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trans-Diiodobis(triphenylphosphine)palladium(II)

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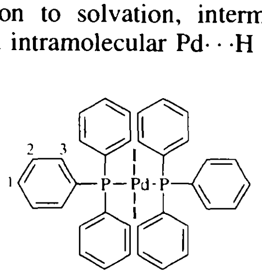
Abstract

The title compound, $[PdI_2\{P(C_6H_5)_3\}_2]$, has the Pd atom located on a crystallographic inversion centre and has a *trans*-square-planar configuration. The Pd—I and Pd—P distances are 2.5975 (3) and 2.3504 (10) Å, respectively. This is the first reported structure of the title compound in an unsolvated form.

Comment

In the course of our studies on the synthesis of novel platinum compounds, we sought to make some new pyridine-type ligands. Our route to these compounds follows the published procedure of using a Grignard reagent with a dihalopyridine, catalyzed by tetrakis(triphenylphosphine)palladium (Minato *et al.*, 1980). The title compound, (I), was isolated as orange crystals from amongst the white crystals of the desired product. It was of interest to investigate the crystal structure of this compound in view of earlier discussions of the red chloroform solvate (Kubota *et al.*, 1991) and the yellow dichloromethane solvate (Debaerdemaeker *et al.*, 1973) in relation to solvation, intermolecular Pd···I interactions and intramolecular Pd···H interactions.



(I)

The molecular structure of the title compound is illustrated in Fig. 1. The Pd atom is located on a crystallographic inversion centre which implies a *trans* geometry with two exactly equal Pd—I distances and two equal Pd—P distances; also, this square-planar complex has the Pd and four ligand donor atoms accurately in a single plane. The Pd—I and Pd—P bond distances are in excellent agreement with those reported previously for the solvates (Table 2). The present structure is devoid of solvent and furthermore does not contain any solvent-accessible spaces (*PLATON*; Spek, 1998).

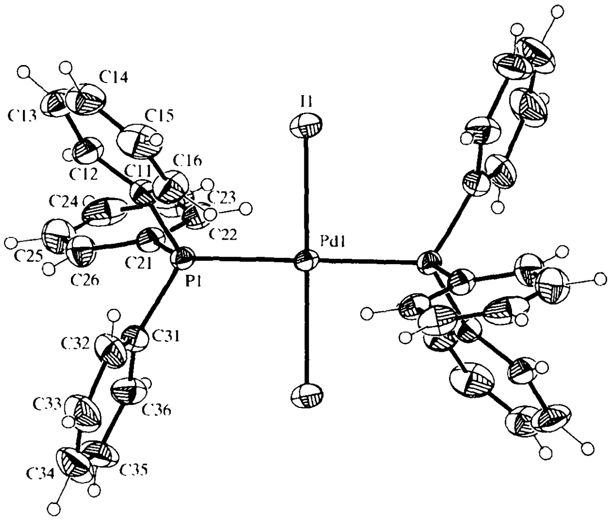


Fig. 1. View of the title molecule showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level.

In the yellow dichloromethane solvate (Debaerdemaeker *et al.*, 1973), a Pd···H separation of 3.18 Å was observed, and this was taken as evidence of octahedral coordination with weak Pd···H interactions. Whilst this distance is greater than the sum of the van der Waals radii of Pd and H, the authors pointed out that since the hydrogen was placed at a calculated position, this bond length is artificial. The real evidence for the Pd···H interaction, they maintain, is the distortion that such an interaction would induce in the phenyl ring; this distortion is observed, with one bond length stretched to 1.491 Å, one reduced to 1.294 Å and the angles deviating substantially from 120°.

The red chloroform solvate (Kubota *et al.*, 1991) is reported to have no intermolecular Pd···I or intramolecular Pd···H interactions, which the authors note is in contrast to the related red complex *trans*-$[PdI_2(PPhMe_2]$ (Bailey & Mason, 1968), which does have intermolecular Pd···I interactions. The title complex, with no intermolecular Pd···I or intramolecular Pd···H interactions, but also no solvation, is orange. This would suggest that the colour is more a function of solvation rather than intermolecular interactions.

