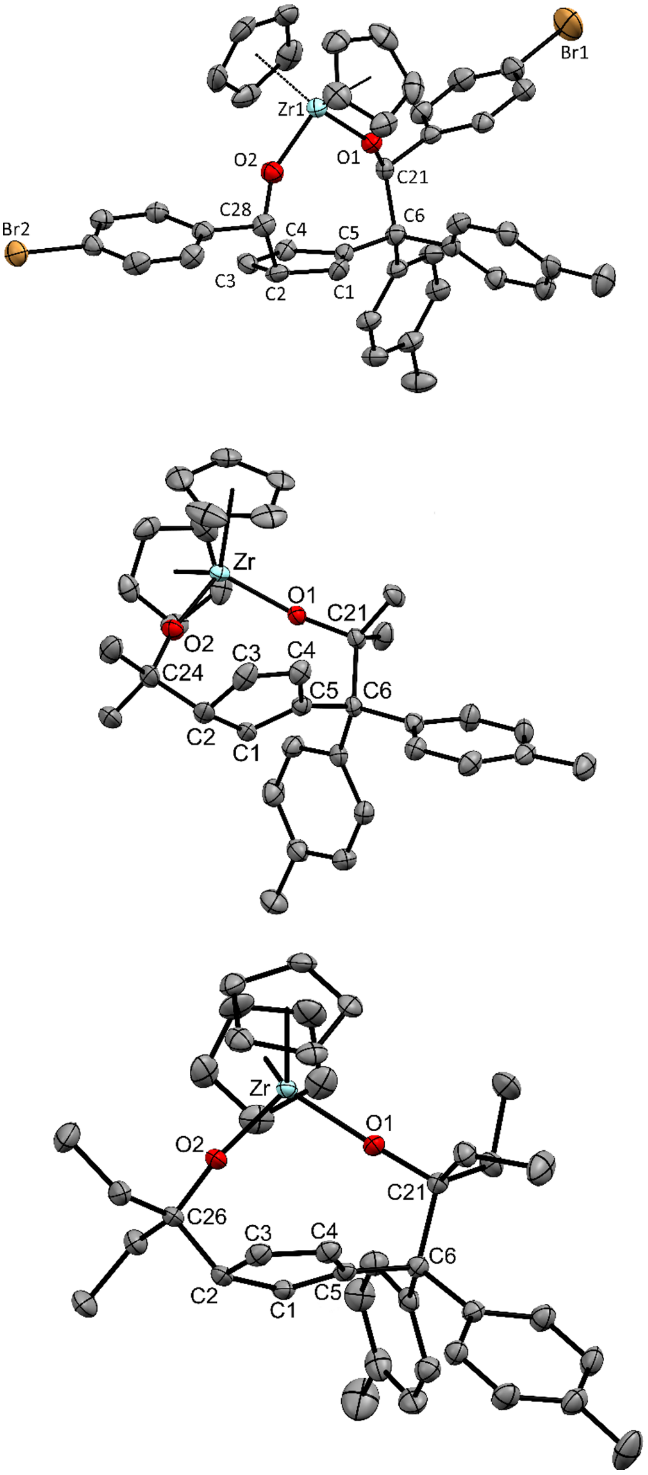


Figure 5. Molecular structures of complexes **3b**,**d**,**e** with 50% probability ellipsoids. Hydrogen atoms and solvent molecules are omitted.

place at the endocyclic positions.[9] A proposed mechanistic pathway for the formation of our double-insertion products is shown in Scheme 3 (stereochemical indications have been neglected for clarity). As the 20-electron complex does not have any available coordination site for the carbonyl group, an electron shift has to occur in **2**, leading presumably to a dienic η^4 coordination mode of zirconium to the fulvene moiety.[13b] The first insertion of the carbonyl group then leads to a zirconium allyl species, which further reacts with a second equivalent of

Table 5. Selected X-ray Data of Complexes 3b,d,e[a]

