Acta Cryst. (1995). C**51**, 1289–1290

trans-Chloro(methyl)bis(triphenylarsine)palladium(II)

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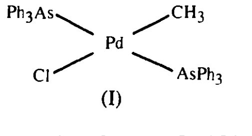
(*Received* 17 *October* 1994; *accepted* 20 *December* 1994)

Abstract

The title compound, [$PdCl(CH_3)(C_{18}H_{15}As)_2$], was obtained as yellow crystals from the reaction of [PdClMe(1,5-cyclooctadiene)] with triphenylarsine. The molecular structure is approximately square planar, with the two arsine ligands in mutually *trans* positions, and Pd—As distances of 2.3989 (5) and 2.4067 (5) Å, and Pd—Cl and Pd—C distances of 2.4086 (11) and 2.095 (4) Å, respectively.

Comment

Platinum complexes of the type [PtCl*R*(cod)] (where *R* is alkyl or aryl and cod is 1,5-cyclooctadiene) are convenient and widely used precursors to other organoplatinum derivatives, but of the corresponding palladium diolefin complexes only the methyl species has been reported to date (Rulke, Ernsting, Spek, Elsevier, van Leeuwen & Vrieze, 1993; Ladipo & Anderson, 1994). Our studies of the reactions of [PdClMe(cod)] with neutral ligands have revealed that the cyclooctadiene ligand may be displaced by one ligand to generate dimeric complexes of the type [$Pd_2(\mu\text{-}Cl)_2Me_2L_2$], or by two ligands to give *trans*-[$PdClMeL_2$]. Treatment of the bis(ligand) complex with additional [PdClMe(cod)] regenerates the appropriate dimeric compound. During the course of this work, we isolated *trans*-[$PdClMe(AsPh_3)_2$], (I), as a crystalline solid.



(I)

The structure analysis of *trans*-[$PdClMe(AsPh_3)_2$] reveals that each molecule adopts approximate square-planar geometry, with a *trans* disposition of the two arsine ligands (Fig. 1). The two As—Pd—C angles are slightly greater than 90°, whereas the As—Pd—Cl angles are less than 90°. The As—Pd—As and C—Pd—Cl vectors are distorted slightly from linearity [177.53 (2) and 176.54 (12)°, respectively]. The two Pd—As distances are 2.3989 (5) and 2.4067 (5) Å, and the Pd—C and Pd—Cl bond lengths are 2.095 (4) and 2.4086 (11) Å, respectively. The molecular structures of only three other bis(arsine) organopalladium complexes have been reported and two of these have mutually *cis* arsine ligands (Kemmitt, McKenna, Russell & Sherry, 1985; Skelton & White, 1980). The only *trans* complex, [$PdCl\{C_6H_2(NO_2)_3\text{-}2,4,6\}(AsPh_3)_2$], exhibits Pd—As distances of 2.406 (3) and 2.427 (3) Å, and shorter Pd—C [1.97 (2) Å] and Pd—Cl [2.329 (5) Å] bond lengths (Vicente, Arcas, Borrachero, de Goicoechea, Lanfranchi & Tiripiccio, 1990). The longer Pd—Cl distance in the present compound reflects the stronger *trans* influence of the methyl group compared with the trinitrophenyl moiety.

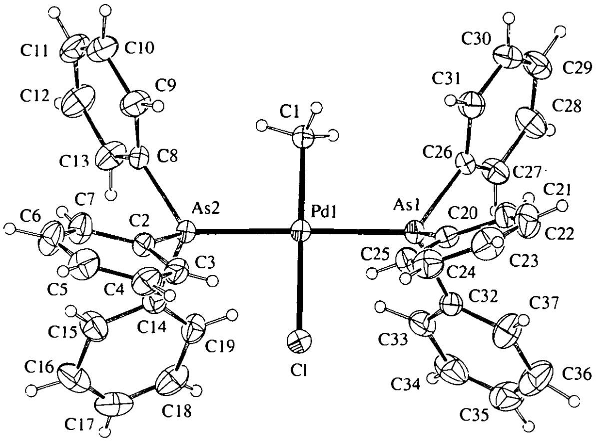


Fig. 1. View of the title compound showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 30% probability levels.

