Dalton
Transactions

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View Article Online
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Cite this: *Dalton Trans.*, 2013, **42**, 14673

Received 5th June 2013,
Accepted 11th July 2013

DOI: 10.1039/c3dt51497h

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Formation and structural characterization of a five-membered zirconacycloallenoid[†,‡]

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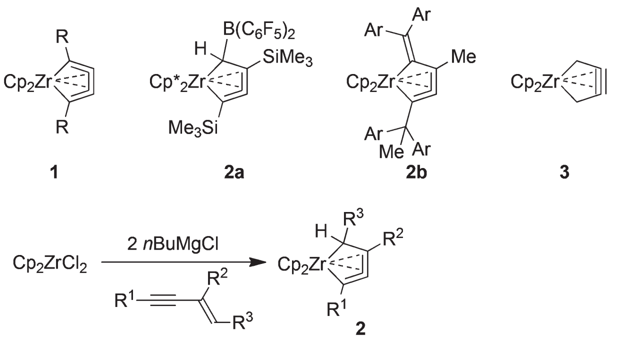
A conjugated enyne reacts with *in situ* generated zirconocene to yield a five membered zirconacycloallenoid that was characterized by X-ray diffraction.

Zirconocene complexes of conjugated dienes, enynes or diynes strongly favour metallacyclic five-membered ring structures over their conventional π-complex resonance forms, which indicates a very pronounced backbonding component for these Group 4 bent metallocene complexes.[1] Rosenthal's metallacyclocumulenes[2] (**1**) and Suzuki's metallacycloalkynes[3] (**3**) are very typical examples. Recently, we[4] and shortly thereafter Suzuki[5] had described the formation and structural characterization of two substituted examples of the zirconacycloallenoids (**2**) that were taking a position in between complexes **1** and **3** in this unique general class of compounds[6] (Scheme 1).

Conjugated diene zirconocenes can be synthesised by reacting the respective substituted butadiene magnesium reagents with, *e.g.*, Cp_2ZrCl_2[7] or by reductive coupling of bis(alkenyl)zirconocenes.[8] A convenient method is the trapping of a conjugated diene ligand by *in situ* generated zirconocene.[1,9] Both the latter reaction types had also been used to prepare 'Rosenthal-zirconacyclocumulenes' as well.[2] Suzuki and subsequently we had prepared examples of the zirconacycloallenoids by generating zirconocene by variants of the Negishi method[10] in the presence of conjugated enynes,[11] and we had used that to carry out typical subsequent reactions.[12] However, to the best of our knowledge, a simple derivative of the general complex class of the zirconacycloallenoids (**2**) had so far not been characterized by X-ray diffraction so that an ample structural description of these conceptual links between the well characterized metallacyclocumulenes (**1**) and the metallacycloalkynes (**3**) was still missing. We have now prepared a suitable example of a five-membered zirconacycloallenoid bearing only simple substituents and have characterized it by X-ray diffraction. We also carried out a few reactions of this compound (actually with an unusual outcome) that will be described in this paper.



Scheme 1

We treated Cp_2ZrCl_2 with two molar equivalents of *n*-butylmagnesium chloride in the presence of the enyne **4** (5.5 : 1 *trans–cis*-mixture, one equiv.). After keeping the mixture for 1 h at 60 °C, workup eventually gave compound **2c** as yellow-orange crystals in 58% yield.¶

The X-ray crystal structure analysis shows that the enyne **4** has become η^4-coordinated to the *in situ* generated zirconocene unit. It shows a central unit that is probably best described as a resonance hybrid between a Cp_2Zr(enyne) π-complex and a five-membered metallacycloallene (see Scheme 2). The bonds between the zirconium atom and the pair of former acetylene carbon atoms are short (Zr1–C1 2.304(8) Å, Zr1–C2 2.321(7) Å). The Zr–C(olefin) linkages are also rather short (Zr1–C3 2.446(8) Å, Zr1–C4 2.461(7) Å) but markedly longer than the former pair of Zr–C bonds (for comparison, the Zr–C(Cp) bond lengths of compound **2c** are in a range between 2.488(9) Å and 2.55(2) Å). The C1–C2 bond is still short at 1.269(10) Å, while the C3–C4 bond is slightly longer (1.415(11) Å), both reminding us of their acetylenic and

