Communications

Preparation and X-ray Structure of $[Cp_2Zr(\mu\text{-}I)]_2$. A Thermally Unstable Zirconium(III) Complex

Ytsen Wielstra, Sandro Gambarotta,* Auke Meetsma, and Jan L. de Boer

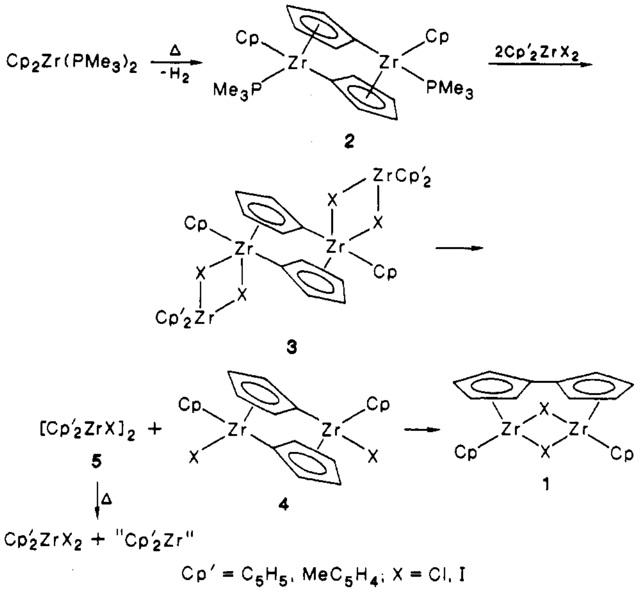
Laboratorium voor Anorganische Chemie
Rijksuniversiteit Groningen, Nijenborgh 16
9747 AG Groningen, The Netherlands

Received September 19, 1988

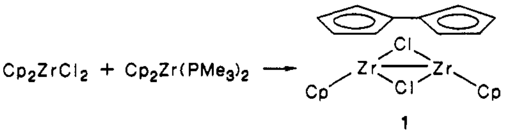
Summary: The comproportionation reaction between $Cp_2Zr^{IV}I_2$ and $Cp_2Zr^{II}(PMe_3)_2$ leads to a mixture of $(\eta^5{:}\eta^5\text{-}C_{10}H_8)[(\eta^5\text{-}C_5H_5)Zr(\mu\text{-}I)]_2$ (**1**) and $[Cp_2Zr(\mu\text{-}I)]_2$ (**5**) which have been isolated in pure form. The structure of the thermally unstable **5** has been determined by X-ray diffraction methods. Complex **5** crystallizes in the tetragonal space group $P4_2nm$ (No. 102) with a = 8.500 (3) Å, c = 13.774 (1) Å, V = 995.2 (5) Å^3, and Z = 2. The long Zr⋯Zr distance [3.669 (2) Å] suggests that no Zr–Zr bond occurs in this diamagnetic complex.

Although the chemistry of group IVB transition metals has been well-established, the oxidation state of (+III) remains quite elusive in the case of zirconium and virtually unknown for hafnium.[1] A puzzling question arises, for example, from the ability of zirconium and hafnium d^1 complexes, to form dinuclear species ligated by a single metal–metal bond. The presence of this bond is in fact a postulate commonly accepted to explain the diamagnetism of Zr(III) complexes.[2] However, only two structural determinations supporting this idea have been reported for zirconium so far,[3a–c] showing moreover quite elongated Zr–Zr bonds. Furthermore, the long intermetallic distances, which have been observed in a recent crystallographic characterization of two bis(cyclopentadienyl)zirconium(III) complexes,[4] suggest that not necessarily a metal–metal bond should occur in the dinuclear and diamagnetic d^1 species. Apart from the nonmarginal question of the real existence of Zr–Zr bond, the chemical behavior of Zr(III) remains poorly understood. Undoubtedly, the absence of suitable synthetic pathways has been the limiting step for the development of this chemistry.[5]

Scheme I



We previously reported that equilibration reactions between tetravalent and divalent compounds, commonly used for the preparation of Ti(III) complexes,[6] can be used as a successful synthetic pathway to fulvalene-bridged Zr(III) complexes (eq 1).[3c] A gentle heating (40–45°) is necessary to start the reaction. Under these conditions, $Cp_2Zr(PMe_3)_2$ releases one molecule of PMe_3, forming the dimeric $[(\eta^1{:}\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)Zr(PMe_3)]_2$ (Scheme I).[7] We have verified that the final fulvalene complex **1** can be formed by direct reaction of this complex with Cp_2ZrCl_2. The reaction probably involves the same intermediates **3** and **4** individuated by Schwartz in the controlled oxidation of Zr(II).[8]



