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CLEAVAGE OF THE TETRAMERIC PALLADIUM(II) COMPLEX $[Pd_4(PPr^n_3)_4(NO_2)_4(ONO)_4]$ WITH NUCLEOPHILES. X-RAY CRYSTAL STRUCTURES OF THE PRODUCTS *TRANS*-$[Pd(PPr^n_3)(NO_2)_2Cl][As(C_6H_5)_4]$ AND $[Pd_2(PPr^n_3)_2Cl_2(NO_2)_2]$

G. BRUNO,* S. CAMPAGNA, M. CUSUMANO, A. GIANNETTO
and V. RICEVUTO

Dipartimento di Chimica Inorganica e Struttura Molecolare, Salita Sperone 31, Vil.S.Agata,
98016 Messina, Italy

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Abstract—The tetrameric complex $[Pd_4(PPr^n_3)_4(NO_2)_4(ONO)_4]$ readily reacts with the nucleophiles NO_2^- and Cl^- to give a variety of palladium(II) square-planar complexes of PPr^n_3. A scheme for these reactions is proposed. The crystal structures of *trans*-$[Pd(PPr^n_3)(NO_2)_2Cl][As(C_6H_5)_4]$, obtained by reaction of the tetramer with $[As(C_6H_5)_4]NO_2$, and of $[Pd_2(PPr^n_3)_2(NO_2)_2Cl_2]$, obtained by reaction of the tetramer with the bridged complex $[Pd_2(PPr^n_3)_2Cl_4]$ have been determined by single crystal X-ray diffraction: (1) $[Pd(PPr^n_3)(NO_2)_2Cl][As(C_6H_5)_4]$, $M_r = 777.45$, orthorhombic, $P2_12_12_1$, $a = 17.723(2)$, $b = 14.890(1)$, $c = 13.178(1)$ Å, $V = 3477.7(5)$ Å^3, $Z = 4$, $D_x = 1.48$ Mg m^{-3}, λ(Mo-K_α) = 0.71069 Å, $\mu = 0.78$ cm^{-1}, $F(000) = 1584$, $T = 293$ K, $R = 0.053$ for 1710 independent reflections with $I > 3\sigma(I)$. (2) $[Pd_2(PPr^n_3)_2Cl_2(NO_2)_2]$, $M_r = 696.2$, monoclinic, $P2_1/n$, $a = 13.665(2)$, $b = 7.855(1)$, $c = 13.704(2)$ Å, $\beta = 101.4(1)$, $V = 1441.8(4)$ Å^3, $Z = 4$, $D_x = 1.60$ Mg m^{-3}, λ(Mo-K_α) = 0.71069 Å, $\mu = 0.74$ cm^{-1}, $F(000) = 704$, $T = 293$ K, $R = 0.030$ for 1993 independent reflections with $I > 3\sigma(I)$.

We have recently shown[1] that by reaction of the bridged complex $[Pd_2(PPr^n_3)_2Cl_4]$ with $NaNO_2$ in methanol the tetrameric compound $[Pd_4(PPr^n_3)_4(NO_2)_4(ONO)_4]$ is obtained. In this species an approximate square of Pd atoms is joined together by nitro–nitrito bridges; a nitro group and a tri-*n*-propylphosphine complete the coordination. This complex is very labile and is promptly cleaved, in different solvents, by nucleophiles to give various square-planar complexes of PPr^n_3. In this paper we describe the reaction of $[Pd_4(PPr^n_3)_4(NO_2)_4(ONO)_4]$ with the nucleophiles Cl^- and NO_2^- and report the crystal structure of one of the products of the reaction with the latter nucleophile, *trans*-$[Pd(PPr^n_3)(NO_2)_2Cl][As(C_6H_5)_4]$, and of the complex $[Pd_2(PPr^n_3)_2(NO_2)_2Cl_2]$ obtained by reaction of the tetramer with $[Pd_2(PPr^n_3)_2Cl_4]$.

