Inorganica Chimica Acta, 86 (1984) 121–125

Synthesis and Characterization of an Hexamethylphosphortriamide Derived Palladium Complex: Crystal Structure of Dichloro Bis(dimethylamine)Palladium(II)

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Received October 18, 1983

When a solution of palladium(II) chloride in hexamethylphosphortriamide (HMPA = $(Me_2N)_3PO$) was heated, a sec-alkylamine (L) palladium complex —of the type PdL_2Cl_2— was isolated and characterized on the basis of analytical and spectral data. The crystal structure of the title compound was carried out by X-ray diffraction data: it crystallizes in a monoclinic cell $P2_1/c$, with $a = 7.699(2)$, $b = 5.999(1)$, $c = 10.454(3)$ Å, $\beta = 98.3(1)°$, $Z = 2$. Final R values: $R = 0.035$ and $R_w = 0.035$ for 1059 independent reflections. A trans *square planar coordination geometry around the palladium atom was ascertained. An alternative synthetic route to the complex is reported, together with the possible reasons for its formation.*

Introduction

As part of a series of investigations into new transition metal derivatives as heterogenized catalysts in organic synthesis [1–3], we wish to report the unexpected formation of an amine–palladium complex which was isolated by heating palladium(II) chloride in hexamethylphosphortriamide (HMPA). Our initial aim was to coordinate a soft acid, such as $PdCl_2$, with the powerful electron donor HMPA [4], acting at the same time as a polar aprotic solvent, in order to obtain a weakly interactive, although efficient, catalytic system for the selective liquid phase hydrogenation of carbon–carbon triple bonds [5, 6].

There are no reports in the literature about reactions between palladium salts and HMPA, although several investigators have already pointed out that other transition metals, such as Fe, Co, Ni, etc., form coordination complexes with HMPA in non-aqueous media; co-ordination generally involves the phosphorous–oxygen functionality of the ligand molecule [4, 7–12]. In our case however the behaviour of HMPA was somehow different, in that the preliminary formation of an amine ligand occurred under the experimental conditions adopted, to yield subsequently a simpler coordination complex, *i.e.* dichloro bis(dimethylamine)palladium(II) (*1*). The present paper describes its synthesis, isolation, spectral characterization and structure as determined by X-ray diffraction.

The reaction reported here provides an alternative synthetic route to the amine complexes of the type $M(Alkylamine)X_2$, where M = Pd, Pt, etc. and X = halogen, whose importance is well established [13].

Results and Discussion

The title compound (*1*) was prepared by reacting palladium(II) chloride in solution with HMPA. Specific conditions are needed to obtain the complex, *i.e.* a large excess of the ligand precursor, acting also as a solvent, should be used. Furthermore, the temperature has to be kept constant at not less than 80–85 °C. The oily residue was left standing after solvent evaporation and gave yellow crystals which are not sensitive to light and moisture.

The thermal analysis' dynamic curve of the complex showed a sublimation pattern from 120 °C to the m.p. value (212–4 °C) and further peaks up to 320 °C, which are due to partial decomposition, sublimation and high m.p. value indicate a fair degree of stability of the complex, as well as the typical behaviour of monomeric species. Stoichiometry has been established by elemental analysis; the data are consistent with a metal to ligand 1:2 addition compound, of the type PdL_2X_2 whose formula is $Pd(C_4H_{14}N_2)Cl_2$. Molar conductivity is very low, compared to values of 1:1 electrolytes, thus indicating that the complex is essentially non-ionic.

Spectroscopic evidences suggested an alkylamine–palladium species for (*1*). The electronic spectrum of the complex under examination (Table I) exhibits two ligand field bands at 26316 and 29851 cm^{-1}, due to $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_g$ transitions re-

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0020-1693/84/$3.00

TABLE I. Infrared and Electronic Spectral Data of $Pd(Me_2NH)_2Cl_2$ (*1*).

