Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1121). Services for accessing these data are described at the back of the journal. Full structural data for the chlorine analog have also been deposited and are included in the CIF.

References

Enraf–Nonius (1988). *CAD-4 Manual*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Flack, H. D. (1977). *Acta Cryst.* A33, 890–898.

Flack, H. D. (1983). *Acta Cryst.* A39, 876–881.

Okechukwu, R. C., Fun, H.-K., Teoh, S.-G., Teo, S.-B. & Chinnakali, K. (1993). *Acta Cryst.* C49, 368–370.

Ruddick, J. N. R. & Sams, J. R. (1973). *J. Organomet. Chem.* **60**, 233–246.

Sheldrick, G. M. (1990). *SHELXTL/PC*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Smith, P. J. & Dodd, D. (1971). *J. Organomet. Chem.* **32**, 195–199.

Teoh, S.-G., Yeap, G., Loh, C.-C., Foong, L.-W., Teo, S.-B. & Fun, H.-K. (1997). *Polyhedron*, **16**, 2213–2221.

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(1,1-Dimercaptoethene-2,2-dicarbonitrilato-S,S')bis(triphenylphosphine)palladium(II) Diacetonitrile Solvate

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Abstract

The title palladium(II) compound, [Pd(PPh$_3$)$_2${S$_2$C=C-(CN)$_2$}].2CH$_3$CN or [Pd(C$_4$N$_2$S$_2$)(C$_{18}$H$_{15}$P)$_2$].2C$_2$H$_3$N, was obtained from the reaction of PPh$_3$, PdCl$_2$ and K$_2$S$_2$C=C(CN)$_2$ (i-mnt) in CH$_3$CN. The Pd atom is coordinated by two P and two S atoms in a distorted square-planar arrangement. The average Pd—P and Pd—S distances are 2.3184 (11) and 2.3420 (11) Å, respectively, the P—Pd—P and S—Pd—S angles are 99.11 (4) and 74.68 (4)°, respectively.

Comment

Transition metal complexes with phosphine ligands have been studied extensively, not only due to the variation in their geometric and electronic structures and properties, but also because of their application for homogeneous or heterogeneous catalytic functions (Puddephatt, 1983; Cotton *et al.*, 1987; Kiress & Eisenberg, 1989). Metal–thiolate complexes are known as ubiquitous biological electron-transfer mediators and have been studied for two decades (Blower & Dilworth, 1987). However, complexes blending both phosphine and thiolate ligands have received attention only in recent years. Many palladium complexes containing such mixed ligands (Fenn & Segrott, 1972; Dance, 1986; Wolf *et al.*, 1980) have been structurally characterized. Recently, studies of metal–thiolate–phosphine complexes began in our laboratory, resulting in a series of palladium(II) complexes, such as [Pd$_2$(SC$_2$H$_4$S)$_2$(PPh$_3$)$_2$] (Cao *et al.*, 1995), [Pd$_2$(HOC$_6$H$_4$S)$_2$(PPh$_3$)$_2$Cl$_2$] (Cao *et al.*, 1996) and [Pd(SC$_3$H$_6$S){Ph$_2$P(CH$_2$)$_3$PPh$_2$}] (Su *et al.*, 1996). We report herein the synthesis and crystal structure of a mononuclear palladium complex, namely, (1,1-dimercaptoethene-2,2-dicarbonitrilato-S,S')bis(triphenylphosphine)palladium(II) diacetonitrile solvate, [Pd(PPh$_3$)$_2${S$_2$C=C(CN)$_2$}].2CH$_3$CN, (I).

