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Transformation of a 1-Zirconacyclopent-3-yne, a Five-Membered Cycloalkyne, into a 1-Zirconacyclopent-3-ene and Formal “1-Zirconacyclopenta-2,3-dienes”**

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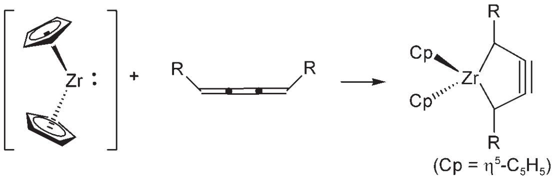
Cycloalkynes smaller than seven-membered rings are generally unstable and difficult to isolate, whereas the synthesis and reactivity of cyclopentynes, five-membered cycloalkynes, have been studied extensively.[1] Most reactions of the labile species involved formal 1,2-addition to the triple bond. There have been some reports of cyclopent-1-en-3-ynes,[2] but 1,4-addition to these compounds has not been shown. Cyclopentynes conjugated with alkylidene moieties have not been reported to date. We were interested in investigating the reactivity of cyclopentynes with alkylidene groups.

We described previously the synthesis and reactivity of 1-metallacyclopent-3-yne compounds, five-membered cycloalkynes, and showed that these compounds were surprisingly stable in pure form at room temperature [Eq. (1)].[3a,b]



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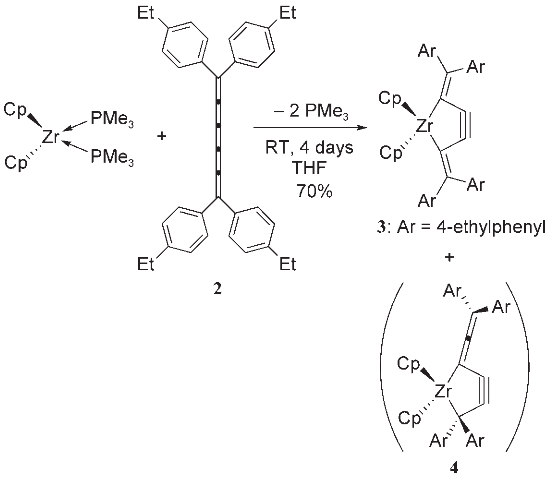
(1)

Titanium and hafnium analogues have also been prepared.[3c,4a] Several reactions of these unique molecules have been reported;[3–5] however, their transformation into cycloalkenes or cycloallenes has not been shown. We reasoned that 1-metallacyclopent-3-ynes of conjugated systems would show more varied reactivities. We report herein the synthesis of a 2,5-bisalkylidene-1-metallacyclopent-3-yne compound and its transformation into 1-metallacyclopent-3-ene and formal “1-metallacyclopenta-2,3-diene” compounds.

The treatment of a low-valent zirconocene–bisphosphine complex, $[Cp_2Zr(PMe_3)_2]$,[6] with 1,1,6,6-tetrakis(4-ethylphenyl)-1,2,3,4,5-hexapentaene (**2**)[7] at room temperature for 4 days gave the 2,5-bisalkylidene-1-zirconacyclopent-3-yne compound **3** in 70 % yield [Eq. (2)]. The reaction gave **3** predominantly, and the possible isomer 2-allenylidene-1-zirconacyclopent-3-yne (**4**) was not obtained, probably because of the steric hindrance of the aryl groups. Although several transition-metal complexes of hexapentaenes have been reported, none of them have 1-metallacyclopent-3-yne structures.[8] The molecular structure of **3** is shown in Figure 1.[9] The triple bond in **3** (C3–C4) is significantly longer than that in the nonsubstituted 1-zirconacyclopent-3-yne complex **1** (R = H; 1.237(5) Å),[3e] whereas the adjacent single bonds (C2–C3 and C4–C5) are slightly shorter in **3** than in **1** (1.406–1.408 Å in **1**). These differences may reflect differences between the bond lengths of hexapentaene **2** and those of butatrienes: Compound **2** has a longer central bond (1.311(2) Å),[7,10] whereas butatrienes have a shorter central bond (1.22–1.28 Å). The alkylidene moieties are bent away from the metal center; the four carbon atoms C2–C5 and the Zr center are coplanar, and C1 and C6 are located 0.24 and 0.27 Å from this plane, respectively.



