Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Bis[μ-4-(diphenylphosphino)but-3-ene-2-thiolato]bis[bis(η^5-cyclopentadienyl)-zirconium(IV)] dichloromethane disolvate

Esteban Ortega,[a]* Nadine Pirio,[a] Philippe Meunier[a] and Philippe Richard[b]

[a]LSEO Faculté des Sciences, B, bd. Gabriel, 21000 Dijon, France, and [b]LSEO Faculté des Sciences, 9 av. Alain Savary, BP 47870, 21078 Dijon, France

Correspondence e-mail:
prichard@u-bourgogne.fr

Received 22 December 2003
Accepted 13 January 2004
Online 23 January 2004

Key indicators

Single-crystal X-ray study
T = 110 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.038
wR factor = 0.092
Data-to-parameter ratio = 18.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

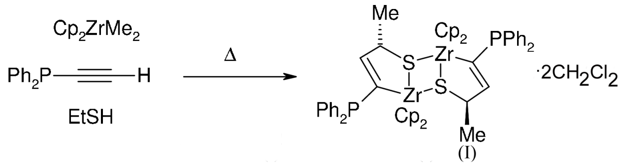
The title compound, $[Zr_2(C_5H_5)_4(C_{16}H_{15}PS)_2]\cdot 2CH_2Cl_2$, was prepared by insertion of diphosphinoacetylene into the Zr—C bond of the transient (η^2-thioaldehyde)zirconocene formed by treatment of Cp_2ZrMe_2 with one equivalent of ethanediol. The sulfonium zirconocenate complex exhibits a centrosymmetric sulfur-bridged dimeric structure.

Comment

(η^2-Aldehyde) complexes and derived group 4 metallocenes exhibit a wide variety of interesting structural and chemical features. Moreover, they show a high tendency to form dinuclear systems in which the O atom serves as a bridging atom (Erker *et al.*, 1986; Erker, Mena *et al.*, 1991; Erker & Noe, 1991; Stephan, 1991; Gau *et al.*, 1993; Rosenthal *et al.*, 1993; Peulecke *et al.*, 1996). (η^2-Thioaldehyde) and related zirconocene complexes are also readily available (Buchwald *et al.*, 1987). In contrast to their chalcogen homologues, the zirconocene thiametallocycles are mostly mononuclear.

Reaction of Cp_2ZrMe_2 with one equivalent of thiol has been shown to proceed *via* elimination of methane, affording the complex $Cp_2Zr(Me)SR$. In the case of a thiolate fragment with α-H atoms, alkylthiozirconocene leads to the unstable thioaldehydezirconocene by thermolysis.

We report here the formation of an unprecedented 18-electron bissulfonium zirconocenate (Miquel *et al.*, 1998; Cadierno *et al.*, 1999; Miquel *et al.*, 2000; Cadierno *et al.*, 2002) complex, (I) (Fig. 1). Dimer (I) can be prepared by regioselective insertion of diphosphinoacetylene (Charrier *et al.*, 1964) into the Zr—C bond of the transient (η^2-thioaldehyde)zirconocene formed by treatment of Cp_2ZrMe_2 (Samuel & Rausch, 1973) with one equivalent of ethanethiol.



(I)

The sulfonium zirconocenate complex in the title compound adopts a centrosymmetric dimeric structure. The *Cg*1—Zr—*Cg*2 angle (where *Cg*1 and *Cg*2 are the geometrical centers of the Cp rings) is 126.3 (1)° and a C atom and two bridging S atoms complete the coordination sphere of the Zr atoms. The C1—Zr—S and S—Zr—S^i angles (for the symmetry code see Table 1), and the Zr—C1 bond length, are 70.33 (6)°, 61.07 (2)° and 2.381 (3) Å, respectively. These values are comparable to those found in related oxygen-bridged zirconocene dimers, where these mean values are equal to 71°, 64° and 2.38 Å, respectively (Rosenthal *et al.*, 1993; Rosenthal *et*

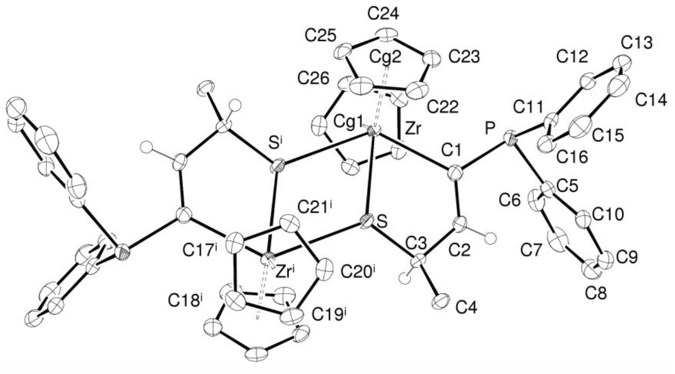


Figure 1
*ORTEP*III (Burnett & Johnson, 1996) view of the title compound, showing displacement ellipsoids at the 50% probability level. Only the major disorder component is shown. For clarity, the solvent molecule is not represented and only relevant H atoms are shown.

