

Preliminary communication

Hydrogen-bonding 'Pd(OH) ... 2(HOAr)' and '[Pd(OH<sub>2</sub>)<sup>+</sup> ... <sup>-</sup>OAr]<sub>2</sub>',  
and protonation of a hydroxo-ligand by pentafluorophenol  
in organopalladium(IV) chemistry. Structural studies  
of the pallada(IV) cyclopentane adducts  
[Pd(OH)(C<sub>4</sub>H<sub>8</sub>){((pz)<sub>3</sub>BH}.2(3-MeC<sub>6</sub>H<sub>4</sub>OH)]  
and [Pd(OH<sub>2</sub>)(C<sub>4</sub>H<sub>8</sub>){((pz)<sub>3</sub>BH}.(C<sub>6</sub>F<sub>5</sub>O)]<sub>2</sub>  
[(pz)<sub>3</sub>BH = tris(pyrazol-1-yl) borate]

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Abstract

The pallada(IV)cyclopentane complex [Pd(OH)(C<sub>4</sub>H<sub>8</sub>){(pz)<sub>3</sub>BH}] crystallizes with *m*-cresol to form [Pd(OH)(C<sub>4</sub>H<sub>8</sub>){(pz)<sub>3</sub>BH}.2(3-MeC<sub>6</sub>H<sub>4</sub>OH)], in which the hydroxopalladium(IV) group is hydrogen-bonded to two *m*-cresol groups and to the more acidic pentafluorophenol to form [Pd(OH<sub>2</sub>)(C<sub>4</sub>H<sub>8</sub>){(pz)<sub>3</sub>BH}.(C<sub>6</sub>F<sub>5</sub>O)]<sub>2</sub>, in which the aquapalladium(IV) group is strongly hydrogen-bonded to two C<sub>6</sub>F<sub>5</sub>O<sup>-</sup> ions in a centrosymmetric dimer. These first structural studies in diorganopalladium(IV) chemistry include the first examples of hydroxo- and aqua-palladium(IV) complexes, and also provide models for possible pallada(IV)cyclic intermediates in organic synthesis involving palladium complexes as catalysts.

**Keywords:** Palladium; Hydroxo-ligand; Crystal structure; Hydrogen bonding; Metallacycle; Water

The chemistry of oxidation state +IV for palladium in its organometallic chemistry has been developed only recently [1], and the first stable diorganopalladium(IV) complex was obtained by the oxidation of a palladium(II) complex by water [2]. Extensive efforts to characterize this pallada(IV)cyclopentane species [Pd(OH)(C<sub>4</sub>H<sub>8</sub>){(pz)<sub>3</sub>BH}] [(pz)<sub>3</sub>BH = tris(pyrazol-1-yl)borate] crystallographically were unsuccessful, but we have now found that the complex forms crystalline adducts from solutions containing substituted phenols. The adducts provide models for the hydrogen-bonding interaction of phenols with coordinated hydroxo-ligands, and of phenolate ions with coordinated aqua-ligands,