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When a red solution of **3** in tetrahydrofuran was treated with lithium powder or potassium graphite at room temperature, the color of the solution changed to deep blue. Protonation of this solution with catechol (1 equiv) gave the 1-zirconacyclopent-3-ene compound **6** as the major product [46 % yield (as determined by ^1H NMR spectroscopy), M = K; Eq. (3)]. This result indicates the formation of a dianionic species **5** upon the treatment of **3** with alkali metals.[11] The ^1H NMR signals for the vinyl hydrogen atoms of **6** appeared

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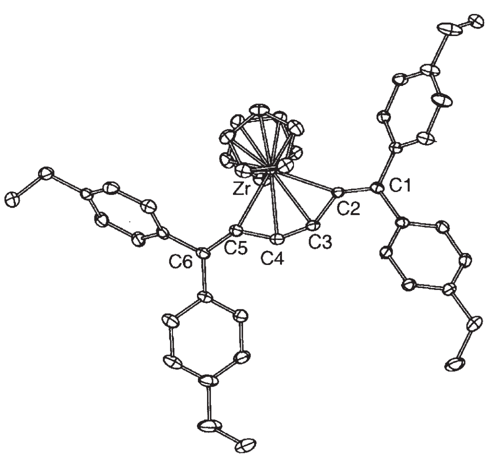
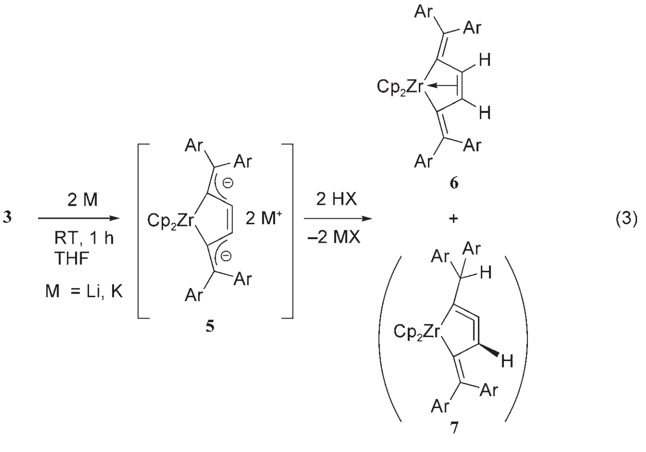


Figure 1. Molecular structure of **3**. Hydrogen atoms are omitted. Selected bond lengths [Å] and angles [°]: Zr–C2 2.347(2), Zr–C3 2.338(2), Zr–C4 2.336(2), Zr–C5 2.341(2), C1–C2 1.351(2), C2–C3 1.390(2), C3–C4 1.263(2), C4–C5 1.388(2), C5–C6 1.355(2); C2-Zr-C5 100.4(1), C1-C2-C3 131.9(2), C2-C3-C4 147.3(2), C3-C4-C5 147.3(2), C4-C5-C6 133.5(2).



at $\delta = 6.29$ ppm, and the corresponding signals for the methine carbon atoms appeared at $\delta = 123.2$ ppm in the ^{13}C NMR spectrum. This result is the first example of the formal hydrogenation of a 1-zirconacyclopent-3-yne to give a 1-zirconacyclopent-3-ene.[12] The molecular structure of **6** was determined by an X-ray diffraction study.[13] The 1-zirconacyclopent-3-ene ring in **6** is bent at the α carbon atoms by 35°. This bend angle is significantly smaller than those observed in *s-cis*-1,3-diene complexes (60–67°),[14a] which indicates that the central double bond coordinates weakly to the metal.[14] ^{1}H NMR spectra of the reaction mixture suggested the formation of the formal "1-zirconacyclopenta-2,3-diene" compound **7** as a minor product (18% yield by ^{1}H NMR spectroscopy). Non-equivalent Cp signals at $\delta = 5.20$ and 5.26 ppm and a singlet at $\delta = 4.1$ ppm assignable to a β hydrogen atom were consistent with the formation of **7**, although this complex has not yet been identified unequivocally.

