

Tableau 3. Valeurs des angles ($^{\circ}$) entre le vecteur Cl(1)–Cl(2) et les vecteurs Ca–Ca' des cycles pyridiniques

Cl(1)–Cl(2)/C(11)–C(15)	47,6 (2)
Cl(1)–Cl(2)/C(21)–C(25)	38,1 (2)
Cl(1)–Cl(2)/C(31)–C(35)	47,1 (2)

à des répulsions plus importantes entre les atomes de chlore qu'entre les atomes de chlore et ceux d'azote, du fait de la plus grande dimension du chlore. Toutefois, si l'angle N(1)–Fe–N(2), égal à $84,9 (1)^{\circ}$, est normalement le plus petit de tous, il est surprenant de constater que l'angle N(1)–Fe–N(3), $88,4 (1)^{\circ}$, lui est nettement supérieur alors que ces deux angles correspondent *a priori* à des dispositions identiques; l'explication peut être trouvée dans l'examen des contacts Cl...H et N...H, cet hydrogène étant celui du carbone en α par rapport à l'azote de la pyridine.

Les cycles pyridiniques sont disposés en hélice (Fig. 1); ils se déduisent approximativement l'un de l'autre par une rotation de $\pi/2$ autour de l'axe Cl(1)–Cl(2) (Tableau 3). Les cycles en position *trans* l'un par rapport à l'autre, font un angle dièdre de $93,5 (3)^{\circ}$; de plus, la projection de ces cycles sur le plan équatorial [Cl(1), Cl(2), Cl(3), N(1)] montre que leurs plans sont orientés de telle sorte qu'ils contiennent les bissectrices des angles définis par les directions Cl(3)–N(1) et Cl(1)–Cl(2) (Fig. 2). Une telle disposition, déjà observée dans les composés similaires [MoCl₃L₃] (Brenčič & Leban, 1980) vise à diminuer les interactions liées à l'encombrement stérique entre les atomes Cl(1), Cl(2), Cl(3), N(1) d'une part et les atomes d'hydrogène situés sur les carbones en α par rapport aux azotes pyridiniques N(2) et N(3) d'autre part. La position la plus stable est celle pour laquelle ces interactions sont minimales, c'est à dire lorsque chacun de ces atomes d'hydrogène est le plus loin possible de ses voisins immédiats soit deux chlores, soit un chlore et un azote.

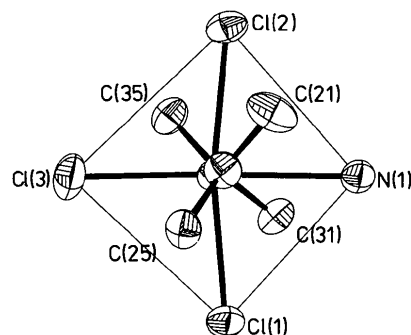


Fig. 2. Projection de la molécule sur le plan Cl(1), Cl(2), Cl(3), N(1). Pour des raisons de clarté du dessin seul les atomes de carbone en α des atomes d'azote 2 et 3 ont été représentés.

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Tetra- μ -nitrito(*O,N*)-tetrakis[nitro(tri-*n*-propylphosphine)palladium(II)], [Pd₄(NO₂)₄(ONO)₄{P(C₃H₇)₃}]₄

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Abstract. $M_r = 1434.6$, monoclinic, $P2_1/n$, $a = 12.870 (6)$, $b = 27.642 (10)$, $c = 8.565 (5) \text{ \AA}$, $\beta = 101.0 (1)^{\circ}$, $U = 2991 (3) \text{ \AA}^3$, $Z = 2$ tetrameric units, $D_x = 1.59 \text{ g cm}^{-3}$, $\mu(\text{Mo } K\alpha) = 12.3 \text{ cm}^{-1}$, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $F(000) = 1456$, $T = 298 \text{ K}$, final $R = 0.052$ and $R_w = 0.063$ for 1997 reflections. The tetramer consists of an approximate square of Pd atoms joined together by nitro–nitrito bridges. The coor-

dination polyhedron around Pd is square planar, a nitro group and a tri-*n*-propylphosphine completing the coordination.

Introduction. During the course of our studies on the photochemical behaviour of planar tetracoordinate palladium(II) complexes of the type *trans*-[Pd(PPrⁿ)₂X₂] (*X* = Cl, Br, I) it has been shown that (i) irradiation of the *trans* complexes on the range 254–405 nm causes *trans*→*cis* isomerization and (ii) further irradiation of the *cis* complexes give rise to bridged complexes [Pd₂(PPrⁿ)₂X₄] (Cusumano, Guglielmo, Ricevuto, Sostero, Traverso & Kemp, 1981). In particular, by reaction of the complex [Pd₂(PPrⁿ)₂Cl₄] with NaNO₂ in methanolic solution, a compound, which analyses as Pd(NO₂)₂(PPrⁿ)₂, is obtained. Its spectroscopic properties were indicative of a nitro-bridged derivative. In order to obtain further information about this compound a crystal structure determination was undertaken.

