CRYSTAL STRUCTURE OF TRIS(TRIPHENYLPHOSPHINE) PALLADIUM

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The authors have made an x-ray structural investigation [λMo, 5655 reflections, anisotropic (Pd, P)-isotropic (C) method of least squares to R = 0.088] of the reaction product of $Pd_2(PPh_3)_2 \cdot (\mu\text{-}CO)(OAc)_2$ with a tertiary amine, identified in the course of x-ray structural analysis as $Pd(PPh_3)_3$. The crystals are triclinic: a = 11.659, b = 14.803, c = 15.843 Å, α = 109.31, β = 95.17, γ = 90.49°, ρ_{calc} = 1.154 g/cm³, Z = 2, space group $P\bar{1}$. In the structure the coordination unit PdP_3 has the form of a strongly distorted trigonal pyramid. The Pd atom is raised a little above the plane of P_3 and is 0.160 Å from it. The spacings of Pd—P are 2.307-2.322 Å, and the values of the angles PPdP are 115.0-126.5°. The short intramolecular contacts Pd...H (2.82-2.03 Å) to the ortho atoms of the Ph rings lie above and below the plane P_3, blocking the axial positions at the Pd atoms. The results are compared with the literature data on complexes of zero-valent palladium with phosphine ligands.

The dimer carbonyl-containing complex of univalent palladium, $Pd_2(PPh_3)_2(\mu\text{-}CO)(OAc)_2$ (I), is obtained by reacting palladium (1+) carbonylacetate $Pd_4(CO)_4(OAc)_4$ with PPh_3. Complex I is unstable in solution and on standing decomposes to a compound of Pd(2+) and the complex of zero-valent palladium of unknown composition (II). The same result is produced by processing I with tertiary amines [1].

EXPERIMENTAL

The dark green crystals of $Pd(PPh_3)_3$ form irregular cubes and are triclinic. The lattice parameters are: a = 11.659(3), b = 14.803(4), c = 15.843(4) Å, α = 109.31(2), β = 95.17(2), γ = 90.49(2)°, V = 2567.9(10) Å³, ρ_{calc} = 1.154(2) g/cm³, μ_{Mo} = 4.9 cm⁻¹, Z = 2, space group $P\bar{1}$

The experimental material for XSA was obtained from a single crystal measuring 0.35 × 0.40 × 0.45 mm on a Syntex $P2_1$ automatic four-circle diffractometer at room temperature (λMo Kα radiation, graphite monochromator). The reflections were scanned by the θ/2θ method ($2\theta_{max}$ = 45°). The drift of the intensity was monitored by periodic (every 100 reflections) measurement of the intensity of the control reflections 040 and 002. Anisotropy of the absorption was taken into account experimentally from the curve of azimuthal scanning for the reflections 200 and 600. For the atoms Pd and P a correction was made for anomalous scattering. In the course of the exposure the crystal, under the influence of the x-rays and atmospheric moisture, gradually broke up from the surface and changed color from dark to light green, leading to a systematic reduction in the intensity of the control reflections (totally ~20%).

The full set of diffraction data included 6738 independent reflections; to determine the structure we used 5655 reflections with $I \geq 1.96\,\sigma(I)$. All the calculations were made by means of the XTL program complex on a Nova-1200 minicomputer.

The structure was solved by the heavy-atom method and refined by the method of least squares in the full-matrix approximation, anisotropic for the Pd and P atoms and isotropic for the C atoms, with inclusion of the atoms H(Ph) in the computed positions (starting from sp^2 hybridization of the C atoms and the given distances C—H = 1.05 Å). The final value of R was 0.088. In the zeroth Fourier synthesis we found several unidentified peaks, possibly relating to a strongly disordered solvent molecule (most likely triethylamine).