EXPERIMENTAL

The preparation of $[Pd_4(PPr^n_3)_4(NO_2)_4(ONO)_4]$ has already been reported.[1] $[Pd(PPr^n_3)(NO_2)_3][As(C_6H_5)_4]$ was obtained by reacting $[Pd_4(PPr^n_3)_4(NO_2)_4(ONO)_4]$ in methanol, in the presence of $[As(C_6H_5)_4][NO_3]$ in a ratio of 1 : 10, with a large excess of $NaNO_2$. The solution was stirred for 1 h and the solvent evaporated off. The residue, after washing several times with water, was crystallized from methanol–diethyl ether.

$[Pd_2(PPr^n_3)_2Cl_4]$. The tetrameric compound $[Pd_4(PPr^n_3)_4(NO_2)_4(ONO)_4]$, dissolved in methanol, was treated with a large excess of LiCl. The resulting solution was left under magnetic stirring for 24 h and the solvent was evaporated off. The solid residue was washed with water and crystallized from cold ethanol.

The complexes *trans*-$[Pd(PPr^n_3)(NO_2)_2Cl][As(C_6H_5)_4]$, $[Pd(PPr^n_3)(NO_2)Cl_2][As(C_6H_5)_4]$ and $[Pd(PPr^n_3)Cl_3][As(C_6H_5)_4]$ were prepared by reacting $[Pd_4(PPr^n_3)_4(NO_2)_4(ONO)_4]$ with $[As(C_6H_5)_4][NO_2]$, in the appropriate ratio in methanol. The resulting solution was stirred for 1 h and the solvent evaporated off. The residue was dissolved in CH_2Cl_2 and the product was precipitated as a crystalline solid by the addition of diethyl ether.

$[Pd_2(PPr^n_3)_2(NO_2)_2Cl_2]$ was obtained as a crystalline solid by reacting the tetramer with $[Pd_2$

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*Author to whom correspondence should be addressed.

$(PPr^n_3)_2Cl_4]$, in methanol, in a ratio of 1 : 2. LiCl, NaCl and $NaNO_2$, as well as all the solvents used, were of reagent grade.

UV–vis spectra were recorded using a Perkin–Elmer Lambda 5 spectrophotometer. IR spectra in the range 250–4000 cm^{-1} were recorded as Nujol mulls on a Perkin–Elmer 783 spectrometer. Conductivity measurements were carried out with a Radiometer CDM3 conductivity bridge.

Diffraction data, for **1** and **2**, were collected on a Siemens–Stoe Four Circle diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å). Accurate unit cell dimensions and crystal orientation matrices were obtained from least-squares refinement of 2θ, ω, χ and ψ values of 20 strong reflections in the range $14 < 2\theta \langle 24^\circ$. Three standard reflections were monitored periodically during the course of the data collection as a check of the crystal stability, and these varied by less than 3% for both compounds. Of 3800 and 3950 independent reflections measured by the ω–2θ scan technique, in the range $3 < 2\theta < 50$, 1710 and 1993 ($R_{int} = 0.022$, 0.018) having net intensity $I > 3\sigma(I)$ were used in the solution and refinement of the structure. Corrections for Lorentz and polarization effects were made, but not those for absorption ($\mu = 16.3$ and 15.5 cm^{-1}). Both the structures were solved by using standard Patterson methods. The Fourier difference synthesis phased with the heavy-atom positions allowed the location of the non-hydrogen atoms in **1** and **2**. Full-matrix least-squares refinement of the models was carried out by minimizing the function $\Sigma\, w(|F_o| - |F_c|)^2$. The weighting scheme used in the last refinement cycles were $w = 0.7186/[\sigma^2(F_o) + 0.005366F_o^2]$ for **1** and $w = 0.6979/[\sigma^2(F_o) + 0.001878F_o^2]$ for **2**, which showed reasonable consistency in a test of $w\Delta^2$ for data sectioned with respect to both F_o and $\sin\theta/\lambda$. Anisotropic temperature factors were introduced for all non-hydrogen atoms; in compound **1** the phenyl rings of the triphenylarsine cation were refined as rigid groups and restricted to their normal geometry (D_{6h} symmetry; $d_{C—C} = 1.395$ Å) by using the group refinement procedure. Each ring was assigned an individual isotropic thermal parameter. Hydrogen atoms were added at calculated positions and included in the structure factor calculations with a common thermal parameter ($U = 0.06$ Å^2). Both models reached convergence with $R = [\Sigma|F_o| - |F_o|]/\Sigma|F_o| = 0.053$ and 0.030 $wR[\Sigma\, w(|F_o| - |F_c|)^2/\Sigma\, w|F_o|^2]^{1/2} = 0.056$ and 0.036 for **1** and **2**, respectively. Scattering factors for non-hydrogen atoms were taken from ref. 2 and for hydrogen atoms from ref. 3. Anomalous dispersion corrections for Pd, Cl and P atoms were taken from ref. 4.