Experimental

The title compound was obtained by addition of a benzene solution (25 ml) of [PdClMe(cod)] (0.248 g, 0.936 mmol) to solid $AsPh_3$ (0.572 g, 1.87 mmol). The product began to precipitate immediately and after stirring for 2 h the pale yellow microcrystalline material was filtered off, washed with pentane and air dried (0.489 g, 68%). ^1H NMR ($CDCl_3$): δH 0.13 (*s*, CH_3), 7.40 (*m*) and 7.67 (*m*) (C_6H_5). Crystals suitable for X-ray diffraction analysis were grown from benzene solution.

Crystal data

[$PdCl(CH_3)(C_{18}H_{15}As)_2$]
$M_r = 769.32$
Monoclinic
$P2_1/n$
$a = 11.793 (3)$ Å
$b = 23.267 (3)$ Å
$c = 12.7130 (10)$ Å
$\beta = 111.48 (2)°$
$V = 3246.0 (10)$ Å^3
$Z = 4$
$D_x = 1.574$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 23 reflections
$\theta = 11.18\text{–}19.49°$
$\mu = 2.702$ mm^{-1}
$T = 298 (2)$ K
Rectangular
0.55 × 0.35 × 0.30 mm
Yellow–orange

Data collection

Siemens *R*3 diffractometer
$\theta/2\theta$ scans
Absorption correction:
  ψ scan (*XEMP*; Sheldrick, 1991)
  $T_{min} = 0.266$, $T_{max} = 0.363$
8371 measured reflections
7957 independent reflections
4500 observed reflections
  $[I > 2\sigma(I)]$

$R_{int} = 0.0630$
$\theta_{max} = 30.07°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 32$
$l = -17 \rightarrow 16$
3 standard reflections
  monitored every 50 reflections
  intensity decay: 2%

Refinement

Refinement on F^2
$R(F) = 0.0365$
$wR(F^2) = 0.0807$
$S = 0.815$
7955 reflections
491 parameters
Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0380P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.598$
$\Delta\rho_{max} = 0.746$ e Å^{-3}
$\Delta\rho_{min} = -0.358$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
Pd1	0.17422 (3)	0.152425 (12)	0.49726 (2)	0.03961 (9)
As1	0.18040 (4)	0.17225 (2)	0.68446 (3)	0.04087 (11)
As2	0.16166 (4)	0.12934 (2)	0.30877 (3)	0.03909 (11)
Cl	0.19688 (10)	0.05164 (4)	0.54353 (8)	0.0536 (3)
C1	0.1659 (4)	0.2406 (2)	0.4621 (3)	0.0466 (10)
C2	0.0236 (3)	0.0827 (2)	0.2191 (3)	0.0425 (9)
C3	−0.0391 (4)	0.0508 (2)	0.2714 (4)	0.0519 (11)
C4	−0.1365 (5)	0.0169 (2)	0.2084 (4)	0.0631 (13)
C5	−0.1720 (5)	0.0152 (2)	0.0937 (4)	0.0690 (15)
C6	−0.1109 (5)	0.0463 (2)	0.0411 (4)	0.073 (2)
C7	−0.0133 (5)	0.0798 (2)	0.1028 (4)	0.0603 (13)
C8	0.1524 (4)	0.1902 (2)	0.2010 (3)	0.0451 (10)
C9	0.0438 (5)	0.2197 (2)	0.1529 (4)	0.0674 (14)
C10	0.0331 (6)	0.2634 (2)	0.0756 (4)	0.0729 (15)
C11	0.1303 (6)	0.2781 (2)	0.0486 (4)	0.073 (2)
C12	0.2373 (6)	0.2500 (3)	0.0958 (5)	0.079 (2)
C13	0.2477 (5)	0.2058 (2)	0.1724 (4)	0.0631 (13)
C14	0.3021 (4)	0.0848 (2)	0.3121 (3)	0.0416 (9)
C15	0.3003 (5)	0.0507 (2)	0.2236 (4)	0.0664 (14)
C16	0.3996 (6)	0.0182 (2)	0.2302 (6)	0.078 (2)
C17	0.5014 (6)	0.0203 (2)	0.3249 (6)	0.074 (2)
C18	0.5063 (5)	0.0541 (3)	0.4108 (5)	0.069 (2)
C19	0.4074 (4)	0.0867 (2)	0.4064 (4)	0.0561 (12)
C20	0.0379 (4)	0.1452 (2)	0.7123 (3)	0.0434 (9)
C21	0.0041 (5)	0.1674 (2)	0.7973 (4)	0.0599 (12)
C22	−0.0984 (6)	0.1474 (3)	0.8120 (5)	0.074 (2)
C23	−0.1675 (5)	0.1055 (3)	0.7435 (5)	0.075 (2)
C24	−0.1330 (5)	0.0823 (2)	0.6607 (5)	0.0646 (14)
C25	−0.0321 (4)	0.1023 (2)	0.6444 (4)	0.0507 (11)
C26	0.1999 (4)	0.2504 (2)	0.7435 (3)	0.0417 (9)
C27	0.3107 (4)	0.2697 (2)	0.8163 (4)	0.0570 (12)
C28	0.3244 (5)	0.3252 (2)	0.8576 (5)	0.0652 (14)
C29	0.2277 (5)	0.3615 (2)	0.8270 (4)	0.0640 (13)
C30	0.1154 (5)	0.3426 (2)	0.7545 (4)	0.0660 (14)
C31	0.1021 (4)	0.2879 (2)	0.7117 (4)	0.0573 (12)
C32	0.3188 (4)	0.1370 (2)	0.7990 (3)	0.0437 (10)
C33	0.4261 (5)	0.1348 (2)	0.7803 (4)	0.0646 (13)
C34	0.5349 (5)	0.1177 (2)	0.8667 (5)	0.079 (2)
C35	0.5311 (7)	0.1010 (2)	0.9673 (5)	0.088 (2)
C36	0.4245 (6)	0.1023 (3)	0.9872 (5)	0.092 (2)
C37	0.3185 (5)	0.1212 (3)	0.9016 (4)	0.073 (2)

