

# Intermolecular hydrogen...metal interactions. The crystal structure of $\{cis-[PdCl_2(TPA)_2]\}_2 \cdot H_2O$ , a water-soluble palladium(II) tertiary phosphine complex

Elmer C. Alyea,\* George Ferguson and Shanmugaperumal Kannan

Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada, N1G 2W1

The single-crystal X-ray structural determination of  $\{cis-[PdCl_2(TPA)_2]\}_2 \cdot H_2O$  (TPA = 1,3,5-triaza-7-phosphaadamantane) establishes that pairs of  $cis-[PdCl_2(TPA)_2]$  molecules are linked about inversion centres by intermolecular Pd...H...C three-centre-four-electron interactions (2.86, 3.00 Å for the two independent dimers); the water molecule links these dimers via O-H...N hydrogen bonds to form infinite chains extending in the *c*-direction in the crystal lattice.

Attention has focused recently on complexes of the air-stable water-soluble phosphine 1,3,5-triaza-7-phosphaadamantane (TPA) with transition metal ions.<sup>1,2</sup> Darensbourg and co-workers have shown the high catalytic activity of certain ruthenium and rhodium complexes towards the hydrogenation of alkenes and the conversion of unsaturated aldehydes to saturated aldehydes or unsaturated alcohols.<sup>1b,c,f</sup> Given the potential for applications of water-soluble palladium and platinum complexes in catalysis, *e.g.*  $[Pd(TPPTS)_4]$  [TPPTS =  $P(m-C_6H_4SO_3Na)_3$ ] is used for the telomerization of dienes<sup>3</sup> and  $cis-[PtCl_2(TPPTS)_2]$  for the functionalization of dienes,<sup>4</sup> we are currently extending our preliminary investigations of group 10 complexes of TPA.<sup>2a,c</sup> We report here our discovery that the crystal structure of the square-planar water-soluble palladium(II) complex of TPA,  $\{cis-[PdCl_2(TPA)_2]\}_2 \cdot H_2O$  **1** contains rare intermolecular C...H...Pd interactions; such C...H...M interactions, originally postulated in the literature as possible examples of agostic bonding, are best described as three-centre-four-electron (3c-4e) hydrogen bonds.<sup>5</sup>

The analytically pure compound was synthesized by the reaction of solid  $PdCl_2$  with an excess of TPA in water.<sup>6</sup> The analytical, <sup>1</sup>H and <sup>31</sup>P NMR spectral data† of the isolated greenish-yellow product **1** show that the TPA ligand is bonded through its phosphorus atom to the metal ion in a 2:1 ratio. In contrast, a similar reaction employing  $PtCl_2$  gave a product having the formula  $[Pt(TPA)_3Cl]Cl$ .<sup>2c</sup> Crystals of **1** suitable for X-ray diffraction analysis were obtained from a  $H_2O$ -MeCN-MeOH mixture by slow evaporation.‡ Our preliminary studies show that this complex is unstable in water, giving TPA oxide, but it is relatively stable in the presence of an excess of TPA. The mechanism of decomposition, which also occurs for the analogous Ni and Pt complexes, is under further investigation.<sup>6</sup>

Compound **1** crystallised in the triclinic space group  $P\bar{1}$  and the asymmetric unit contains two molecules of  $cis-[PdCl_2(TPA)_2]$  and a water molecule which links the two Pd complexes via O-H...N hydrogen bonds [O(1)-H(1)...N(13), O...N 2.916(6); O(1)-H(2)...N(33), O...N 2.914(6) Å]. A view of this hydrogen-bonded complex is in Fig. 1. The two independent Pd complexes have essentially identical stereochemistry and conformation; each palladium atom is surrounded by two chlorine and two TPA ligands, giving the expected square-planar geometry. It is well established that *cis*- and *trans*-isomerization in palladium(II) trialkylphosphine complexes of the type  $[PdX_2L_2]$  (X = halogen, L = trialkylphosphine) is mainly determined by the phosphine size.<sup>7-9</sup> Thus, the  $PMe_3$  (cone angle  $\theta = 118^\circ$ ) complex is *cis*,<sup>7</sup> whereas larger