(1)

What remains unclear, is which pair of cyclopentadienyl rings is used by the metal for the formation of the fulvalene ligand. In an attempt to gain insights into the reaction pathway, we have reacted $Cp_2Zr(PMe_3)_2$ with Cp'_2ZrCl_2 (Cp' = MeC_5H_4), where the cyclopentadienyl rings are labelled by the presence of a methyl substituent. The reaction leads to the formation of **1** (45% in NMR tube

---

[1] (a) Bottrill, M.; Gavens, P. D.; McMeeking, J. *Comprehensive Organometallic Chemistry*; Pergamon Press: Oxford, 1982; Vol. 3, p 281. (b) Cardin, D. J.; Lappert, M. F.; Raston, C. L.; Riley, P. I. *Comprehensive Organometallic Chemistry*; Pergamon Press: Oxford, 1982; Vol. 3, p 549. (c) Fay, C. F. *Comprehensive Coordination Chemistry*, Pergamon Press: Oxford, 1987; Vol. 3, p 363. (d) McAuliffe, C. A.; Barratt, S. *Comprehensive Coordination Chemistry* Pergamon Press: Oxford, 1987; Vol. 3, p 323. (e) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of organozirconium and -hafnium compounds*; Ellis Horwood Ltd.: Chichester, 1986. (f) Fay, R. C. *Coord. Chem. Rev.* **1983**, *52*, 285.

[2] (a) Issleib, K.; Hackert, H. *Z. Naturforsch.* **1966**, *21B*, 519. (b) Wade, S. R.; Wallbridge, G. M. H.; Willey, G. R. *J. Chem. Soc., Dalton Trans.* **1983**, 2555. (c) Cuenca, T.; Herrmann, W. A.; Ashworth, T. V. *Organometallics* **1986**, *5*, 2514. (d) Herrmann, W. A.; Cuenca, T.; Menjon, B.; Herdtweeck, E. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 697. (e) Fochi, G.; Guidi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1984**, 1253.

[3] (a) Wengrovius, J. H.; Schrock, R. R.; Day, C. S. *Inorg. Chem.* **1981**, *20*, 1844. (b) Cotton, F. A.; Diebold, M. P.; Kibala, P. A. *Inorg. Chem.* **1988**, *27*, 799. (c) Gambarotta, S.; Chiang, M. Y. *Organometallics* **1987**, *6*, 897. (d) Cotton, F. A.; Kibala, P. A.; Roth, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 298.

[4] Chiang, M. Y. N.; Gambarotta, S.; van Bolhuis, F. *Organometallics* **1988**, *7*, 1864.

[5] Wielstra, Y.; Gambarotta, S.; Chiang, M. Y. N. *Recl. Trav. Chim. Pays-Bas*, in press.

[6] (a) Floriani, C.; Fachinetti, G. *J. Chem. Soc., Dalton Trans.* **1973**, 1954. (b) Wailes, P. C.; Weigold, H. *J. Organomet. Chem.* **1971**, *28*, 91.

[7] (a) Kool, L. B.; Rausch, M. D.; Alt, H. G.; Herberhold, M.; Thewalt, V.; Wolf, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 394. (b) Kool, L. B.; Rausch, M. D.; Honold, B. *J. Organomet. Chem.* **1986**, *310*, 27.

[8] (a) Gell, I. K.; Harris, T. V.; Schwartz, J. *Inorg. Chem.* **1981**, *20*, 481. (b) Williams, G. M.; Schwartz, J. *J. Am. Chem. Soc.* **1982**, *104*, 1122. (c) Williams, G. M.; Gell, I. K.; Schwartz, J. *J. Am. Chem. Soc.* **1980**, *102*, 3660.