Reversing the sign of the imaginary anomalous scattering component for **1**, which has the non-centrosymmetric space group $P2_12_12_1$, increased R from 0.053 to 0.071. This difference is highly significant, and therefore the model has the correct absolute configuration.

All calculations were performed with the *SHELX 76*[5] and *PARST*[6] set of programs on the IBM 4341 computer at the "Centro di Calcolo dell' università di Messina". Atomic coordinates, anisotropic temperature factors and calculated and observed structure factors are available as supplementary material. Atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

On addition of excess nitrite or chloride to a methanol or dichloromethane solution of $[Pd_4(PPr^n_3)_4(NO_2)_4(ONO)_4]$, an immediate reaction occurs as shown by the large spectral variation, in the UV region, associated with the process. However, when using NaCl or LiCl as the nucleophile only the starting complex is recovered if the solvent is evaporated off. The reaction product in the case of NO_2^-, $[Pd(PPr^n_3)(NO_2)_3]^-$, can be obtained in the solid state as a pure compound, providing the nucleophile/complex ratio is $\geqslant 4$, in the presence of a bulky counter ion such as $[As(C_6H_5)]^+$. When the nucleophile is Cl^-, various substances are obtained as a function of the chloride concentration. Thus, when the chloride/complex ratio is 4 only $[Pd(PPr^n_3)(NO_2)_2Cl]^-$ forms in solution; with a large excess of chloride (over 100-fold with respect to the complex) either $[Pd(PPr^n_3)Cl_3]^-$ or the chloro-bridged complex $[Pd_2(PPr^n_3)_2Cl_4]$ are the reaction products. The former, as well as $[Pd(PPr^n_3)(NO_2)_2Cl]^-$, precipitates in the presence of $[AS(C_6H_5)_4]^+$; the latter substance is obtained, using LiCl or NaCl as the nucleophile, when the solvent is evaporated off. Intermediate Cl^- concentrations lead to a mixture of variously substituted complexes of PPr^n_3 including a substance which precipitates in the presence of $[As(C_6H_5)_4]NO_3$ and can be formulated, on the basis of elemental analysis, as $[Pd(PPr^n_3)(NO_2)Cl_2][As(C_6H_5)_4]$. In this compound, the two chlorides most likely occupy mutual *cis* positions; the IR spectrum (Nujol mull) shows in fact two stretching frequencies at 265 and 329 cm^{-1} assignable to the Pd—Cl *trans* and *cis*, respectively, to phosphine.[7] In addition, reaction of a 1 : 1 ratio of this complex and PPr^n_3 does not lead to *trans*-$[Pd(PPr^n_3)_2Cl_2]$ as expected if NO_2 were *trans* to phosphine but to $[Pd(PPr^n_3)_2ClNO_2][As(C_6H_5)_4]$. The IR spectrum of this product shows a stretching frequency Pd—Cl at 285 cm^{-1} characteristic of Cl *trans* to phosphine[7] and only one Pd—P stretching frequency at 425 cm^{-1} as expected for phosphines *trans* to each other.