The addition of iodomethane (2 equiv) to **5** afforded selectively the formal "1-zirconacyclopenta-2,3-diene" compound **8a**, whose molecular structure was determined unambiguously (Figure 2), in 83% yield [Eq. (4)]. One methyl group attacked the metallacycle, whereas the other reacted at

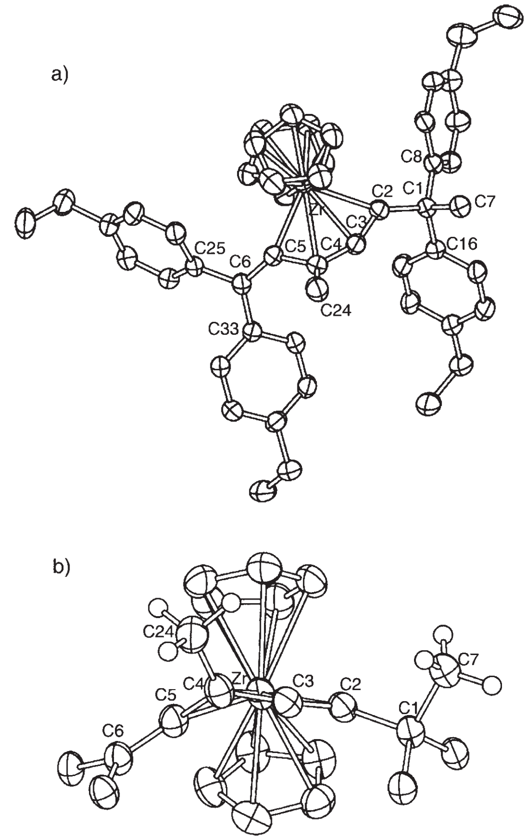
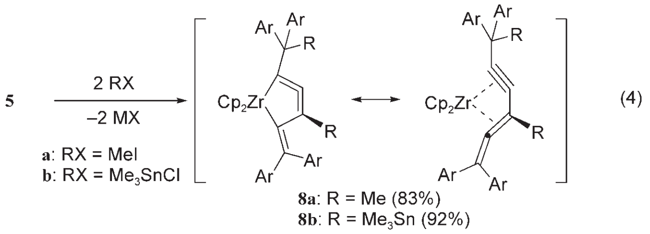
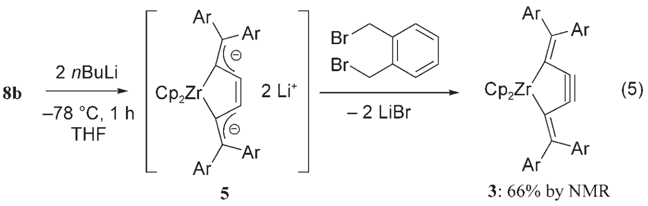


Figure 2. Molecular structure of **8a**. a) Top view; hydrogen atoms are omitted. b) Front view; aryl groups and some of the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zr–C2 2.323(3), Zr–C3 2.333(2), Zr–C4 2.495(2), Zr–C5 2.299(2), C1–C2 1.522(2), C2–C3 1.286(4), C3–C4 1.372(4), C4–C5 1.439(4), C5–C6 1.348(4); C2-Zr-C5 94.1(1), C1-C2-C3 129.9(2), C2-C3-C4 153.6(3), C3-C4-C5 120.5(2), C4-C5-C6 113.0(2), C3-C4-C24 120.5(3), C5-C4-C24 117.5(3).



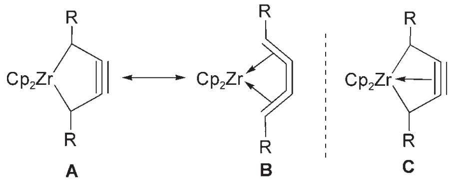
a benzylic position, probably because of steric hindrance by the first methyl group. This reaction is a formal 1,4-addition to a conjugated cyclopentyne. Trimethyltin chloride reacted similarly with **5** to give **8b** in 92% yield. In the NMR spectra, the signals for the methyl hydrogen atoms in **8b** appeared at $\delta_H = -5.70$ and -6.19 ppm, and signals for quaternary carbon atoms coupled with tin atoms were observed at $\delta_C = 54.0$ and 67.3 ppm.

Thus, the 1-zirconacyclopent-3-yne **3** was transformed into the 1-zirconacyclopent-3-ene **6** and the formal "1-zirconacyclopenta-2,3-diene" **8**. Rosenthal proposed the possibility of the isomerization of a "1-metallacyclopenta-2,3-diene" to a 1-metallacyclopent-3-yne.[5d] Such a transformation has not been reported to date. Therefore, we examined the retrotransformation of **8** into **3** [Eq. (5)].



n-Butyllithium (2 equiv) was added to a solution of **8b** in THF at −78 °C. The reaction mixture turned blue, which is an indication of the formation of **5** (M = Li). α,α′-Dibromo-*o*-xylene was added to this mixture to produce **3** in 66 % yield according to NMR spectroscopic analysis of the mixture (44 % yield of isolated **3**).

