$\mathrm{Li[Cp_2Zr(C{\equiv}CPh)(\eta^2{:}1,2\text{-}PhC_2C{\equiv}CPh)]}$: an anionic zirconium(II) intermediate for carbon–carbon coupling

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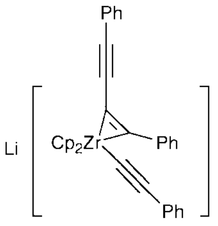
The unexpected anionic $\mathrm{Zr^{II}}$ complex $\mathrm{[Cp_2Zr(C{\equiv}CPh)(\eta^2{:}1,2\text{-}PhC_2C{\equiv}CPh)]^-}$ was isolated from $\mathrm{LiC{\equiv}CPh}$ and $\mathrm{Cp_2ZrCl_2}$ in THF, giving clear evidence for a CC coupling between two alkynyl moieties, one of them being η^2-bonded to the zirconium atom.

New prospects towards non linear optical (NLO) materials have induced, in recent years, a resurgence of interest in the chemistry of acetylenic transition metals complexes.[1] Numerous studies have focused on the CC coupling of the acetylenic moieties, which underlies the synthesis of the building block of the poly-ynes.[2] We have been interested in the reaction of vanadocene with poly-ynes.[3] An unexpected heterodimetallic complex $\mathrm{Cp_2V(\mu{:}\eta^2{:}\eta^4\text{-}PhC{\equiv}CC{\equiv}CPh))ZrCp_2}$, containing a butadiene framework with two internal planar tetracoordinate carbons was isolated from $\mathrm{Cp_2V}$ and $\mathrm{Cp'_2Zr(C{\equiv}CPh)_2}$ ($\mathrm{Cp'}$ = $\mathrm{C_5H_5}$, $\mathrm{C_5H_4Me}$, $\mathrm{C_5H_4Bu^t}$, $\mathrm{C_5H_4SiMe_3}$).[4,5] The chemistry of these bis(alkynyl)metallocene precursors has previously been detailed[6–8] and their synthesis, generally in diethyl ether solvent, well described.[6] On the other hand, a CC bond forming reaction was reported by Negishi *et al.*[9] as resulting from the reaction of $\mathrm{Cp_2ZrCl_2}$ with 3 equiv. of $\mathrm{LiC{\equiv}CPh}$ in THF followed by hydrolysis affording the isomerically pure (*Z*)-1,4-diphenylbut-1-ene-3-yne. In this process, $\mathrm{Li[Cp_2Zr(C{\equiv}CPh)_3]}$ was postulated as an intermediate species.[9] The authors underline the necessity of the third equiv. of $\mathrm{LiC{\equiv}CPh}$ to $\mathrm{Cp_2Zr(C{\equiv}CPh)_2}$ to produce the CC coupling. More recently, the $\mathrm{[Zr(C{\equiv}CR)_3]^-}$ anion moiety was suggested as being an intermediate species in the trimerization of *tert*-butyl acetylene to 1,3,6-tri(*tert*-butyl)fulvene.[10] We report here the X-ray structure of the intermediate anion species $\mathrm{Li[CpZr(C{\equiv}CPh)(\eta^2{:}1,2\text{-}PhC_2C{\equiv}CPh)]}$ and some aspects of its formation mechanism.



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When the reaction of $\mathrm{Cp_2ZrCl_2}$ with 2 equiv. of $\mathrm{LiC{\equiv}CPh}$ is carried out in THF, followed by slow diffusion of pentane, the unexpected $\mathrm{Zr^{II}}$ lithium salt species $\mathrm{Li[Cp_2Zr(C{\equiv}CPh)(\eta^2{:}1,2\text{-}PhC_2C{\equiv}CPh)]}$ **1**,† was obtained as a red crystalline complex and fully characterized by an X-ray structure determination (Fig. 1).‡ The main feature of this structure gives clear evidence for a CC coupling between two alkynyl moieties, one of them being η^2-bonded to the zirconium atom. A titanium complex related to **1**, namely $\mathrm{(C_5Me_5)_2Ti(\eta^2{:}1,2\text{-}RC_2C{\equiv}CR)]}$ was also recently isolated by Rosenthal *et al.* by Mg reduction of $\mathrm{(C_5Me_5)_2TiCl_2}$ in the presence of $\mathrm{Me_3SiC_4SiMe_3}$.[11a] Depending on the ratio of the reactants, this reaction also affords either the tweezer $\mathrm{Ti^{III}}$ complex $\mathrm{[(C_5Me_5)_2Ti(\eta^1\text{-}C{\equiv}CSiMe_3)_2][Mg(THF)Cl)]}$ (A) or $\mathrm{[(C_5Me_5)_2Ti((\eta^3\text{-}Me_3SiC_3{=}C(C{\equiv}CSiMe_3)SiMe_3]}$[11b] (B). The tweezer $\mathrm{Ti^{III}}$ complex (A) could be described as an intermediate for the formation of complex (B).