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TABLE 1. Atomic Coordinates (in lattice fractions) and Temperature Factors B_{eq}* of Pd and P Atoms, and B_j of C Atoms (in Å²)

Atom	x	y	z	$B_{eq}(B_j)$
Pd	—0,0045(1)	0,14451(9)	0,24381(9)	3,01
P(1)	—0,1657(4)	0,2111(3)	0,3106(3)	3,6
P(2)	0,1253(4)	0,2468(3)	0,2137(3)	3,3
P(3)	0,0628(4)	—0,0060(3)	0,2317(3)	3,3
C(1)	—0,2288(14)	0,3125(12)	0,2842(11)	3,8(4)
C(2)	—0,1637(15)	0,3941(13)	0,3000(12)	4,4(4)
C(3)	—0,2079(18)	0,4711(15)	0,2767(13)	5,8(5)
C(4)	—0,3154(20)	0,4655(17)	0,2357(15)	7,0(5)
C(5)	—0,3859(20)	0,3824(18)	0,2145(16)	7,5(6)
C(6)	—0,3418(18)	0,3031(15)	0,2416(14)	6,0(5)
C(7)	—0,2928(14)	0,1379(13)	0,3090(12)	4,2(4)
C(8)	—0,3091(14)	0,0470(12)	0,2463(11)	4,2(4)
C(9)	—0,4070(17)	—0,0119(14)	0,2446(13)	5.5(4)
C(10)	—0,4876(17)	0,0235(15)	0,3066(14)	6,1(5)
C(11)	—0,4733(18)	0,1173(15)	0,3718(14)	6,2(5)
C(12)	—0,3738(17)	0.1753(14)	0,3749(13)	5,7(5)
C(13)	—0,1242(14)	0,2654(12)	0,4329(11)	4,1(4)
C(14)	—0,0536(16)	0,2064(14)	0,4704(13)	5.3(4)
C(15)	—0,0157(19)	0,2431(16)	0.5635(15)	6,7(5)
C(16)	—0,0458(19)	0,3340(17)	0.6132(15)	6,9(5)
C(17)	—0,1141(19)	0,3893(16)	0,5766(16)	7,1(6)
C(18)	—0,1548(17)	0,3569(15)	0.4850(14)	6,0(5)
C(19)	0,2107(14)	0,3214(12)	0.3151(11)	3,8(4)
C(20)	0,1609(15)	0,3415(13)	0,3954(12)	4,6(4)
C(21)	0,2220(18)	0,3978(15)	0,4789(14)	6,2(5)
C(22)	0,3322(20)	0,4278(16)	0.4809(16)	7,1(6)
C(23)	0,3838(22)	0,4095(19)	0.4025(18)	8,6(7)
C(24)	0,3200(18)	0,3553(15)	0.3143(14)	6,1(5)
C(25)	0,0630(13)	0,3321(11)	0,1662(10)	3,5(3)
C(26)	0,1137(16)	0,4212(14)	0,1829(13)	5,4(4)
C(27)	0,0544(19)	0,4836(16)	0,1403(15)	6,8(5)
C(28)	—0,0500(18)	0,4501(16)	0,0833(14)	6,4(5)
C(29)	—0,0998(17)	0,3614(15)	0,0676(14)	6,1(5)
C(30)	—0,0387(15)	0,3032(13)	0,1118(12)	4,7(4)
C(31)	0,2368(13)	0,1994(11)	0,1364(10)	3,4(3)
C(32)	0,3225(15)	0,1494(12)	0,1647(11)	4,3(4)
C(33)	0,4067(16)	0,1109(14)	0,1074(13)	5,4(4)
C(34)	0,3982(17)	0,1189(14)	0,0197(14)	5,8(5)
C(35)	0,3059(18)	0,1656(15)	—0,0086(14)	6,3(5)
C(36)	0,2274(16)	0,2067(13)	0,0515(12)	4,9(4)
C(37)	0,1519(14)	—0,0013(12)	0,3347(11)	3,7(3)
C(38)	0,2000(15)	0,0897(13)	0,3885(12)	4,4(4)
C(39)	0,2673(16)	0,0988(14)	0,4718(13)	5,4(4)
C(40)	0,2857(17)	0,0211(15)	0,4990(14)	6,1(5)
C(41)	0,2403(19)	—0,0689(16)	0,4431(15)	6,8(5)
C(42)	0,1724(16)	—0,0843(14)	0,3594(13)	5,4(4)
C(43)	—0,0291(13)	—0,1132(11)	0,2158(11)	3,5(3)
C(44)	—0,1080(15)	—0,1026(13)	0,2786(12)	4,6(4)
C(45)	—0,1837(17)	—0,1814(14)	0,2706(13)	5,5(5)
C(46)	—0,1798(17)	—0,2664(15)	0,1975(14)	5,7(5)
C(47)	—0,1014(17)	—0,2699(14)	0,1366(13)	5,4(4)
C(48)	—0,0254(15)	—0,1959(13)	0,1451(12)	4,4(4)
C(49)	0,1546(13)	—0,0551(11)	0.1409(11)	3,4(3)
C(50)	0,1260(14)	—0,0331(12)	0,0654(12)	4,3(4)
C(51)	0,1856(18)	—0,0665(15)	—0,0109(14)	5,8(5)
C(52)	0,2759(18)	—0,1286(15)	—0;0069(14)	6,3(5)
C(53)	0,3069(18)	—0,1499(16)	0,0732(15)	6,7(5)
C(54)	0,2462(15)	—0,1133(13)	0,1506(12)	4,8(4)
H(14)**	—0,031	0,138	0,430	6
H(20)	0,077	0,315	0,395	6
H(30)	—0,074	0,234	0,102	6
H(38)	0,187	0,150	0,368	6
H(50)	0,056	0,011	0,064	6