(I)
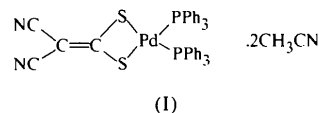
Selected bond distances and angles are listed in Table 1. The molecular structure of the complex consists of a discrete monopalladium complex and two CH$_3$CN solvent molecules. As depicted in Fig. 1, the complex molecule does not possess any crystallographic symmetry. The Pd atom is surrounded by two
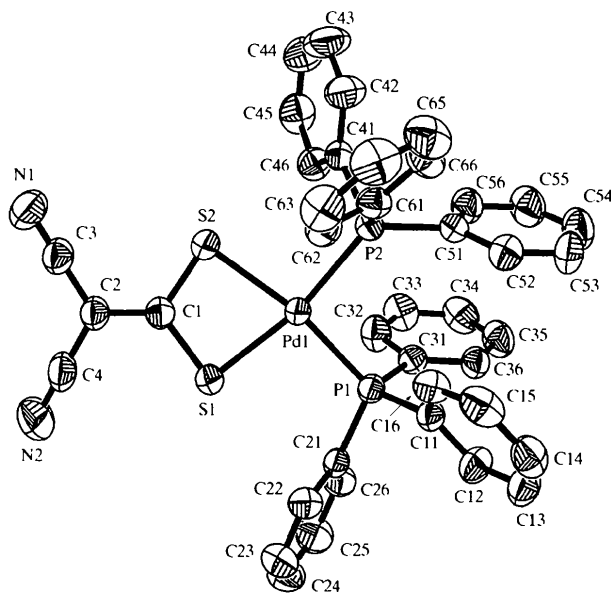

Fig. 1. The crystal structure of [Pd(PPh$_3$)$_2${S$_2$C=C(CN)$_2$}], with displacement ellipsoids plotted at the 50% probability level.

P and two S atoms in a distorted square-planar geometry. The five atoms Pd1 (0.0365 Å), S1 (0.114 Å), S2 (−0.130 Å), P1 (−0.109 Å) and P2 (0.088 Å) are essentially planar. The average Pd—S—C angle in the chelate ring [87.34 (13)°] is much smaller than 109° because of the constraint of the four-membered ring. The average Pd—S and Pd—P bond lengths [2.3420 (11) and 2.3184 (11) Å, respectively], and the P—Pd—P and S—Pd—S angles [99.11 (4) and 74.68 (4)°, respectively], are in agreement with those of similar Pd–dithiolate complexes, while the C—S bond distance [1.728 (4) Å] is slightly shorter than those in the related complexes (1.77 Å; Cao *et al.*, 1995, 1996; Su *et al.*, 1996).

Experimental

The title compound was obtained from the reaction of PdCl₂, PPh₃, and K₂S₂C=C(CN)₂ (i-mnt) (molar ratio 1:2:1) in CH₃CN. To a solution of PPh₃ (1.04 g, 4 mmol) and K₂S₂C=C(CN)₂ (0.44 g, 2 mmol) in MeCN (30 ml) was added anhydrous PdCl₂ (0.35 g, 2 mmol). The solution turned brown gradually. After stirring for 24 h, the yellow–red solution was filtered. The filtrate was kept in an icebox for two weeks to yield yellow–red prisms of the title complex. Crystals suitable for X-ray diffraction analysis were obtained by recrystallization from CH₃CN at room temperature.

Crystal data

[Pd(C₄N₂S₂)(C₁₈H₁₅P)₂].-
2C₂H₃N
$M_r = 853.23$
Monoclinic
$P2_1/c$
$a = 13.957 (3)$ Å
$b = 13.877 (3)$ Å
$c = 21.831 (4)$ Å
$\beta = 102.90 (3)°$
$V = 4121.5 (15)$ Å³
$Z = 4$
$D_x = 1.375$ Mg m⁻³
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 4524
reflections
$\theta = 7.5–15.0°$
$\mu = 0.665$ mm⁻¹
$T = 293$ K
Prism
$0.35 \times 0.25 \times 0.20$ mm
Yellow

Data collection

Siemens SMART CCD
diffractometer
ω scans
Absorption correction:
semi-empirical from
equivalent reflections
(*XEMP* in *SHELXTL*;
Sheldrick, 1994)
$T_{min} = 0.784, T_{max} = 0.875$
15 630 measured reflections

7175 independent reflections
5829 reflections with
$F > 2\sigma(F)$
$R_{int} = 0.022$
$\theta_{max} = 25.04°$
$h = -16 \rightarrow 10$
$k = -8 \rightarrow 16$
$l = -25 \rightarrow 23$
Intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.037$
$wR(F^2) = 0.070$
$S = 1.122$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.654$ e Å⁻³
$\Delta\rho_{min} = -0.554$ e Å⁻³
Extinction correction: none