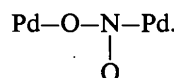
Experimental. 0.558 mmol of Pd₂(PPrⁿ)₂Cl₄ was allowed to react for 24 h with 2 ml of a saturated aqueous solution of NaNO₂ at room temperature under constant stirring. The initially insoluble complex converted into a pink oily substance. The supernatant liquid was removed and 18 ml of H₂O added to the oil. The mixture was left overnight with stirring. The yellow substance obtained was filtered and thoroughly washed with water until there was no indication of free Cl⁻ and NO₂⁻ ions. By dissolving the crude material in a mixture of ethanol and diethyl ether and leaving the solution for two days at room temperature, yellow crystals (m.p. with decomposition 446–448 K) suitable for X-ray study were obtained. The infrared spectrum of the substance in hexachlorobutadiene shows two stretching frequencies at 1485 and 1245 cm⁻¹ in agreement with the formulation of the complex as a bridged nitro–nitrito complex.

Prismatic crystal, 0.2 × 0.3 × 0.2 mm, 20 reflections with 6 < θ < 12° used for measuring lattice parameters, reflections collected at room temperature in the scan range 2θ = 3–50° (–15 ≤ *h* ≤ 14, 0 ≤ *k* ≤ 30, 0 ≤ *l* ≤ 10) on a Siemens Stoe four-circle diffractometer, using graphite-monochromatized Mo *K*α radiation and employing the ω–θ scan technique, with a 0.5 s count at each of 120 steps of 0.01° for each reflection and a 10 s background count at each end of the scan range; no reflections sufficiently intense to require the insertion of attenuators into the beam; two standard reflections (3 $\bar{2}$ 4 and 1,1 $\bar{2}$,1) measured after approximately 150 data reflections showed no significant intensity variation; 2430 measured reflections, 1997 with *I* > 2.5σ(*I*) used for solution and refinement of the structure, Lp correction. Structure solved by Patterson and Fourier methods and refined by full-matrix least-squares procedure, $\sum w|F_o| - |F_c|^2$ minimized, *w* =

0.1867/[σ²(*F*_o) + 2.674 × 10⁻² *F*_o²] used in the last refinement cycles. Anisotropic temperature factors assigned to Pd, P, N, O atoms, isotropic to the C atoms; P–C and C–C bond distances of *n*-propyl groups constrained to the values 1.80 (2) and 1.53 (2) Å respectively because of the disordering in the C-atom positions; C(13), C(15), C(16) and C(17) refined in two alternative positions with occupancy factors 0.6 and 0.4 respectively, the latter labelled as C(131), C(151), C(161), C(171); final conventional *R* = 0.052, *R*_w = 0.063, scattering factors from *International Tables for X-ray Crystallography* (1974) (Pd and P treated as anomalous scatterers); final (Δ/σ)_{max} = 0.1, some peaks of the order of 0.6 e Å⁻³ in the final difference Fourier map in the proximity of the P(1) *n*-propyl chain; computations carried out using *SHELX* (Sheldrick, 1976) on an IBM 4341 computer.

Discussion. Final coordinates for non-hydrogen atoms are in Table 1, bond lengths and angles in Table 2.*

The structure consists of discrete tetrameric units lying on inversion centres; the Pd atoms are joined by a bridging nitro–nitrito group of the type



The coordination geometries around the two independent Pd atoms are both about square planar, with identical ligating atoms. Each Pd is surrounded by a P atom of the tri-*n*-propylphosphine ligand, an N of a terminal nitro group, and an O and an N belonging to bridging NO₂ ligands. In Fig. 1 is shown the asymmetric unit, with atom-numbering scheme, and in Fig. 2 the molecular packing. The bond distances in the two coordination spheres are equal within the limits of the errors. The two Pd–N(nitro) [Pd–N 2.015 (4)_{av} Å] are not significantly different from the two Pd–N(bridging) [Pd–N 2.031 (4)_{av} Å], and are comparable with the values for Pd–N(nitro) of 1.984 (8) Å reported in the cationic complex [Pd(NO₂)₂(NH₃)₂]⁺ (Boer, Carter & Turley, 1971) and of 2.007 (5) Å in Pd(NO₂)₂(PPhMe₂)₂ and Pd(NO₂)₂(PEt₃)₂ respectively (Tack, Hubbard, Kriek, Dubrawski & Enemark, 1981).

