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Preliminary Communication

Oxidation reactions using water, hydrogen peroxide and halogens to give pallad(IV)cyclopentane complexes $PdX(C_4H_8)\{(pz)_3BH\}$ (X = OH, Cl, Br, I). The crystal structure of the hydroxoplatinum(IV) complex $Pt(OH)Me_2\{(pz)_3BH\}$, formed by use of water as an oxidant

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Abstract

The pallada(II)cyclopentane reagent $[Pd(C_4H_8)\{(pz)_3BH\}]^-$, generated by addition of potassium tris(pyrazol-1-yl)borate to the tetramethylethylenediamine analogue, reacts with water or hydrogen peroxide to give the hydroxopalladium(IV) complex $Pd(OH)(C_4H_8)\{(pz)_3BH\}$. Similar oxidation reactions occur with phenyliodonium dichloride, bromine and iodine to give $PdX(C_4H_8)\{(pz)_3BH\}$ (X = Cl, Br, I). The hydroxoplatinum(IV) complex $Pt(OH)Me_2\{(pz)_3BH\}$ has been obtained by reaction of $[PtMe_2(SEt_2)]_2$ with $K[(pz)_3BH]$, followed by addition of water, and its structure determined by an X-ray diffraction study.

Keywords: Palladium; Hydroxoplatinum; Oxidation; Crystal structure; Water; Metallacycle

Nucleophilic centres in some coordination complexes can undergo oxidative addition reactions with water; e.g. $[Ir(PMe_3)_4]^+$ reacts with water to form the iridium(III) complex *cis*-$[IrH(OH)(PMe_3)_4]^+$ [1]. Metal–carbon σ-bonded organometallic compounds are also potentially capable of similar reactions, but in the limited number of cases reported the substrates employed did not yield hydride complexes, presumably as a result of subsequent hydrolysis [2–5], e.g. $PtMe_2(bipy)$ forms $[Pt(OH)Me_2(bipy)(OH_2)][OH]$ (bipy = 2,2′-bipyridyl) [2].

The anion $[PdMe_2\{(pz)_3BH\}]^-$ reacts with water in a complex manner to give the triorganopalladium(IV) complex $PdMe_3\{(pz)_3BH\text{-}N,N',N''\}$ and a $Pd^{II}Me$ product [5]. This reaction is believed to involve formation of an undetected hydroxopalladium(IV) intermediate $Pd(OH)Me_2\{(pz)_3BH\}$, followed by a redox reaction in which Me^+ transfer occurs from the intermediate to nucleophilic $[PdMe_2\{(pz)_3BH\}]^-$ [5]. In a strategy aimed at preventing the alkyl transfer reaction we have commenced studies of oxidation reactions involving use of pallada(II)cyclopentane reagents. We report here the first isolation of a hydroxopalladium(IV) complex, together with the crystal structure of a closely related platinum(IV) complex formed by water oxidation, and the oxidation of organopalladium(II) complexes by other oxidants to form stable diorganopalladium(IV) complexes.

The pallada(II)cyclopentane reagent $Pd(C_4H_8)$(tmeda), containing the easily replaceable tetramethylethylenediamine ligand [6,7], decomposes in the presence of water. However, initial reaction with $K[(pz)_3BH]$ in dry acetone (4 hr, 0°C) gives a solution of $[Pd(C_4H_8)\{(pz)_3BH\}]^-$, which on addition of water reacts slowly (12 hr) to give $Pd(OH)(C_4H_8)\{(pz)_3BH\}$. The complex was isolated in 59% yield [8], and a ^1H NMR study of the reaction in $(CD_3)_2CO$ revealed no other organopalladium products.

The strong oxidizing agent hydrogen peroxide was found to react with $[Pd(C_4H_8)\{(pz)_3BH\}]^-$ within a few seconds to give $Pd(OH)(C_4H_8)\{(pz)_3BH\}$, and the mild chlorine-transfer agent phenyliodonium dichloride ($PhICl_2$), bromine, and iodine all react rapidly to form palladium(IV) products, which were isolated in

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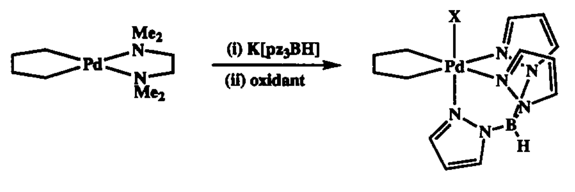

Scheme 1.

yields of 30–80% (Scheme 1) [8]. All of the complexes may be stored in the solid state at −20°C, and their solutions are stable at ambient temperature for several hours.

