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Edge-bridged half-open zirconocenes: Synthesis, characterization, and reaction with diphenylacetylene

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Abstract

The synthesis and characterization of the new, 16 electron half-open zirconocenes, $Zr(C_5H_5)(c\text{-}C_8H_{11})(PR_3)$ (R = Me, Et) are reported, together with a structural study of the PEt_3 complex. As with other low valent half-open zirconocenes, the Zr–C distances are significantly shorter on average for the electronically open dienyl ligand than those for the C_5H_5 ligand, 2.343 vs. 2.512 Å. Reaction of either of these compounds with PhC_2Ph led to the incorporation of two equivalents of the alkyne, resulting in a formally 14 electron complex with coordination from cyclopentadienyl, allyl, σ-alkyl, and σ-vinyl units.

Keywords: Pentadienyl; Coupling reaction; Zirconium complex

1. Introduction

The chemistry of low valent half-open titanocenes has proven to be very rich, yielding for example numerous products of coupling reactions between the pentadienyl ligands and ketones [1], imines [2], nitriles [3], isonitriles [1], alkynes [4], and even combinations of these substrates [5]. A number of these reactions are quite similar to reactions observed for the earlier investigated zirconium diene compounds [6]. The reactions for the electronically open pentadienyl ligands are especially interesting given that it has been demonstrated that these ligands, whether edge-bridged or not, are more strongly bound than their "stabilizing" cyclic counterparts [7]. Several reasons suggest that an extension to the larger, more electropositive zirconium would lead to even more promising opportunities. As the large girth of the pentadienyl ligands leads to a reduced degree of orbital overlap relative to C_5H_5, the larger zirconium center would be ideal for minimizing this loss, resulting in even more effective bonding. In addition, the more electropositive nature of zirconium should serve even better to promote coupling reactions with the heteroatom-containing substrates listed above, while still retaining favorability for coupling with alkynes, due to the conversion of π C–C bonds to σ bonds. Indeed, some of these expectations have already been borne out for the 2,4-C_7H_{11} [8] and 6,6-dmch [9] ligands (C_7H_{11} = dimethylpentadienyl; dmch = dimethylcyclohexadienyl). Herein we report on the extension of these studies to half-open zirconocenes containing the c-C_8H_{11} (cyclooctadienyl) ligand.

2. Experimental

All reactions were carried out under a nitrogen atmosphere in Schlenk apparatus. Hydrocarbon and aromatic solvents were dried by passage through activated alumina columns under a nitrogen atmosphere, while THF was dried by distillation from sodium benzophenone ketyl under a nitrogen atmosphere. Elemental analyses were obtained from Desert Analytics. 1,3-Cyclooctadiene was prepared by the catalytic isomerization of 1,5-cyclooctadiene [10], and thereafter converted to $K(c\text{-}C_8H_{11})$ by standard procedures [11]. $Zr(C_5H_5)Cl_2Br$ was prepared as

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previously described [9]. NMR assignments for **2** were confirmed by 2D spectra.

2.1. *(Trimethylphosphine)(cyclopentadienyl)-(cyclooctadienyl)zirconium, $Zr(C_5H_5)(\eta^5\text{-}c\text{-}C_8H_{11})$-$(PMe_3)$ (**1a**)*

To a solution of $Zr(C_5H_5)Cl_2Br$ (0.50 g, 1.6 mmol) in 40 mL THF under a nitrogen atmosphere at −78 °C was added PMe_3 (0.17 mL, 1.6 mmol) yielding a pale pink solution. To the resulting solution was added dropwise K(*c*-C_8H_{11}) (0.70 g, 4.9 mmol) in 50 mL of THF. The resulting red solution was allowed to warm to room temperature and a color change to green-blue was observed. Then the solvent was removed in vacuo and the crude product extracted with three portions of 20 mL pentane and filtered through a Celite pad on a coarse frit. Concentration in vacuo of the green-blue filtrate was carried out until incipient crystallization. Cooling of the mixture to −90 °C for one day afforded 0.42 g of an air-sensitive blue crystalline solid (mp 95–96 °C) in 65% yield.

^1H NMR (benzene-d_6, ambient): δ 6.95 (dt, 1H, H-3, $J = 10.1$, 4.2 Hz), 6.28 (s, 5H, C_5H_5), 5.30 (dt, 2H, H-2,4, $J = 10.1$, 4.2 Hz), 2.50 (m, 2H, H-1,5), 0.6–1.0 (m, 6H, H-(6–8)), 0.33 (d, 9H, PMe_3, $J = 5.4$ Hz).