	3b	3d	3e
C1–C2	1.498(6)	1.490(4)	1.5072(19)
C2–C3	1.497(6)	1.493(5)	1.496(2)
C3–C4	1.335(6)	1.323(5)	1.331(2)
C4–C5	1.487(5)	1.483(4)	1.4849(19)
C5–C1	1.346(6)	1.344(4)	1.338(2)
C5–C6	1.517(5)	1.522(4)	1.5358(19)
C6–C21	1.595(5)	1.634(4)	1.625(2)
C2–C24/26/28	1.573(6)	1.555(4)	1.566(2)
Zr–O1	1.979(3)	1.959(2)	1.9582(10)
Zr–O2	1.971(3)	1.9374(19)	1.9332(10)
O1–C7	1.408(4)	1.408(4)	1.4268(17)
O2–C24/26/28	1.403(5)	1.401(3)	1.4047(18)
Ct–Zr	2.269, 2.271	2.261, 2.287	2.272, 2.302
Ct–Zr–Ct	127.0	124.1	123.0
O1–Zr–O2	103.70(11)	101.77(8)	101.74(4)
Zr–O1–C21		168.42(19)	170.17(9)
Zr–O2–C24/26/28	155.7(3)	169.4(2)	171.69(9)
C21–C6–C1	151.4(2) 103.4(3)	106.2(2)	106.43(11)

[a] Bond lengths are given in Å and angles in deg.

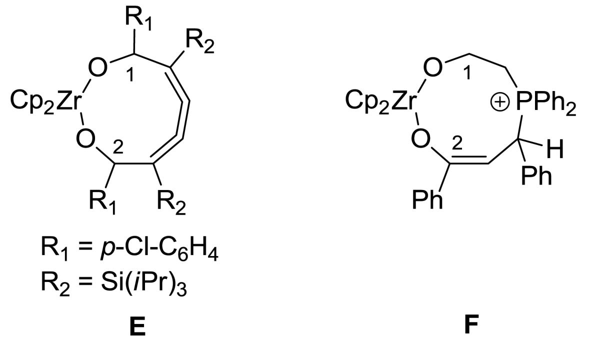
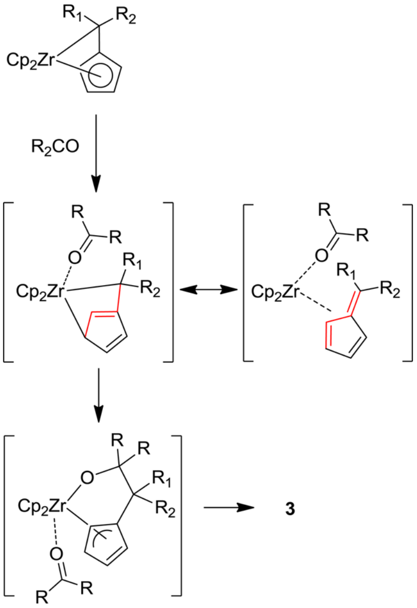


Figure 6. Other nine-membered zirconocene–diolate complexes.[16,17]

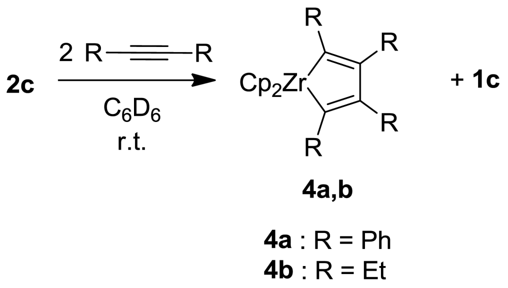
Scheme 3. Mechanistic Proposal for the Double Insertion of Carbonyl Compounds into Zirconocene–Fulvene Complexes



carbonyl compound to yield the observed complexes **3**. Under the conditions described above, the monoinsertion product could not be observed and the reaction goes straight to the bis-insertion product.

Reactivity toward Alkynes. In 2008, Mach reported the insertion of internal alkynes into the Ti−C6 bond of a Cp*FvTi complex.[10a] In analogy, we have investigated the reaction of complex **2c** with 1 equiv of diphenylacetylene in C_6D_6. After 1 h, the solution had turned from pale yellow to pale orange and the ^{1}H NMR spectrum indicated the presence of a new singlet peak at 6.0 ppm as well as the appearance of signals corresponding to the free fulvene in addition to remaining starting complex. Addition of another 1 equiv of diphenylacetylene led to full conversion of **2c** and only the peak at 6.0 ppm remained as a signal for the Cp ligands, which can be attributed to the zirconacyclopentadiene **4a**,[14b] arising from the reductive dimerization of the alkyne at the low-valent zirconium center.[18] Quenching the reaction mixture with HCl and analysis of the obtained solution indicated the formation of 1,2,3,4-tetraphenyl-1,3-butadiene (Scheme 4). The same reaction outcome was observed when 2 equiv of 3-hexyne was reacted with **2c** to form zirconacyclopentadiene **4b**.[19]

Scheme 4. Reductive Dimerization of Alkynes with Complex 2c



Despite the supposedly strong coordination of the fulvene moiety to the zirconocene fragment, which we have described as dianionic according to NMR and X-ray studies, the fulvene keeps some triene character and can therefore be displaced from the metal center by more strongly π-complexating ligands. The synthetic potential of complexes **2** as new isolable Zr(II) equivalents needs to be investigated further.