0276-7333/89/2308-0250$01.50/0

Organometallics **1989**, *8*, 251-253

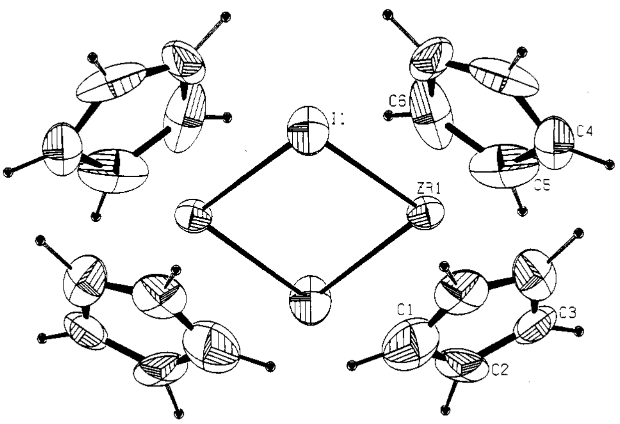


Figure 1. Molecular structure of $[Cp_2ZrI]_2$ showing thermal ellipsoids drawn at 50% level probability. Selected bond lengths (Å) and angles (deg) (estimated standard deviation in parentheses): Zr(1)–I(1) = 2.916 (1); I(1)–Zr(1)–I(1A) = 102.03 (3); Zr(1)–I(1)–Zr(1A) = 77.97 (3); Cp^1–Zr(1)–Cp^2 = 115.68 (3); Zr(1)···Zr(1A) = 3.669 (2).

experiments) as the only fulvalene-containing product. Considerable amounts of Cp'_2ZrCl_2 (35%, by NMR) remain unreacted, and new signals tentatively assigned to "Cp'_2Zr" have also been observed.[12]

This result clearly indicates that the fulvalene ligand originates only from the two cyclopentadienyl rings of the $Cp_2Zr(PMe_3)_2$ molecule. On the other hand, it is obvious that the bridging chlorine atoms of the complex **1** are provided by Cp'_2ZrCl_2. However, we were unable to understand why considerable amounts of unreacted Cp'_2ZrCl_2 invariably were present in the reaction mixtures, in spite of our effort to adjust the stoichiometry. In order to better clarify the role played by Cp'_2ZrCl_2 in this respect, we have carried out a comproportionation reaction between Cp_2ZrI_2 and $Cp_2Zr(PMe_3)_2$ in toluene. The reaction proceeds at room temperature, forming a deep purple solution. When the reaction progress is monitored by ^1H NMR, the disappearance of the starting materials is observed along with the formation of the fulvalene-bridged $(\eta^5{:}\eta^5\text{-}C_{10}H_8)[(\eta^5\text{-}C_5H_5)Zr(\mu\text{-}I)]_2$[8a] and a growing narrow singlet at 4.97 ppm in the ^1H NMR spectrum [45% considering the singlet belonging to a bis(cyclopentadienyl) moiety]. The resulting solution was concentrated to a small volume, yielding black greenish[9] crystals (25%) upon cooling to −30 °C. The fulvalene-free compound showed the presence of a singlet at 4.97 ppm in the ^1H NMR spectrum (300 MHz) and a doublet at 102.04 ppm in the ^{13}C NMR spectrum (75 MHz). Analytical data were consistent with the formulation $[Cp_2ZrI]_2$ (**5**).

The structure of the molecule has been demonstrated by an X-ray diffraction analysis.[10] The unit-cell contains two discrete dimeric units, with the usually bent Cp_2Zr moieties linked by two bridging iodine atoms (Figure 1). The value of the intermetallic distance [3.669 (2) Å] is similar to those found in $[Cp_2Zr(\mu\text{-}PMe_2)]_2$[4] and $[Cp_2Zr(\mu\text{-}Cl)][Cp_2Zr(\mu\text{-}PMe_3)]$,[4] excluding once more the presence of a Zr–Zr bond. All the bond distances and angles are normal.

By analogy with $[ZrCl_3(PR_3)_2]_2$ complexes,[3a,d] $[Cp_2ZrI]_2$ is thermally unstable. It slowly disproportionates in solution at room temperature to Cp_2ZrI_2 and "Cp_2Zr".[12] Full decomposition can be achieved within few hours at 100 °C. This result tentatively suggests that the formation of Cp_2ZrCl_2 and "Cp_2Zr", observed in the comproportionation with Cp_2ZrCl_2, might be ascribed to the intermediate formation of the elusive $[Cp_2ZrCl]_2$. A higher thermal instability possibly might be responsible for the failure to characterize this species.[13] Further attempts to prepare $[Cp_2ZrCl]_2$ by the reaction between $[ZrCl_3(PR_3)_2]_2$ and CpNa in either ether or toluene at low temperature (−80/−30 °C) led only to mixtures of Cp_2ZrCl_2 and $Cp_2Zr(PR_3)_2$.

A full investigation on the reactivity of $[Cp_2ZrI]_2$ is in progress at the moment.