^{13}C NMR (benzene-d_6, ambient): δ 135.6 (d, C-3, $J = 150$ Hz), 106.1 (d, C_5H_5, $J = 169$ Hz), 80.6 (d, C-2,4, $J = 161$ Hz), 76.0 (d, C-1,5, $J = 134$ Hz), 38.4 (t, C-6,8, $J = 122$ Hz), 21.1 (t, C-7, $J = 124$ Hz), 18.5 (dq, PMe_3, $J = 121$, 15 Hz).

Anal. Calc. for $C_{16}H_{25}PZr$: C, 56.59; H, 7.42. Found: C, 56.71; H, 7.39%.

2.2. *(Triethylphosphine)(cyclopentadienyl)(cyclooctadienyl)zirconium, $Zr(C_5H_5)(\eta^5\text{-}c\text{-}C_8H_{11})$$(PEt_3)$ (**1b**)*

To a solution of $Zr(C_5H_5)Cl_2Br$ (0.50 g, 1.6 mmol) in 40 mL THF under a nitrogen atmosphere at −78 °C was added PEt_3 (0.25 mL, 1.6 mmol), yielding a pale pink solution. To the resulting solution was added dropwise K(*c*-C_8H_{11}) (0.70 g, 4.9 mmol) in 50 mL of THF. The resulting red solution was allowed to warm to room temperature and a color change to green-blue was observed. Then the solvent was removed in vacuo and the crude product extracted with several portions of pentane and filtered through a Celite pad on a coarse frit. Concentration in vacuo of the blue filtrate was carried out until incipient crystallization. Cooling of the mixture to −90 °C for one day afforded 0.40 g of an air-sensitive blue crystalline solid (mp 127–128 °C) in 62% yield.

^1H NMR (benzene-d_6, ambient): δ 6.95 (br, 1H, H-3), 6.28 (s, 5H, C_5H_5), 5.32 (m, 2H, H-2,4), 2.51 (m, 2H, H-1,5), 0.8–1.2 (m, 6H, H-(6–8)), 0.75 (m, 6H, PEt_3), 0.30 (m, 9H, PEt_3).

^{13}C NMR (benzene-d_6, ambient): δ 136.0 (d, C-3, $J = 157$ Hz), 106.2 (d, C_5H_5, $J = 169$ Hz), 80.6 (d, C-2,4, $J = 164$ Hz), 76.4 (d, C-1,5, $J = 135$ Hz), 38.5 (t, C-6,8, $J = 122$ Hz), 20.7 (t, C-7, $J = 124$ Hz), 17.3 (t, PEt_3, $J = 129$ Hz), 7.9 (q, PEt_3, $J = 127$ Hz).

Anal. Calc. for $C_{19}H_{31}PZr$: C, 59.71; H, 8.19. Found: C, 59.54; H, 7.97%.

2.3. *Bis(diphenylacetylene)/$Zr(C_5H_5)(c\text{-}C_8H_{11})$ coupling product, "$Zr(C_5H_5)(c\text{-}C_8H_{11})(PhCCPh)_2$" (**2**)*

0.21 g (0.056 mmol) of $Zr(C_5H_5)$(*c*-C_8H_{11})(PEt_3) were partially dissolved in 40 mL of hexane in a 100 mL Schlenk flask. 0.22 g (1.2 mmol) of diphenylacetylene was added as a solid under nitrogen and the flask was swirled several times. The originally bright blue-green solution rapidly converted to a dark red color and was left to sit undisturbed for 18 h. Bright red needle-like crystals precipitated from the solution and were collected by syringing off the supernatant, washing with 3 × 10 mL pentane, and drying in vacuo. Yields ranged from 50% to 70% depending on the purity of the starting materials. The title compound can also be synthesized from the PMe_3 adduct with similar results. Crystals suitable for an X-ray crystallographic study were grown by carefully layering a dilute, filtered solution of the phosphine adduct in hexane with a dilute solution of the acetylene in the same solvent.

