SHORT-FORMAT PAPERS

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Structure of *cis*-[PdCl$_2$*L*] (*L* = 1,4,7-Trithiacyclononane)

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Abstract. [PdCl$_2$(C$_6$H$_{12}$S$_3$)], $M_r = 357{\cdot}7$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}5768\ (12)$, $b = 12{\cdot}2058\ (22)$, $c = 12{\cdot}2464\ (22)$ Å, $V = 1132{\cdot}6$ Å^3, $Z = 4$, $D_x = 2{\cdot}097$ Mg m^{-3}, $\bar{\lambda}$(Mo $K\alpha$) = 0·71069 Å, $\mu = 2{\cdot}575$ mm^{-1}, $F(000) = 704$, $T = 298$ K, $R = 0{\cdot}0181$ for 798 independent observed reflections. The Pd atom occupies a somewhat distorted square-planar environment with the two coordinated thia donors mutually *cis* [Pd—S = 2·2672 (17), 2·2457 (17) Å] and *trans* to the two chlorides [Pd—Cl = 2·3316 (21), 2·3326 (21) Å]. An average shortening in the Pd—S$_{\rm eq}$ distances of 0·065 Å compared with the [PdL_2]$^{2+}$ cation is observed. The remaining potential thia donor is remote from the metal centre [Pd···S = 3·1400 (21) Å] and no significant interaction occurs: it is notable that unlike in [PdL_2]$^{2+}$ the $\langle$S$_{\rm ax}$PdS$_{\rm eq}\rangle$ values of 78·42 (5) and 81·14 (5)° are inequivalent.

Experimental. Compound prepared by refluxing PdCl$_2$ and *L* (*L* = 1,4,7-trithiacyclononane) in CH$_3$CN/CH$_2$Cl$_2$ (3:1) under N$_2$ for 16 h, crystals obtained by recrystallization from CH$_3$NO$_2$. Dark-red, flattened needle, 0·462 × 0·154 × 0·058 mm, Stoe–Siemens AED-2 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, cell parameters from 14 reflections with $13 < \theta < 14°$. For data collection ω–2θ scans with ω-scan width $(1{\cdot}05 + 0{\cdot}35\tan\theta)°$, $\theta_{\max} = 22{\cdot}5°$, h 0→8, k 0→13, l 0→13, no significant variation in intensity of three standard reflections, semi-empirical absorption correction (transmission factors 0·180–0·253). 906 unique reflections, 798 with $F > 6\sigma(F)$ for structure solution [Patterson synthesis (Pd) followed by *DIRDIF* (Beurskens *et al.*, 1983) yielding all non-H-atom positions] and refinement [using full-matrix least squares on *F* (Sheldrick, 1976)]. Anisotropic thermal parameters for all non-H atoms, H atoms in calculated positions. At convergence $R = 0{\cdot}0181$, $wR = 0{\cdot}0253$,

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters with e.s.d.'s*

$$U_{\rm eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	*y*	*z*	$U_{\rm eq}$(Å^2)
Pd	0·19275 (6)	0·13813 (4)	0·12680 (4)	0·0299 (2)
Cl(1)	0·4204 (3)	0·01794 (17)	0·17215 (18)	0·0617 (12)
Cl(2)	0·0403 (3)	0·00763 (13)	0·02449 (17)	0·0586 (11)
S(1)	−0·01931 (25)	0·16188 (15)	0·34584 (15)	0·0475 (10)
C(2)	0·1558 (9)	0·2398 (6)	0·4116 (5)	0·045 (4)
C(3)	0·3340 (9)	0·2429 (6)	0·3559 (5)	0·044 (4)
S(4)	0·34429 (20)	0·27367 (14)	0·21185 (13)	0·0362 (9)
C(5)	0·2110 (9)	0·3983 (5)	0·1974 (6)	0·044 (4)
C(6)	0·0960 (10)	0·3939 (5)	0·0961 (6)	0·054 (4)
S(7)	−0·00916 (21)	0·26101 (13)	0·07182 (13)	0·0339 (8)
C(8)	−0·1922 (9)	0·2555 (7)	0·1653 (5)	0·047 (4)
C(9)	−0·1628 (9)	0·2661 (7)	0·2872 (6)	0·050 (4)