Different crossing reactions were monitored by ^{1}H NMR to gain an understanding of the formation of **1**.§ When the reaction of $\mathrm{Cp_2ZrCl_2}$ and 2 equiv. of $\mathrm{LiC{\equiv}CPh}$ is carried out in THF and in the absence on sunlight, $\mathrm{Cp_2Zr(C{\equiv}CPh)_2}$ **2** was obtained as the sole product and can be kept unchanged at least one week in the dark, whereas in presence of daylight only **1** is formed.[12] Starting from **2** and the solid lithium salt $\mathrm{LiC{\equiv}CPh}$ in THF-d_8, complete consumption of the Li salt gives **1** nearly immediately and quantitatively in absence or in presence of daylight. We checked that in the absence of daylight no reaction occurs in $\mathrm{C_6D_6}$ between **2** and $\mathrm{LiC{\equiv}CPh}$ (1 : 1) whereas still in the absence of daylight the addition of THF-d_8 in the NMR tube, which dissolves the lithium salt, immediately generates **1**.

Complementary hydrolysis experiments on complex **1** containing the preformed CC coupling were performed to ensure that the 1,4-diphenylbut-1-en-3-yne is also formed in this case. In presence of HCl and at room temperature, hydrolysis of **1** leads to the formation of *E* and *Z* isomers of the enyne $\mathrm{PhCH{=}CHC{\equiv}CPh}$ with a high selectivity when the reaction is carried out in toluene (toluene: *Z*:*E* = 98:2; THF: *Z*:*E* = 30:70).¶ Adding $\mathrm{LiC{\equiv}CBu^t}$ to **2** followed by HCl hydrolysis gives *Z* enynes, namely $\mathrm{PhCH{=}CHC{\equiv}CBu^t}$, $\mathrm{PhC{\equiv}CCH{=}CHBu^t}$ and $\mathrm{PhCHCHC{\equiv}CPh}$ (roughly 30, 15, 55% respectively, characterized by GC/MS and ^{1}H NMR).‖ This result suggests that the first step of the reaction is the formation of the

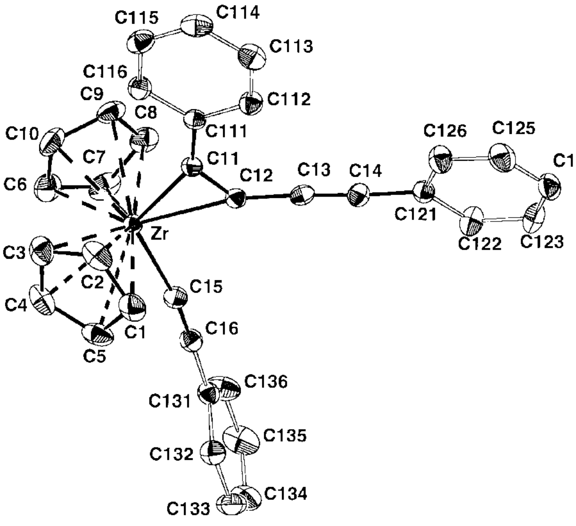

Fig. 1 Molecular structure of anionic $[\mathbf{1}]^-$ with selected bond distances (Å) and angles (°), hydrogen atoms omitted. Zr–C(11) 2.206(2), Zr–(C12) 2.342(1), Zr–C(15) 2.314(2), C(11)–C(12) 1.335(2), C(12)–C(13) 1.412(2), C(13)–C(14) 1.208(2), C(15)–C(16) 1.223(2), Zr–Cp 2.252(av.); Zr–C(11)–C(111) 147.8(1), Zr–C(15)–C(16) 171.9(1), Zr–C(12)–C(13) 127.9(1), C(12)–C(13)–C(14) 177.5(2), C(11)–Zr–C(12) 33.97(6), C(12)–Zr–C(15) 88.60(5), C(11)–Zr–C(15) 122.53(5), Zr–C(15)–C(16) 171.9(1), C(15)–C(16)–C(166) 176.3(2), Cp–Zr–Cp 129.57(av.) [Cp are the centroids of the $\mathrm{C_5H_5}$ rings C(1)–C(5), C(6)–C(10)].