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*$B_{eq} = 1/3(B_{11} + B_{22} + B_{33})$.

**We give coordinates only for those hydrogen atoms for which the contacts Pd...H ≤ 3.1 Å.

In Table 1 we give the coordinates of the atoms, the temperature factor constants B_{eq} for the Pd and P atoms and B_j for the C atoms. Tables of the anisotropic temperature factors B_{ij}, the structure factors $F^2(hk\ell)$, the atomic coordinates of the H atoms, and the deviations of the atoms from the median planes can be obtained from the authors.

TABLE 2. Examples of Structurally Studied Phosphines of Complexes of Zero-Valent Palladium with Various Coordinations of Metal

Compound	Coordination number	Geometry of coordination unit	Mean length of Pd–P bond	Angle PPdP (av.)	References
$Pd\{PPh(\textit{mpem}\text{-}Bu)_2\}_2$	2	Linear	2,285(2)	176,6(1)	[3]
$Pd\{P(C_6H_{11})_3\}_2$	2	Bent	2,295(7)	158,4(3)	[4]
$Pd(PPh_3)_2(CS_2)$	3 *	Planar-trigonal	2,365(8)	108,8(3)	[5]
$[Pd\{C_2(CO_2Me)_2\}(PPh_3)_2]$	3 **	»	2,325(2)	107,43(6)	[6]
$[Pd(PPh_3)(\mu\text{-}Ph_2PC{\equiv}CCF_3)_2]_2$	3 **	»	2,317(4) (PPh_3) 2,298(4) $(\mu\text{-}PPh_2PC{\equiv}CCF_3)$	—	[7]
$Pd(PPh_3)_3$	3	Flattened-pyramidal	2,316(5)	119,6(2)	Present authors
$[Pd(PPh_3)_4]\cdot C_6H_6$	4	Tetrahedral	2,450(4)	109,5(1)	[8]

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*We assume that the bidentate (S, C) ligand CS_2 occupies one coordination site.

**The acetylene bond C≡C of the olefin type occupies one coordination site.

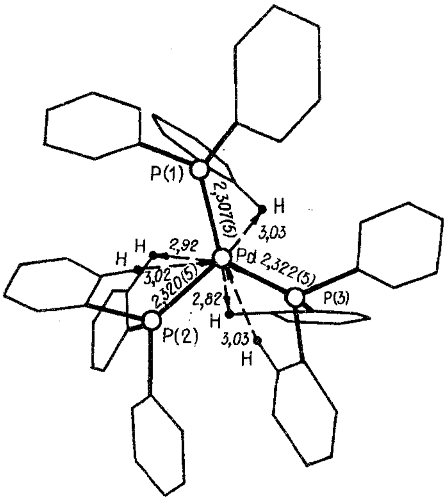

Fig. 1. Structure of complex $Pd(PPh_3)_3$ (projection on plane of three P atoms).

RESULTS AND DISCUSSION

The structure of the complex $Pd(PPh_3)_3$ (II) is shown in Fig. 1 (projection on plane of three P atoms).

The palladium atom is coordinated by three phosphorus atoms from three PPh_3 ligands. The coordination unit PdP_3 has the form of a strongly flattened trigonal pyramid. The Pd atom is raised a little above the P_3 plane and is spaced 0.160 Å from it. The complex $Pt\cdot(PPh_3)_3$ [2], in which the platinum atom is spaced 0.1 Å away from the plane of the three phosphorus atoms, has a similar structure.