Frequency (cm^{-1})	Relative intensity	Assignment[a]	Frequency (cm^{-1})	ϵ_{max} (m^{-1} cm^{-1})	Assignment
3210	m	ν(N–H)	26316	193	$^1A_{1g} \rightarrow {}^1B_{1g}$
2967	m	ν(C–H)	29851	217	$^1A_{1g} \rightarrow {}^1E_g$
2924	s	ν(C–H)	45249	27169	charge transfer
2875	sh	ν(C–H)			
2785	m	ν(C–H) in N–Me			
2090	w				
1640	w,b				
1455	s	ν(C–H) in N–Me			
1427	m	δ(N–H) ?			
1418	m				
1396	m				
1258	m				
1207	w				
1135	m	ν(C–N)			
1048	s				
1024	m				
900	s	ω(N–H)			
803	w				
512	m	ν(Pd–N)			
340	s	ν(Pd–Cl)			
255	m	δ(Pd–N) ?			

[a] The notation is according to R. S. Mulliken [20].

spectively [14], and a strong charge-transfer band at 45249 cm^{-1}, observed in all the palladium complexes [15]. The most relevant i.r. absorption bands maxima of complex (*1*) and their assignments are also given in Table I. The whole spectrum exhibits a similar pattern to that of dimethylamine [16], in the 3400–2000 cm^{-1} (N–H and C–H stretching) and 1650–700 cm^{-1} (N–H and C–H bending and C–N stretching) regions; of these only frequencies at 3210, 1427 and 900 cm^{-1} are associated with N–H vibration modes and are lowered by *ca.* 50–90 cm^{-1} on complexation, indicating that coordination to the metal occurs through the amine nitrogen atom, as expected. The other bands in the region 1500–600 cm^{-1} are mostly due to the ligand skeletal vibrations and seem to be coordination-insensitive. The far-i.r. spectrum reveals a strong absorption band at 340 cm^{-1}, assigned to a Pd–Cl bond stretching, in agreement with a *trans*-orientation of the halogens in a square planar palladium complex [17]. Two medium absorptions at 512 and 255 cm^{-1} have been tentatively associated to stretching and bending modes of Pd–N respectively of the alkylamine palladium complex [18, 19].

In the ^1H n.m.r spectrum of the complex (see Experimental) two unequal signals are observed in the methyl region (intensity ratio $\simeq$2:1). If compared to the single methyl signal in free ligand (δ = 2.76 ppm), both resonances are slightly shifted towards higher fields, in agreement with a differentiated shielding effect related to coordination of the amine to the metal. Moreover, it can be inferred that in solution the complex has a stereosymmetric structure, where only a pair of hydrogen atoms for each conformationally mobile methyl group are in turn magnetically equivalent, whilst the third hydrogen is differently shielded and therefore not magnetically equivalent to the others. A *trans* configuration of ligand molecules is thus favoured also by n.m.r. considerations.

An X-ray structural determination of the complex established definitively that in the solid state its structure is identical to that proposed above. Fig. 1 shows a view of the molecule. The final atomic parameters are in Table II. Table III shows the interatomic distances and angles.

The $Pd(Me_2NH)_2Cl_2$ molecule lies on a crystallographic inversion center and the PdN_2Cl_2 moiety is consequently *trans* and planar. The Pd–N and Pd–Cl bond distances of 2.055(4) and 2.305(1) Å respectively are comparable with the values reported for analogous compounds [21]. All the C–H lengths are in the range 0.1–1.1 Å. In the coordination plane the only departure from the exact square-planar configuration is given by the different values of the two Cl–Pd–N angles (87.7° and 92.3° respectively). This could be justified by some degree of repulsion between Cl and C(1) carbon atom, the distance C(1)···Cl (3.563 Å) being shorter than the sum of the van der Waals radii.

The C sp^3-N bond values, 1.481(7) and 1.468(7) Å, are standard single bonds. The crystal packing

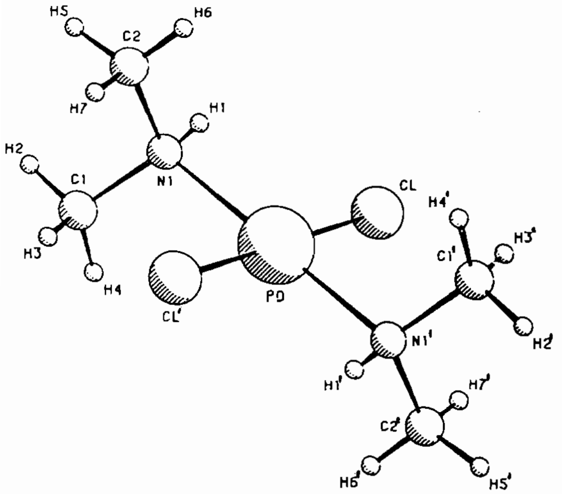

Fig. 1. Perspective view of the molecule.