The two Pd–P distances, 2.247 (1) Å, are shorter than those found in the two *trans* complexes (Tack *et al.*, 1981) Pd(NO₂)₂(PPhMe₂)₂ and Pd(NO₂)₂(PEt₃)₂ of 2.352 (2) and 2.338 (1) Å respectively, but are comparable with the value of 2.252 (4) Å found in μ-(CN)Pd₂(SCN)₂(NCS)(PPrⁿ)₃ (Bombieri, Bruno, Guglielmo & Ricevuto, 1984) for the Pd–P bond distance *trans* to the bridging cyano group.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39033 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The Pd—O bond distances, $2.14(1)_{\text{av}} \text{ \AA}$, are significantly larger than those found in $\text{Pd}(\text{NO}_3)_2(\text{MeSO})_2$ (Langs, Hare & Little, 1967) where the two monodentate nitrito groups have Pd—O = 2.066 \AA . This lengthening in the Pd—O distance *trans* to the PPR_3^{r} ligand could be related either to the '*trans* influence' of the phosphine ligand, or to some strain due to the fact that the oxygen involved belongs to the bridging nitro-

nitrito group. However, considering that the Pd—N bond distances (nitro and bridging) are comparable (in the limits of errors) it is more likely that the lengthening of the Pd—O distance is due to the '*trans* influence'.

The coordination angles are all close to 90° . The Pd(1) coordination square shows significant distortions from planarity towards a tetrahedral arrangement. The deviations from the weighted least-squares plane (Nardelli, Musatti, Domiano & Andreetti, 1965) through Pd(1)P(1)O(22)N(3)N(4) are Pd(1) $-0.005(1)$, P(1) $0.037(4)$, N(3) $-0.06(2)$, N(4) $-0.07(2)$ and O(22) $0.29(1) \text{ \AA}$, while in the Pd(2) coordination square the deviations from planarity are of the order of 0.03 \AA . The two coordination planes make an angle of $14.5(3)^\circ$. The two bridging nitro-nitrito groups N(4)—O(41)—O(42) and N(2)—O(21)—O(22) are inclined with respect to the Pd(1) coordination plane by $80(1)$ and $85(1)^\circ$ respectively, while the terminal nitro group, N(3)—O(31)—O(32), is rotated with respect to the same plane by $105(1)^\circ$. With the Pd(2) coordination plane, N(2)O(21)O(22) and N(4')O(41')O(42') form angles of $90(1)$ and $65(1)^\circ$ respectively and the terminal nitro group N(1)O(11)O(12) forms an angle of $82(1)^\circ$.

The distances Pd(1)—Pd(2)' and Pd(1)—Pd(2) are the same with values of $4.886(2)$ and $4.888(6) \text{ \AA}$. There are no significant contacts, less than normal van der Waals interactions, between the different tetrameric units.

Table 1. Atomic coordinates ($\times 10^4$) and isotropic and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^2$) for non-hydrogen atoms, with *e.s.d.*'s in parentheses

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j \text{ (for values with an asterisk).}$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>K</i>	<i>U</i> _{eq} or <i>U</i> _{iso}
Pd(1)	3649 (1)	4126.9 (4)	2397 (1)		4.02 (4)*
Pd(2)	6646 (1)	4129.0 (4)	6867 (1)		4.11 (4)*
P(1)	2251 (3)	4201 (2)	390 (5)		5.7 (2)*
P(2)	6743 (3)	3318 (1)	7029 (5)		4.2 (1)*
N(1)	8139 (10)	4149 (5)	8165 (19)		5.7 (5)*
O(11)	8836 (10)	4218 (6)	7389 (19)		9.3 (7)*
O(12)	8290 (12)	4145 (7)	9498 (20)		12.2 (8)*
N(2)	5165 (10)	4099 (5)	5503 (17)		5.2 (5)*
O(21)	4346 (9)	4100 (6)	5959 (15)		8.7 (6)*
O(22)	5149 (8)	4080 (5)	4039 (14)		6.5 (5)*
N(3)	3414 (15)	3412 (5)	2481 (20)		6.6 (6)*
O(31)	2833 (14)	3228 (5)	3097 (20)		10.8 (8)*
O(32)	4074 (17)	3130 (6)	2022 (23)		12.5 (9)*
N(4)	3841 (13)	4854 (5)	2425 (17)		5.2 (5)*
O(41)	3274 (10)	5099 (4)	3147 (13)		5.7 (5)*
O(42)	4475 (14)	5063 (5)	1846 (22)		10.7 (8)*
C(11)	1813 (16)	3709 (6)	-864 (24)		9.0 (6)
C(12)	2642 (22)	3496 (11)	-1706 (36)		15.0 (1)
C(13)	1870 (51)	3192 (25)	-2969 (70)	0.6	18.0 (3)
C(131)	2321 (84)	3071 (28)	-2866 (101)	0.4	15.0 (4)
C(14)	2289 (22)	4713 (8)	-824 (28)		12.0 (1)
C(15)	1926 (32)	4771 (14)	-2583 (32)	0.6	11.0 (1)
C(151)	3156 (31)	4736 (18)	-1701 (36)	0.4	6.0 (1)
C(16)	2289 (33)	5231 (13)	-3306 (45)	0.6	10.0 (1)
C(161)	2949 (7)	5191 (22)	-2742 (90)	0.4	14.0 (3)
C(17)	1134 (16)	4467 (8)	1023 (27)	0.6	6.7 (7)
C(171)	1009 (27)	4001 (18)	874 (50)	0.4	10.0 (2)
C(18)	848 (28)	4220 (11)	2431 (31)		15.0 (1)
C(19)	228 (33)	4362 (18)	3690 (51)		25.0 (2)
C(20)	5576 (13)	3012 (6)	5909 (19)		5.4 (4)
C(21)	5642 (16)	2440 (7)	6091 (23)		7.9 (6)
C(22)	4680 (16)	2230 (8)	4971 (25)		8.4 (6)
C(23)	7881 (13)	3089 (6)	6264 (20)		5.7 (4)
C(24)	7834 (19)	3218 (8)	4528 (28)		9.7 (7)
C(25)	8960 (24)	3058 (10)	4011 (36)		14.0 (1)
C(26)	6925 (13)	3105 (6)	9116 (20)		6.0 (5)
C(27)	5898 (18)	3214 (8)	9842 (26)		8.8 (6)
C(28)	5825 (18)	3746 (8)	10346 (27)		9.2 (7)