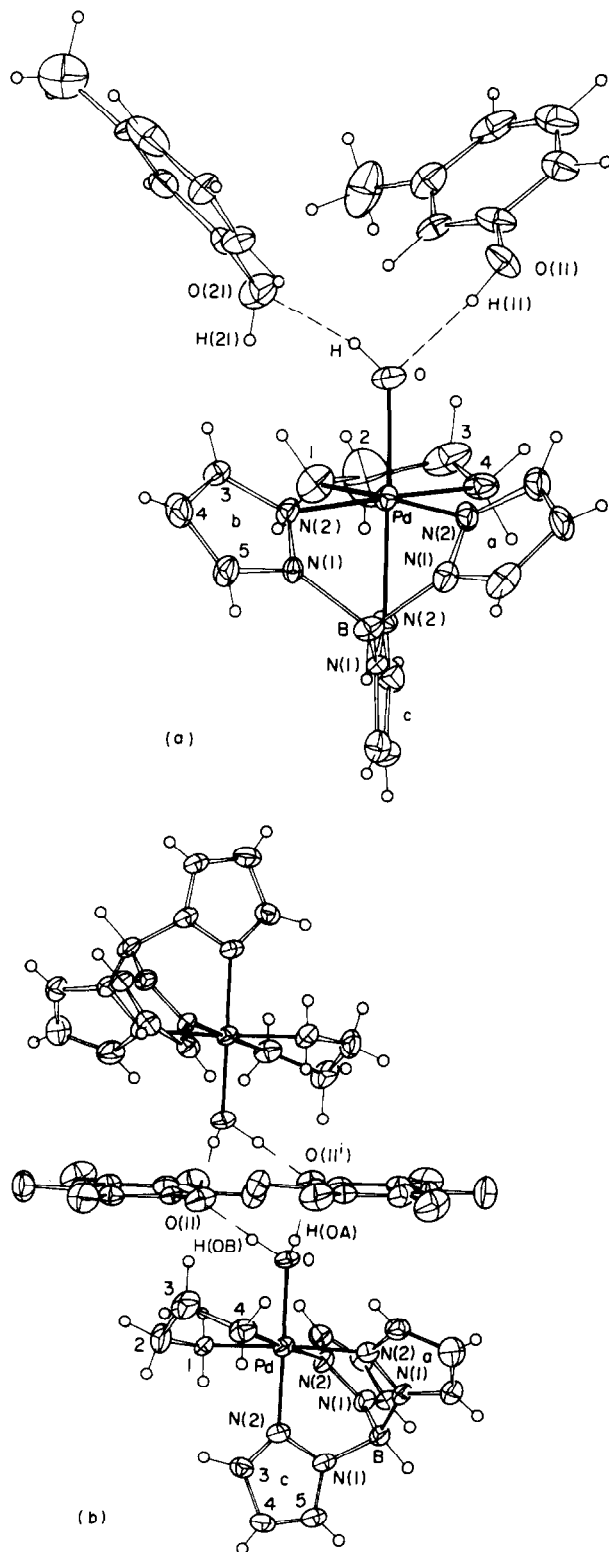
and thus they are relevant to current interest in hydrogen-bonding between alcohols and alcoholato-ligands in transition metal complexes [3].

The pallada(IV)cyclopentane complex [Pd(OH)(C<sub>4</sub>H<sub>8</sub>){(pz)<sub>3</sub>BH}], isolated after addition of water to a solution of the palladium(II) complex ion [Pd(C<sub>4</sub>H<sub>8</sub>){(pz)<sub>3</sub>BH}]<sup>-</sup> [2], dissolves in acetone and, on addition of a 1–1.5 molar ratio of *m*-cresol or pentafluorophenol, colourless crystals can be isolated [4]. X-ray structural studies of these [5] show them to be [Pd(OH)(C<sub>4</sub>H<sub>8</sub>){(pz)<sub>3</sub>BH}.2(3-MeC<sub>6</sub>H<sub>4</sub>OH)] (**1**) and [Pd(OH<sub>2</sub>)(C<sub>4</sub>H<sub>8</sub>){(pz)<sub>3</sub>BH}.(C<sub>6</sub>F<sub>5</sub>O)]<sub>2</sub> (**2**), respectively (Fig. 1). All hydroxylic hydrogen atoms for **1** and **2** refined meaningfully in (*x*, *y*, *z*, *U*<sub>iso</sub>), and the Figures show all significant inter- or intramolecular interactions.

Both adducts have distorted octahedral geometry for palladium in which the puckered palladacyclic rings

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exhibit C(1)–Pd–C(4) angles of 84.8(5)° (**1**) and 85.2(3)° (**2**), and the tridentate ligand forms ‘bite’ angles of 85.7(3)–86.8(4)° (**1**) and 85.2(2)–89.3(2)° (**2**). The remaining interligand angles at palladium fall in the ranges 88.9(5)–95.0(4)° (**1**) and 88.3(2)–95.3(2)° (**2**).



Adduct **1** has a coordinated hydroxo-group which is hydrogen-bonded to two *m*-cresol groups in such a way that the oxygen atom geometry is planar in the unit ‘Pd(OH)(H(11))’, which has Pd–O–H 132(6)°, Pd–O...H(11) 130(3)°, and O–H 0.88(8) Å. The interaction O(11)–H(11)...O, with an O(11)...O distance of 2.69(1) Å and an O(11)–H(11)...O angle of 171(10)°, may be regarded as a hydrogen-bond of medium strength [6]. The other hydrogen-bond, involving an O...O(21) distance of 2.65(1) Å is however, weak, since the O–H...O(21) angle of 123(8)° is well removed from the ideal hydrogen-bond geometry of 180° [6].