Table 2. *Selected geometric parameters* (Å, °)

Pd1—C1	2.095 (4)	As1—C20	1.945 (4)
Pd1—As1	2.3989 (5)	As1—C26	1.949 (4)
Pd1—As2	2.4067 (5)	As2—C14	1.940 (4)
Pd1—Cl	2.4086 (11)	As2—C2	1.941 (4)
As1—C32	1.927 (4)	As2—C8	1.945 (4)
C1—Pd1—As1	90.29 (10)	C14—As2—Pd1	110.89 (11)
C1—Pd1—As2	91.46 (10)	C2—As2—Pd1	116.23 (11)
As1—Pd1—As2	177.53 (2)	C8—As2—Pd1	120.38 (11)
C1—Pd1—Cl	176.54 (12)	C3—C2—As2	120.0 (3)
As1—Pd1—Cl	89.12 (3)	C7—C2—As2	121.6 (3)
As2—Pd1—Cl	89.24 (3)	C13—C8—As2	123.2 (3)
C32—As1—C20	105.9 (2)	C9—C8—As2	118.5 (3)
C32—As1—C26	99.1 (2)	C15—C14—As2	122.3 (3)
C20—As1—C26	102.7 (2)	C19—C14—As2	119.5 (3)
C32—As1—Pd1	112.16 (12)	C25—C20—As1	118.6 (3)
C20—As1—Pd1	113.83 (12)	C21—C20—As1	122.5 (3)
C26—As1—Pd1	121.19 (11)	C27—C26—As1	120.9 (3)
C14—As2—C2	103.9 (2)	C31—C26—As1	120.5 (3)
C14—As2—C8	103.4 (2)	C37—C32—As1	122.8 (4)
C2—As2—C8	100.1 (2)	C33—C32—As1	117.8 (3)

The structure was solved by the Patterson method and refined successfully in the monoclinic space group $P2_1/n$. The non-H atoms were refined anisotropically. Phenyl H atoms were refined freely (C—H = 0.77–1.02 Å) with isotropic displacement parameters. The methyl H atoms were treated as an idealized group with tetrahedral angles and C—H = 0.96 Å using the *AFIX*137 option in *SHELXL*93 (Sheldrick, 1993).

Data collection: Siemens *P*3 data collection software. Cell refinement: Siemens *P*3 data collection software. Data reduction: *XDISK* (Siemens, 1991). Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXTL-Plus*.

This work was supported by a grant from the National Science Foundation (CHE-9101834).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1047). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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