Supplementary Material Available: Tables of crystal data, anisotropic thermal parameters, atomic coordinates, bond lengths, bond angles, and torsion angles (8 pages); a listing of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

---

[9] Complex **5** is a deep red-purple solid. The emerald-green appearance of crystalline samples is a common feature for red Zr(III) derivatives.[3c,4]

[10] Crystal data: deep purple prism; crystal size (mm), 0.14 × 0.30 × 0.06; tetragonal; space group $P4_2nm$ (No. 102); a = 8.500 (3) Å, c = 13.774 (1) Å; $Z = 2$; V = 995.2 (5) Å^3; d(calcd) = 2.325 g cm^{-3}, μ(Mo) = 41.0 cm^{-1}; $F(000) = 652$; scan mode = $\omega/2\theta$; scan width = 0.85 + 0.35 tan θ; T = 298 K; measured reflections 4178, range of hkl = h, $-10 \rightarrow 10$, k $0 \rightarrow 10$, l, $-16 \rightarrow 16$ ($2\theta_{max}$ = 52°); number of unique reflections, 561; number of reflections used in analysis, 522 [$I > 2.5\sigma(I)$]; structure solved by heavy-atom method; all the non-hydrogen atom positions were located and refined anisotropically; the carbon atoms of the cyclopentadienyl rings showed quite large thermal parameters probably due to libration motions as a common features for the complexes having this type of structure;[11] hydrogen atom positions were calculated and refined in the riding mode; number of variables 61; $R = 0.026$; $R_w = 0.031$, GOF = 1.806; $\omega = 1/[\sigma^2]$; largest remaining peak, −0.58, 0.80 e/Å^3; a final difference Fourier map did not show any significant residual feature; largest shift/esd, final cycle, 0.313.

[11] (a) Atwood, J. L.; Smith, K. D. *J. Chem. Soc., Dalton Trans.* **1973**, 2487. (b) Evans, W. J.; Sollberger, M. S.; Khan, S. I.; Bau, R. *J. Am. Chem. Soc.* **1988**, *110*, 439. (c) Blake, P. C.; Lappert, M. F.; Taylor, R. G.; Atwood, J. L.; Hunter, W. E.; Zhong, H. *J. Chem. Soc., Chem. Commun.* **1986**, 1394. (d) Jungst, R.; Sekutowski, D.; Davis, J.; Luly, M.; Stucky, G. *Inorg. Chem.* **1977**, *16*, 1645.

[12] Broad and undiagnostic signals have been reported for "Cp_2Zr".[8a] In our experiments "Cp_2Zr" showed a clean and well-solved NMR spectrum [^1H NMR (C_6D_6, δ (ppm)): "Cp_2Zr", 5.95 (s), 5.62 (s), 5.07 (pseudo-t), 4.33 (pseudo-t); "Cp'_2Zr", 5.67 (m), 1.91 (m)]. However, attempts to isolate this species were unsuccessful so far, and the structure remains not defined.

[13] Both green[13a] and red[13b–d] colors have been claimed for $[Cp_2ZrCl]_2$. (a) Fochi, G.; Guidi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1984**, 1253. (b) Cuenca, T.; Royo, P. *J. Organomet. Chem.* **1985**, *295*, 159. (c) Cuenca, T.; Royo, P. *J. Organomet. Chem.* **1985**, *293*, 61. (d) Samuel, E.; Guery, D.; Vedel, J.; Basile, F. *Organometallics* **1985**, *4*, 1073.

Isolation and X-ray Structure of an Intermediate in the Reaction of $(\mu\text{-}S)_2Fe_2(CO)_6$ with Thiolates: The $[(\mu\text{-}S)(\mu\text{-}S_2\text{-}t\text{-}Bu)Fe_2(CO)_6]^-$ Ion

Xintao Wu,[1] K. S. Bose, E. Sinn, and B. A. Averill*

Department of Chemistry, University of Virginia
Charlottesville, Virginia 22901

Received August 15, 1988

Summary: Reaction of $(\mu\text{-}S_2)Fe_2(CO)_6$ (**1**) with 1 equiv of thiolate RS^- (R = Ph, $PhCH_2$, *i*-Pr) results in formation of the $[Fe_4S_4(CO)_{12}]^{2-}$ ion (**2**) containing two $[(\mu\text{-}S)_2Fe_2(CO)_6]^-$ units linked by a disulfide bond. Use of *t*-BuS$^-$ results instead in a new green mixed disulfide, the $[(\mu\text{-}S)(\mu\text{-}S_2\text{-}t\text{-}Bu)Fe_2(CO)_6]^-$ ion (**3**), the structure of which has been determined as the Ph_4As^+ salt. These results suggest that similar mixed disulfides are intermediates in the reaction of thiolates with **1** to produce **2**.

---

[1] Current address: Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, People's Republic of China.

0276-7333/89/2308-0251$01.50/0