None of the diorganopalladium(IV) complexes could be obtained in a form suitable for X-ray crystallography. There appear to be no reports of X-ray studies of organometallic hydroxo complexes formed using water as an oxidant [2–5], and thus a suitable hydroxoplatinum(IV) analogue was sought for structural analysis. The facile alkyl group exchange reactions that occur between palladium(IV) complexes and nucleophilic organopalladium(II) complexes [5,12,13] do not appear to occur readily in organoplatinum chemistry [4], and thus $[PtMe_2\{(pz)_3BH\}]^-$ was selected as a substrate. The anion, generated from $[PtMe_2(SEt_2)]_2$ and $K[(pz)_3BH]$, reacted readily with water in acetone (2 h at ambient temperature) to give $Pt(OH)Me_2\{(pz)_3BH\}$, which was recrystallized from chloroform/hexane in 45% yield. In the solid state (Fig. 1) the complex has a crystallographic mirror plane [14] containing the Pt–O bond [Pt–O 1.984(5) Å] with the pyrazole group trans to it. The Pt–N bonds trans to the methyl groups are ~ 0.13 Å longer than the Pt–N bonds trans to the hydroxo group, reflecting the stronger trans influence of the methyl groups.

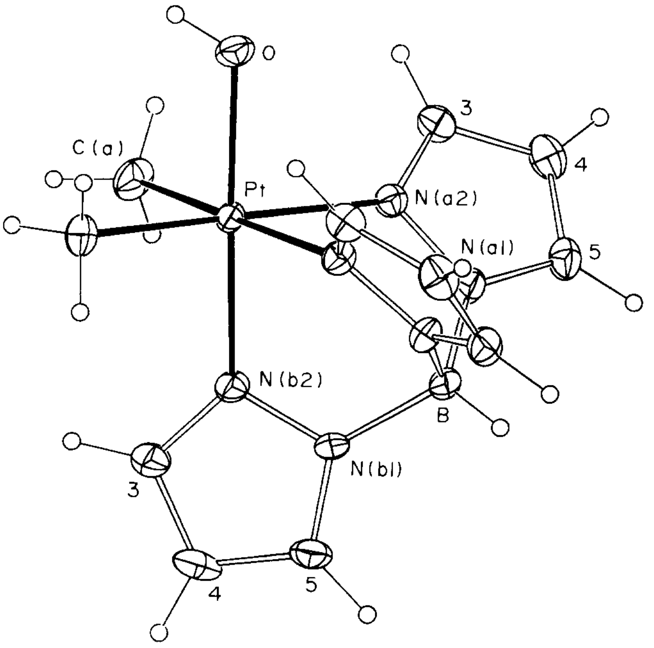

Fig. 1. Projection of the complex $Pt(OH)Me_2\{(pz)_3BH\}$ showing selected atom numbering; 20% thermal ellipsoids are shown for the non-hydrogen atoms. Selected bond distances (Å) and angles (°): Pt-O, 1.984(5), Pt-C(a), 2.048(5), Pt-N(a2, b2), 2.151(3), 2.022(5) Å, C(a)-Pt-C(a'), 89.1(2), C(a)-Pt-N(a2, b2), 177.6(2), 91.7(2), C(a)-Pt-O, 89.9(2), O-Pt-N(a2, b2), 90.4(1), 177.8(2), N(a2)-Pt-N(a2', b2), 84.4(1), 88.0(1)°.

Tables of atom coordinates, bond lengths and angles, and thermal parameters have been deposited in the Cambridge Crystallographic Data Centre. Structure factors are available from the authors.

Acknowledgements

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[14] Crystal data: $Pt(OH)Me_2\{(pz)_3BH\}$, $C_{11}H_{17}BN_6OPt$, orthorhombic, space group *Pnma* (No 62), $a = 15.056(12)$, $b = 11.259(5)$, $c = 8.730(3)$ Å, $U = 1480(1)$ Å^3, D_c $(Z = 4) = 2.04$ g cm^{-3}, $F(000) = 864$, $R = 0.035$, $R_w = 0.039$ (statistical weights) for 2600 'observed' reflections with $I > 3\sigma(I)$. The structure was determined from diffractometer data (Mo Kα radiation, $\lambda = 0.7107_3$ Å, $2\theta_{max} = 70°$, $\mu = 95$ cm^{-1}) collected at 295 K on an Enraf-Nonius CAD-4 diffractometer in conventional $2\theta/\theta$ scan mode. Full matrix least squares refinements were employed after analytical absorption correction and solution of the structure by vector methods. The OH hydrogen atom was located in difference maps and lies on the crystallographic mirror plane that passes through the molecule.