^1H NMR (benzene-d_6, ambient): δ 7.35–6.65 (m, 20H, Ph), 6.03 (t, 1H, $J = 8$ Hz, H3), 5.75 (s, 5H, Cp), 4.91 (t, 1H, $J = 9$ Hz, H5), 4.69 (dd, 1H, $J = 11.5$, 9.5 Hz, H4), 4.60 (dd, 1H, $J = 7.2$, 2.1 Hz, H6), 3.82 (d, 1H, $J = 8$ Hz, H2), 3.53 (s, 1H, H10), 3.05 (t, 1H, $J = 7$ Hz, H6), 2.50–2.34 (1H, $H7_{endo}$), 1.98–1.84 (m, 1H, $H7_{exo}$), 1.54–1.34 (m, 2H, H8a,b).

^{13}C NMR (benzene-d_6, ambient): δ 154.4 (s, 1C), 152.0 (s, 1C), 149.0 (s, 1C), 145.7 (s, 1C), 139.4 (s, 1C), 127.7 (d, 1C, $J = 162$ Hz, C4), 111.4 (d, 5C, $J = 171$ Hz, Cp), 107.8 (d, 1C, $J = 164$ Hz, C3), 96.1 (d, 1C, $J = 157$ Hz, C5), 90.6 (d, 1C, $J = 125$ Hz, C10), 69.0 (s, 1C, C9), 60.0 (d, 1C, $J = 136$ Hz, C6), 59.8 (d, 1C, $J = 136$ Hz, C1), 46.4 (d, 1C, $J = 131$ Hz, C2), 37.8 (t, 1C, $J = 130$ Hz, C7), 30.2 (t, 1C, $J = 129$ Hz, C8).

Anal. Calc. for $C_{41}H_{36}Zr$: C, 79.43; H, 5.85. Found: C, 79.23; H, 6.07%.

2.4. *Crystallographic studies*

Crystal, data collection, and refinement parameters are presented in Table 1. Single crystals of each compound were examined under Paratone oil. Suitable crystals were then transferred to a Nonius Kappa diffractometer for study, which in the case of **2** was equipped with a CCD detector. Initial structural solutions came from direct methods using SIR-97 [12], while SHELXL-97 [13] was used for the location of additional atoms and structural refinements. All nonhydrogen atoms were refined anisotropically. The hydrogen atoms in **1b** were placed in idealized positions while those in **2** were successfully refined isotropically.

Table 1
Crystallographic parameters for $Zr(C_5H_5)(c\text{-}C_8H_{11})(PEt_3)$ (**1b**) and the bis(diphenylacetylene) coupling product, **2**

Formula	$C_{19}H_{31}PZr$	$C_{41}H_{36}Zr$
Formula weight	381.65	619.92
Temperature (K)	173(1)	200(1)
λ (Å)		
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
Unit cell dimensions		
a (Å)	8.289(2)	13.0909(4)
b (Å)	9.770(5)	15.8198(5)
c (Å)	12.656(7)	14.2531(3)
α (°)	95.68(6)	90
β (°)	105.27(5)	91.4619(16)
γ (°)	108.72(3)	90
Volume ($Å^3$)	917.4(8)	2950.79(14)
Z	2	4
D_{calc}	1.382	1.395
Absorption coefficient (cm^{-1})	6.68	4.02
θ Range (°)	2.0–24.0	3.3–25.3
Limiting indices	$0 \leqslant h \leqslant 9$, $-11 \leqslant k \leqslant 10$, $-14 \leqslant l \leqslant 13$	$-15 \leqslant h \leqslant 15$, $-19 \leqslant k \leqslant 17$, $-17 \leqslant l \leqslant 17$
Reflections collected	3081	9924
Independent reflections	2455	5374
n: $I > n\sigma(I)$	3	2
$R(F)$	0.0632	0.0407
$R_w(F^2)$	0.0830	0.0824
Maximum difference Fourier peak ($e\,Å^{-3}$)	1.79	0.40

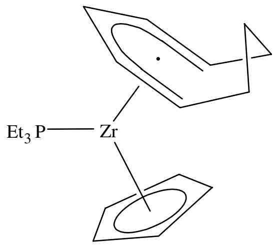
3. Results and discussion

The reaction of $Zr(C_5H_5)Cl_2Br$ with three equivalents of $K(c\text{-}C_8H_{11})$ in the presence of PMe_3 or PEt_3 yields the respective 16 electron $Zr(C_5H_5)(c\text{-}C_8H_{11})(PR_3)$ complexes (Eq. (1); R = Me, Et)

$$Zr(C_5H_5)Cl_2Br + 3K(c\text{-}C_8H_{11}) + PR_3 \rightarrow Zr(C_5H_5)(c\text{-}C_8H_{11})(PR_3) \quad R = Me, Et \tag{1}$$

