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Preliminary Communication

Formation of [cp$_2$Zr(C=C–SiMe$_3$)]$_2$ from the reaction of zirconocene with trimethylsilylacetylene

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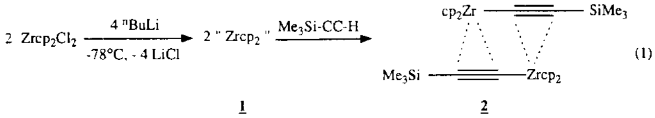
Abstract

Zirconocene, generated *in situ*, reacts with trimethylsilylacetylene to form the dimeric complex [cp$_2$Zr(C ≡ C–SiMe$_3$)]$_2$ as a byproduct. This compound has been fully characterized and its solid-state structure established by an X-ray single crystal structure analysis.

Since Negishi and coworkers [1] devised an easy experimental procedure for the *in situ* generation of zirconocene, "cp$_2$Zr" (**1**), there has been a considerable synthetic interest in its reactions. It has proved to be useful not only for organic synthesis [2], but also for the formation of new Main Group heterocycles [3] as well as for the bicyclization of phosphaalkynes [4]. Although the reaction tolerates many functional groups (R$_3$Si, R$_3$Sn, amino, ether and sulfoxy groups have been employed) and can be carried out in various solvents (hydrocarbons and ethers give very similar yields) [2,5], and (by use of ^{t}BuLi [6]) can be applied to alkenes as successfully as to alkynes RC≡CR′, no identifiable products have ever been isolated from the reaction of "cp$_2$Zr" with 1-H-alkynes, so that it has been stated that "it is therefore necessary to use terminally substituted alkyne derivatives" [2a].

However, when we treated zirconocene **1** with two equivalents of trimethylsilylacetylene following standard procedures, we were able to isolate 1.1% of the dimeric complex [cp$_2$Zr(C≡C–SiMe$_3$)]$_2$, as dark-brown crystals after recrystallization of the product mixture at −78°C from toluene/hexane (1:1) [7*]. The dimeric nature of the complex was established by an X-ray single crystal structure analysis [8*] (see Fig. 1).



Scheme 1.

The two zirconium atoms and the atoms C1, C2, C6, C7 form a plane (maximum deviation 2.4 pm), and the Zr2–C6–C7 plane is folded by 5.4° relative to the Zr1–C1–C2 plane. The zirconium atoms lie almost symmetrically over their π-bonded alkyne moiety, with Zr–C bond lengths ranging from 239.9(5) to 242.6(5) pm. This is in sharp contrast with the analogous Ti compound [cp$_2$Ti(C≡C–SiMe$_3$)]$_2$ [9], in which the Ti–C2 bond is more than 7 pm shorter than the Ti–C1 bond. However, most of the other features, including bond angles and the C≡C triple bond length, are fairly similar in the two structures. Erker and coworkers reported the first example of a dimeric phenylethinyl-zirconocene complex **3** in 1986 [10]. Their compound, which

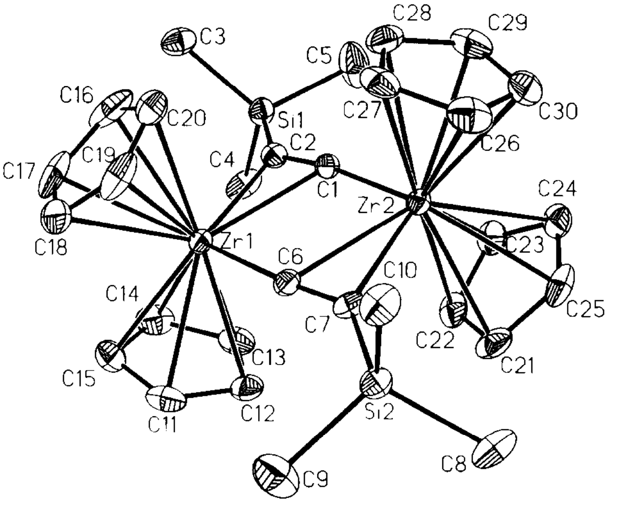


Fig. 1. ORTEP plot of **1**. Selected bond lengths (Å) and angles (°) are: Zr1–C2 2.399(5), Zr1–C1 2.420(5), Zr1–C6 2.191(5), Zr2–C7 2.407(5), Zr2–C6 2.426(5), Zr2–C1 2.191(5), Si1–C2 1.846(5), Si1–C4 1.852(7), Si2–C7 1.845(5), Si1–C2 1.846(6), Zr1–Zr2 3.522(2), C1–C2 1.249(7), C6–C7 1.260(7); Zr1–C2–C1 75.9(3), C1–Zr1–C2 30.0(2), Zr1–C2–Si1 141.4(3), Si1–C2–C1 142.5(4), Zr2–C1–C2 172.7(4), Zr1–C1–Zr2 99.5(2).