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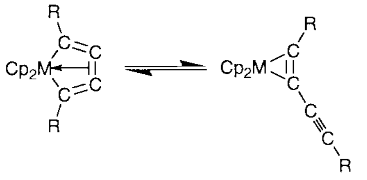

Scheme 1

Li[Cp$_2$Zr(C≡CPh)$_2$(C≡CBu^t)] intermediate which could give three possible species such as Li[Cp$_2$Zr(C≡CPh)(η^2:1,2-PhC$_2$C≡CBu^t)], Li[Cp$_2$Zr(C≡CPh)(η^2:1,2-Bu^{t}C$_2$C≡CPh] and Li[Cp$_2$Zr(C≡CBu^t)(η^2:1,2-PhC$_2$C≡CPh)], the formation of the latter being favoured by the presence of the less steric R = Ph group on the η^2 chain.**

The CC coupling between two alkynyl moieties from Cp′$_2$Zr(C≡CR)$_2$ (Cp′ = C$_5$H$_5$, R = Bu^t; Cp′ = C$_5$Me$_5$, R = Ph, SiMe$_3$) has already been demonstrated by Rosenthal *et al.*[11,13,14] This reaction occurs under *hν* irradiation or sunlight to give the zirconacyclocumulene complex Cp′$_2$Zr(η^4:1,2,3,4-RC=C=C=CR).†† Thus (C$_5$H$_5$)$_2$Zr(η^4:1,2,3,4-PhC=C=C=CPh) **3** should be an excellent candidate for explaining the formation of **1**. Starting from **3**, generated by *hν* daylight in THF-d$_8$ from **2**,[12] addition of one equiv. of LiC≡CPh gives **1**. This experiment is indicative of an equilibrium between the zirconacyclocumulene and a (η^2:1,2-PhC$_2$C≡CPh) containing species (Scheme 1) as already mentioned by Rosenthal *et al.*[13] Nevertheless the formation of the zirconacumulene species must be catalysed either by daylight, or by the B(C$_6$F$_5$)$_3$ borane,[15] or by the Cp$_2$V vanadocene for at least one day. By contrast, the formation of the (η^2:1,2-PhC$_2$C≡CPh) moiety in **1** is immediate in THF when adding the third LiC≡CPh equiv. to the bis(alkynyl)zirconocene complex. No catalytic reaction from **2** to **3** with LiC≡CPh as catalyst was observed by ^{1}H NMR.

At this stage we are not in a position to prove the involvement of LiC≡CPh in a photoassisted reaction with **2** leading to **1**. However, it is noteworthy that when the reaction is carried out in the dark, it yields only **2**. Our results clearly suggest that the alkynyl coupling reaction is induced by a third alkynyl ligand *via* the formation of the unstable ‘ate’ intermediate Zr^{IV} species Li[Cp$_2$Zr(C≡CPh)$_3$], or an assumed tweezer Zr species [Cp$_2$Zr(C≡CPh)$_2$][Li(C≡CPh)], which may subsequently rearrange to **1**.[16]

Notes and references

† *Spectroscopic data* for C$_{42}$H$_{41}$LiO$_2$Zr **1**: M = 675.9, Calc: C, 74.55; H, 6.06. Found: C, 74.72; H, 5.86%; (40% yield based on 2 equiv. LiC≡CPh; 75% yield when the reaction is performed with 3 equiv. LiC≡CPh). IR (Nujol): ν(C≡C) 2063, 2110 cm^{-1}; ^{1}H NMR (C$_6$D$_6$, δ/ppm) 8.26 (pseudo triplet, 2H, *o*-Ph from the η^2-PhC$_2$-bonded to the zirconium atom), 7.54–6.9 (m, 13H, Ph), 5.78 (s, 10H, Cp), 3.36, 0.95 (m, 16H, THF). A ^{1}H NMR VTP of the complex from −80 to +80 °C does not show any change in the solution structure. Assignement of the ^{13}C NMR spectrum of **1** in THF-d$_8$ (δ/ppm, J(Hz)) could be tentatively done with a JMOD and 2D heteronuclear correlation technique (inverse HMQC (LR), gradient selected). Li[Cp$_2$Zr(C$_\alpha$≡C$_\beta$Ph)(η^2-PhC$_a$≡C$_b$-C$_c$≡C$_d$Ph)], **1**: 205.9 (s, $^3J_{CH}$ = 4 Hz, C$_b$), 134.9, 130.4, (s, C$_a$/C$_\alpha$), 97.6 (s, C$_c$), 126.4/107.4 (t, $^3J_{CH}$ = 4–5 Hz, C$_\beta$/C$_d$), 142.5, 127.9, 128.3 (t, ^2J = 7–8 Hz, C$_{ipso}$), 130.8, 129.8, 129.0, 128.4, 128.2, 128.0, 126.1, 126.0, 125.8 (d, $^1J_{CH}$ = 158–162 Hz, Ph), 105.0 (d, $^1J_{CH}$ = 171 Hz, Cp).