The question could be raised as to whether these products **8** should be regarded as η^4-1,3-enyne complexes or 1-metallacyclopenta-2,3-dienes [Eq. (4)]. Five-membered cycloallenes have been reported only as short-lived species,[15] whereas complex **8** is very stable at room temperature if kept under argon. The same question has been discussed in relation to 1-metallacyclopent-3-ynes. Lin and Lam proposed the contribution of the η^4 π,π coordination mode (**B**, Scheme 1),[16] whereas Jemmis et al. suggested donation from the triple bond to the metal (**C**).[17] Our experimental study showed that structure **B** must contribute, although structure **A** is more important.[18]



Scheme 1. Coordination modes in 1-zirconacyclopent-3-ynes.

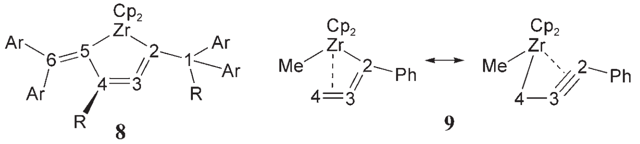
Rosenthal and co-workers have studied extensively the synthesis and reactivity of 1-metallacyclopenta-2,3,4-trienes.[5b,c,19] They predicted the possibility of preparing 1-metallacyclopenta-2,3-diene compounds either from metal species and 1,3-enynes or from alkynyl vinyl metal complexes.[5d] There have been two reports of η^4-1,3-enyne complexes.[20] The only example structurally characterized was a η^6-1,3,5-dienyne–ruthenium complex, although this complex is unstable at room temperature.[20b] The possibility of preparing a 1-metallacyclopenta-2,3-diene structure has not been discussed for these complexes.[21]

We examined the structure of **8a** to shed light on this issue. The five-membered metallacycle plane is folded at the Zr–C4 bond in such a way that the compound looks like a 50/50 mixture of a 1-metallacyclopenta-2,3,4-triene and a 1-metallacyclopent-3-ene. The C2–C3 distance and the C2-C3-C4 angle are within the range of those observed for 1-metallacyclopenta-2,3,4-trienes (1.28–1.30 Å, 147–152°).[19a,22] The C3–C4 and C4–C5 distances, on the other hand, resemble those in 1-metallacyclopent-3-enes (1.38–1.40 and 1.45–1.47 Å, respectively), as does the C3-C4-C5 angle (122.7–123.5°).[14a] Summation of the three bond angles at C4 (358.4°) indicates its sp^2 character. On the basis of these considerations, the C3–C4 bond could be a double bond that is longer as a result of coordination to the metal, as observed in 1-zirconacyclopent-3-enes.

Wojcicki and co-workers reported a η^3-phenylallenyl zirconocene complex **9** (Table 1) for which they proposed a combination of η^3-propargyl and η^3-allenyl resonance structures.[23] The lengths C2–C3 and C3–C4 in **9** were 1.259 and 1.354 Å, respectively, with a C2-C3-C4 bond angle of 155.4°. The structural similarity of **8** and **9** implies that **8** should also have such resonance structures.

The chemical shifts in the ^{13}C NMR spectra of **8a**,**b** are summarized in Table 1. The two Cp rings in **8**, as well as the four aryl groups, are non-equivalent. We prepared ^{13}C-enriched **8** (**8-^{13}C$_4$**) with four ^{13}C atoms (> 99 %) at positions C2–C5 to enable the assignment of each signal on the basis of ^{13}C,^{13}C coupling constants.

Table 1: Chemical shifts [ppm] in the ^{13}C NMR spectra of **8a**,**b** and **9**.



	8a (R = Me)[a]	**8b** (R = SnMe$_3$)[a]	**9**[b]
C1	51.7	54.0	
C2	149.3	126.8	120.5
C3	128.8	123.3	114.1
C4	81.6	67.3	55.5
C5	185.6	187.7	
C6	146.6	141.3	
Cp	104.1 105.9	103.4 106.5	107.2

[a] Solvent: C$_6$D$_6$. [b] Solvent: CD$_2$Cl$_2$; ref. [23].

Signals for the central carbon atoms of allenes generally appear downfield, at around 200 ppm.[24] However, the signal for C3 appeared at 128.8 (**8a**) and 123.3 ppm (**8b**). These values seem inconsistent with an allene structure. Again, the chemical shifts observed for **8** were similar to those of **9**, for which the signal for the quaternary carbon C3 was observed at 114.1 ppm.