■ CONCLUSION

In this work we have described the synthesis of the first metallocene−pentafulvene type complexes using either the Negishi reagent or the bimetallic system Cp_2ZrCl_2/Mg with a variety of pentafulvenes. These formal 20-electron complexes were characterized in the solid state by X-ray diffraction studies and in solution by NMR spectroscopy, showing in both cases a $\eta^5{:}\eta^1$ binding mode of the fulvene to the zirconium metal. DFT studies confirmed this description as well as the inversion of polarity at the exocyclic fulvene carbon upon complexation. The reactivity of these new complexes was explored toward carbonyl compounds and alkynes. In the former case, a new double-insertion reaction was observed, leading to zirconocene−diolate complexes with excellent diastereoselectivity in the case of aldehydes. With alkynes, fulvene displacement occurred with concomitant reductive dimerization to yield the corresponding zirconacyclopentadienes. Further work to elucidate the reaction mechanism of the double insertion and the scope of reactivity of this new class of metal−fulvene complexes is currently underway.

■ EXPERIMENTAL SECTION

General Considerations. All reactions were conducted under an atmosphere of argon with rigorous exclusion of oxygen and moisture using standard glovebox and Schlenk techniques. Solvents were freshly distilled over sodium/benzophenone ketyl or collected from a PURSOLV MD-3 (Innovative Technologies Inc.) solvent purification unit. C_6D_6 was stored over activated 4 Å molecular sieves. Zirconocene dichloride was purchased from Strem Chemicals. Aldehydes and *n*-butyllithium (2.5 M solution in hexanes) were purchased from Aldrich and used as received. Fulvenes were prepared according to literature procedures.[20] ^{1}H and ^{13}C NMR spectra were recorded in C_6D_6 on a 500 MHz Bruker Avance III spectrometer equipped with a BBFO+ probe. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) and referenced to residual protons of the solvent. Elemental analyses were carried out on a EuroEA 3000 Elemental Analyzer. High-resolution ESI-MS spectra were recorded on a hybrid tandem quadrupole/time-of-flight (Q-TOF) instrument, equipped with a pneumatically assisted electrospray (Z-spray) ion source (Micromass, Manchester, U.K.) operated in positive mode. Low-resolution EI-MS spectra were obtained by direct introduction on a GCT Premier mass spectrometer with orthogonal acceleration time-of-flight detector using an electron impact source (Micromass, Manchester, U.K.) or on a Finnigan-MAT 95 spectrometer using the LIFDI method.

Single crystals were coated in Paratone-N oil and mounted on a loop. Data were collected at 150.0(1) K on a Nonius Kappa CCD or a Stoe IPDS diffractometer using a Mo Kα (λ= 0.71070 Å) X-ray source and a graphite monochromator. All data were measured using ψ and ω scans. The crystal structures were solved using SIR 97 and refined using Shelx 2014.[21,22]

General Procedure (GP-1) for the Synthesis of Cp_2ZrFv Complexes 2 Using the Negishi Reagent. In a Schlenk tube under argon, a solution of zirconocene dichloride (292 mg, 1.0 mmol) in THF (8 mL) was reacted at −78 °C with *n*-butyllithium (2.5 M in hexanes, 0.8 mL, 2.0 mmol) for 30 min. A solution of fulvene (1 mmol) in THF (2 mL) was added to the reaction mixture at −60 °C, and the solution was slowly warmed to room temperature over 2 h. The reaction was further stirred at this temperature for the given time to result in a dark orange-red solution. THF was evaporated under vacuum, and toluene (10 mL) was added to the resulting yellow-orange solid. The white precipitate of LiCl was removed by centrifugation. Then toluene was evaporated under vacuum and the solid washed with hexanes (10 mL). Further drying of the solid under vacuum yielded complexes **2**.