These complexes are of interest for several reasons. Their deep blue colors are quite unique among related open and half-open metallocenes. Further, half-open zirconocenes with other pentadienyl ligands thus far have incorporated two phosphorus donor centers, as in $Zr(C_5H_5)$(6,6-dmch)$(PMe_3)_2$ [9] and $Zr(C_5H_5)(2,4\text{-}C_7H_{11})$(dmpe) [8]. In this respect, the $Zr(C_5H_5)(c\text{-}C_8H_{11})(PR_3)$ complexes resemble analogous 16 electron titanium complexes [1], in which only one donor center has thus far been observed, whether the accompanying pentadienyl ligand is $2,4\text{-}C_7H_{11}$, 6,6-dmch, or $c\text{-}C_8H_{11}$. The formation of 16 electron half-open zirconocenes with the $c\text{-}C_8H_{11}$ ligand must be due to the $c\text{-}C_8H_{11}$ ligand being more sterically demanding than either $2,4\text{-}C_7H_{11}$ or 6,6-dmch. It has been recognized for some time that the edge-bridged ligands such as 6,6-dmch and $c\text{-}C_8H_{11}$ are more sterically demanding than $2,4\text{-}C_7H_{11}$ [1d,7,14]. That $c\text{-}C_8H_{11}$ is more sterically demanding than 6,6-dmch can readily be explained on the basis of differences between the separations between the dienyl termini (C1, C5). For $Ti(C_5H_5)(c\text{-}C_8H_{11})(PMe_3)$, the C1–C5 separation is 3.08 Å [15], whereas for $Ti(C_5H_5)$(6,6-dmch)(PMe_3) [1d], the separation is 2.43 Å. Not only does this increase in girth make $c\text{-}C_8H_{11}$ more sterically demanding, but that extra girth also geometrically requires a closer approach of the dienyl ligand plane to the metal, just to maintain similar M–C distances. For these two complexes, the respective deviations of the titanium center from the open dienyl planes are 1.50 and 1.72 Å, vs. 2.07 and 2.06 Å for the C_5H_5 ligands.

The structure of $Zr(C_5H_5)(c\text{-}C_8H_{11})(PEt_3)$ (**1b**, Fig. 1 and Table 2, $c\text{-}C_8H_{11}$ = cyclooctadienyl) is observed to be similar to that of $Ti(C_5H_5)$(6,6-dmch)(PMe_3) (dmch = dimethylcyclohexadienyl) in that the phosphine ligand resides near the central carbon atom (C3) of the electronically open dienyl ligand, whereas for related species without edge-bridges, the phosphine would be positioned by the open edge. Similar to related early metal complexes [16], the Zr–C bonds for the electronically open dienyl ligand (2.260(7)–2.428(7) Å, avg. 2.343 Å) are significantly shorter than those for the aromatic C_5H_5 ligand (2.491(10)–2.534(10) Å, avg. 2.512 Å). This translates into a substantial difference in the deviations of the zirconium center from the dienyl planes (vide infra). For the $c\text{-}C_8H_{11}$ ligand, the Zr–C distances differ significantly, with average values for the three types of carbon atom positions being 2.268(5) Å for C(1,5), 2.374(5) Å for C(2,4), and 2.428(7) Å for C3. This trend may be attributed to the location of the phosphine ligand (Zr–P = 2.755(2) Å) near the C3 atom. One observes significant tilts of the hydrogen atom substituents below the $c\text{-}C_8H_{11}$ plane, averaging 22.4° for H(1,5), 11.3° for H(2,4), and 3.0° for H3. The related $Ti(C_5H_5)(c\text{-}C_8H_{11})(PMe_3)$ complex displays respective tilts of 23.0°, 15.0°, and 4.6° [15]. For purposes of comparison with the $Ti(C_5H_5)(c\text{-}C_8H_{11})(PMe_3)$ and $Ti(C_5H_5)$(6,6-dmch)(PMe_3) complexes discussed above, $Zr(C_5H_5)(c\text{-}C_8H_{11})(PEt_3)$ displays a C1–C5 separation of 3.16 Å, and respective deviations of the zirconium center by 2.233 and 1.609 Å from the C_5H_5 and $c\text{-}C_8H_{11}$ planes. For the 18 electron $Zr(C_5H_5)$(2,6,6-tmch)$(PMe_3)_2$ complex, the corresponding distances were found to be 2.37, 2.220, and 2.024 Å [9].