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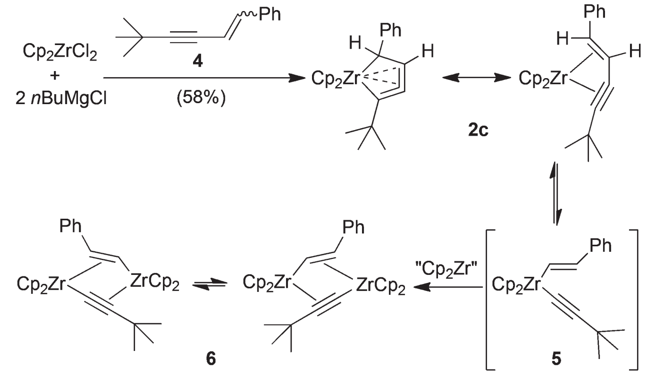
[†] Dedicated to Professor Carl Krüger on the occasion of his 80th birthday.

[‡] Electronic supplementary information (ESI) available: Experimental and analytical details. CCDC 938715–938717. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt51497h

[§] X-ray crystal structure analyses.



Scheme 2

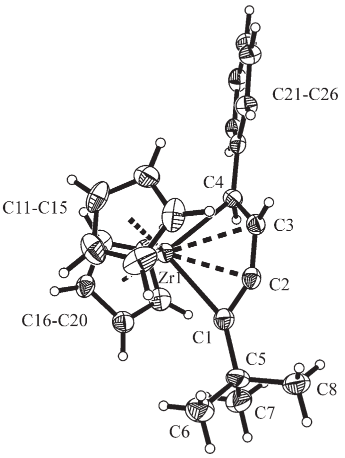


Fig. 1 A view of the molecular structure of the zirconacycloallenoid **2c** (thermal ellipsoids are shown with 30% probability).

olefinic origin, respectively. However, their connecting bond is remarkably short at an intermediate value between the former C–C pair at C2–C3 1.383(11) Å, as one would probably have expected it for a structure featuring some allenoid character (see Fig. 1). The central framework of the zirconacycloallenoid **2c** is non-planar.[4,5] It features a *trans*-arrangement of the substituents at the former carbon–carbon double bond (C3–C4): θ = C1–C2–C3–C4 −68.2(2)°, θ = C2–C3–C4–C21 −177.6(7)° (angles C2–C3–C4 121.7(8)°, C3–C4–C21 123.8(7)°, Zr1–C4–C21 133.9(5)°). The former acetylene moiety features a marked transoid distortion (θ = C3–C2–C1–C5 −173.1(13)°, angles C3–C2–C1 150.5(8)°, C2–C1–C5 132.8(7)°, Zr1–C1–C5 151.4(6)°).

In solution (C_6D_6), complex **2c** shows characteristic ^{13}C NMR resonances of the framework at δ 162.5 (C1), 116.7 (C2), 92.8 (C3) and 68.5 (C4). The corresponding 4-H ^{1}H NMR signal was observed at δ 2.72 and the adjacent 3-H signal at δ 5.04 (AX, $^{3}J_{HH}$ = 13.9 Hz). These values indicate a marked participation of the metallacyclic allenoid resonance structure as it is often observed for such zirconocene complexes. The Cp NMR features of complex **2c** occur at δ 5.39 and 4.87 (^{1}H, each 5H; ^{13}C: δ 104.8, 102.7) and the ^{1}H NMR ^{t}Bu signal is at δ 1.38.

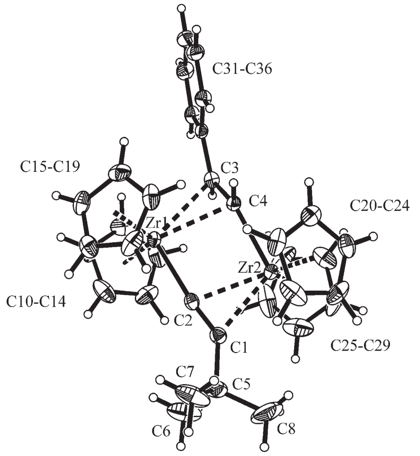
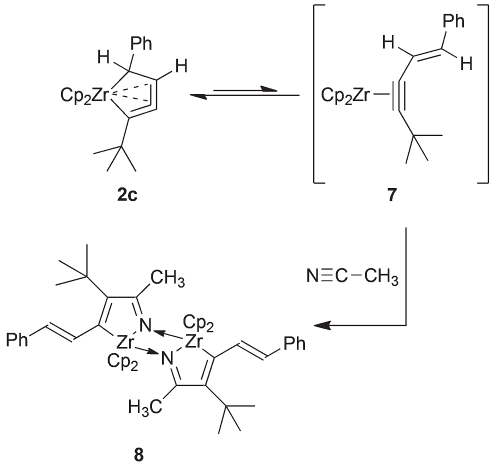


Fig. 2 Molecular structure of complex **6** (thermal ellipsoids are shown with 30% probability).