General Procedure (GP-2) for the Synthesis of Cp_2ZrFv Complexes Using the Bimetallic Approach. In a Schlenk tube under argon was prepared a mixture of zirconocene dichloride (1 equiv) and Mg (1 equiv). A solution of fulvene (1 equiv) in THF (100 mL) was added at room temperature, and the reaction mixture was stirred for 12 h. THF was evaporated under vacuum, and toluene (70 mL) was added onto the resulting yellow-orange solid. After filtration, toluene was evaporated under vacuum and the solid washed with small amounts of hexanes. Further drying of the solid under vacuum yielded complexes **2**.

Cp_2Zr(6-*tert*-butylfulvene) (2a). According to GP-1, 6-*tert*-butylfulvene (134 mg, 1.0 mmol) was reacted for 6 h to give complex **2a** as a yellow solid in 73% yield (260 mg, 0.7 mmol). ^{1}H NMR (500 MHz, C_6D_6): δ 5.52 (s, 1H, H2), 5.46 (s, 1H, H3), 5.39 (s, 5H, Cp), 5.21 (s, 5H, Cp), 4.25 (s, 1H, H4), 3.58 (s, 1H, H1), 3.17 (s, 1H, H6), 1.42 (s, 9H, *t*Bu). ^{13}C NMR (125 MHz, C_6D_6): δ 114.9 (C), 111.9 (CH), 111.8 (CH), 111.4(CH), 106.5(CH), 106.4(CH), 105.1(CH), 94.6(CH), 35.8(C), 34.1(CH_3). LR-MS (EI, *m*/*z*, relative intensity): 354 ([M$^+$], 8), 289 ([M$^+$ − Cp], 7), 220 ([M$^+$ − Fv], 12), 134 ([M$^+$ − Cp_2Zr], 25), 119 ([Fv − CH_3^+], 100). No correct elemental analysis of the bulk product was obtained, despite several attempts.

Cp_2Zr(6,6-adamantylidenefulvene) (2b). According to GP-1, 6,6-adamantylidenefulvene (198 mg, 1.0 mmol) was reacted for 15 h to give complex **2b** as a yellow solid in 72% yield (290 mg, 0.7 mmol). ^{1}H NMR (600 MHz, C_6D_6): δ 5.52 (t, *J* = 2.6 Hz, 2H, H2 + H3), 5.23 (s, 10H, Cp), 3.85 (t, *J* = 2.6 Hz, 2H, H1 + H4), 2.38 2.32 (m, 2H, CH_2(Ad)), 2.32 2.26 (m, 3H, CH_2 + CH(Ad)), 2.21 2.14 (m, 3H, CH_2 + CH(Ad)), 2.08 2.03 (m, 2H, CH_2(Ad)), 1.82 (m, 2H, 2CH(Ad)). ^{13}C NMR (151 MHz, C_6D_6): *δ* 117.7 (C), 108.2 (CH), 106.7 (CH), 106.5 (C), 106.2 (CH), 44.3 (CH_2), 39.0 (CH_2), 38.8 (CH_2), 36.9 (CH), 29.6(CH), 29.1 (CH). LR-MS (EI, *m*/*z*, relative intensity): 418 ([M^+], 5), 353 ([M^+ − Cp], 3), 220 ([M^+ − Fv], 15), 198 ([M^+ − Cp_2Zr], 100). No correct elemental analysis of the bulk product was obtained, despite several attempts.

Cp_2Zr(6,6-di-*p*-tolylfulvene) (2c). According to GP-1, 6,6-di-*p*-tolylfulvene (258 mg, 1.0 mmol) was reacted for 4 h to give complex **2c** as an orange-yellow powder in 50% yield (240 mg, 0.5 mmol). ^{1}H NMR (500 MHz, C_6D_6): *δ* 7.79 (d, *J* = 8.2 Hz, 4H, *o*-CH), 7.03 (d, *J* = 7.9 Hz, 4H, *m*-CH), 5.49 (t, *J* = 2.6 Hz, 2H, H2 + H3), 5.13 (s, 10H, Cp), 4.50 (t, *J* = 2.6 Hz, 2H, H1 + H4), 2.17 (s, 6H, CH_3). ^{13}C NMR (126 MHz, C_6D_6): *δ* 146.3 (C), 134.1 (C), 129.8 (CH), 128.7 (CH), 117.5 (C), 109.8 (CH), 109.1 (CH), 108.8 (CH), 103.8 (C), 21.0 (CH_3). LR-MS (EI, *m*/*z*, relative intensity (%)): 478 ([M^+], 26), 258 ([M^+ − Cp_2Zr], 100), 220 ([M^+ − Fv], 76). No correct elemental analysis of the bulk product was obtained, despite several attempts. Crystals of complex **2c** suitable for X-ray studies were grown from a concentrated C_6D_6 solution.

