

cis-Dichloro(dimethylamino-methylene)(triphenylphosphine)-palladium(II) acetone solvate

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Received 1 March 2000

Accepted 10 March 2000

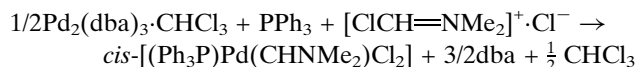
Data validation number: IUC0000069

The synthesis and X-ray structural analysis of the title compound, $[\text{PdCl}_2(\text{C}_3\text{H}_7\text{N})(\text{C}_{18}\text{H}_{15}\text{P})]\cdot\text{C}_3\text{H}_6\text{O}$, are described. The crystal structure contains discrete monomeric molecules of the carbene complex and solvent molecules separated by normal van der Waals distances. The Pd atom is four-coordinate in an essentially square-planar environment, with the chlorine ligands mutually *cis*; Pd—P = 2.2495 (7), Pd—Cl = 2.3508 (7) and 2.3600 (7), Pd—C 1.948 (2) and N—C(carbene) 1.274 (3) Å.

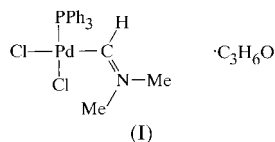
Comment

The reaction of the Vilsmeier salt, chloromethylenedimethylammonium chloride, with formally low-valent nucleophilic transition metal species has been used for the synthesis of a range of transition metal dimethylaminomethylene complexes (Cucciolo *et al.*, 1999; Hartshorn *et al.*, 1978; Rendina *et al.*, 1995).

We have now used this reaction to prepare the title palladium complex, (I), according to the following sequence (dba = dibenzylideneacetone):



Complex (I) was required for comparison with the platinum analogue, *cis*- $[(\text{Ph}_3\text{P})\text{Pt}(\text{CHNMe}_2)\text{Cl}_2]$, (II), which has been obtained by two different routes (Barefield *et al.*, 1982; Ferguson *et al.*, 1999), and for which an X-ray crystallographic study has been reported (Barefield *et al.*, 1982).



The crystal structure of (I) contains discrete monomeric molecules of the carbene complex and solvent molecules separated by normal van der Waals distances. Principal dimensions are collected in Table 1 and mean-plane data are in the CIF. The Pd atom is four-coordinate in an essentially square-planar environment with the chlorine ligands mutually *cis*. The framework atoms of the carbene ligand (C1/N1/C2/C3) are close to being coplanar, and the dihedral angle between this plane and the coordination plane (Pd1/P1/C11/C12/C1) is 72.30 (10)° [*cf.* 84° for the Pt analogue (II)].

The interatomic distances in (I) are very similar to those reported (Barefield *et al.*, 1982) for (II), except that the M—P bond length is somewhat greater for M = Pd [2.2495 (7) Å] than for M = Pt [2.220 (2) Å]. Similar differences have been found for other pairs of Pd and Pt complexes containing phosphine ligands (McCrindle *et al.*, 1995). The Pd1—C1 [1.948 (2) Å] and C1—N1 [1.274 (3) Å] bonds are relatively short, consistent with π -bonding within the metal-carbene moiety comparable with those observed in other Pd-carbene complexes (Dixon & Dixon, 1995).

Experimental

A solution of $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (517.5 mg, 0.500 mmol) and PPh_3 (262.3 mg, 1.00 mmol) in dry CH_2Cl_2 (20 ml) was added dropwise to a cooled (263 K) suspension of $[\text{ClHC}=\text{CNMe}_2]\text{Cl}$ [generated *in situ* from dimethylformamide (80 mg, 1.1 mmol) and oxalyl chloride (127 mg, 1.00 mmol) in CH_2Cl_2 (3 ml) with stirring under nitrogen]. The temperature of the reaction mixture was allowed to rise to ambient and stirring was continued for 16 h. The solvent was then removed *in vacuo*, the residue was washed with benzene to remove dibenzylideneacetone, and the insoluble fraction was crystallized from CH_2Cl_2 /pentane to give *cis*- $[(\text{Ph}_3\text{P})\text{Pd}(\text{CHNMe}_2)\text{Cl}_2]$ as very fine white needles (194.5 mg, 39.1% yield). Analysis calculated for $\text{C}_{21}\text{H}_{22}\text{Cl}_2\text{NPPd}$: C 50.78, H 4.46, N 2.82%; found: C 50.90, H 4.32, N 2.79%. NMR (CDCl_3), ^1H : δ 9.25 (1H, *d*, $^3J_{\text{PH}} = 7.6$ Hz), 7.65–7.75 (6H, *m*), 7.35–7.48 (9H, *m*), 3.59 (3H, *s*), 2.85 (3H, *s*); ^{13}C : δ 221.2, 134.2 (*d*, $^2J_{\text{PC}} = 11$ Hz), 131.4 (*d*, $^4J_{\text{PC}} = 2.5$ Hz), 129.6 (*d*, $^1J_{\text{PC}} = 54$ Hz), 128.8 (*d*, $^3J_{\text{PC}} = 11$ Hz), 51.48, 49.71; ^{31}P : δ 25.6. Recrystallization of the material from acetone gave well formed colourless blocks, one of which was selected for X-ray crystallographic examination.

