# Dimethylallenediyl as an $\eta^1,\eta^2$-Bridging Ligand in a Dizirconocene Complex

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Treatment of ($\eta^2$-ethene)(trimethylphosphane)zirconocene **1** with 3,3-dimethylcyclopropene **2** leads to the formation of a new type of bis(ethylzirconocene) complex **3** with 3,3-dimethylallenediyl as a $\mu^1,\mu^2$-bridging ligand; the crystal structure of **3** is determined by X-ray analysis.

The multifunctional behaviour of cyclopropenes is now well documented.[1] They can act either as $\eta^2$-ligands in low-valent transition metal complexes by complexation of the strained C–C double bond[2] or as $\eta^1$-ligands resulting from opening of the three-membered ring. In the latter case, metallacyclo-butenes[3] or vinylcarbene metal complexes[4] are formed. The ability of cyclopropenes to act as proton donors has been observed in organometallic chemistry only in metallation reactions with main group metallorganic compounds, *e.g.* butyllithium, LDA (lithium diisopropylamide) or Grignard reagents.[1]
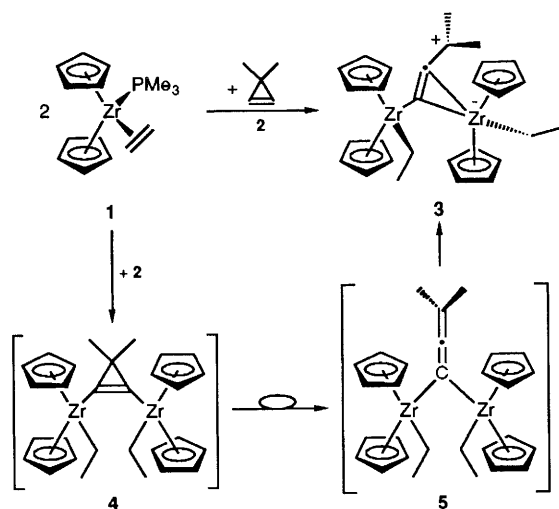
We now report for the first time the protonation of an $\eta^2$-ethene metal complex by a cyclopropene to give an ethylmetal compound. Two molecules of $\eta^2$-ethene zircon-ocene, prepared *in situ* from its trimethylphosphane complex **1** by addition of one equivalent of triethylborane, reacts with one equivalent of 3,3-dimethylcyclopropene **2** at room temperature with formation of the new 1,1-(ethylzirconocenyl)-allene complex **3** in 56% yield as yellow crystals. The characteristic feature of compound **3** is the bridging 3,3-

dimethylallenediyl group which forms a single bond to one zirconium atom and an $\eta^2$-bond to the other one, Scheme 1.

The formation of complex **3** is best explained by invoking the intermediate of the dizirconated cyclopropene **4**, which rearranges immediately to give the product **3**. Support for this assumption is given by the observation that 1,2-dilithio-3,3-diphenylcyclopropene rearranges spontaneously to 1,1-di-lithio-3,3-diphenylallene[5] whereas 1,2-dilithio-3-phenyl-3-methylcyclopropene can be prepared at 0 °C in diethyl ether.[6] Both dilithio compounds react with dichlorotitanocene in the presence of trimethylphosphane to yield the corresponding allenylidene(trimethylphosphane)titanocenes.[5] It is note-worthy that the more acidic acetylene and alk-1-ynes react with complex **1** through oxidative coupling to give zircona-cyclopentene derivatives whereas ethanol protonates the $\pi$-bonded ethene in **1** to yield ethylethoxyzirconocene.[7]
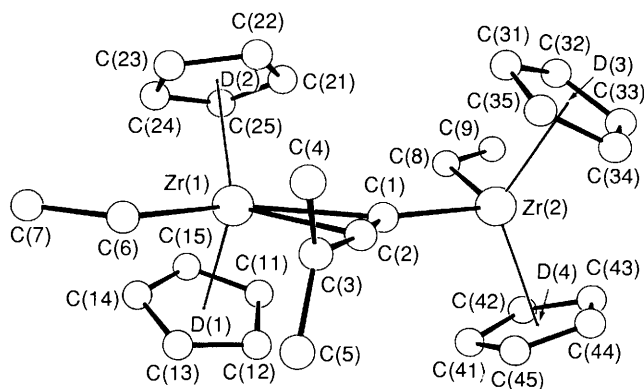
It is also worth mentioning that other $\eta^2$-alkene or $\eta^2$-alkyne zirconocene complexes react with **2** in a different manner. For example, the reaction of the $\eta^2$-butene(trimethylphos-phane)zirconocene leads to replacement of butene by **2**[4] whereas alkyne(trimethylphosphane)zirconocene and **2** gives a 2-zirconabicyclo[3.1.0]hex-3-ene derivative through oxida-tive coupling.[8]