al., 1994; Peulecke *et al.*, 1996; Kempe *et al.*, 1998). Because the Zr—S bond length is longer, the S—Zr—S^i angle is slightly smaller than the corresponding angle in the oxo series. As expected for such a coordination mode, two different Zr—S bond lengths are observed, *viz*. Zr—S = 2.6124 (7) Å and Zr—S^i = 2.7380 (7) Å. Atom C3 is a chiral center and, having a center of inversion, the complex exhibits a *meso* configuration. However, owing to an inversion of chirality at C3, we observe disorder in the structure affecting atoms C2, C3 and C4 [occupancies 0.84 (1):0.16 (1)].

Experimental

The experiment was conducted under a dry argon atmosphere with standard Schlenk techniques. Solvents were freshly distilled under an argon atmosphere from solutions of $NaK_{2.8}$/benzophenone (pentane), $NaK_{2.8}$ (toluene) or CaH_2 (CH_2Cl_2). Reagents were purchased from commercial suppliers and used without further purification, except for ethanethiol, which was distilled and stored under an argon atmosphere. For the preparation of the title complex, to a solution of dimethylzirconocene (0.53 g, 2.1 mmol) in toluene (25 ml) was added diphenylphosphinoacetylene (0.44 g, 2.1 mmol) and a stoichiometric amount of ethanethiol (0.16 ml, 2.1 mmol). The resulting solution was transferred into an autoclave because of the high volatility of the mercaptan and stirred for 24 h at 383 K. The mixture was cooled to room temperature, transferred in to a flask and concentrated *in vacuo*, and pentane (20 ml) was added. The resulting solid product was washed with pentane (5 × 10 ml) and vacuum dried. Yield 0.61 g (59%), beige powder. Recrystallization from a CH_2Cl_2 solution afforded colorless crystals suitable for X-ray analysis. The NMR spectrum could not be recorded owing to a lack of solubility in common solvents. Analysis calculated for $C_{52}H_{50}P_2S_2Zr_2$, CH_2Cl_2: C 59.57, H 4.91, S 6.00%; found: C 59.24, H 4.99, S 5.80%.

Crystal data

$[Zr_2(C_5H_5)_4(C_{16}H_{15}PS)_2]\cdot 2CH_2Cl_2$
$M_r = 1153.29$
Monoclinic, $P2_1/n$
$a = 12.2116$ (5) Å
$b = 12.4090$ (6) Å
$c = 17.2983$ (9) Å
$\beta = 107.526$ (2)°
$V = 2499.6$ (2) Å^3
$Z = 2$
$D_x = 1.532$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1776 reflections
$\theta = 1.0$–27.5°
$\mu = 0.82$ mm^{-1}
$T = 110$ (2) K
Prism, colorless
0.50 × 0.40 × 0.25 mm

Data collection

KappaCCD diffractometer
φ scans ($\kappa = 0$) and additional ω scans
9529 measured reflections
5521 independent reflections
4454 reflections with $I > 2\sigma(I)$
$R_{int} = 0.043$
$\theta_{max} = 27.4°$
$h = -11 \rightarrow 15$
$k = -16 \rightarrow 9$
$l = -22 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.092$
$S = 1.03$
5521 reflections
302 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0361P)^2 + 2.0399P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.75$ e Å^{-3}
$\Delta\rho_{min} = -0.91$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zr—*Cg*1	2.242 (3)	P—C1	1.856 (3)
Zr—*Cg*2	2.242 (4)	S—C3	1.811 (3)
Zr—S	2.6124 (7)	C1—C2	1.347 (4)
S—Zr^i	2.7380 (7)	C2—C3	1.502 (4)
Zr—C1	2.381 (3)		
*Cg*1—Zr—Ct2	126.3 (1)	C1—Zr—S^i	130.68 (7)
*Cg*1—Zr—S	113.22 (7)	C3—S—Zr	107.30 (10)
*Cg*1—Zr—S^i	103.22 (7)	C3—S—Zr^i	124.54 (10)
*Cg*1—Zr—C1	102.88 (9)	Zr—S—Zr^i	118.93 (2)
*Cg*2—Zr—S	120.43 (7)	C1—C2—C3	125.1 (3)
*Cg*2—Zr—S^i	99.52 (7)	C2—C3—S	106.9 (2)
*Cg*2—Zr—C1	97.7 (1)	P—C1—Zr	119.15 (12)
S—Zr—S^i	61.07 (2)	C2—C1—P	116.6 (2)
C1—Zr—S	70.33 (6)	C2—C1—Zr	122.3 (2)

Symmetry code: (i) $-x, -y, -z$.

