Molecular and Crystal Structure of *trans*-(Dicyanato)-bis(triphenylphosphine)palladium(II)

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The triphenylphosphine (PPh₃) displaces the acetonitrile from [PdCl₂(CH₃CN)₂], and subsequent addition of the potassium cyanate causes substitution of the chloro ligand by NCO⁻ to yield *trans*-[Pd(NCO)₂(PPh₃)₂]. The complex was characterized by elemental analysis, IR spectroscopy and single-crystal X-ray diffraction. The title compound was crystallized in a triclinic system, space group *P* $\bar{1}$ with *a* = 9.213(3) Å, *b* = 9.781(7) Å, *c* = 10.483(5) Å, α = 111.39(5)°, β = 93.49(3)°, γ = 103.81(4)°, *V* = 845.0(1) Å³, *Z* = 1. The coordination geometry around Pd(II) in this complex is nearly square-planar, with the ligands in a *trans* relationship.

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The molecular and crystal structures of square-planar complexes of general formulae [PdX₂(PPh₃)₂] (X = halide or pseudohalide, PPh₃ = triphenylphosphine) have been determined by many authors.¹⁻⁴ In particular, the complex [Pd(NCO)₂(PPh₃)₂] was firstly prepared by Norbury and Sinha⁵ in 1967 by the displacement of pyridine from [Pd(NCO)₂(py)₂] by 2 equivalents of PPh₃. However, the formulation of this compound was based only on infrared evidence. Focusing our interest on the coordination and supramolecular chemistry of Pd(II) compounds bearing halides and pseudohalides,^{6,7} we describe in this work the synthesis and X-ray structural study of the complex *trans*-(dicyanato)bis(triphenylphosphine)palladium(II) (Fig. 1).

Triphenylphosphine (202 mg; 0.77 mmol) in 7 mL of CHCl₃ was added to a deep-orange solution of [PdCl₂(MeCN)₂] (100 mg; 0.38 mmol) in 20 mL of CHCl₃. After stirring the resulting orange solution for 5 min, KNCO (62.5 mg; 0.77 mmol) in 2 mL of CH₃OH/H₂O (1:1) was added and the solution became yellow. Slow evaporation of the solution gave yellow crystals in high yield and of good quality for X-ray diffraction studies. Yield, 65%; M.p., 205°C (dec.). *Anal.* Calcd. for C₃₈H₃₀N₂O₂P₂Pd(%): C, 63.83; N, 3.92; H, 4.23. Found: C,

63.72; N, 3.86; H, 4.20. Selected IR frequencies ($\bar{\nu}$ /cm⁻¹): 3055, ν CH; 2222, $\nu_{\text{as}}\text{NCO}$; 1434, ν_{ring} ; 752, γCH .

The crystal data for the compound *trans*-[Pd(NCO)₂(PPh₃)₂] were taken in an Enraf-Nonius CAD4 diffractometer, at room temperature. Using 25 reflections automatically centered, the cell parameters were obtained and refined. Table 1 gives a summary of the data-collection and refinement conditions. The structure was solved and refined by the WinGX⁸ system, using

Table 1 Summary of data collection and refinement for *trans*-[Pd(NCO)₂(PPh₃)₂]

CCDC	643595
Formula; formula weight	C ₃₈ H ₃₀ N ₂ O ₂ P ₂ Pd; 692.98 g mol ⁻¹
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> (Å); <i>b</i> (Å); <i>c</i> (Å)	9.213(3); 9.781(7); 10.483(5)
α (°); β (°); γ (°)	111.39(5); 93.49(3); 103.81(4)
<i>Z</i>	1
<i>V</i> (Å ³)	845.0(1)
<i>D</i> _c (g cm ⁻³)	1.362
Crystal size (mm)	0.15 × 0.20 × 0.10
Crystal color	yellow
μ (mm ⁻¹)	0.678
<i>K</i> _α Mo, λ (Å)	0.71073
Scan mode	ω -2 θ
Temperature (K)	293
θ range (°)	2.3 – 23.4
Reflections collected; <i>R</i> _{int}	2111; 0.026
Unique reflections	1956
Reflections observed (<i>I</i> > 2 σ (<i>I</i>))	1685
<i>R</i> ; <i>wR</i> ₂	0.0319; 0.0797
GOF	1.07
Refinement method	full-matrix least-squares on <i>F</i> ²
No. of parameters refined	205
Largest diff. peak and hole (e/Å ³)	−0.38, 0.40

Fig. 1 Chemical structure of *trans*-[Pd(NCO)₂(PPh₃)₂].