1b

While several coupling products have been readily isolated from the reactions of $Ti(C_5H_5)(c\text{-}C_8H_{11})(PR_3)$

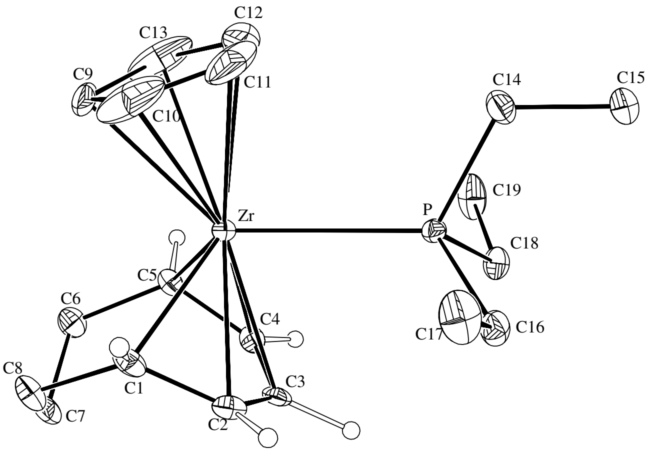
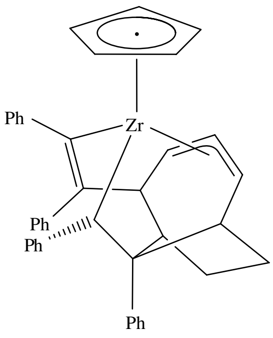


Fig. 1. Solid state structure of $Zr(C_5H_5)(c\text{-}C_8H_{11})(PEt_3)$ (**1b**).

Table 2
Selected bond distances (Å) and angles (°) for $Zr(C_5H_5)(c\text{-}C_8H_{11})(PEt_3)$ (**1**)

Bond distances (Å)			
Zr–P	2.755(2)	C1–C8	1.530(10)
Zr–C1	2.276(7)	C2–C3	1.417(11)
Zr–C2	2.367(7)	C3–C4	1.409(10)
Zr–C3	2.428(7)	C4–C5	1.438(10)
Zr–C4	2.382(8)	C5–C6	1.531(10)
Zr–C5	2.260(7)	C6–C7	1.514(11)
Zr–C9	2.510(9)	C7–C8	1.509(11)
Zr–C10	2.520(10)	C9–C10	1.429(20)
Zr–C11	2.491(10)	C9–C13	1.413(19)
Zr–C12	2.505(11)	C10–C11	1.337(21)
Zr–C13	2.534(10)	C11–C12	1.267(20)
C1–C2	1.437(11)	C12–C13	1.309(20)
Bond angles (°)			
Zr–P–C14	117.7(3)	C1–C2–C3	126.7(7)
Zr–P–C16	115.2(2)	C2–C3–C4	130.6(7)
Zr–P–C18	115.8(2)	C3–C4–C5	126.3(7)

(R = Me, Et) complexes with PhC_2SiMe_3, the corresponding reactions for the analogous zirconium complexes have been more complicated, thereby leading to an attempt with another alkyne, Ph_2C_2. Notably, with either $Zr(C_5H_5)(c\text{-}C_8H_{11})(PR_3)$ complex (R = Me, Et), a single, identical di(alkyne) coupling product resulted, **2**, whose complexity required a single crystal X-ray-diffraction study for its elucidation. In contrast, $Ti(C_5H_5)(c\text{-}C_8H_{11})(PMe_3)$ and $Ti(C_5H_5)(c\text{-}C_8H_{11})(PEt_3)$ each gave rise to its own coupling product(s) with PhC_2SiMe_3 at least, incorporating two [4b] and three (and/or four) [15] equivalents of alkyne, respectively.