‡ *Crystallographic data* for **1**: C$_{34}$H$_{25}$LiZr·2THF M = 675.95, monoclinic, space group $P2_1/c$, a = 14.986(2), b = 10.4594(8), c = 22.028(2) Å, β = 102.07(1)°, V = 3376(1) Å^3, D = 1.33 g cm^{-3}, μ = 3.61 cm^{-1}, R(Rw) = 0.0272 (0.0722) for 4701 unique data and 415 parameters, G.O.F. = 1.04. Data collection were performed at *ca.* 160 K on a IPDS STOE diffractometer using graphite monochromatized Mo-Kα radiation. The structure was solved by direct methods and subsequent difference Fourier maps. CCDC 182/1708. See htpp://www.rsc.org/suppdata/cc/b0/b004478o/ for crystallographic files in .cif format.

§ A suspension of Cp$_2$ZrCl$_2$ (0.900 g, 3.08 mmol) was treated with 2 equiv. solid LiC≡CPh (0.665 g, 6.16 mmol) in benzene for 4 h and species such as Cp$_2$ZrCl$_2$, Cp$_2$ZrCl(C≡CPh) and **2** were identified by ^{1}H NMR (in nearly 1:4:1 ratio respectively). After 24 h stirring and work-up, **2** was obtained as a crystalline solid (0.840 g, 64% yield). With 3 equiv. LiC≡CPh for 24 h, in the same experimental conditions, a red solution is obtained with the appearance of a paramagnetic Zr^{III} species (g = 1.997, a(^{91}Zr) = 37 G, 20%) which broadens the ^{1}H NMR signals of the solution (the main peak observed at 5.6 ppm could not be assigned). Different experiments were conducted in THF and in absence of daylight (to avoid the formation of the zirconacyclocumulene species) between (C$_5$H$_4$R)$_2$Zr(C≡CPh)$_2$ (R = Me, SiMe$_3$) and LiC≡CPh. ^{13}C NMR spectroscopy shows the characteristic peak of the (η^2:1,2-PhC$_2$C≡CPh) moiety at 208 and 205 ppm for R = Me and SiMe$_3$, respectively which suggests the *in situ* formation of Li[(C$_5$H$_4$R)$_2$Zr(C≡CPh)(η^2:1,2-PhC$_2$C≡CPh)] (R = Me, SiMe$_3$) (for Cp*$_2$Ti(η^2:1,2-Me$_3$SiC$_2$C≡CSiMe$_3$[11] two peaks were observed at 227 and 205 ppm). Hydrolysis of the THF mixture with HCl gives the *Z/E* enynes (30:70).

¶ It is of note that Cp$_2$ZrCl$_2$ + 3 equiv. LiC≡CPh in toluene at room temperature for 24 h selectively affords, after hydrolysis, the *Z* isomer whereas the same reaction carried out in THF gives a mixture of *Z/E* isomers (40:60). The *Z* isomer was selectively obtained in THF when the reaction is carried out at −80 °C.[9]

‖ Hydrolysis experiments with HCl on (C$_5$H$_4$R)$_2$Zr(η^4:1,2,3,4-PhC=C=C=CPh) (R = H, Me, SiMe$_3$) give in toluene or in THF solution nearly 100% of the *E* isomer PhCH=CH-C≡CPh, in contradiction with the described results in which the η^2 coordination is involved.

** LiC≡CBu^t was added to **2** in THF; after stirring for 4 h, the solvent was evaporated to dryness and replaced by toluene. Hydrolysis with HCl (3 equiv. in solution in diethyl ether) gives Z enynes; ^{1}H NMR (δ/ppm, CDCl$_3$, 250 MHz), MS: PhCH=CHC≡CBu^t: 6.55, 5.69, (d, CH=CH, J = 12 Hz), 1.32 (s, Bu^t), MS: 184; PhC≡CCH=CHBu^t: 5.87, 5.60, (d, CH=CH, J = 12 Hz), 1.26 (s, Bu^t), MS: 184; PhCH=CHC≡CPh: 6.70, 5.92, (d, CH=CH, J = 12 Hz), MS: 204. When HCl hydrolysis was performed in THF, a mixture of *Z/E* enynes was observed by GC/MS but not further characterized.

†† ^{1}H and ^{13}C{^{1}H} NMR of the reaction show complex spectra in which three main cyclopentadienyl signals can be observed at 5.76, 5.71, 5.67/105.0, 104.9, 104.7 ppm; low field quaternary carbons at 228, 225.9, 208.2, 205.9, 203, 202 ppm were also observed.

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