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Fig. 2 ORTEP representation of *trans*-[Pd(NCO)₂(PPh₃)₂], showing the labeling of the atoms. Displacement ellipsoids are drawn at the 50% probability level.

Table 2 Selected bond lengths (Å) and bond angles (°) for the title complex

Bond distances (Å)		Bond angles (°)	
Pd-P	2.338(1)	P-Pd-N	92.30(13)
Pd-N	2.033(4)	P-Pd-N*	87.70(13)
N-C	0.961(7)	P-Pd-P*	180
O-C	1.288(8)	N-Pd-N*	180
P-C1	1.809(5)	Pd-N-C	155.4(6)
P-C7	1.807(5)	O-C-N	178.8(8)
P-C13	1.815(5)	Pd-P-C1	111.04(16)

full-matrix least squares and Fourier synthesis (SHELXL). The hydrogen atoms were located at their ideal positions, and not refined with thermal vibration equal to 1.3-times the isotropic equivalent B of the attached atom. A structural analysis was performed by the PLATON system. The crystal data are deposited at Cambridge Crystallographic Data Centre, CCDC 643595.

The molecular structure of *trans*-[Pd(NCO)₂(PPh₃)₂] (Fig. 2) showed that the palladium atom is on the crystallographic inversion center. The coordination geometry around Pd(II) is nearly square-planar, with two nitrogen atoms from cyanate ions and two phosphorus atoms from triphenylphosphine ligands, in a *trans* configuration. The PPh₃ ligands display a staggered conformation with respect to the P-P* axis.

The bond angles deviate slightly from 90° (P-Pd-N = 92.3(1)° and P-Pd-N1* = 87.7(1)°), as shown in Fig. 2. Selected bond lengths and bond angles are given in Table 2.

The Pd-N bond distance of 2.033(4) Å is significantly shorter than that found for [Pd(*C,N*-dmmba)(NCO)(2,3-lutidine)] (2.158(7) Å) (dmmba = *N,N*-dimethylbenzylamine).⁶ The cyanate

Fig. 3 Crystal packing of *trans*-[Pd(NCO)₂(PPh₃)₂].

ion is essentially linear with the N-C-O angle equal to 178.8(8)°. The N-C and C-O bond lengths of 0.961(7) and 1.288(8) Å, respectively, indicate the dominance of the mesomeric forms, N=C=O and N≡C-O. In fact, the Pd-N-C angle of 155.4(6)° ranges between the expected values for sp- and sp²-hybridization for the nitrogen atom. The Pd-P bond length, equal to 2.338(1) Å, agrees well with values found for the complexes *trans*-[PdCl₂(PPh₃)₂]·1/2(*p*-C₆H₄Cl₂) (2.345(1) Å),¹ *trans*-[PdI₂(PPh₃)₂]·CHCl₃ (2.343(2) Å),² *trans*-[Pd(N₃)₂(PPh₃)₂] (2.347(1) Å)³ and *trans*-[Pd(CN)₂(PPh₃)₂]·CH₂Cl₂ (2.3333(6) Å).⁴ The crystal packing of *trans*-[Pd(NCO)₂(PPh₃)₂] is shown in Fig. 3.

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References

1. Y. Kitano, Y. Kinoshita, R. Nakamura, and T. Ashida, *Acta Cryst.*, **1983**, C39, 1015.
2. M. Kubota, S. Ohba, and Y. Saito, *Acta Cryst.*, **1991**, C47, 1727.
3. W. Beck, W. P. Fehlhammer, K. Feldl, T. M. Klapötke, G. Kramer, P. Mayer, H. Piotrowski, P. Pöllmann, W. Ponikwar, T. Schütt, E. Schuierer, and M. Vogt, *Z. Anorg. Allg. Chem.*, **2001**, 627, 1751.
4. R. Hua, M. Goto, and M. Tanaka, *Anal. Sci.*, **2001**, 17, 469.
5. A. H. Norbury and A. I. P. Sinha, *Inorg. Nucl. Chem. Lett.*, **1967**, 3, 355.
6. S. R. Ananias, A. E. Mauro, K. Zutin, C. M. C. Picchi, and R. H. A. Santos, *Trans. Metal Chem.*, **2004**, 29, 284.
7. E. T. de Almeida, A. E. Mauro, A. M. Santana, S. R. Ananias, A. V. G. Netto, J. G. Ferreira, and R. H. A. Santos, *Inorg. Chem. Commun.*, **2007**, 10, 1394.
8. L. J. Farrugia, *J. Appl. Cryst.*, **1999**, 32, 837.