Crystallographic and spectroscopic studies have been car-ried out to characterize the static and dynamic behaviour of complex **3**. The result of the crystal X-ray study† is shown in Fig. 1. This reveals an asymmetric bonding mode of the



**Scheme 1**

**Fig. 1** Molecular structure of **3**: selected distances (Å) and angles (°): Zr(1)–C(1) 2.433(4), Zr(1)–C(2) 2.420(4), Zr(1)–C(6) 2.368(4), Zr(2)–C(1) 2.245(4), Zr(2)–C(8) 2.286(4), C(1)–C(2) 1.256(5), C(2)–C(3) 1.352(6), C(3)–C(4) 1.503(8), C(3)–C(5) 1.499(7), C(6)–C(7) 1.541(6), C(8)–C(9) 1.514(7); D(2)–Zr(1)–D(1) 127.2(1), C(6)–Zr(1)–C(1) 128.3(1), C(2)–Zr(1)–C(1) 30.0(1), D(4)–Zr(2)–D(3) 129.4(1), C(8)–Zr(2)–C(1) 103.9(2), C(2)–C(1)–Zr(2) 138.9(3), C(2)–C(1)–Zr(1) 74.5(2), Zr(2)–C(1)–Zr(1) 146.7(2), C(3)–C(2)–C(1) 167.8(4), C(3)–C(2)–Zr(1) 92.3(3), C(1)–C(2)–Zr(1) 75.6(2), C(7)–C(6)–Zr(1) 120.4(3), C(9)–C(8)–Zr(2) 123.7(3)



**Scheme 2**
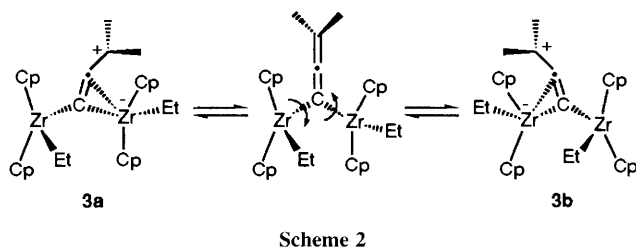
allenediyl ligand to the two zirconium atoms. Zr(2) is bonded by a shortened Zr(2)–C(1) bond [2.245(4) Å], whereas Zr(1) shows a π-interaction with C(1) and C(2) [Zr(1)–C(1) 2.433(4), Zr(1)–C(2) 2.420(4) Å]. Only a small interaction may exist between Zr(1) and C(3) because of the large separation [Zr(1)–C(3) 2.819(5) Å] of these two atoms. The allenediyl fragment is distinctly bent toward Zr(1) [C(1)–C(2)–C(3) angle, 167.8(4)°] compared to the strictly linear arrangement adopted by σ,σ-bonded allene derivatives. The special bonding situation in this molecule is also reflected in high Zr(1)–C(1)–Zr(2) [146.7(2)°] and Zr(2)–C(1)–C(2) [138.9(3)°] angles, a small Zr(1)–C(1)–C(2) [74.5(2)°] angle and in the distances C(1)–C(2) [1.256(5) Å] and C(2)–C(3) [1.352(6) Å], which correspond to a π-bonded triple bond[9] and a double bond. The two methyl substituents are situated perpendicular to the Zr$_2$ [μ-C(1)] plane.

The 200 MHz ^{1}H and 50.5 MHz ^{13}C NMR spectra of **3**‡ at 30 °C reveal only one set of ethyl signals and one Cp-signal (Cp = cyclopentadienyl). Provided that the solid-state structure is retained in solution, a rapid exchange of the environment of

the Cp(Et)Zr-fragment on the NMR time scale must be taking place as shown in Scheme 2. However, the only direct evidence of such an exchange is a slight broadening of the methylene carbon signal of the ethyl groups in the 75.5 MHz ^{13}C NMR spectrum at −80 °C. All other signals remain sharp at this temperature.

In the literature, several examples of mononuclear allenylidene metal complexes of Ru,[10] Cr, W,[11] Mn[12] and Ti[5] are described and also dinuclear metal complexes of the allene fragment with different kinds of metal–carbon bonding are referred to.[13] All of the hitherto reported dinuclear allene complexes are prepared by methods different from the presently described synthesis of **3** nor is the bonding mode of the two zirconium atoms in **3** comparable with those of the previously reported bimetallic allene derivatives.

## References

1 For recent reviews, see: B. Halton and M. G. Banwell in *The Chemistry of the Cyclopropyl Group*, ed. Z. Rappoport, Wiley, 1987, p. 1224; M. S. Baird, *Top. Curr. Chem.*, 1988, **144**, 137; P. Binger and H. M. Büch, *Top. Curr. Chem.*, 1987, **135**, 77.