Crystal data

$[\text{PdCl}_2(\text{C}_3\text{H}_7\text{N})(\text{C}_{18}\text{H}_{15}\text{P})]\cdot\text{C}_3\text{H}_6\text{O}$	$Z = 2$
$M_r = 554.74$	$D_x = 1.465 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.9821 (14) \text{ \AA}$	Cell parameters from 25 reflections
$b = 10.8560 (18) \text{ \AA}$	$\theta = 9.39\text{--}10.65^\circ$
$c = 14.3002 (19) \text{ \AA}$	$\mu = 1.029 \text{ mm}^{-1}$
$\alpha = 91.279 (16)^\circ$	$T = 294 (1) \text{ K}$
$\beta = 107.901 (16)^\circ$	Lath, colourless
$\gamma = 107.173 (15)^\circ$	$0.40 \times 0.25 \times 0.14 \text{ mm}$
$V = 1257.9 (3) \text{ \AA}^3$	

Data collection

Enraf-Nonius CAD-4 diffractometer	4660 reflections with $I > 2\sigma(I)$
$\theta/2\theta$ scans	$\theta_{\text{max}} = 27.5^\circ$
Absorption correction: Gaussian	$h = -11 \rightarrow 10$
(<i>ABSO</i> in <i>NRCVAX</i> ; Gabe <i>et al.</i> , 1989)	$k = 0 \rightarrow 14$
$T_{\text{min}} = 0.810$, $T_{\text{max}} = 0.907$	$l = -18 \rightarrow 18$
5768 measured reflections	3 standard reflections
5768 independent reflections	frequency: 120 min
	intensity decay: 0.8%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0275P)^2 + 0.3092P]$
$R[F^2 > 2\sigma(F^2)] = 0.028$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.063$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.024$	$\Delta\rho_{\max} = 0.38 \text{ e } \text{Å}^{-3}$
5768 reflections	$\Delta\rho_{\min} = -0.32 \text{ e } \text{Å}^{-3}$
274 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.0132 (5)

Table 1
Selected geometric parameters (Å, °).

Pd1—P1	2.2495 (7)	P1—C31	1.821 (2)
Pd1—C11	2.3508 (7)	C1—N1	1.274 (3)
Pd1—C12	2.3600 (7)	C1—H1	0.93
Pd1—C1	1.948 (2)	N1—C2	1.463 (4)
P1—C11	1.819 (2)	N1—C3	1.473 (3)
P1—C21	1.818 (2)		
C11—Pd1—C12	91.73 (3)	Pd1—P1—C21	110.47 (8)
C11—Pd1—P1	89.09 (3)	Pd1—P1—C31	115.00 (8)
C11—Pd1—C1	174.55 (7)	Pd1—C1—N1	130.27 (19)
C12—Pd1—P1	179.16 (2)	C1—N1—C2	122.3 (2)
C12—Pd1—C1	88.37 (7)	C1—N1—C3	122.2 (2)
P1—Pd1—C1	90.80 (7)	C2—N1—C3	115.5 (2)
Pd1—P1—C11	114.45 (8)		

The title compound crystallized in the triclinic system; space group $P\bar{1}$ was assumed and confirmed by the analysis. All H atoms of the Pd complex were resolved in difference maps and were treated as riding atoms (C—H 0.93–0.96 Å) during refinement. The H atoms of the acetone solvate molecule were not at all clearly resolved and these were allowed for in the final calculations by placing six 0.5 occupancy H atoms around the C5 and C6 atoms with appropriate geometry constraints and C—H = 0.96 Å. Examination of the structure with *PLATON* (Spek, 2000) showed that there were no solvent-accessible voids in the crystal lattice. The acetone of solvation fills what would otherwise have been a void in the crystal lattice.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992); cell refinement: *SET4* and *CELDIM* in *CAD-4-PC Software* (Enraf–

Nonius, 1992); data reduction: *DATRD2* in *NRCVAX96* (Gabe *et al.*, 1989); program(s) used to solve structure: *NRCVAX96* via Patterson heavy-atom method; program(s) used to refine structure: *NRCVAX96* and *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *NRCVAX96*, *SHELXL97* and *WordPerfect* macro *PREP8* (Ferguson, 1998).

We thank Dr J. F. Gallagher and Dublin City University for the funds to purchase the X-ray tube used in the data collections.

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