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Experimental

2,4-Dihexyloxychlorobenzene (15.0 g, 48.0 mmol) was added dropwise to a stirred solution of magnesium (1.22 g, 50.0 mmol) and methyl iodide (0.30 g, 2.11 mmol) in THF (25 ml) under an inert atmosphere. The resulting Grignard was transferred *via* a cannula to a stirred solution of 2,6-dichloropyridine (2.96 g, 20.0 mmol) and tetrakis(triphenylphosphine)palladium (0.45 g, 0.50 mmol) in THF (25 ml). The reaction mixture was then refluxed for 24 h under an inert atmosphere. Excess Grignard was destroyed with dilute acid. The neutralized reaction mixture was extracted with diethyl ether (2 × 200 ml) and dried (saturated NaCl and magnesium sulfate). The solvent was removed under vacuum and the products recrystallized from ethyl acetate. The expected product, 2,6-bis(4-hexyloxyphenyl)pyridine, crystallized out as white needle-like crystals (yield 95%, 12.0 g, 19.0 mmol) and the diiodobis(triphenylphosphine)palladium(II) complex formed as orange needles (yield 46%, 0.2 g, 0.23 mmol). The two products were separated manually. Crystals of X-ray quality were obtained by recrystallization from hot ethyl acetate. FAB MS (in NBA): m/z 885 (calculated for $[PdI_2\{P(C_6H_5)_3\}_2]$ 885); ^1H NMR [$CDCl_3$, 250.13 MHz, with assignments as show in (I)]: δ 7.38 (H1 and H3, *m*, 18H), 7.69 (H2, *m*, 12H); ^{13}C NMR ($CDCl_3$, 100.577 MHz); δ 128.08 (C3), 130.58 (C1), 134.33 (C4), 135.65 (C2); ^{31}P NMR ($CDCl_3$, 161.923 MHz): δ 13.57.

Crystal data

$[PdI_2(C_{18}H_{15}P)_2]$
$M_r = 884.74$
Triclinic
$P\bar{1}$
$a = 9.3761\ (6)$ Å
$b = 9.4407\ (5)$ Å
$c = 10.7822\ (6)$ Å
$\alpha = 71.424\ (3)°$
$\beta = 87.87\ (1)°$
$\gamma = 67.852\ (3)°$
$V = 834.18\ (2)$ Å^3
$Z = 1$
$D_x = 1.761$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 3679 reflections
$\theta = 2.00–28.66°$
$\mu = 2.526$ mm^{-1}
$T = 160\ (2)$ K
Block
0.40 × 0.14 × 0.04 mm
Orange

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (Sheldrick, 1996)
$T_{min} = 0.625$, $T_{max} = 0.928$
4960 measured reflections
3608 independent reflections

2793 reflections with $I > 2\sigma(I)$
$R_{int} = 0.016$
$\theta_{max} = 28.66°$
$h = -9 \rightarrow 12$
$k = -11 \rightarrow 12$
$l = -10 \rightarrow 14$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.094$
$S = 1.012$
3608 reflections
187 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0530P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 1.055$ e Å^{-3}
$\Delta\rho_{min} = -0.951$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Pd1—P1	2.3504 (10)	P1—C21	1.826 (4)
Pd1—I1	2.5975 (3)	P1—C11	1.828 (4)
P1—C31	1.826 (4)		
P1—Pd1—I1	88.45 (3)		

Table 2. *Comparison of $[PdI_2(PPh_3)_2]$ structures*

	Space group	Colour	Pd—I (Å)	Pd—P (Å)
$[PdI_2(PPh_3)_2]^a$	$P\bar{1}$	Orange	2.5975 (3)	2.3504 (10)
$[PdI_2(PPh_3)_2]\cdot CHCl_3{}^b$	$C2/c$	Red	2.6029 (5)	2.343 (2)
$[PdI_2(PPh_3)_2]\cdot 2CH_2Cl_2{}^c$	$P2_1/c$	Yellow	2.587 (1)	2.331 (2)

References: (*a*) this work; (*b*) Kubota *et al.* (1991); (*c*) Debaerdemaeker *et al.* (1973).

The temperature of the crystal was controlled using an Oxford Cryosystems Cryostream Cooler (Cosier & Glazer, 1986). Data were collected over a hemisphere of reciprocal space by a combination of three sets of exposures. Each set had a different φ angle for the crystal and each exposure of 10 s covered 0.3° in ω. The crystal-to-detector distance was 5.01 cm. Coverage of the unique set was over 81% complete to at least 28° in θ. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analysing the duplicate reflections. H atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms. H atoms were given $U_{iso} = 1.2U_{eq}(C)$.