Cp_2Zr(6,6-diphenylfulvene) (2d). According to GP-2, Cp_2ZrCl_2 (2.34 g, 8.0 mmol), Mg (0.19 g, 8.0 mmol), and 6,6-diphenylfulvene (1.84 g, 8.0 mmol) were reacted to give complex **2d** as an orange-yellow powder in 65% yield (2.35 g, 5.2 mmol). ^{1}H NMR (500 MHz, C_6D_6): *δ* 7.83 (m, 4H, phenyl), 6.94−7.20 (m, 6H, phenyl), 5.45 (t, $^3J_{HH}$ = 2.6 Hz, 2H, H2 + H3), 5.08 (s, 10H, Cp), 4.44 (t, $^3J_{HH}$ = 2.6 Hz, 2H, H1 + H4). ^{13}C NMR (126 MHz, C_6D_6): *δ* 148.9 (C), 129.8 (CH), 128.5 (CH), 125.0 (CH), 117.2 (C), 109.8 (CH), 109.1 (CH), 108.9 (CH), 103.9 (C). LR-MS (EI, *m*/*z*, relative intensity (%)): 450 ([M^+], 16), 385 ([M^+ − Cp], 7), 230 ([M^+ − Cp_2Zr], 100), 220 (([M^+ − Fv], 69). No correct elemental analysis of the bulk product was obtained, despite several attempts. Crystals of complex **2d** suitable for X-ray studies were grown from a toluene solution at −15 °C. The compound crystallizes with 0.5 equiv of toluene.

Cp_2Zr(6,6-di-*p*-fluorophenylfulvene) (2e). According to GP-2, Cp_2ZrCl_2 (2.00 g, 6.84 mmol), Mg (0.17 g, 6.84 mmol), and 6,6-di-*p*-fluorophenylfulvene (1.82 g, 6.84 mmol) were reacted to give complex **2e** as an orange-yellow powder in 72% yield (2.41 g, 4.92 mmol). ^{1}H NMR (500 MHz, C_6D_6): *δ* 7.50 (m, $^3J_{HH}$ = 8.5 Hz, $^4J_{HF}$ = 5.6 Hz, 4H, *o*-CH), 6.83 (m, $^3J_{HH}$ = 8.5 Hz, $^3J_{HF}$ = 9.0 Hz, 4H, *m*-CH), 5.44 (t, $^3J_{HH}$ = 2.6 Hz, 2H, H2 + H3), 5.03 (s, 10H, Cp), 4.26 (t, $^3J_{HH}$ = 2.6 Hz, 2H, H1 + H4). ^{13}C NMR (126 MHz, C_6D_6): *δ* 160.8 ($^1J_{CF}$ = 244 Hz, C), 144.9 ($^4J_{CF}$ = 3.0 Hz, C), 129.8 ($^3J_{CF}$ = 7.0 Hz, CH), 117.2 (C), 114.7 ($^2J_{CF}$ = 21.0 Hz, CH), 109.7 (CH), 109.1 (CH), 109.0 (CH), 101.1 (C). ^{19}F NMR (300 MHz, C_6D_6): *δ* −118.1. LR-MS (EI, *m*/*z*, relative intensity (%)): 486 ([M^+], 13), 421 ([M^+ − Cp], 2), 220 ([M^+ − Fv], 100). Anal. Calcd for $C_{31.5}H_{26}F_2Zr$: C, 70.88; H, 4.91. Found: C, 70.72; H, 5.14. Crystals of complex **2e** suitable for X-ray studies were grown from a toluene solution at 4 °C. The compound crystallizes with 0.5 equiv of toluene.

General Procedure (GP-3) for Reaction of Cp_2ZrFv Complex 2c with Carbonyl Compounds (Bulk Reaction). To a solution of complex **2c** (1 equiv) in toluene was added the carbonyl compound (2 equiv), and the reaction mixture was stirred at room temperature for a given time. The solvent was then removed under vacuum, and the residue was washed with small amounts of hexanes, filtered, and further dried under vacuum to yield **3**.