The observed ^{13}C,^{13}C coupling constants between C2 and C3 were 79 (**8a**) and 83 Hz (**8b**); the ^{13}C,^{13}C coupling constants between C3 and C4 were 73 (**8a**) and 65 Hz (**8b**). These values are smaller than the typical values for allenes (99–103 Hz)[25a,b] or acetylene (170 Hz), but a little larger than the value for ethylene (68 Hz).[25c] Although the $^1J_{C,C}$ values in bent allenes have not been studied well, the observed coupling constants may support the resonance structure in Equation (4). HMBC spectra showed that hydrogen atoms on the Cp rings couple with atoms C2 and C5, but not with C3 or C4, and thus suggest that the compound forms a five-membered ring. A weak absorption at 1604 cm^{-1}, which is characteristic of zirconium-coordinated alkynes (1611 cm^{-1} for $[Cp_2Zr(Me_3Si{-}C{\equiv}C{-}tBu)(thf)]$), was observed in the infrared spectrum of **8a**.[26]

Hydrocarbyl cyclopentynes are reported to have low energy barriers to racemization via biradical intermediates.[27] When **8a** was heated in $[D_8]$toluene to 100 °C, the coalescence of two Cp or two geminal aryl signals in the ^1H NMR spectrum was not observed. Thus, no racemization occurred; nor did **7** undergo racemization under these conditions.[28]

These results suggest that the complexes **8** would be better described as η^4-1,3-enyne complexes than as 1-zirconacyclopenta-2,3-dienes, although the latter structures might contribute to some extent. The structural description of the complexes must await further investigation. Structural data suggest that the Ru–η^6-1,3,5-dienyne complex of O'Connor et al. may also belong to the same category.[20b] The preparation of various derivatives of **3** and **8**, and investigations of their reactivity, are now in progress.

Experimental Section

Preparation of **8a**: Complex **3** (75.3 mg, 0.105 mmol) and KC_8 (46 mg; K atoms: 0.25 mmol) were suspended in THF (1.5 mL) at room temperature, and the resulting mixture was stirred for 1 h. The deep blue mixture was then cooled to −78 °C, and iodomethane (68 mg, 0.48 mmol) was added dropwise. The mixture immediately turned brown. It was warmed to room temperature and stirred for 1 h. ^1H NMR spectroscopy showed clean formation of **8a** (83 %). Volatiles were removed in vacuo, and the residue was dissolved in hexane. The solution was filtered, and the filtrate was concentrated and cooled at −30 °C to give **8a** as red crystals (53.2 mg, 68 %). ^1H NMR (600 MHz, C_6D_6, Me_4Si): $\delta = 1.08$ (t, $J = 7.6$ Hz, 3H), 1.12 (t, $J = 7.6$ Hz, 3H), 1.16 (t, $J = 7.6$ Hz, 3H), 1.18 (t, $J = 7.6$ Hz, 3H), 1.62 (s, 3H), 2.19 (s, 3H), 2.45 (q, $J = 7.6$ Hz, 2H), 2.51 (q, $J = 7.6$ Hz, 2H), 2.54 (q, $J = 7.6$ Hz, 2H), 2.58 (q, $J = 7.6$ Hz, 2H), 5.01 (s, 5H), 5.45 (s, 5H), 7.09 (d, $J = 8.5$ Hz, 2H), 7.11 (d, $J = 8.1$ Hz, 2H), 7.16 (d, $J = 7.5$ Hz, 2H), 7.16 (d, $J = 7.6$ Hz, 2H), 7.53 (d, $J = 8.1$ Hz, 2H), 7.62 (d, $J = 8.5$ Hz, 2H), 7.70 (d, $J = 7.6$ Hz, 2H), 7.73 ppm (d, $J = 7.5$ Hz, 2H).

Compound **8b** was prepared similarly by using trimethyltin chloride. (**Caution!** Trimethyltin chloride is highly toxic and must be handled in a fume hood.)

Crystallographic data of **8a**: $C_{50}H_{52}Zr$, FW = 744.18, monoclinic, space group $P2_1/c$ (no. 14), $a = 19.486(4)$, $b = 8.6745(14)$, $c = 23.967(4)$ Å, $\beta = 105.982(12)°$, $V = 3897.6(12)$ Å^3, $Z = 4$, $\rho_{calc} = 1.269$ gcm^{-3}, $\mu = 3.159$ cm^{-1}, $\lambda = 0.71073$ Å, $T = 90$ K, 8946 unique ($R_{int} = 0.071$) and 669 refined parameters, $R = 0.0457$, $wR^2 = 0.1107$.[9].

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Keywords: alkali metals · alkynes · allenes · cyclopentynes · zirconium

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