Because of an inversion of chirality at C3, atoms C2, C3 and C4 are disordered. The occupancies for the disordered groups are 0.84 (1):0.16 (1). The C atoms of the disordered minor component were refined isotropically. All H atoms were included in calculated positions (C—H = 0.93–0.97 Å) and treated using a riding model, with $U_{iso} = 1.2U_{eq}$ ($1.5U_{eq}$ for the methyl group) of the carrier atom.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97 and *WinGX* (Farrugia, 1999).

The award of a thesis grant (EO) from the Ministère de l'Education Nationale de la Recherche et la Technologie (MENRT) is gratefully acknowledged. The authors thank S. Royer for her helpful technical assistance.

References

Buchwald, S. L., Nielsen, R. B. & Dewan, J. C. (1987). *J. Am. Chem. Soc.* **109**, 1590–1591.

Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Cadierno, V., Zablocka, M., Donnadieu, B., Igau, A. & Majoral, J.-P. (1999). *Organometallics*, **18**, 1882–1886.

Cadierno, V., Zablocka, M., Donnadieu, B., Igau, A. & Majoral, J.-P. (2002). *Organometallics*, **21**, 3215–3220.

m202 Esteban Ortega *et al.* • $[Zr_2(C_5H_5)_4(C_{16}H_{15}PS)_2]\cdot 2CH_2Cl_2$ *Acta Cryst.* (2004). E**60**, m201–m203

Charrier, C., Simonnin, M. P., Chodkiewicz, W. & Cadiot, P. (1964). *C. R. Acad. Sci.* **258**, 1537–1540.

Erker, G., Dorf, U., Czisch, P. & Peterson, J. L. (1986). *Organometallics*, **5**, 668–676.

Erker, G., Mena, M., Krueger, C. & Noe, R. (1991). *J. Organomet. Chem.* **402**, 67–75.

Erker, G. & Noe, R. (1991). *J. Chem. Soc. Dalton Trans.* pp. 685–692.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Gau, H. M., Chen, C. A., Chang, S. J., Shih, W. E., Yang, T. K., Jong, T. T. & Chien, M. Y. (1993). *Organometallics*, **12**, 1314–1318.

Kempe, R., Spannenberg, A., Peulecke, N. & Rosenthal, U. (1998). *Z. Kristallogr. New Cryst. Struct.* **213**, 793.

Miquel, Y., Cadierno, V., Donnadieu, B., Igau, A. & Majoral, J.-P. (2000). *Organometallics*, **19**, 54–61.

Miquel, Y., Igau, A., Donnadieu, B., Majoral, J.-P., Pirio, N. & Meunier, P. (1998). *J. Am. Chem. Soc.* **120**, 3504–3505.

Nonius. (1997). *KappaCCD Server Software.* Nonius BV, Delft. The Netherlands.

Otwinowski, Z.& Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Peulecke, N., Ohff, A., Tillack, A., Baumann, W., Kempe, R., Burlakov, V. V. & Rosenthal, U. (1996). *Organometallics*, **15**, 1340–1344.

Rosenthal, U., Ohff, A., Braumann, W., Kempe, R., Tillack, A. & Burlakov, V. V. (1994). *Angew. Chem. Int. Ed. Engl.* **33**, 1850.

Rosenthal, U., Ohff, A., Michalik, M., Goerls, H., Burlakov, V. V. & Shur, V. B. (1993). *Organometallics*, **12**, 5016–5019.

Samuel, E. & Rausch, M. D. (1973). *J. Am. Chem. Soc.* **95**, 6263–6267.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Stephan, D. W. (1991). *Organometallics*, **10**, 2037–2045.

Acta Cryst. (2004). E**60**, m201–m203 Esteban Ortega *et al.* • $[Zr_2(C_5H_5)_4(C_{16}H_{15}PS)_2]\cdot 2CH_2Cl_2$ **m203**