We generated Cp_2Zr in the presence of 0.5 molar equivalent of the enyne **4** and isolated a different compound, namely the alkynyl/alkenyl-bridged bis-zirconocene **6**. It was isolated in *ca.* 50% yield. We assume that in this reaction the zirconacycloallenoid **2c** is formed first and that this can then react with an additional Cp_2Zr equivalent *via* its (σ-alkenyl, σ-alkynyl)$ZrCp_2$ isomer **5** formed by C–C bond cleavage. Similar reactions had previously been observed in bis(alkynyl)zirconocene/‘Rosenthal-zirconacyclocumulene’ chemistry.[13]

Complex **6** was characterized by NMR spectroscopy and X-ray diffraction. The structural and spectroscopic features of the (alkyne)$ZrCp_2$ and (alkene)$ZrCp_2$ structural subunits of **6** are markedly different from those of the respective zirconacycloallenoid **2c**. The molecular structure of complex **6** shows an alkynyl ligand that is σ-bonded to Zr1 (Zr1–C2 2.181(4) Å) and π-bonded to Zr2 (Fig. 2). The bond lengths of this unit amount to 1.242(6) Å (C1–C2), 2.376(4) Å (Zr2–C1) and 2.403(4) Å (Zr2–C2). The C2–C1–C5 “substituent angle” of complex **6** was found at 140.8(5)° (Zr1–C2–C1 172.8(4)°). Zirconium atom Zr2 has the *trans*-styryl-ligand σ-bonded to it (Zr2–C4 2.258(4) Å, C3–C4 1.396(6) Å, θ = Zr2–C4–C3–C31 −162.2(4)°). This ligand is π-coordinated to Zr1 (Zr1–C3 2.576(5) Å, Zr1–C4 2.514(4) Å, angles Zr2–C4–C3 142.2(3)°, C4–C3–C31 128.6(4)°).

Compound **6** shows sharp NMR signals in solution at 213 K (C_7D_8). The ^{1}H/^{13}C NMR features of the pair of σ/π-ligands in **6** are quite different from those of the corresponding subunits of **2c**. Compound **6** shows the ^{13}C NMR resonances of the σ/π-acetylide moiety at δ 215.0 (C2) and δ 170.9 (C1), respectively. The ^{1}H NMR signals of the σ/π-*trans*-styryl ligand occur at δ 9.66 and 5.41 (AX, $^{3}J_{HH}$ = 19.7 Hz) with corresponding ^{13}C NMR resonances at δ 209.6 (C4) and 105.6, respectively. The chiral bis(zirconocene) complex **6** exhibits two pairs of diastereotopic Cp-ligands; consequently we have observed four sharp ^{1}H NMR Cp-signals (δ 5.43, 5.09, 5.02, 4.62). Increasing the monitoring temperature leads to a pairwise coalescence of the ^{1}H NMR Cp signals. This probably indicates a mutual exchange of the σ-alkenyl/σ-alkynyl pair of ligands between



Scheme 3

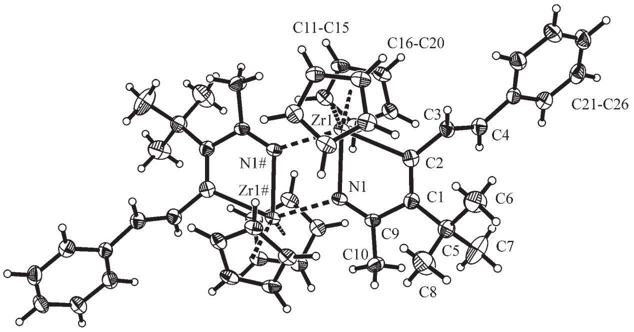


Fig. 3 Molecular structure of complex **8** (thermal ellipsoids are shown with 30% probability).

the pair of zirconocene units[9] (see Scheme 2) [$\Delta G^{\neq}_{\mathrm{rearr}}$(273 K) = 12.1 ± 0.2 kcal mol^{-1} (for details see the ESI‡)].