In our structure II the distances Pd–P lie in the interval 2.307-2.322(5) Å, and the angles PPdP in the interval 115.0-126.5(2)°. In the triphenylphosphine ligands, as usual, the angles PdPC [107.9-124.9(6)°] are mainly larger, and the angles CPC [99.5-105.2(8)°] are less than the ideal tetrahedral value 109.5°. The distances P–C are 1.80-1.85(2) Å, C–C are 1.35-1.49(3) Å, the angles PCC are 114-124(1)°, CCC are 114-123(2)°. The plane (within ±0.01-0.03 Å) phenyl rings are rotated through 40-97° relative to the plane P_3. In each triphenylphosphine ligand the Ph rings are arranged like propeller blades; the range of angles between their planes is 58-121°.

In structure II there are a number of short intramolecular Pd...H contacts. The five shortest of these at distances of 2.82-3.03 Å include the ortho atoms of H of five of the nine rings [one for atom P(1), and two for atoms P(2) and P(3)]. These hydrogen atoms lie above and below the plane P_3 (spaced from it by 2.18-2.36 Å), blocking the axial positions for the Pd atoms. Short intramolecular contacts Pd...H with ortho-atoms of H(Ph) and hydrogen atoms of tert-butyl groups (2.70-2.83 Å) are also found for complexes of zero-valent palladium with linear geometry of the metal atom $Pd(PPh(\text{tert-Bu})_2)_2$ [3].

The compound $Pd(PPh_3)_3$ is the first structurally studied example of a complex of zero-valent palladium with trigonal-pyramidal geometry. Table II gives examples of complexes Pd(0) with phosphine ligands having various geometries of the coordination unit [3-8]. The mean distance Pd–P in our compound $Pd(PPh_3)_3$ (2.316 ± 0.009 Å) falls in a fairly wide interval of mean values (2.285-2.365 Å) for five other double and triple coordination complexes Pd(0) with phosphine ligands [3-7]. An exception is the complex $Pd(PPh_3)_4\cdot C_6H_6$ [8] with tetrahedral coordination of the metal atom, in which the Pd–P bonds (mean value 2.450 Å) are increased owing to spatial hindrances due to the presence of four bulky triphenylphosphine ligands in the coordination sphere.

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CRYSTAL STRUCTURE OF ORGANOSILICON COMPOUNDS.

XLV.* 1-(BROMODIMETHYLSILYLMETHYL)-2-PIPERIDONE

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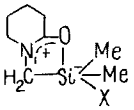
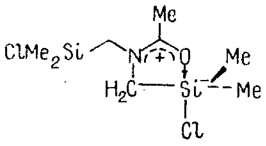
An x-ray diffraction structural study was carried out on 1-(bromodimethylsilylmethyl)-2-piperidone (R = 0.079 relative to 1772 reflections). A rearrangement of the silicon bonds in the crystal was unexpectedly discovered: a strong covalent Si—O bond is formed with 1.800(4) Å bond length and the Si—Br bond is weakened with its conversion to a weak donor—acceptor Si...Br interaction; the length of this weak bond, which is reported for the first time, is 3.122(2) Å. The silicon atom has distorted trigonal-bipyramidal coordination.

INTRODUCTION

Pentacoordinated silicon compounds have attracted attention in light of their high biological activity [2], structural features without analogy among carbon compounds [2-5] and as possible intermediates in nucleophilic substitution at silicon [6, 7]. We have recently described a new type of pentacoordinated silicon derivatives, namely, N-(halodimethylsilylmethyl)lactams (I), which feature intermolecular coordination between the silicon and oxygen atoms [8]. Such coordination in their "acyclic" analog, (O-Si)-chloro-[(N-chlorodimethylsilylacetamido)methyl]dimethylsilane (II) was establsihed by x-ray diffraction structural analysis [9]. The formation of an Si ← O coordination bond leads to a redistribution of electron density in II characterized by the predominant contribution of a resonance form with positive charge on the $N\underline{\cdots}C\underline{\cdots}O$ fragment and negative charge on the silicon atom. A significant contribution of this form could also be proposed for I upon realization of the Si ← X coordination bond.



I; X=Cl(a), Br(b)



II

On the other hand, comparison of the IR spectra of I and of N-(halodimethyldilylmethyl)-amides II [10] shows that these spectra for chlorides and bromides differ significantly. Conductometric studies of I also show a difference in the corrrsponding chlorides and bromides. The physicochemical data indicate the formation of an Si—O covalent bond and weaker

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*For XLIV, see [1].

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