2 J. P. Visser, A. J. Schipperijn, L. Lukas, R. Bright and J. J. de Boer, *J. Chem. Soc., Chem. Commun.*, 1971, 1266; L. S. Isaeva, T. A. Peganova, P. V. Petrovskii, I. G. Bolesov and D. N. Kravtsov, *Izv. Akad. Nauk SSSR*, 1987, 2053; *Engl. Transl.*, 1988, 1904; L. S. Isaeva, T. A. Peganova, P. V. Petrovskii and D. N. Kravtsov, *Organomet. Chem., USSR*, 1989, **2**, 221; C. G. Kreiter, M. Wenz and W. Michels, *Z. Naturforsch, Teil B*, 1989, **44**, 1247.

3 R. C. Hemond, R. P. Hughes, D. J. Robinson and A. L. Rheingold, *Organometallics*, 1988, **7**, 2239; R. P. Hughes, M. E. King, D. J. Robinson and J. M. Spotts, *J. Am. Chem. Soc.*, 1989, **111**, 8919; R. P. Hughes and D. J. Robinson, *Organometallics*, 1989, **8**, 1015; P. Binger, P. Müller, A. T. Herrmann, P. Philipps, B. Gabor, F. Langhauser and C. Krüger, *Chem. Ber.*, 1991, **124**, 2165.

4 P. Binger, P. Müller, R. Benn and R. Mynott, *Angew. Chem.*, 1989, **101**, 647; *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 610; H. Fischer, J. Hofmann and E. Mauz, *Angew. Chem.*, 1991, **103**, 1013; *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 998; for vinylketene complex formation via CO insertion into a vinylcarbene complex see: M. G. Newton, N. S. Pantaleo, R. B. King and C. K. Chu, *J. Chem. Soc., Chem. Commun.*, 1979, 10; P. Binger, B. Cetinkaya and C. Krüger, *J. Organomet. Chem.*, 1978, **159**, 63; G. Detlaf, U. Behrens and E. Weiss, *Chem. Ber.*, 1978, **111**, 3019; T. Valéri, F. Meier and E. Weiss, *Chem. Ber.*, 1988, **121**, 1083.

5 P. Binger, P. Müller, R. Wenz and R. Mynott, *Angew. Chem.*, 1990, **102**, 1070; *Angew. Chem., Int. Ed. Engl.*, 1990, **29** 1037.

6 P. Binger and R. Wenz, unpublished results.

7 H. G. Alt and C. E. Denner, *J. Organomet. Chem.*, 1989, **368**, C15.

8 P. Binger, P. Müller and F. Langhauser, unpublished results; see P. Müller, Dissertation, University of Kaiserslautern, 1989; F. Langhauser, Dissertation, University of Kaiserslautern, 1991.

9 S. L. Buchwald and R. B. Nielson, *Chem. Rev.*, 1988, **88**, 1047.

10 J. P. Selegue, *Organometallics*, 1982, **1**, 217; H. LeBozee, K. Ouzzine and P. H. Dixneuf, *J. Chem. Soc., Chem. Commun.*, 1989, 219; A. Romero, D. Peron and P. H. Dixneuf, *J. Chem. Soc., Chem. Commun.*, 1990, 1410.

11 E. O. Fischer, H. J. Kalter, A. Frank, F. H. Köhler and G. Huttner, *Angew. Chem.*, 1976, **88**, 683; *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 623.

12 H. Berke, *Angew. Chem.*, 1976, **88**, 684; *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 624; H. Berke, *Chem. Ber.*, 1980, **113**, 1370.

13 H. Berke, *J. Organomet. Chem.*, 1980, **185**, 75; H. Berke, P. Härter, G. Huttner and L. Zsolnai, *Chem. Ber.*, 1982, **115**, 695; N. E. Kolobova, L. L. Ivanov, O. S. Zhvanko, G. G. Aleksandrov and Y. T. Strukhov, *J. Organomet. Chem.*, 1982, **228**, 265; S. F. T. Froom, M. Green, R. J. Mercer, K. R. Nagle, A. G. Orpen and S. Schwiegk, *J. Chem. Soc., Chem. Commun.*, 1986, 1666.

‡ *Selected NMR spectroscopic data* for **3**: [1]H (200 MHz, [2H$_8$]THF; 30 °C) δ 5.86 (s, 5H, C$_5$H$_5$), 1.44 (t, 6H, *Me*CH$_2$), $J_{HH}$ 7.6 Hz), 1.30 (s, 6H, Me), 0.72 (q, 4H, *CH$_2$*Me); [13]C (50.5 MHz, [2H$_8$]THF, 30 °C), δ 168.6 (C$_α$). 141.6 (C$_β$), 75.3 (C$_γ$), 18.3 (CH$_3$, $J_{CH}$ 123 Hz), 34.3 (*CH$_2$*Me, $J_{CH}$ 117 Hz), 21.9 (*Me*CH$_2$, $J_{CH}$ 126 Hz), 109.5 (C$_5$H$_5$, $J_{CH}$ 172 Hz).