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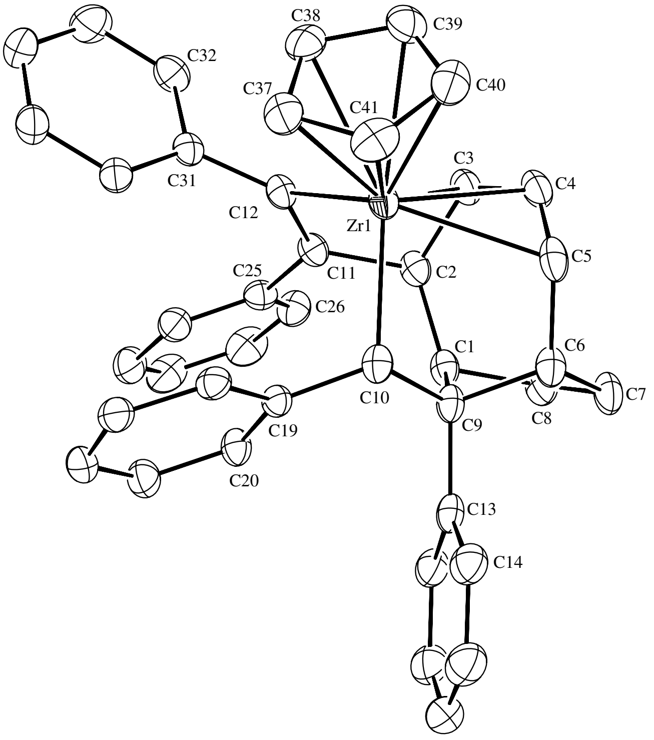


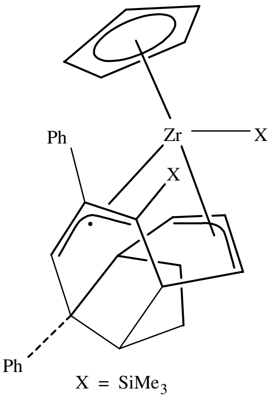
Fig. 2. Structure of the $Zr(C_5H_5)(c\text{-}C_8H_{11})/bis(Ph_2C_2)$ coupling product, **2**.

The structure of compound **2** is presented in Fig. 2, while pertinent bonding parameters are given in Table 3. The zirconium center is coordinated by a cyclopentadienyl ligand, an allyl fragment (C3–C5), a σ-alkyl ligand (C10), and a formally σ-vinyl ligand (C12). The Zr–C σ-bond distances are shortest at 2.249(3) Å for C12 and 2.264(3) Å for C10. The shorter σ-vinyl coordination is in accord with the greater s character on the bound carbon atom, sp^2 vs. sp^3. The Zr–C distances for the cyclopentadienyl ligand are fairly regular, averaging 2.524 Å, while the allyl coordination is decidedly asymmetric, with the respective Zr–C(3–5) distances being 2.385(3), 2.439(3), and 2.505(3) Å. The similarity of the C3–C4 and C4–C5 distances (1.385(5), 1.393(5) Å) nonetheless suggests little if any contribution from a σ-allyl resonance form. As a result of the above-mentioned ligand coordinations, the complex has a formal 14 electron count, an extremely low value for a zirconium center. Based on the results obtained for related electron deficient coupling products [15a,17], the possibility of the presence of (C–H) → Zr agostic interactions needs to be considered. There is, in fact, one C–H bond in a position to engage in an agostic interaction, although structural parameters do not suggest it to be very strong (e.g., Zr–H10, 2.60 Å; Zr–C10–H10, 100(2)°; C10–H10, 0.94(3) Å).

Table 3
Selected bond distances (Å) and angles (°) for the bis(diphenylacetylene) coupling product

Bond distances (Å)			
Zr–C3	2.385(3)	C1–C2	1.566(4)
Zr–C4	2.439(3)	C1–C9	1.570(4)
Zr–C5	2.505(3)	C2–C3	1.525(4)
Zr–C10	2.264(3)	C2–C11	1.536(4)
Zr–C12	2.249(3)	C3–C4	1.385(5)
Zr–C37	2.500(3)	C4–C5	1.393(5)
Zr–C38	2.532(3)	C5–C6	1.523(5)
Zr–C39	2.556(4)	C6–C9	1.550(4)
Zr–C40	2.530(3)	C9–C10	1.562(4)
Zr–C41	2.500(3)	C11–C12	1.347(4)
Bond angles (°)			
C10–Zr–C12	97.36(11)	C2–C1–C9	120.6(2)
Zr–C10–C9	106.8(2)	C11–C2–C3	108.8(3)
Zr–C12–C11	105.7(2)	C1–C2–C3	119.8(3)
C10–C9–C6	106.8(2)	C2–C3–C4	126.5(3)
C10–C9–C1	119.3(2)	C3–C4–C5	126.9(3)
C12–C11–C2	116.4(3)	C4–C5–C6	126.9(3)
C11–C2–C1	115.8(2)	C5–C6–C9	113.7(3)