Table 2. *Bond lengths* (Å), *angles* (°) *and torsion angles* (°) *with e.s.d.'s*

Pd—Cl(1)	2·3316 (21)	C(3)—S(4)	1·805 (7)
Pd—Cl(2)	2·3326 (21)	S(4)—C(5)	1·835 (7)
Pd—S(4)	2·2672 (17)	C(5)—C(6)	1·517 (10)
Pd—S(7)	2·2457 (17)	C(6)—S(7)	1·831 (7)
S(1)—C(2)	1·820 (7)	S(7)—C(8)	1·800 (7)
S(1)—C(9)	1·821 (8)	C(8)—C(9)	1·515 (10)
C(2)—C(3)	1·513 (10)		
Cl(1)—Pd—Cl(2)	93·71 (7)	Pd—S(4)—C(5)	106·38 (22)
Cl(1)—Pd—S(4)	88·57 (7)	C(3)—S(4)—C(5)	104·1 (3)
Cl(1)—Pd—S(7)	174·64 (7)	S(4)—C(5)—C(6)	111·4 (5)
Cl(2)—Pd—S(4)	174·76 (7)	C(5)—C(6)—S(7)	114·5 (5)
Cl(2)—Pd—S(7)	87·58 (7)	Pd—S(7)—C(6)	104·25 (24)
S(4)—Pd—S(7)	89·74 (6)	Pd—S(7)—C(8)	108·02 (24)
C(2)—S(1)—C(9)	104·1 (3)	C(6)—S(7)—C(8)	105·4 (3)
S(1)—C(2)—C(3)	117·7 (5)	S(7)—C(8)—C(9)	120·7 (5)
C(2)—C(3)—S(4)	118·9 (5)	S(1)—C(9)—C(8)	114·6 (5)
Pd—S(4)—C(3)	105·98 (23)		
Cl(1)—Pd—S(4)—C(3)	−70·24 (24)	C(2)—S(1)—C(9)—C(8)	123·4 (5)
Cl(1)—Pd—S(4)—C(5)	179·43 (23)	S(1)—C(2)—C(3)—S(4)	48·2 (7)
Cl(2)—Pd—S(4)—C(3)	173·9 (7)	C(2)—C(3)—S(4)—Pd	−61·9 (5)
Cl(2)—Pd—S(4)—C(5)	63·6 (8)	C(2)—C(3)—S(4)—C(5)	50·1 (6)
S(7)—Pd—S(4)—C(3)	114·84 (24)	Pd—S(4)—C(5)—C(6)	−27·0 (5)
S(7)—Pd—S(4)—C(5)	4·51 (23)	C(3)—S(4)—C(5)—C(6)	−138·7 (5)
Cl(1)—Pd—S(7)—C(6)	−57·4 (8)	S(4)—C(5)—C(6)—S(7)	41·9 (6)
Cl(1)—Pd—S(7)—C(8)	−169·1 (7)	C(5)—C(6)—S(7)—Pd	−35·9 (5)
Cl(2)—Pd—S(7)—C(6)	−161·43 (25)	C(5)—C(6)—S(7)—C(8)	77·7 (6)
Cl(2)—Pd—S(7)—C(8)	86·8 (3)	Pd—S(7)—C(8)—C(9)	52·6 (6)
S(4)—Pd—S(7)—C(6)	14·07 (25)	C(6)—S(7)—C(8)—C(9)	−58·3 (6)
S(4)—Pd—S(7)—C(8)	−97·7 (3)	S(7)—C(8)—C(9)—S(1)	−59·6 (7)
C(9)—S(1)—C(2)—C(3)	−105·1 (5)		