phosphines such as  $PEt_3$ ,  $PPR_3$ ,  $PMe_2Ph$ , *etc.*, form isomeric mixtures<sup>8</sup> and the  $PCy_3$  ( $\theta = 170^\circ$ ) complex is *trans*.<sup>9</sup> Since the cone angle of TPA is only  $102^\circ$ ,<sup>1a</sup> not surprisingly, in the present complex the two TPA ligands are arranged in a *cis*-orientation, and indeed the P-Pd-P bond angles [93.25(5), 93.58(5)°] are the smallest found for any  $cis-[Pd(PR_3)_2X_2]$  complexes.<sup>7-10</sup> The P-Pd-P angle for the  $PMe_3$  analogue is reported as  $94.7(1)^\circ$  in the solid state.<sup>7</sup> Comparable values for *trans*-P-Pd-Cl bond angles also show that less distortion is present in the TPA complex, mean  $176.8(4)^\circ$  compared with a mean value of  $172.5(1)^\circ$  in the  $PMe_3$  complex.<sup>7</sup> The observed Pd-P [2.2392(13)-2.2551(13) Å] and Pd-Cl bond distances [2.3467(14)-2.3777(13) Å] are similar to those in  $cis-[Pd(PMe_3)_2Cl_2]$  [av. 2.257(2) and 2.368(3) Å respectively] and other analogous complexes.<sup>7-10</sup>

Although bridging hydrogen-palladium interactions are known for a few palladium-phosphine complexes,<sup>5</sup> {*e.g.*  $Pd \cdots H$  2.8 Å in  $[Pd(PPhMe_2)_2I_2]$  and 2.92 Å in  $[Pd(PEt_3)_2Cl(C_6H_4CMeN_2HPh)]$ } in most cases the interaction is purely an intramolecular one. Examination of the crystal structure of **1** with PLATON<sup>11</sup> shows that each Pd complex lies close to an

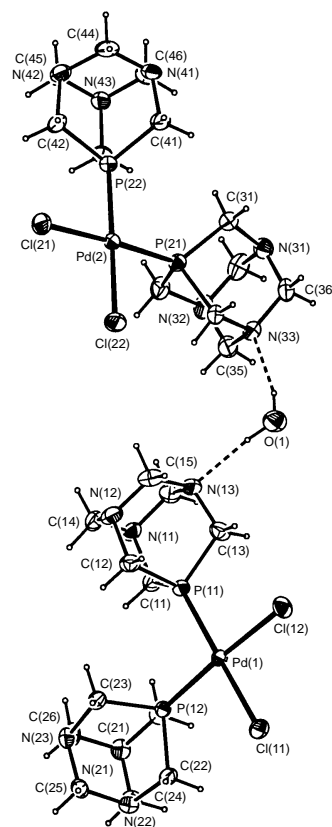
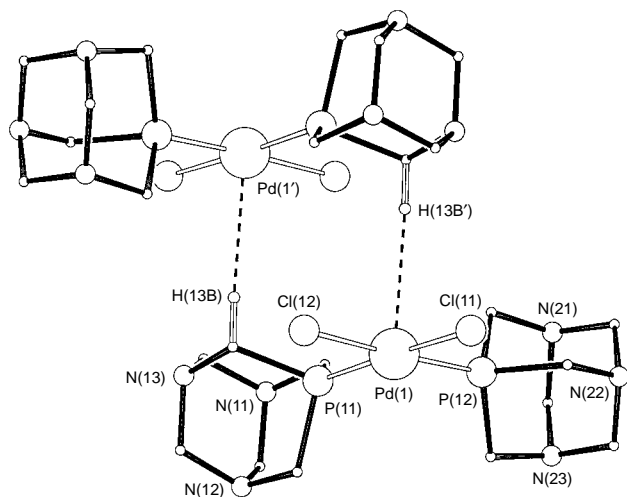


Fig. 1 A view of the asymmetric unit of **1** with our numbering scheme. Anisotropic displacement ellipsoids are drawn at the 40% probability level.