Data collection: *SMART* (Siemens, 1994*a*). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL/PC* (Siemens, 1994*b*). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

We wish to acknowledge the use of the EPSRC's Chemical Database Service at Daresbury Laboratory (Fletcher *et al.*, 1996) for access to the Cambridge Structural Database (Allen & Kennard, 1993). The authors also wish to thank the EPSRC for financial support (to GWVC) and Johnson–Matthey for the loan of chemicals.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1284). Services for accessing these data are described at the back of the journal.

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Nonacarbonyl-μ_2-hydrido-μ_2-(*N*-methylcarboxamido)-*C*:*O*-(*N*-trimethylamine)triosmium(3 *Os*—*Os*)

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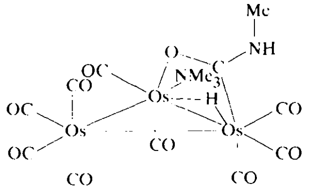
Abstract

In the title compound, nonacarbonyl-$1\kappa^2C,2\kappa^3C,3\kappa^4C$-$\mu$-hydrido-$1{:}2\kappa^2H$-$\mu$-(*N*-methylcarboxamido)-$1{:}2\kappa^2O{:}C$-(*N*-trimethylamine-$1\kappa N$)triosmium(3 *Os*—*Os*), $[Os_3H(C_2H_4NO)(C_3H_9N)(CO)_9]$, the MeHNCO ligand forms a μ_2-C:O bridge between two metal centers, which are also linked by a μ-hydride ligand. These two groups are at opposite sides of the plane defined by the Os atoms. Bond lengths between Os atoms are 2.8149 (8), 2.8777 (8) and 2.9278 (8) Å. The structure shows two metal centers which are heptacoordinated and one which is hexacoordinated.

Comment

The labile triosmium carbonyl clusters can be prepared by the reaction of $Os_3(CO)_{12}$ with Me_3NO (trimethylamine oxide) in the presence of a coordinating solvent such as CH_3CN (acetonitrile) affording the mono- and disubstituted metal clusters $[Os_3(CO)_{11}(MeCN)]$ and $[Os_3(CO)_{10}(MeCN)_2]$, respectively (Johnson *et al.*, 1981). However, if the above-mentioned reaction is performed in a less strongly coordinating solvent, *e.g.* THF (tetrahydrofuran), the amine derivative is obtained (Dawson *et al.*, 1982).

Under our reaction conditions, a novel disubstituted carbonyl cluster, (I), is obtained. In this new compound, one carbonyl group has been replaced by a trimethylamine ligand. Also, a nucleophilic attack occurred at one of the axial carbonyls producing a μ-O—C group that bridges two Os atoms as shown in Fig. 1.



(I)

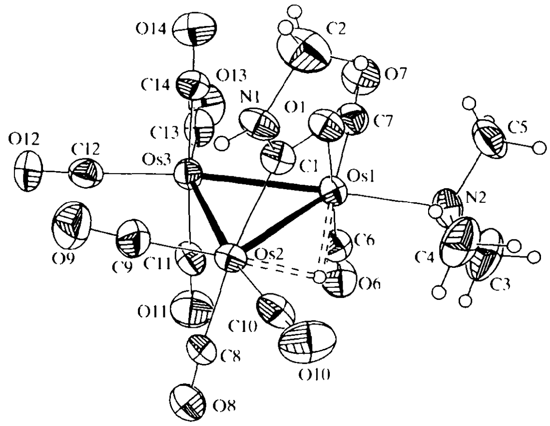


Fig. 1. The molecular structure of the title compound showing 30% probability displacement ellipsoids and the atomic numbering scheme.

The title compound, $[Os_3H(C_3H_9N)(C_2H_4NO)(CO)_9]$, has a triosmium triangular core. Two osmium centers (Os1 and Os2) are heptacoordinated and the other one (Os3) is hexacoordinated. The hexacoordinated Os atom shows a distorted octahedral coordination geometry and the heptacoordinated ones have distorted face-capped octahedral coordination environments. The face-capping ligand is a hydride ligand that bridges Os1 and Os2. In all cases, the 'equatorial' octahedral plane corresponds approximately to the plane defined by the triosmium core.

The apical positions (at the same face of the triosmium core) at Os1 and Os2 are occupied by O and C atoms (O1 and C1), respectively, defining a μ-carbox-

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