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* References with asterisk indicates a note in the list of references.

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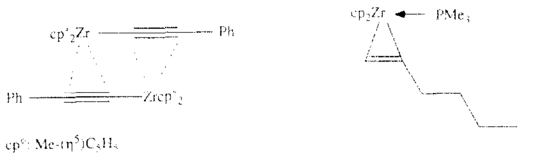

3 4

Scheme 2.

was prepared in 60% yield by the reaction of a bis(alkynyl)zirconocene with the zirconocene-butadiene complex has essentially the same structural parameters as **2**.

When the structural parameters of **2** are compared with those of the zirconocene-1-hexyne-trimethylphosphine adduct **4** [11] it is obvious that **2** is better described as an alkyne-π-complex with fairly long Zr–C π-bonds and a C≡C triple bond length of about 125 pm, whereas **4** shows a longer C≡C bond (128.6(5) pm) and shorter Zr–C bond lengths (221.1(3) and 224.4(3) pm). These are even shorter than the Zr–C distances in 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenyl-zirconacyclopentadiene [12].

The conclusion that **2** should be described as a dimeric zirconium-alkyne π-complex rather than as a zirconacyclopropene is further supported by a comparison of the infrared data for **2** and **4**: The C≡C triple bond stretching frequency is lowered, to 1751 cm^{-1} ($[cp_2Ti(C{\equiv}C{-}SiMe_3)]_2$: 1798 cm^{-1}), from that for the free alkyne, but is 1660 cm^{-1} in the trimethylphosphine-zirconacyclopropene adduct **4** (expected for C=C double bonds: 1680–1620 cm^{-1}).

Although the mechanism of the formation of **2** remains unclear, the isolation and characterization of this $[cp_2Zr(C{\equiv}C{-}SiMe_3)]_2$ complex from the reaction of zirconocene with trimethylsilylacetylene is of considerable interest, since to our knowledge the product is the first characterized compound from the zirconocene-mediated reaction with unsubstituted 1-H-alkynes.

Acknowledgements

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References and notes

1 E. Negishi, F.E. Cederbaum and T. Takahashi, *Tetrahedron Lett.*, *27* (1986) 2829.

2 E. Negishi, S.J. Holmes, J.M. Tour, J.A. Miller, F.E. Cederbaum, D.R. Swanson and T. Takahashi, *J. Am. Chem. Soc.*, *111* (1989) 3336; A.S. Guram and R.F. Jordan, *Organometallics*, *10* (1991) 3470. For two reviews, see also E. Negishi and T. Takahashi, *Synthesis*, (1988) 1 and S.L. Buchwald and R.B. Nielsen, *Chem. Rev.*, *88* (1988) 1047.

3 P.J. Fagan, E.G. Burns and J.C. Calabrese, *J. Am. Chem. Soc.*, *110* (1988) 2979; P.J. Fagan and W.A. Nugent, *J. Am. Chem. Soc.*, *110* (1988) 2310; S.C. Sendlinger, B.S. Haggerty, A.L. Rheingold and K.H. Theopold, *Chem. Ber.*, *124* (1991) 2453.

4 P. Binger, F. Wettling, R. Schneider, F. Zurmühlen, U. Bergsträßer, J. Hoffmann, G. Maas and M. Regitz, *Angew. Chem.*, *103* (1991) 208, *Angew. Chem., Int. Ed. Engl.*, *30* (1991) 207.