7175 reflections
478 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0542P)^2 + 3.1350P]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Pd1—P1	2.2968 (10)	P1—C31	1.827 (4)
Pd1—S1	2.3297 (10)	P1—C21	1.836 (4)
Pd1—P2	2.3401 (11)	P2—C41	1.823 (4)
Pd1—S2	2.3542 (11)	P2—C61	1.825 (4)
S1—C1	1.727 (4)	P2—C51	1.830 (4)
S2—C1	1.729 (4)	C1—C2	1.375 (5)
N1—C3	1.145 (6)	C2—C3	1.418 (6)
N2—C4	1.151 (6)	C2—C4	1.426 (6)
P1—C11	1.808 (4)		
P1—Pd1—S1	93.87 (4)	C21—P1—Pd1	114.99 (11)
P1—Pd1—P2	99.11 (4)	C41—P2—C61	106.1 (2)
S1—Pd1—P2	166.81 (3)	C41—P2—C51	101.9 (2)
P1—Pd1—S2	165.99 (4)	C61—P2—C51	104.9 (2)
S1—Pd1—S2	74.68 (4)	C41—P2—Pd1	109.25 (12)
P2—Pd1—S2	92.78 (4)	C61—P2—Pd1	110.17 (13)
C1—S1—Pd1	87.76 (13)	C51—P2—Pd1	123.14 (11)
C1—S2—Pd1	86.91 (13)	C2—C1—S1	124.9 (3)
C11—P1—C31	109.4 (2)	C2—C1—S2	124.5 (3)
C11—P1—C21	102.3 (2)	S1—C1—S2	110.6 (2)
C31—P1—C21	104.7 (2)	C1—C2—C3	121.8 (4)
C11—P1—Pd1	116.83 (12)	C1—C2—C4	120.6 (4)
C31—P1—Pd1	107.91 (12)	C3—C2—C4	117.6 (4)

Data collection: *SMART* (Siemens, 1994). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1994). Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

References

Blower, P. J. & Dilworth, J. R. (1987). *Coord. Chem. Rev.* **76**, 121–185.
Cao, R., Hong, M.-C., Jiang, F.-L. & Liu, H.-Q. (1995). *Acta Cryst.* C**51**, 1280–1282.
Cao, R., Hong, M.-C., Jiang, F.-L., Xie, X.-L. & Liu, H.-Q. (1996). *Polyhedron*, **15**, 2661–2670.
Cotton, F. A., Dunbar, K. R. & Verbruggen, M. G. (1987). *J. Am. Chem. Soc.* **109**, 5498–5506.
Dance, I. G. (1986). *Polyhedron*, **5**, 1037–1104.
Fenn, R. H. & Segrott, G. R. (1972). *J. Chem. Soc. Dalton Trans.* pp. 330–333.
Kiress, R. V. & Eisenberg, R. (1989). *Inorg. Chem.* **28**, 3372–3378.
Puddephatt, R. J. (1983). *Chem. Soc. Rev.* **12**, 99–127.
Sheldrick, G. M. (1994). *SHELXTL. Structure Determination Programs.* Version 5. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1994). *SMART* and *SAINT. Data Collection and Intergration Programs.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

$[Pd(C_4N_2S_2)(C_{18}H_{15}P)_2] \cdot 2C_2H_3N$

Su, W.-P., Hong, M.-C., Zhou, Z.-Y., Xue, F., Liu, H.-Q. & Mak, T. C. W. (1996). *Acta Cryst.* C52, 2691–2693.

Wolf, T. E., Berg, J. M., Power, P. P., Hodgson, K. O. & Holm, R. H. (1980). *Inorg. Chem.* 19, 430–437.

(I)

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Dicyclopentadienyl Complexes of Samarium(III): [Sm(η5-C5H4SiMe3)2(μ-Cl)]2

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Abstract

The title compound, di-μ-chloro-bis[(η5-trimethylsilylcyclopentadienyl)samarium(III)], [SmCl2(C8H13Si)4], which has been characterized by single-crystal X-ray diffraction, is isostructural with its ytterbium analogue. The geometrical parameters of the lanthanide atoms are compared in the two compounds. Results and conclusions reported for [Yb(η5-C5H4SiMe3)2(μ-Cl)]2 are entirely corroborated by the present structure analysis.