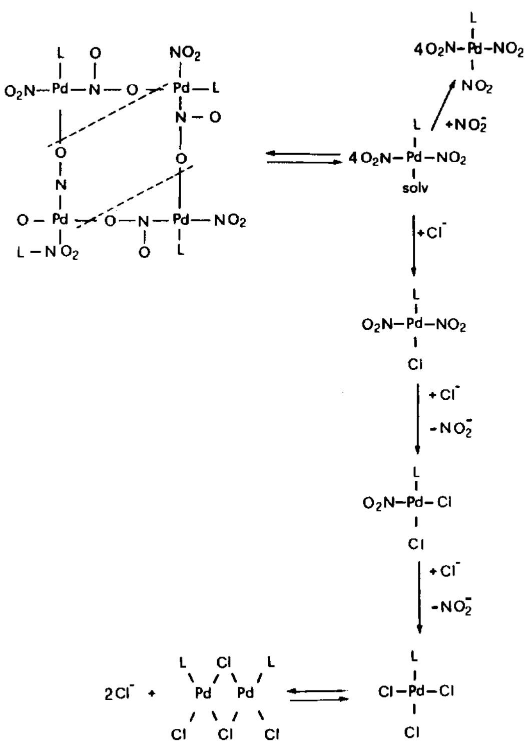
The IR spectrum of $[Pd(PPr^n_3)(NO_2)_2Cl][As(C_6H_5)_4]$ exhibits a band at 285 cm^{-1} attributable to Pd—Cl with the chloride *trans* to phosphine. This type of structure has been conclusively confirmed by X-ray analysis of the substance. The structure of $[Pd_2(PPr^n_3)_2(NO_2)_2Cl_2]$ has also been established by single crystal determination. On the basis of the nature of the reaction products a possible reaction scheme is predicted in Scheme 1.

The existence of an equilibrium between the tetramer and a solvo-species is supported by the conductivity data. A methanol solution of the tetramer (1×10^{-4} M) exhibits a molar conductance of about 9 Ω^{-1} cm^2 M^{-1} which is unexpected for a neutral complex.[8]

By reacting the tetramer with the bridged complex $[Pd_2(PPr^n_3)_2Cl_4]$, $[Pd_2(PPr^n_3)_2(NO_2)_2Cl_2]$ is obtained:

$$[Pd_4(PPr^n_3)_4(NO_2)_4(ONO)_4] + 2[Pd_2(PPr^n_3)_2Cl_4] \rightarrow 4[Pd_2(PPr^n_3)_2(NO_2)_2Cl_2]. \quad (2)$$

The structure of $[Pd_2(PPr^n_3)_2(NO_2)_2Cl_2]$ has also been established by single crystal determination.



Scheme 1.

Molecular structure of $[Pd_2(PPr^n_3)(NO_2)_2Cl][As(C_6H_5)_4]$ (1)

The crystal structure of **1**, depicted in Fig. 1 with the atomic labelling, consists of a discrete

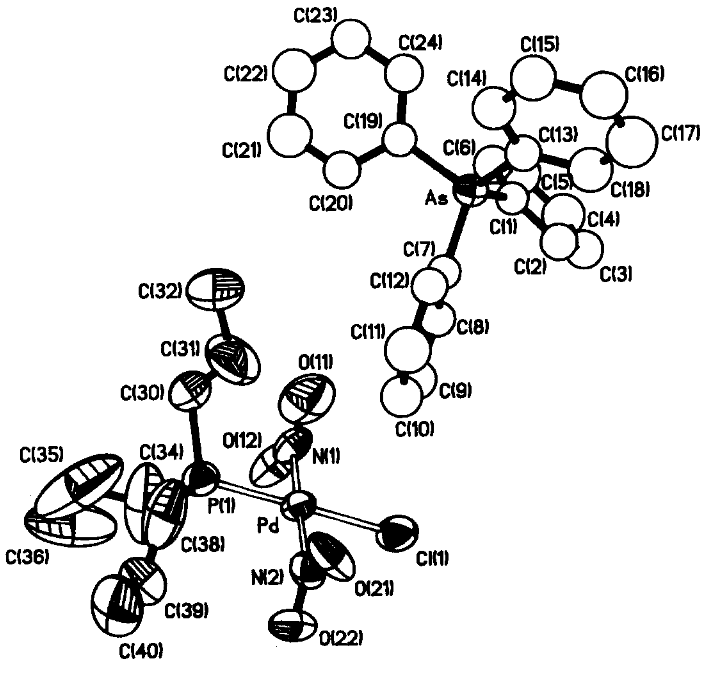


Fig. 1. Molecular structure of *trans*-$[Pd(PPr^n_3)(NO_2)_2Cl][As(C_6H_5)_4]$.