In contrast, adduct **2** has a coordinated aqua-group with pyramidal geometry at the oxygen atom [Pd–O–H(OA,OB) 118(4), 120(4)°; H(OA)–O–H(OB) 98(6)°] which is hydrogen-bonded to two pentafluorophenolate ions in a centrosymmetric dimer. The angles O–H(OA)...O(11) and O–H(OB)...O(11<sup>i</sup>) are 175(6) and 166(6)°, respectively, and the O...O(11,11<sup>i</sup>) distances of 2.607(7) and 2.577(6) Å indicate that the hydrogen-bonding is strong [6]. The O...O distances are similar to those reported for square-planar d<sup>8</sup> species containing M–OR...H–OR’ hydrogen-bonding [O...O = 2.544(6)–2.64(4) Å] [3a–e,g,i]. The pentafluorophenolate oxygen atom, O(11), is in an approximately planar environment with H(OA)...O(11)...H(OB<sup>i</sup>) 97(3)° and C(11)–O(11)...H(OA,OB<sup>i</sup>) angles of 133(3) and 123(2)°. The presence of C<sub>6</sub>F<sub>5</sub>O<sup>−</sup> rather than C<sub>6</sub>F<sub>5</sub>OH is reflected in the occurrence of a C–O bond distance [1.300(7) Å] which is shorter than that for both coordinated C<sub>6</sub>F<sub>5</sub>O<sup>−</sup> [1.314(5) Å] and hydrogen-bonded C<sub>6</sub>F<sub>5</sub>OH [1.344(4) Å] in the palladium(II) complex *trans*-PdH(OC<sub>6</sub>F<sub>5</sub>)(PCy<sub>3</sub>)<sub>2</sub>·C<sub>6</sub>F<sub>5</sub>OH [3b], and shorter than for hydrogen-bonded C<sub>6</sub>F<sub>5</sub>OH in C<sub>6</sub>F<sub>5</sub>OH...O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O...HOC<sub>6</sub>F<sub>5</sub> [1.348(1) Å] [8a] and C<sub>6</sub>F<sub>5</sub>OH...OPPh<sub>3</sub> [1.348(3) Å] [8b].

The crystallization of **1** as a hydroxo-complex, but **2** as an aqua-complex in which the potential ligand C<sub>6</sub>F<sub>5</sub>O<sup>−</sup> is not coordinated to palladium, presumably results from a complex interplay of several factors,

Fig. 1. Projections of (a) [Pd(OH)(C<sub>4</sub>H<sub>8</sub>)(pz<sub>3</sub>BH)·2(3-MeC<sub>6</sub>H<sub>4</sub>OH)] (**1**) and (b) [Pd(OH<sub>2</sub>)(C<sub>4</sub>H<sub>8</sub>)(pz<sub>3</sub>BH)·(C<sub>6</sub>F<sub>5</sub>O<sup>−</sup>)<sub>2</sub>] (**2**) showing selected atom numbering; 20% thermal ellipsoids are shown for the non-hydrogen atoms, and hydrogen atoms have been given an arbitrary radius of 0.1 Å. Selected distances (Å) and angles (°): **1**: C(21)–O(21) 1.37(2), C(11)–O(11) 1.35(2), O–H 0.88(8), O(21)–H(21) 0.9(2), O(11)–H(11) 0.8(1), O...H(11) 1.9(1), O(21)...H 2.06(9), Pd–O 2.011(8), Pd–N(2a,2b,2c) 2.18(1), 2.172(8), 2.036(9), Pd–C(1,4) 2.04(1), 2.02(1), Pd–O–H 132(6), Pd–O...H(11) 130(3), O–H...O(21) 123(8), O...H(11)–O(11) 171(10). **2**: C(11)–O(11) 1.300(7), O–H(OA,OB) 1.00(7), 0.78(6), O(11)...H(OA) 1.60(8), O(11<sup>i</sup>)...H(OB) 1.81(6), Pd–O 2.035(4), Pd–N(2a,2b,2c) 2.206(5), 2.168(5), 2.020(4), Pd–C(1,4) 2.041(7), 2.046(8), Pd–O–H(OA,OB) 120(4), 118(4), H(OA)–O–H(OB) 98(6), O–H(OA)...O(11) 175(6), O–H(OB)...O(11<sup>i</sup>) 166(6), H(OA)–O(11)–H(OB<sup>i</sup>) 97(3); i = 1 – x, 1 – y, 2 – z.

including the higher acidity of pentafluorophenol ( $pK_a$  5.49) than of *m*-cresol ( $pK_a$  10.08) [9] and the formation of complex structures containing hydrogen-bonding.

The structures reported here provide the first examples of hydroxo-, aqua-, and diorganopalladium(IV) complexes in organopalladium(IV) chemistry, and suggest that it may be possible to develop a rich aqueous solution organometallic chemistry for palladium(IV). The complexes also provide structural models that are relevant to proposals that pallada(IV)cyclic intermediates are involved in organic synthesis [1,10].