We[12b] and others[14] had previously shown that five-membered zirconacycloallenoids often insert organic nitriles into the Zr–C bond[15] with the formation of the corresponding seven-membered metallacycloallenoid products. Complex **2c** behaves differently. It seems that complex **2c** reacts with acetonitrile by means of a metallacyclic cycloaddition reaction *via* its reactive η^2-alkyne isomer **7** (see Scheme 3). Treatment of **2c** with acetonitrile overnight at r.t. gave product **8**. The X-ray crystal structure analysis shows the presence of the doubly unsaturated five-membered metallaheterocyclic cores (Zr1–N1A 2.247(5) Å, N1A–C9A 1.286(8) Å, C9A–C1A 1.498(9) Å, C1A–C2A 1.347(9) Å, Zr1–C2A 2.402(7) Å) to which the remaining *trans*-styryl substituent is bonded (C3A–C4A 1.337(10) Å, θ = C1A–C2A–C3A–C4A 69.1(11)°, θ = C2A–C3A–C4A–C21A 173.3(7)°, see Fig. 3). The overall structure of compound **8** is dimeric[16] with monomeric entities being connected by means of intramolecular Zr–N coordination (Zr1–N1# 2.359(5) Å, angle Zr1–N1A–Zr1# 109.7(2)°).

In solution the typical ^{1}H NMR features of the *trans*-styryl substituent have been observed (δ 7.36, 5.80, AX, $^3J_{\mathrm{HH}}$ = 15.8 Hz). The ^{13}C NMR resonance of the endocyclic N═C moiety was located at δ 193.4; the adjacent C═C bond shows its ^{13}C NMR resonances at δ 205.2 (ZrC═) and 148.7, respectively. Complex **8** shows a sharp ^{1}H NMR Cp resonance at δ 5.83 and the ^{t}Bu ^{1}H NMR signal at δ 1.42.

Conclusions

Our study has provided us with some detailed structural information about the very special class of the metallacycloallenoid complexes. It has revealed some interesting new reactivities, be it in its reaction with an additional zirconocene equivalent or the addition of acetonitrile. The metallacycloallenoids **2** occupy an interesting position between Rosenthal's metallacyclocumulenes **1** and Suzuki's metallacycloalkynes **3**. They seem to show an interesting chemical behavior towards unsaturated organic and organometallic reagents, as shown by the examples described in this study.

Acknowledgements

Financial support from the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Notes and references

¶Preparation of complex **2c**: *N*-butylmagnesium chloride (0.68 ml, 2 M diethyl ether solution, 1.36 mmol, 2 eq.) was added to a solution of bis(η^5-cyclopentadienyl)zirconium dichloride (200 mg, 0.68 mmol, 1 eq.) and enyne **4** (153 mg, 0.83 mmol, 1.2 eq.) in THF (8 ml) at −78 °C. After heating for 1 h at 60 °C, the volatiles of the deep red mixture were removed *in vacuo* and the residue was extracted with diethyl ether (3 × 10 ml). The red coloured filtrate was concentrated and cooled to −30 °C. Compound **2c** was obtained as yellow-orange crystals (161 mg, 58%). ^{1}H NMR (500 MHz, 299 K, [d_6]-benzene): δ = 7.26 (m, 2H, *m*-Ph), 7.21 (m, 2H, *o*-Ph), 6.98 (m, 1H, *p*-Ph), 5.39 (s, 5H, Cp$^{\mathrm{A}}$), 5.04 (d, $^3J_{\mathrm{HH}}$ = 13.9 Hz, 1H, 3-H), 4.87 (s, 5H, Cp$^{\mathrm{B}}$), 2.72 (d, $^3J_{\mathrm{HH}}$ = 13.9 Hz, 1H, 4-H), 1.38 (s, 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (126 MHz, 299 K, [d_6]-benzene): δ = 162.5 (C-1), 146.4 (i-Ph), 128.9 (*m*-Ph), 123.6 (*o*-Ph), 123.0 (*p*-Ph), 116.7 (C-2), 104.8 (Cp$^{\mathrm{A}}$), 102.7 (Cp$^{\mathrm{B}}$), 92.8 (C-3), 68.5 (C-4), 36.2 (^{t}Bu), 33.4 (^{t}Bu).

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