anion, in which the metal atom is fully coordinated, and separated from the cation $[As(C_6H_5)_4]^+$ by normal van der Waals interactions. Bond distances and angles are reported in Table 1. The local anion geometry is, as expected, square-planar slightly distorted as the atom-to-plane deviations are all lower than 0.02 Å. The two nitrogen atoms of the nitro groups *trans* to each other form an angle [N(1)—Pd(1)—N(2)] of 178.1(6)°. Both the Pd(1)—N(1) and Pd(1)—N(2) bond distances are comparable (2.037(19) and 2.007(18) Å) with the corresponding values in $[Pd(PPr^n_3)(NO_2)_3][As(C_6H_5)_4]$[9] and other nitro complexes.[10,11] The geometry of the nitrite groups is characterized by N—O distances (mean 1.16(3) Å) and the O—N—O angle of 122.6(2)°. In addition, the planes of the nitrite groups are nearly perpendicular to the coordination plane, being rotated by 88.7(9) and 91.9(8)° with respect to it. The Pd(1)—P(1) bond distance of 2.243(6) Å is comparable with the corresponding value of 2.262(6) Å in $[Pd(PPr^n_3)(NO_2)_3][As(C_6H_5)_4]$[9] and 2.248(4) Å in $[Pd_4(PPr^n_3)_4(NO_2)_4(ONO)_4]$[1] and is much lower than the value of 2.327(3) Å in $[Pd_2(PPr^n_3)_2(NCS)(SCN)_2(\mu\text{-}CN)]$[11] where the two phosphines are mutually *trans*. The Pd(1)—Cl bond distance of 2.347(5) Å is slightly lower than the value of 2.359(1) Å found for Pd—Cl *trans* to $As(C_6H_5)_3$ in *cis*-$[Pd(SNNMe_2)(As(C_6H_5)_3)Cl_2]$[12] and is significantly longer than the value of 2.300 Å mediated over a series of Pd—Cl bonds[13] where two chlorine atoms are *trans* to each other.

Table 1. Selected bond lengths (Å) and bond angles (°) for *trans*-$[Pd(PPr^n_3)(NO_2)_2Cl]$ $[As(C_6H_5)_4]$

Bond distances (Å)			
Pd(1)—Cl(1)	2.347(6)	Pd(1)—N(1)	2.037(19)
Pd(1)—N(2)	2.007(18)	Pd(1)—P(1)	2.243(6)
N(1)—O(11)	1.085(36)	N(1)—O(12)	1.156(28)
N(2)—O(21)	1.185(24)	N(2)—O(22)	1.220(23)
P(1)—C(30)	1.865(27)	P(1)—C(34)	1.978(36)
P(1)—C(38)	1.813(28)		
Angles (°)			
N(2)—Pd(1)—P(1)	92.3(4)	N(1)—Pd(1)—P(1)	89.6(5)
N(1)—Pd(1)—N(2)	178.1(6)	Cl(1)—Pd(1)—P(1)	178.6(2)
Cl(1)—Pd(1)—N(2)	88.6(5)	Cl(1)—Pd(1)—N(1)	89.5(5)
Pd(1)—N(1)—O(12)	116.1(20)	Pd(1)—N(1)—O(11)	119.8(20)
O(11)—N(1)—O(12)	124.1(23)	Pd(1)—N(2)—O(22)	117.7(13)
Pd(1)—N(2)—O(21)	120.9(14)	O(21)—N(2)—O(22)	121.2(18)
Pd(1)—P(1)—C(38)	118.4(9)	Pd(1)—P(1)—C(34)	107.7(10)
Pd(1)—P(1)—C(30)	112.5(9)		

Table 2. Selected bond lengths (Å) and bond angles (°) for $[Pd_2(PPr^n_3)_2Cl_2(NO_2)_2]$