TABLE III. Interatomic Distances (Å)* and Angles (°) with their e.s.d. s in Parentheses, and Some Selected Contacts (Å).

Pd–Cl	2.305(1)	Pd–N	2.055(4)
N–C(1)	1.468(7)	N–C(2)	1.481(7)
N–H(1)	0.91(5)	C(1)–H(2)	1.03(7)
C(1)–H(3)	0.88(8)	C(1)–H(4)	1.05(7)
C(2)–H(5)	1.04(6)	C(2)–H(6)	0.93(8)
C(2)–H(7)	0.95(5)		
Cl····N	3.026	N····Cl′	3.149
C(1)····Cl′	3.563	H····Pd	2.425
Cl–Pd–N	87.7(1)	N–Pd–Cl′	92.3(1)
Pd–N–H(1)	103(3)	Pd–N–C(2)	115.1(4)
Pd–N–C(1)	112.1(4)	H(1)–N–C(1)	108(3)
H(1)–N–C(2)	106(3)	C(1)–N–C(2)	111.4(5)

*Primed atoms are centrosymmetrically related to the unprimed.

(Fig. 2) is determined solely by van der Waals forces and none of the intermolecular contact distances are shorter than the sum of the van der Waals radii.

A possible reaction sequence leading to the formation of complex (*1*) involves a preliminary hydrolytic cleavage of N–P bonds in HMPA, promoted by traces of water and catalyzed by a soft acid, such as $PdCl_2$ [22]; phosphoric acid and dimethylamine are formed and have been both detected among the reaction products. Subsequently, two molecules of the resulting nucleophilic ligand coordinate to the transition metal. As expected on the above grounds, the reaction described did not occur when all reagents were carefully dryed and operations were carried out in a dry box, under a nitrogen atmosphere.

Finally, evidence for the proposed reaction path and *trans* geometry of the square planar complex (*1*)

TABLE II. Atomic Coordinates and Thermal Parameters.

a) Atomic coordinates ($\cdot 10^4$), for hydrogen atoms ($\cdot 10^3$) with e.s.d.'s in parentheses.

	x	*y*	*z*		*x*	*y*	*z*
Pd	0	0	0				
Cl	1721(2)	733(2)	−1581(1)				
N	−1898(5)	1981(6)	−1013(4)	H(1)	−132(6)	262(8)	−162(4)
C(1)	−3366(8)	671(12)	−1681(7)	H(2)	−419(8)	164(12)	−231(6)
				H(3)	−388(8)	9(8)	−105(7)
				H(4)	−310(9)	−64(13)	−299(7)
C(2)	−2528(10)	3833(11)	−264(7)	H(5)	−347(9)	468(9)	−89(6)
				H(6)	−162(12)	469(11)	16(9)
				H(7)	−310(7)	326(8)	42(5)

b) Anisotropic and isotropic thermal parameters (Å^2) with e.s.d.'s in parentheses ($\cdot 10^3$).

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd	29.9(2)	32.7(2)	34.6(2)	−2.3(2)	10.0(2)	−2.2(2)
Cl	48.8(6)	49.3(6)	51.4(6)	2.7(6)	25.4(5)	0.6(5)
N	40(2)	42(2)	39(2)	2(2)	10(2)	0(2)
H(1)	35(12)					
C(1)	45(3)	68(4)	58(3)	4(3)	−1(3)	−1(3)
H(2)	73(19)					
H(3)	55(18)					
H(4)	83(22)					
C(2)	74(4)	48(4)	65(4)	−4(3)	20(4)	18(3)
H(5)	60(18)					
H(6)	96(30)					
H(7)	45(14)					