Cp_2Zr[OCH(Ph)C(*p*-tolyl)$_2C_5H_3$CH(Ph)O] (3a). According to GP-3, complex **2c** (0.99 g, 2.06 mmol) was reacted with benzaldehyde (0.44 g, 0.42 mL, 4.12 mmol) in toluene (90 mL) for 2 h to give complex **3a** as a white solid in 78% yield (1.12 g, 1.62 mmol). ^{1}H NMR (500 MHz, C_6D_6): *δ* 6.85−7.84 (m, 18H, *p*-tolyl and phenyl), 6.81 (d, *J* = 5.3 Hz, 1H, H4), 6.27 (m, 1H, H3), 6.06 (s, 5H, Cp), 5.97 (s, 5H, Cp), 5.94 (m, 1H, H1), 5.50, (s, 1H, H21), 5.37 (s, 1H, H28), 3.52 (s, 1H, H_2), 2.19 (s, 3H, CH_3), 2.08 (s, 3H, CH_3). ^{13}C NMR (125 MHz, C_6D_6): *δ* 152.9 (C), 147.7 (C), 144.9 (C), 142.8 (C), 140.8 (C), 136.7 (CH), 136.1 (CH), 135.9 (C), 135.5 (C), 133.8 (CH), 132.2 (CH), 131.9 (CH), 130.3 (CH), 128.5 (CH), 128.3 (CH), 127.9 (CH), 127.7 (CH), 127.2 (CH), 126.9 (CH), 125.6 (CH), 112.0 (CH), 111.6 (CH), 93.0 (CH), 83.4 (CH), 63.0 (C), 62.0 (CH), 21.0 (CH_3), 20.9 (CH_3). LR-MS (EI, *m*/*z*, relative intensity (%)): 690 ([M^+], 7), 584 ([M^+ − C_6H_5CHO], 4), 478 ([M^+ − 2{C_6H_5CHO}], 19), 413 ([M^+ − 2{C_6H_5CHO} − Cp], 7), 326 ([M^+ − {C_6H_5CHO} − Fv], 100), 258 ([Fv^+], 39), 220 ([Cp_2Zr^+], 98), 91 ([C_6H_4-CH_3^+], 91).

Cp_2Zr[OCH(*p*-Br-Ph)C(*p*-tolyl)$_2C_5H_3$CH(*p*-Br-Ph)O] (3b; NMR Experiment). To a C_6D_6 solution of complex **2c** (20 mg, 0.04 mmol) was added *p*-bromobenzaldehyde (15 mg, 0.08 mmol) and after stirring for 30 min ^{1}H NMR confirmed full conversion to complex **3a**. ^{1}H NMR (500 MHz, C_6D_6): *δ* 7.81 (d, *J* = 8.3 Hz, 2H, *m*-CH, Ar), 7.46 (d, *J* = 8.4 Hz, 2H, *m*-CH, Ar), 7.28 (d, *J* = 8.5 Hz, 2H, *m*-CH, *p*-tol), 7.20 (d, *J* = 8.3 Hz, 2H, *m*-CH, *p*-tol), 7.17 (d, *J* = 8.2 Hz, 2H, *o*-CH, Ar), 7.06 (d, *J* = 8.5, 3.0 Hz, 2H, *o*-CH, Ar), 7.06 (d, *J* = 8.5, 3.0 Hz, 2H, *o*-CH, *p*-tol), 6.92 (d, *J* = 8.1 Hz, 2H, *o*-CH, *p*-tol), 6.83 (d, *J* = 5.3 Hz, 1H, H4), 6.22−6.17 (m, 1H, H3), 6.09 (s, 5H, Cp), 5.96 (s, 6H, Cp + H1), 5.40 (s, 1H, H21), 5.22 (s, 1H, H28), 3.42 (s, 1H, H_2), 2.28 (s, 3H, CH_3), 2.16 (s, 3H, CH_3). ^{13}C NMR (125 MHz, C_6D_6) *δ*152.7 (C), 146.5 (C), 143.7 (C), 142.3 (C), 140.4 (C), 136.5 (CH), 136.2 (C), 136.1 (CH), 135.9 (C), 133.5 (CH), 132.0 (CH), 131.9 (CH), 131.7 (CH), 131.6 (CH), 131.0 (CH), 128.3 (CH), 127.8 (CH), 127.3 (CH), 121.3 (C), 120.6 (C), 112.0 (CH), 111.6 (CH), 92.1 (CH), 82.6 (CH), 62.7 (C), 61.6 (CH), 21.0 (CH_3), 20.9 (CH_3). ESI-MS for [$C_{44}H_{38}O_2Br_2ZrK$]$^+$: calcd 884.9923, found 884.9913. Crystals suitable for X-ray studies were grown from a concentrated C_6D_6 solution.