## Acknowledgements

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- [4] For **1** subsequent addition of petroleum ether (b.p. 60–80°C) until cloudiness occurs is required, followed by cooling to –20°, evaporation to low volume, filtration, further slow evaporation and filtration, and crystallization from the filtrate (20–40% yield). For **2** only subsequent evaporation to dryness and recrystallization from acetone/petroleum ether (~100%) is required. The adducts exhibit  $^1\text{H}$  NMR resonances ( $\text{CDCl}_3$ , 300 MHz) for the pallada(IV)cyclopentane and tris(pyrazol-1-yl)borate moieties that are within 0.05 ppm of that for the parent complex  $[\text{Pd}(\text{OH})(\text{C}_4\text{H}_8)(\text{pz})_3\text{BH}]$ , except for the  $\text{PdCH}_2$  resonances which are shifted downfield by 0.07 and 0.14 ppm for **1**, and 0.16 and 0.26 ppm for **2**. Selected NMR data: **1**: d 1.68 (m, 2 H,  $\text{CH}_2$ ), 1.89 (m, 2 H,  $\text{CH}_2$ ), 2.26 (s, 6 H, Me), 3.85 (q, 2 H,  $\text{PdCH}_2$ ), 4.26 (q, 2 H,  $\text{PdCH}_2$ ), 6.24 [m, 2 H, H(4) pz], 6.30 [m, 1 H, H(4) pz], 6.65–7.07 (m, 8 H, Ar), 7.69 [d, 2 H, H(5) pz], 7.71 [d, 1 H, H(5) pz], 7.75 [d, 1 H, H(3) pz], 7.77 [d, 2H, H(3) pz]. **2**: d 1.66 (m, 2 H,  $\text{CH}_2$ ), 1.86 (m, 2 H,  $\text{CH}_2$ ), 3.94 (q, 2 H,  $\text{PdCH}_2$ ), 4.38 (q, 2 H,  $\text{PdCH}_2$ ), 6.24 [m, 2 H, H(4) pz], 6.32 [m, 1 H, H(4) pz], 7.68 [d, 2 H, H(5) pz], 7.71 [d, 1 H, H(5) pz], 7.74 [d, 1 H, H(3) pz], 7.78 [d, 2H, H(3) pz]. Both adducts have satisfactory microanalyses (C, H, N).
- [5] Crystal data: **1**:  $\text{C}_{27}\text{H}_{35}\text{BN}_6\text{O}_3\text{Pd}$ ,  $M = 608.8$ , monoclinic,  $P2_1/n$ ,  $a = 10.945(6)$ ,  $b = 20.07(1)$ ,  $c = 13.359(4)$  Å,  $\beta = 101.17(3)^\circ$ ,  $Z = 4$ . Conventional  $R$ ,  $R_w$  (statistical weights) on  $|F|$  were 0.055, 0.048 for  $N_0 = 2216$  ‘observed’ [ $I > 3\sigma(I)$ ] out of  $N = 5056$  independent absorption-corrected room temperature ( $T \sim 295$ ) diffractometer reflections ( $2\theta_{\text{max}} = 50^\circ$ ). **2**:  $\text{C}_{19}\text{H}_{20}\text{BF}_5\text{N}_6\text{O}_2\text{Pd}$ ,  $M = 576.6$ , monoclinic,  $P2_1/c$ ,  $a = 10.424(3)$ ,  $b = 22.97(2)$ ,  $c = 9.755(3)$  Å,  $\beta = 106.38(2)^\circ$ ,  $Z = 4$ .  $R$ ,  $R_w = 0.038$ ,  $0.038$  for  $N$ ,  $N_0 = 3938$ , 2722. Full matrix least squares refinements were applied, and thermal parameter forms were anisotropic for all non-hydrogen atoms. In **2**, all hydrogen atoms were refined in ( $x$ ,  $y$ ,  $z$ ,  $U_{\text{iso}}$ ); in **1** all hydroxylic hydrogen atoms were refined thus.
- [6] Tables of atom coordinates and thermal parameters and a complete list of bond lengths and angles has been deposited at the Cambridge Crystallographic Data Centre.
- [7] Hydrogen-bonding O–H...O is usually classified according to O...O distances as very strong (< 2.50 Å), strong (2.50–2.65 Å), medium (2.65–2.80 Å) or weak (> 2.80 Å). The energy of bent O–H...O bonds is reduced to ~90% for an angle of 165°, and to less than 10% for an angle of 110°, relative to that for an angle of 180° [7].
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