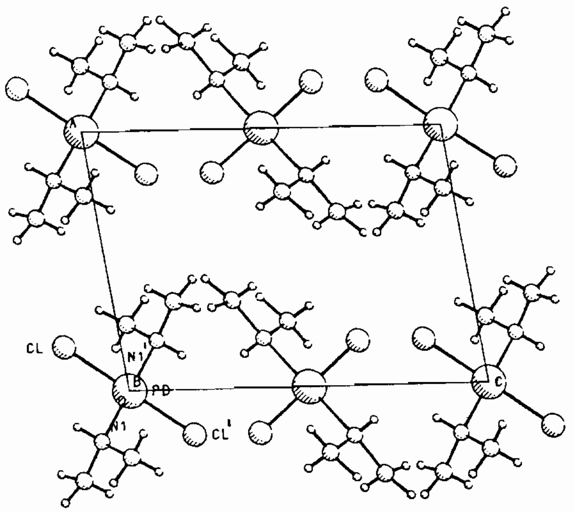

Fig. 2. Unit cell content viewed down *b*.

was also obtained by synthesizing it through a procedure alternative to that reported [23], *i.e.* starting from *trans*-$Pd(PhCN)_2Cl_2$ and aqueous Me_2NH (see Experimental).

Experimental

HMPA (Fluka, purum) and solvents were purified according to standard methods. Palladium(II) chloride (Engelhard, batch n. 5743) and other reagents were used as obtained from commercial sources.

Molar conductivity measurements were made with an Halosis Conductivity Bridge Type SAz, using a dip-type platinum cell. M.p.'s of the compounds were determined in a Köfler hot-stage microscope apparatus. Thermal analyses were performed with a Perkin-Elmer Mod. DSC-2 differential scanning calorimeter; samples were analyzed under nitrogen in open aluminum pans, at the rate of 10 °C min^{-1} in the range 50–350 °C. Electronic spectra (46500–23000 cm^{-1}) were recorded in abs. ethanol with a Cary Mod. 219 u.v.-vis. instrument. Infrared spectra (4000–400 cm^{-1}, nujol and fluorolube mulls) were recorded with a Perkin-Elmer Mod. 557 spectrophotometer, using CsI windows and a polystyrene film for calibration. A Varian 360A spectrometer was used to obtain 60 MHz ^1H n.m.r. spectra, in $CDCl_3$; chemical shifts are quoted in δ units, parts per million, relative to Me_4Si as an internal reference. Elemental analyses were performed by Bernhardt Microanalytisches Laboratorium, Elbach, W. Germany and by the Microanalytical Laboratory of the Institute of Organic Chemistry, Milan, Italy.

The significant electronic and i.r. spectral data, with assignments, are given in Table I.

Preparation of Dichloro Bis(dimethylamine)palladium(II) (1)

(A) A mixture of palladium(II) chloride (0.040 g, 0.22 mmol) and HMPA (4.00 g, 22.3 mmol) in benzene (10 ml) was stirred, at 40 °C, for eight hours. A deep-orange solution was obtained, which changed to yellow when heated for six hours at 100 °C. The typical smell of alkylamines was detected and a colourless viscous oil separated off and was collected by centrifugation (H_3PO_4). Furthermore, the pH of the solution was measured in the course of the reaction and its value was found to be close to 6 for the orange solution, and gradually became stable at *ca.* 2 while yellow coloration was observable.

The solvent was removed from the centrifugate solution by rotary evaporation under reduced pressure and a yellow solid was obtained on standing. This was recrystallized several times from benzene to yield (*1*), as yellow rombic crystals, m.p. 208–210° (0.050 g, 85%). Sublimation at 170 °C/4–5 bar gave a pale-yellow powder, m.p. 212–4 °C. *Anal.* Calcd. for $PdC_4H_{14}N_2Cl_2$: C, 17.95; H, 5.24; N, 10.47; Cl, 26.55; Pd, 39.79%. Found: C, 18.19; H, 5.28; N, 10.56; Cl, 26.23; Pd, 40.48%. ^1H n.m.r. ($CDCl_3$, Me_4Si), δ, ppm: 2.48 (s, 8H) and 2.55 (s, 4H) for Me hydrogens; 3.25 (broad s, 1H) for NH hydrogen of *sec*-amine ligand. I.r. and u.v. spectral data: see Table I. Molar conductance: 2.8 ohm^{-1}.