Bond distances (Å)			
Pd—P	2.232(1)	Pd—Cl	2.316(2)
Pd—Cl′	2.417(1)	Pd—N	1.979(4)
P—C(1)	1.812(5)	P—C(4)	1.809(6)
P—C(7)	1.797(5)	N—O(1)	1.198(7)
N—O(2)	1.162(8)		
Angles (°)			
Cl—Pd—N	176.8(1)	Cl—Pd—Cl′	87.5(1)
P—Pd—N	92.9(1)	P—Pd—Cl′	177.6(1)
P—Pd—Cl	90.3(1)	Pd—P—C(7)	111.1(2)
Pd—P—C(4)	111.1(2)	Pd—P—C(1)	114.5(1)
C(4)—P—C(7)	103.7(2)	C(1)—P—C(7)	107.5(2)
C(1)—P—C(4)	108.3(3)	Pd—Cl—Pd′	92.5(1)
Pd—N—O(2)	118.5(4)	Pd—N—C(1)	118.0(4)
O(1)—N—O(2)	123.1(5)		

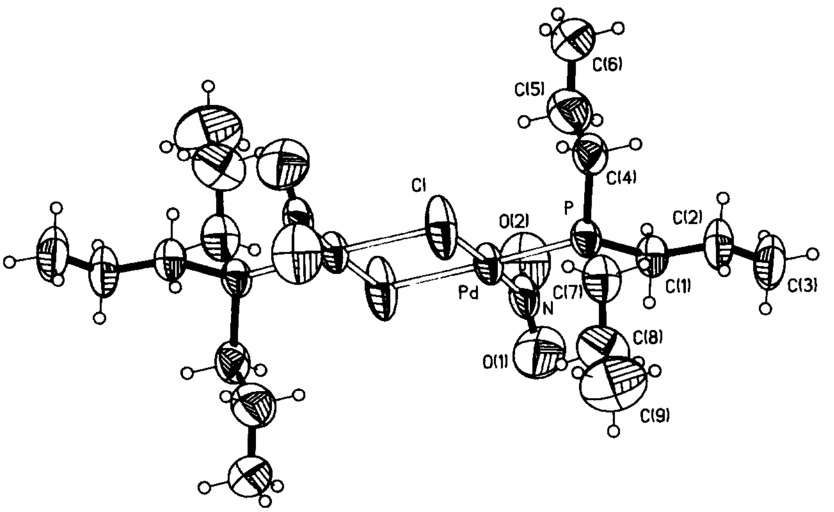


Fig. 2. Molecular structure of $[Pd_2(PPr^n_3)_2Cl_2(NO_2)_2]$.

As—C bond distances (mean value 1.865 Å) and other structural features of $[As(C_6H_5)_4]^+$ and of PPr^n_3 are as usual and require no special comment.

Molecular structure of $[Pd_2(PPr^n_3)_2Cl_2(NO_2)_2]$ (**2**)

The crystal structure of **2** with atomic labelling is depicted in Fig. 2. Bond distances and angles are reported in Table 2. The crystal of compound **2** consists of packing of discrete dimeric molecules $[Pd_2(PPr^n_3)_2Cl_2(NO_2)_2]$ separated by normal van der Waals contacts. Each metal atom is surrounded by a P atom from the PPr^n_3 ligand, an N-bonded nitrite group and two unsymmetrical *cis* chlorine atoms in a planar configuration. The two Pd—Cl bond distances are 2.316(1) and 2.417(1) Å; the latter value refers to a Pd—Cl *trans* to PPr^n_3. The Pd—P bond distance of 2.232(1) Å is at the lower limit found for this type of bond. The two palladium atoms are connected together at a distance of 3.420 Å. The dihedral angle between the two coordination planes is only 1.30(7)°. The P(1)—Pd—Cl(1) and P(1)—Pd—Cl(1′) bond angles are 90.25(4) and 177.58(4)°, respectively. The Pd—N bond distance is 1.979(4) Å slightly shorter than the corresponding values for **1**. Furthermore, the nitro group plane is rotated by 86.0(3)° with respect to the coordination plane. This orientation seems to be the usual one in the absence of steric overcrowding. In the PPr^n_3 ligand the P—C bond distances are as expected and range from 1.797(5) to 1.812(5) Å. The other bond lengths and angles within this ligand, as well as the relatively large thermal motion of the propyl chain, are as usual.

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