5 F. Mohamadi and M.M. Spees, *Organometallics*, *11* (1992) 1398.

6 D.R. Swanson and E. Negishi, *Organometallics*, *10* (1991) 825.

7 To a solution of 2.92 g (10 mmol) of $Zrcp_2Cl_2$ (Merck, Darmstadt) in 40 mL of dry THF (distilled under dinitrogen from K/benzophenone) at −78°C was slowly added 11.8 mL (18.9 mmol) of ^{n}BuLi in hexane. After 2 h stirring at −78°C, a solution of 1.90 g (2.68 mL, 19.4 mmol) of trimethylsilylacetylene (Merck) in 5 mL of dry THF was added, and the mixture slowly warmed to room temperature. After 16 h stirring insoluble materials were removed by filtration under N_2, the THF was distilled from the filtrate *in vacuo*, and the residue was dissolved in 10 mL of dry toluene/hexane (1 : 1). When the clear brown solution was cooled to −78°C, 0.07 g (0.11 mmol, 1.1%) of clear red-brown crystals were obtained, along with a microcrystalline orange-red precipitate that showed several NMR signals in the cp- and in the Me_3Si-region but could not be identified or further separated. Crystals of **2** gave the following data: m.p. 210°C (dec.). IR (nujol/hostaflon): 2951 (m), 1751 (s), 848 (s), 791 (s) cm^{-1}. ^1H NMR (C_6D_6): $\delta = 0.40$ (s, 18 H), 5.21 (s, 20 H). ^{13}C NMR (C_6D_6): $\delta = 1.8$, 102.5 (cp). Since there was only very little material available, not all ^{13}C NMR signals could be detected. Anal. calc. for $C_{30}H_{38}Si_2Zr_2$ (637.53 g/mol): C, 56.55; H, 6.01. Found: C, 53.20; H, 5.78.

8 Crystal structure determination: Crystal size: 0.4 × 0.45 × 0.55 mm^3, monoclinic space group $P2_1/n$, $a = 11.521(6)$ Å, $b = 15.340(5)$ Å, $c = 16.565(7)$ Å, $\beta = 95.92(4)°$, $V = 2912(2)$ Å^3, $Z = 4$ for $C_{30}H_{38}Si_2Zr_2$ (637.2 g/mol) and $\rho_{calc} = 1.453$ Mg/m^3. Data collection was carried out with a Siemens-Nicolet R3m/V four circle diffractometer and Mo-Kα radiation (graphite monochromator) at 298 K. 2 standard reflections were measured every 48 reflections and did not change significantly during the measurement. With ω-scans, 0.9° scan range, $2\theta = 3$–48° and scan speed 2.00–29.30°/min, 4830 reflections were collected in h, k, $+/-l$, of which 4580 proved independent ($R_{int} = 2.44\%$) and 3671 reflections with $F > 3\sigma(F)$ were considered observed. A semi-empirical correction for absorption was carried out, min/max transmision 0.6152/0.6391. Structure solution: Direct methods and full-matrix least-squares refinement, function $\Sigma w(|F_o| - |F_c|)^2$ minimized. The refinement converged (hydrogen atoms riding model with fixed isotropic U, all other atoms anisotropic, weighting scheme $w^{-1} = \sigma^2(F) + 0.0002F^2$), 307 parameters refined, 12:1 data/parameter ratio) at a final $R = 4.34\%$, $R_w = 4.35\%$ (obs. data). The remaining difference Fourier analysis was featureless. All calculations were performed on a MicroVAX II and a personal computer with the SHELXTL PLUS programme package. Further details of the crystal structure determination are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number (obtainable from the authors), the names of the authors, and the journal citation.

9 U. Rosenthal and H. Görls, *J. Organomet. Chem.*, *439* (1992) C36. The Ti-compound was originally reported by G.L. Wood, C.B. Knobler and M.F. Hawthorne, *Inorg. Chem.*, *28* (1989) 382, but Rosenthal and Görls apparently obtained crystals of superior quality, so their more accurate data are used in this paper.
10 G. Erker, W. Frömberg, R. Mynott, B. Gabor and C. Krüger, *Angew. Chem.*, *98* (1986) 456, *Angew. Chem., Int. Ed. Engl.*, *25* (1986) 463.
11 T. Takahashi, D.R. Swanson and E. Negishi, *Chem. Lett.*, (1987) 623.
12 W.E. Hunter and J.L. Atwood, *J. Organomet. Chem.*, *204* (1981) 67.