An alternative procedure, gives (*1*) by dissolving $PdCl_2$ (0.060 g, 0.33 mmol) in HMPA (10 g, 55.5 mmol) as the solvent, and heating the orange solution for 15 min at 115 °C: its colour turns rapidly to yellow. As above, the viscous oil and yellow crystals of (1) separated out on standing for several days (0.080 g, 91%).

(B) $Pd(PhCN)_2Cl_2$ (0.150 g, 0.39 mmol) was dissolved in pure benzene (40 ml), and a 33% aqueous solution of dimethylamine (0.500 g, 3.70 mmol) was added dropwise, while stirring for half an hour at room temperature. The red-brown benzene solution decolorized, while the aqueous phase turned yellowish and gave a yellow precipitate after the usual working up, *i.e. in vacuo* evaporation, filtration and washing with cold benzene.

Yellow rhombic crystals resulted from repeated crystallization from a chloroform–benzene mixture (0.090 g, 86%). Analytical and spectral data of the above compound proved its identity with that of the complex described above.

X-Ray Data Collection and Structure Solution

Yellow crystals of $Pd(Me_2NH)_2Cl_2$, suitable for X-ray diffraction were obtained by slowly cooling a benzene solution. All diffraction measurements were performed on a Siemens-Stoe four-circle diffractometer by using graphite-monochromated MoKα radiation. Twenty reflections of ϑ 10–15° were located by a random search procedure and subsequently centred. These reflections were used as a basis for the indexing. The cell constants and the orientation matrix obtained were refined by a least-squares fit. The crystals were found to be monoclinic with unit cell dimensions $a = 7.699(2)$, $b = 5.999(1)$, $c = 10.454(3)$ Å, $\beta = 98.3(1)^\circ$, U = 477.8 Å^3, F(000) 264, Z = 2, and $D_c = 1.861$ g cm^{-3}, λ(Mo–Kα) = 0.7107 Å, $M_r = 267.4$.

For space group $P2_1/c$ with 2 molecules per cell the molecule must be centrosymmetric with Pd lying in a inversion center.

Intensities were collected at room temperature for all independent reflections in a range $3 < 2\vartheta < 64^\circ$. An ω/ϑ scan was used for each reflection with a scan speed of 0.03° s^{-1}, scan width 1.2° and two 10-s background count at each end of the scan range. No reflections were sufficiently intense to require the insertion of attenuators into the beam. Two standard reflections (−1, −3, −1 and −1, −1, −1) measured after approximately 100 data reflections showed only random fluctuations. Of the 2000 measured reflections, 1059 independent with $I > 3\sigma(I)$ were used for structure solution and refinement. The data were corrected for Lorentz and polarization effects but since the linear absorption coefficient is 22.4 cm^{-1}, no absorption correction was applied. The structure was refined by full matrix least-squares to convergence by using anisotropic thermal parameters for all the non-hydrogen atoms and isotropic for hydrogens.

The function minimized was $\Sigma w\Delta^2$ in which $w = 4.1163/[\sigma^2(F_o) + 19.3 \times 10^{-5}\ (F_o)^2]$ and $\Delta = |F_o| - |F_c|$; discrepancy indices used are $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$ and $Rw = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. Weighting scheme analyses showed no serious dependence of mean $w\Delta^2$ on either (Fo) and $\lambda^{-1} \sin \vartheta$.

A final difference map revealed peaks of about 0.8 e Å^{-3} near the metal positions but was otherwise featureless. A list of observed and calculated structure factors and thermal parameters is available.

Atomic scattering factors were taken from Cromer and Waber's [24] tabulation for all atoms except hydrogen, for which the values of Stewart [25] were used. Anomalous dispersion terms [26] for Pd were included in F_c. The final conventional R values were R = 0.035 and Rw = 0.035.

The calculations were carried out on the IBM computer of the 'Centro di Calcolo', University of Messina, with the 'SHELX 76' system [27] of programs.

Acknowledgements

This work was supported by the Italian National Research Council (CNR, Roma).

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