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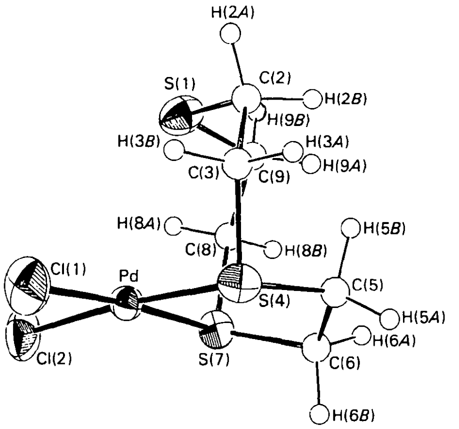

Fig. 1. *ORTEP* plot of the molecule showing atom-labelling scheme. Thermal ellipsoids are shown at the 30% probability level excepting those for C and H, which have artificial radii of 0·15 and 0·10 Å respectively, for clarity.

$S = 1{\cdot}020$ for 109 parameters, $(\Delta/\sigma)_{\max} = 0{\cdot}004$, max. $\Delta\rho = +0{\cdot}34$, min. $= -0{\cdot}36$ e Å^{-3}. No secondary-extinction parameter. Scattering factors inlaid (Sheldrick, 1976) except for Pd (Cromer & Mann, 1968). Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1 while selected molecular parameters appear in Table 2.* The atom-numbering scheme for the structure is shown in Fig. 1, which was generated using *ORTEP* (Mallinson & Muir, 1985). Molecular-geometry calculations were performed using *CALC* (Gould & Taylor, 1985).

Related literature. The corresponding *cis*-[PdBr$_2$*L*] complex is isostructural (Wieghardt, Küppers, Raabe & Krüger, 1986) with Pd—S$_{\rm eq}$ = 2·275 (2), 2·257 (2) and Pd—S$_{\rm ax}$ = 3·125 (1) Å, $\langle$S$_{\rm eq}$PdS$_{\rm ax}\rangle$ = 78·7 (1), 81·7 (1)°. The homoleptic [PdL_2]$^{2+}$ cation shows a closer axial interaction [Pd···S = 2·952 (4) Å] and a significantly different ligand conformation (Blake, Holder, Hyde, Roberts, Lavery & Schröder, 1987; Wieghardt *et al.*, 1986).

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* Lists of structure factors, anisotropic thermal parameters and H-atom positions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44451 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Structure of Pentacarbonyl-μ-[σ:η^4-(1-carbonyl-2-phenyl-2-butenyl)]-(η^5-cyclopentadienyl)diiron(I), $[(CO)_3Fe\{CH_3CHC(C_6H_5)CCO\}Fe(CO)_2Cp]$

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Abstract. $[Fe_2(C_5H_5)(C_{11}H_9O)(CO)_5]$, $M_r = 474{\cdot}036$, $P2_1/n$, $a = 9{\cdot}254$ (3), $b = 17{\cdot}367$ (3), $c = 12{\cdot}601$ (3) Å, $\beta = 95{\cdot}58$ (2)°, $V = 2015{\cdot}6$ (9) Å^3, $Z = 4$, $D_x = 1{\cdot}562$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 14{\cdot}71$ cm^{-1}, $F(000) = 960$, $T = 298$ (2) K, $R = 0{\cdot}041$ for 2746 unique observed reflections. The most striking feature of this structure is the clear example of a C atom of the vinylketene participating in simultaneous σ and π bonding to two otherwise unrelated Fe centers. The Fe···Fe interatomic distance of 3·845 (1) Å precludes any metal–metal bonding. There is an apparent lengthening of the Fe—CO bond *trans* to the α-C of the dienone, indicating that the carbonyl end of the dienone is effectively competing as a back acceptor of electron density from the Fe atom. The four allylic C atoms are coplanar with a maximum deviation from the mean plane of 0·05 Å. The vinylketene O atom is 0·52 Å above this mean plane.

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