**Fig. 2** A view of one of the 'hydrogen-bridged dimers' of *cis*-[PdCl<sub>2</sub>(TPA)<sub>2</sub>] [atom Pd(1') is related to Pd(1) by the symmetry transformation  $-x, -y, 1 - z$ ]

inversion centre and this leads to a short intermolecular Pd...H...C interaction with an H atom of a TPA ligand of a molecule related by the inversion centre. Each Pd complex forms essentially identical dimers in this way with Pd...H distances of 2.86 [Pd(1)...H(13B') (at  $-x, -y, -z$ )] and 3.00 Å [Pd(2)...H(33B'') (at  $-x, -y, 1 - z$ )] some 0.5–0.6 Å less than the sum of the van der Waals radii. A view of the hydrogen-bridged dimer involving Pd(1) is in Fig. 2; a view of the dimer with Pd(2) is given in supplementary material available from the authors. The orientation of the bridging H atoms above the PdP<sub>2</sub>Cl<sub>2</sub> planes is given by *e.g.* the angles P(12)–Pd(1)...H(13B') (99°) and P(22)–Pd(2)...H(33B'') (95°). In the crystal structure, the effect of these Pd...H...C interactions together with the O–H...N hydrogen bonds noted above is to generate infinite chains in the *c*-direction which have 'H-bridged dimers' linked *via* water molecules. These linear C–H...Pd interactions are best described as 3c–4e hydrogen bonds rather than 3c–2e agostic bonds (*i.e.* the out-of-plane Pd *d* orbital is filled), as has been well documented by Brammer.<sup>5b</sup>

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## Notes and References

\* E-mail: alyea@chembio.uoguelph.ca

† *Selected analytical and spectroscopic data for 1*: yield, 250 mg, 87%, mp. 235 °C (decomp.). Anal. Calc. for 2(C<sub>12</sub>H<sub>24</sub>Cl<sub>2</sub>N<sub>6</sub>P<sub>2</sub>Pd)·H<sub>2</sub>O: C, 28.79; H, 5.03; N, 16.79. Found: C, 28.8; H, 4.9; N, 16.7%. FT-Raman: 273, 302 cm<sup>-1</sup>; <sup>31</sup>P{<sup>1</sup>H} [(CD<sub>3</sub>)<sub>2</sub>SO]: δ -18.3. <sup>1</sup>H [(CD<sub>3</sub>)<sub>2</sub>SO]: δ 4.35–4.55 (m, PCH<sub>2</sub>, NCH<sub>2</sub>).

‡ *Crystal data for 1*: 2(C<sub>12</sub>H<sub>24</sub>Cl<sub>2</sub>N<sub>6</sub>P<sub>2</sub>Pd)·H<sub>2</sub>O, *M*<sub>r</sub> = 1001.2, space group *P*1, *a* = 9.6132(6), *b* = 9.8611(5), *c* = 19.5682(8) Å, α = 98.902(4), β = 96.754(4), γ = 90.722(5)°, *U* = 1819.0(2) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.828 g cm<sup>-3</sup>, *F*(000) = 1012, *R*(*F*<sub>o</sub>) = 0.0360 for 4645 observed reflections with *I* > 2σ(*I*), *wR*<sub>2</sub>(*F*<sup>2</sup>) = 0.0822 for all 6381 unique reflections. Data were

collected on an Enraf-Nonius CAD4 diffractometer and corrected for Lorentz, polarization and absorption (Gaussian) effects. The structure was solved using the Patterson heavy-atom method with NRCVAX<sup>12</sup> and refined using SHELXL97.<sup>13</sup> All non-H atoms were allowed anisotropic motion. All H atoms were visible in difference maps and were allowed for as riding atoms. CCDC 182/716.

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