Table 2. Selected bond distances (\AA) and angles ($^\circ$) with *e.s.d.*'s in parentheses

Primed atoms are at $1-x, 1-y, 1-z$.

Pd(1)—P(1)	2.248 (4)	Pd(2)—P(2)	2.247 (4)
Pd(1)—N(3) <i>t</i>	2.00 (1)	Pd(2)—N(1) <i>t</i>	2.03 (1)
Pd(1)—N(4) <i>b</i>	2.02 (1)	Pd(2)—N(2) <i>b</i>	2.04 (1)
Pd(1)—O(22)	2.16 (1)	Pd(2)—O(41')	2.14 (1)
P(1)—C(11)	1.76 (2)	P(2)—C(20)	1.83 (2)
P(1)—C(14)	1.76 (2)	P(2)—C(23)	1.83 (2)
P(1)—C(17)	1.79 (2)	P(2)—C(26)	1.85 (2)
N(1)—O(11)	1.23 (2)	N(3)—O(31)	1.12 (2)
N(1)—O(12)	1.12 (2)	N(3)—O(32)	1.27 (2)
N(4)—O(42)	1.18 (2)	N(2)—O(21)	1.19 (2)
N(4)—O(41) <i>b</i>	1.24 (2)	N(2)—O(22) <i>b</i>	1.25 (2)
P(1)—Pd(1)—N(3)	90.7 (5)	P(2)—Pd(2)—N(1)	87.9 (5)
P(1)—Pd(1)—N(4)	89.8 (4)	P(2)—Pd(2)—N(2)	92.2 (4)
N(3)—Pd(1)—O(22)	92.3 (6)	N(1)—Pd(2)—O(41')	85.9 (6)
N(4)—Pd(1)—O(22)	87.7 (6)	N(2)—Pd(2)—O(41')	93.9 (6)
O(12)—N(1)—O(11)	123 (1)	O(32)—N(3)—O(31)	114 (1)
O(42)—N(4)—O(41)	117 (1)	O(21)—N(2)—O(22)	119 (1)

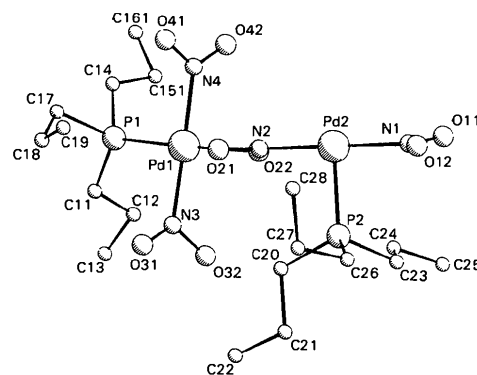


Fig. 1. The asymmetric unit viewed down *c* (only one of the two positions in the *n*-propyl chain is reported).

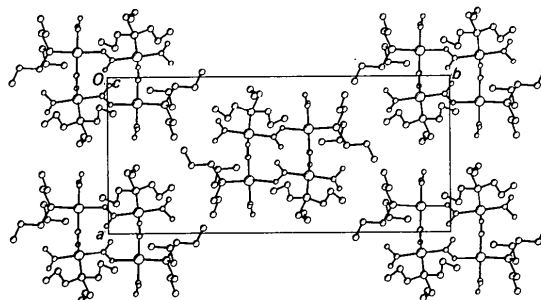


Fig. 2. Projection of the unit-cell contents down *c*.

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