Cp_2Zr[OCH(*p*-MeO-Ph)C(*p*-tolyl)$_2C_5H_3$CH(*p*-MeO-Ph)O] (3c; NMR Experiment). To a C_6D_6 solution of complex **2c** (20 mg, 0.04 mmol) was added *p*-anisaldehyde (11 mg, 0.08 mmol), and after stirring for 30 min ^{1}H NMR confirmed full conversion to complex **3c**. ^{1}H NMR (500 MHz, C_6D_6): *δ* 7.89 (d, *J* = 8.3 Hz, 2H, *o*-CH, *p*-tol), 7.30 (d, *J* = 8.3 Hz, 2H, *o*-CH, *p*-tol), 7.29 (d, *J* = 8.6 Hz, 2H, *o*-CH, anisyl) 7.26 (d, *J* = 8.7 Hz, 2H, *o*-CH, anisyl), 7.17 (d, *J* = 8.3 Hz, 2H, *m*-CH, *p*-tol), 6.94 (d, *J* = 8.6 Hz, 2H, *m*-CH, anisyl), 6.92 (d, *J* = 8.2 Hz, 2H, *m*-CH, *p*-tol), 6.84 (d, *J* = 5.1 Hz, 1H, H4), 6.74 (d, *J* = 8.7 Hz, 2H, *m*-CH, anisyl), 6.35 (d, *J* = 5.4 Hz, 1H, H3), 6.11 (s, 5H, Cp), 6.03 (s, 6H, Cp + H1), 5.52 (s, 1H, H21), 5.40 (s, 1H, H28), 3.55 (s, 1H, H2), 3.43 (s, 3H, OMe), 3.28 (s, 3H, OMe), 2.23 (s, 3H, CH_3), 2.10 (s, 3H, CH_3). ^{13}C NMR (125 MHz, C_6D_6): *δ* 159.1 (C), 159.0 (C), 153.0 (C), 142.9 (C), 141.0 (C), 139.8 (C), 136.9 (C), 136.4 (CH), 136.2 (CH), 135.9 (C), 135.6 (C), 133.9 (CH), 132.2 (CH), 131.9 (CH), 131.3 (CH), 128.3 (CH), 127.7 (CH), 126.7 (CH), 114.0 (CH), 113.5 (CH), 112.0 (CH), 111.5 (CH), 92.4 (CH), 83.1 (CH), 62.9 (C), 62.3 (CH), 54.9 (CH_3), 54.7 (CH_3), 21.1 (CH_3), 20.9 (CH_3). ESI-MS for [$C_{46}H_{44}O_4ZrNa$]$^+$: calcd 773.2184, found 773.2195.

Cp_2Zr[$OCMe_2$C(*p*-tolyl)$_2C_5H_3CMe_2O$] (3d). According to GP-3, complex **2c** (0.89 g, 1.81 mmol) was reacted with acetone (0.21 g, 0.27 mL, 3.62 mmol) in toluene (70 mL) for 2 h to give complex **3d** as a white solid in 75% yield (0.83 g, 1.40 mmol). ^{1}H NMR (500 MHz, C_6D_6): *δ* 7.04−7.52 (m, 8H, *p*-tol), 6.77 (m, 1H, H4), 6.31 (m, 1H, H3), 6.20 (s, 5H, Cp), 6.00 (s, 5H, Cp), 5.70 (s, 1H, H1), 2.84 (s, 1H, H_2), 2.18 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 1.66 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.19 (s, 3H, CH_3). ^{13}C NMR (125 MHz, C_6D_6): *δ* 151.6 (C), 144.9 (C), 142.6 (C), 137.8 (CH), 136.8 (CH), 135.7 (C), 135.4 (C), 133.5 (CH), 131.7 (CH), 128.8 (CH), 127.1 (CH), 111.7 (CH), 111.4 (CH), 87.3 (C), 80.9 (C), 64.8 (C), 62.7 (CH), 32.2 (CH_3), 31.7 (CH_3), 31.4 (CH_3), 30.9 (CH_3), 21.0 (CH_3), 20.9 (CH_3). LR-MS (EI, *m*/*z*, relative intensity (%)): 594 ([M^+], 1), 536 ([M^+ − acetone], 4), 478 ([M^+ − 2 acetone], 25), 413 ([M^+ − 2 acetone − Cp], 35), 278 ([M^+ − acetone − Fv], 87), 220 ([Cp_2Zr^+], 67), 91 ([C_6H_4-CH_3^+], 100). No correct elemental analysis of the bulk product was obtained, despite several attempts. Crystals suitable for X-ray studies were grown from a hexane/toluene solution at −15 °C.