The mechanism responsible for the unique alkyne couplings leading to **2** is of some interest. Although more than one possible pathway could lead to this species, the observation of a somewhat related cage geometry in one of the Zr(C_5H_5)(*c*-C_8H_{11})/PhC_2SiMe_3 coupling products, **3** [15a], suggests a common pathway, thereby helping to narrow the range of possibilities. Notably, while titanium complexes with 2,4-C_7H_{11} and *c*-C_8H_{11} ligands have thus far all undergone 1,5 couplings with alkynes [1c,4,15], the Zr(C_5H_5)(*c*-C_8H_{11})(PR_3) complexes appear to favor instead a 1,2 process. In either case, the initial coupling occurs between a phenyl-substituted alkyne carbon atom and a dienyl terminus (1 position), presumably yielding a species such as **4**, which may incorporate a PR_3 ligand. For the titanium reactions, the other alkyne carbon atom thereafter couples to the other dienyl terminus. The larger size of zirconium, and/or its ability to form stronger bonds, appear(s) to lead its complexes through a different course. One possibility is that activation of a C–H bond on C6, formerly a CH_2 group adjacent to dienyl terminus C5, regenerates a dienyl fragment, together with formation of a Zr–H bond. The new dienyl terminus, C6, then could couple to C9, the alkyne carbon atom involved in the original coupling to C1, yielding after transfer of the hydride to C10, **5** having (as in **4**) a diene ligand formed between carbon atoms C2–C5. The second alkyne could then simply coordinate to the metal center, and couple to a diene terminus, C2, to yield the observed product, **2**. Alternatively, it is also possible that the second alkyne is incorporated just after the coupling of the first alkyne to C1, and that the second alkyne then couples to the other end of the first alkyne (C10 in **4**) and to C2, yielding **6**. Subsequent C6–H activation, hydride transfer to C10, C9–C6 coupling, and C10–C12 bond activation would then yield **2**.



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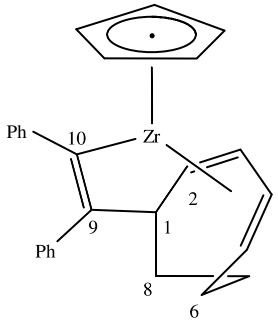
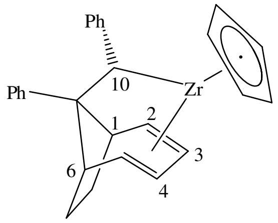
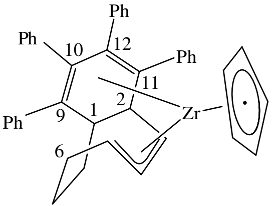


4



5



6

Interestingly, dissolution of **2** in THF for ca. 12 hours leads to its clean conversion to another species, which can also be prepared by carrying out the coupling reaction of **1** with two equivalents of Ph_2C_2 in THF [15a]. The same species is also formed in benzene solutions, but at a much slower rate. It also appears possible to isolate a 1:1 coupling product from **1b** and PhC_2SiMe_3. Neither of these species has as yet been obtained in pure crystalline form, but spectroscopic data suggest they can be formed and isolated as predominant products. It is possible that the nature of the mono(alkyne) coupling product would provide some further indication of the likely mechanism by which **2** is formed.

4. Conclusions

The Zr–C bond distances in $Zr(C_5H_5)(c\text{-}C_8H_{11})(PEt_3)$ reveal clearly that the nonaromatic $c\text{-}C_8H_{11}$ ligand is bound more strongly than the C_5H_5 ligand. Although cyclopentadienyl ligands have been observed to undergo coupling reactions [18], coupling reactions of unsaturated organic molecules with half-open titanocenes or zirconocenes nonetheless involve preferentially the more strongly bound, but nonaromatic, pentadienyl ligands [7]. The reactions of titanium and zirconium pentadienyl complexes with alkynes have led both to compounds having (C–C) → M agostic interactions, and to actual C–C and C–Si bond activations. Given the fact that the bond activations are more common for zirconium, which typically forms stronger bonds than titanium, it can be expected that related hafnium chemistry will also commonly lead to C–C bond activations, and further efforts in that direction should therefore prove fruitful.

5. Supplementary material

CCDC 231988 and 632119 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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