Comment

One important factor affecting the stability of organometallic complexes of the lanthanides is the saturation of the coordination sphere of the metal with bulky ligands in order to sterically block decomposition pathways (Evans, 1982). As the atomic (and ionic) radii decrease when the lanthanide series is traversed from lanthanum to lutetium, it is less difficult to sterically saturate the coordination environment of the elements occurring later in the series. Therefore, Er, Yb and Lu are the most frequently used in synthesis as they form more stable complexes than the larger early members of the lanthanide series. Samarium is a frontier element in terms of obtaining stable organometallic complexes. We reported previously the synthesis and crystal structure analysis of the dimeric complex [Yb(η5-C5H4SiMe3)2(μ-Cl)]2 (Spirlet & Goffart, 1995). The synthesis of the corresponding samarium derivative, (I), and the growing of single crystals suitable for X-ray diffraction allows a comparison of the coordination geometry in the two complexes which have similar bridged samarium dimers.
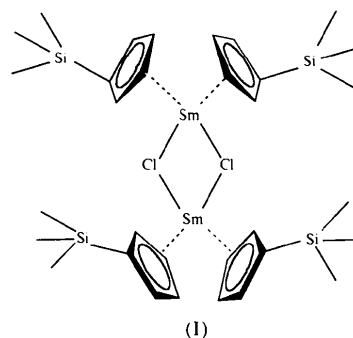
The present X-ray structure analysis reveals that the complex [Sm(η5-C5H4SiMe3)2(μ-Cl)]2 is isostructural with the corresponding Yb derivative (Spirlet & Goffart, 1995). The structural dimeric unit is centrosymmetric with bridging Cl atoms. The pseudo-tetrahedral coordination geometry about the Sm atom, as well as the respective orientation of the ligands in the coordination sphere, are identical in the two compounds. The four centroids of the monosubstituted cyclopentadienyl rings exhibit a square-planar arrangement. The mean bond lengths Sm—Cl [2.754 (3) Å] and Sm—C [2.68 (1) Å] are, as expected (lanthanide contraction), longer than the corresponding Yb—Cl [2.643 (2) Å] and Yb—C [2.599 (9) Å] bond distances in [Yb(η5-C5H4SiMe3)2(μ-Cl)]2. Sm—C distances are in agreement with the values reported for [Sm{C5H3(SiMe3)2}2(μ-OH)]2 (Hitchcock *et al.*, 1991). It has been shown (Evans *et al.*, 1993) that bimetallic tetracyclopentadienylsamarium complexes can adopt either tetrahedral or squareplanar geometries for the four ring centroids depending on the size of the bridging ligands and the degree of substitution on the cyclopentadienyl rings. Complexes containing two crowded (C5Me5)2Sm units and small bridging ligands exhibit structures in which the four pentamethylcyclopentadienyl ring centroids define a tetrahedral geometry rather than a square-planar arrangement as in [Sm(C5Me5)2]2(μ-N2) (Evans *et al.*, 1988), [Sm(C5Me5)2]2(μ-O) (Evans *et al.*, 1985), [Sm(C5Me5)2(μ-H)]2 (Evans *et al.*, 1983) and [Sm(C5Me5)2]2(μ-HNNH) (Evans *et al.*, 1992). Other complexes which possess less steric congestion favour square-planar arrangements of ring centroids as in [Sm(C5H4Me)2(thf)(μ-Cl)]2 (Evans *et al.*, 1993), [Sm(C5H4Me)2C≡CC(Me)3]2 (Evans *et al.*, 1983), [Sm{C5H3(SiMe3)2}2(μ-OH)]2 (Hitchcock *et al.*, 1991), [Sm(C5H3Bu2)2(μ-H)]2 and [Sm(C5H3Bu2)2(μ-BH4)]2 (Gun'ko *et al.*, 1992). The present structure provides further information on how steric effects govern the structures of bimetallic organosamarium complexes. Here, the Sm—Cl—Sm'—Cl' bridging unit is planar like the Sm—O—Sm'—O' unit in the bridged hydroxide, with angles at the lanthanide atom appreciably smaller than at the bridging atom. No unusually short intermolecular contacts are observed.