Cp_2Zr[$OCEt_2$C(*p*-tolyl)$_2C_5H_3CEt_2O$] (3e). According to GP-3, complex **2c** (0.47 g, 0.98 mmol) was reacted with 3-pentanone (0.17 g, 0.21 mL, 1.96 mmol) in toluene (60 mL) for 12 h to give complex **3e** as a white solid in 67% yield (0.43 g, 0.66 mmol). ^{1}H NMR (500 MHz, C_6D_6): *δ* 6.94−7.81 (m, 8H, *p*-tol), 7.09 (m, 1H, H4), 6.31 (m, 1H, H3), 6.26 (s, 5H, Cp), 6.05 (s, 5H, Cp), 5.34 (s, 1H, H1), 2.92 (s, 1H, H_2), 2.32 (m, 1H, CH2CH3, 2.66 (m, 1H, CH_2CH_3), 2.17 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.03 (m, 1H, CH_2CH_3), 1.83 (m, 1H, CH_2CH_3), 1.64 (m, 1H, C*H*$_2$CH$_3$), 1.40−1−56 (m, 3H, C*H*$_2$CH$_3$), 0.98 (t, 3H, CH$_2$C*H*$_3$), 0.75 (t, 3H, CH$_2$C*H*$_3$), 0.57 (t, 3H, CH$_2$C*H*$_3$), 0.27 (t, 3H, CH$_2$C*H*$_3$). ^{13}C NMR (125 MHz, C$_6$D$_6$): δ 152.3 (C), 145.1 (C), 142.1 (C), 138.4 (CH), 137.8 (CH), 136.0 (C), 135.3 (C), 133.1 (CH), 128.3 (CH), 127.9 (CH), 112.1 (CH), 111.7 (CH), 92.2 (C), 86.5 (C), 65.7 (C), 57.8 (CH), 32.3 (CH$_2$), 30.9 (CH$_2$), 30.3 (CH$_2$), 26.9 (CH$_2$), 21.0 (CH$_3$), 20.9 (CH$_3$), 11.6 (CH$_3$), 9.5 (CH$_3$), 9.0 (CH$_3$), 7.6 (CH$_3$). LR-MS (EI, *m*/*z*, relative intensity (%)): 650 ([M$^+$], 5), 621 ([M$^+$ − C$_2$H$_5$], 10), 564 ([M$^+$ − (C$_2$H$_5$)$_2$CO], 35), 535 ([M$^+$ − {(C$_2$H$_5$)$_2$CO} − C$_2$H$_5$], 47), 499 ([M$^+$ − {(C$_2$H$_5$)$_2$CO} − Cp], 36), 413 ([M$^+$ − 2{(C$_2$H$_5$)$_2$CO} − Cp], 22), 305 ([M$^+$ − {(C$_2$H$_5$)$_2$CO} − Fv], 100) 258 ([Fv$^+$], 32). Crystals suitable for X-ray studies were grown from a benzene solution at room temperature. The compound crystallizes with 1.5 molecules of C$_6$D$_6$.

General Procedure for Reaction of Cp$_2$ZrFv Complex 2c with Alkynes (NMR Experiments). To a solution of complex **2c** (15 mg, 0.03 mmol) in C$_6$D$_6$ (0.5 mL) was added a solution of alkyne (0.06 mmol) in C$_6$D$_6$ (0.2 mL). After the mixture was stirred for 12 h at room temperature, the disappearance of complex **2c** was observed in the ^{1}H NMR spectrum with concomitant formation of free fulvene **1c** and the corresponding zirconacyclopentadiene **4**. The ^{1}H NMR data of **4a,b** were in agreement with literature reports.[14b,19]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00213.

Selected crystal data collection parameters, details on DFT calculations, and selected NMR spectra (PDF)

Cartesian coordinates for the calculated structures (XYZ)

Accession Codes

CCDC 1526506−1526507 and 1538922−1538925 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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