Journal of Organometallic Chemistry, 471 (1994) C8–C10

Preliminary Communication

Oxidation of organoplatinum(II) and -palladium(II) complexes by water. The X-ray structure of the trimethylpalladium(IV) complex *fac*-[PdMe$_3${tris(pyrazol-1-yl)borate}] formed on oxidation of a dimethylpalladium(II) reagent

Allan J. Canty, R. Thomas Honeyman,
Andrew S. Roberts and Peter R. Traill

Department of Chemistry, University of Tasmania, Hobart, Tasmania 7001 (Australia)

Ray Colton

Department of Chemistry, La Trobe University, Bundoora, Vic. 3083 (Australia)

Brian W. Skelton and Allan H. White

Department of Chemistry, University of Western Australia, Nedlands, W.A. 6009 (Australia)

(Received November 22, 1993)

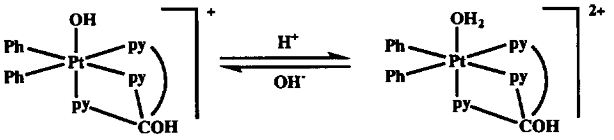
Abstract

Diphenyl{tris(pyridin-2-yl)methanol}platinum(II) reacts with water in acetone to form the platinum(IV) complex [PtPh$_2${(py)$_3$COH}(OH)]-[OH]·nH$_2$O ($n \sim 1$). In contrast, the palladium(II) species [PdMe$_2$-{(py)$_3$COH}] and [PdMeR{tris(pyrazol-1-yl)borate}]$^-$ (R = Me, Ph) react with water to form a mixture of Pd^{IV} and Pd^{II} complexes in reactions involving both oxidation and methyl group transfer. The Pd^{IV} complexes *fac*-[PdMe$_3${(py)$_3$COH}]$^+$ and *fac*-[PdMe$_2$R{(pz)$_3$-BH}] (R = Me, Ph) have been identified as products, together with methylpalladium(II) and phenylpalladium(II) species, and the structure of *fac*-[PdMe$_3${(pz)$_3$BH}] determined by X-ray crystallography.

Key words: Oxidation; Water; Platinum; Palladium; Crystal structure

Few accounts of the oxidation of organometallic compounds by water are available [1], and for d^8 complexes appear to be limited to dimethylplatinum(II) systems [1–4], with the best characterized reactions being those of [PtMe$_2$(L$_2$)] (L$_2$ = 2,2′-bipyridyl or 1,10-phenanthroline) to give [PtMe$_2$(L$_2$)(OH)(OH$_2$)]-[OH] [2]. We report here an example of a reaction of this type that leads to the isolation of a monohydroxoplatinum(IV) complex, and the first demonstration that water can oxidize palladium(II) in remarkable reactions involving conversion of diorganopalladium(II) into triorganopalladium(IV) species.

The reaction of [PtPh$_2$(μ-SEt$_2$)]$_2$ with tris(pyridin-2-yl)methanol in 1:2 mol ratio in refluxing dry acetone for 30 min under nitrogen followed by cooling gives the expected complex [PtPh$_2${(py)$_3$COH}]. A similar procedure for the same reagent mixture or for [PtPh$_2${(py)$_3$-COH}] in acetone containing water gives a white product that has microanalysis and ^{1}H NMR data consistent with "[PtPh$_2${(py)$_3$COH}(OH$_x$)(OH$_y$)][OH$_z$]". The structure is assigned as [PtPh$_2${(py)$_3$COH}(OH)][OH]·nH$_2$O ($n \sim 1$) containing the hydroxo species (1), since the electrospray mass spectrum in methanol [5*] gives a strong peak centred at m/z 629 (with the correct isotope pattern) corresponding to the intact ion [PtPh$_2${(py)$_3$COH}(OH)]$^+$, and the ^{1}H NMR spectrum in CD$_3$OD changes on addition of CF$_3$CO$_2$D and reverts back on subsequent addition of NaOH. Both spectra exhibit pyridine ring environments in 2:1 ratio, and in acidic solution the complex is assumed to be present as [PtPh$_2${(py)$_3$COH}(OH$_2$)]$^{2+}$ (2).



(1) (2)

A similar procedure to that above using [PdMe$_2$-(pyridazine)] [6] and (py)$_3$COH as reagents in acetone containing water resulted in the isolation of a white powder, for which electrospray mass spectra indicate presence of the cations [PdMe$_3${(py)$_3$COH}]$^+$ and [PdMe{(py)$_3$COH}(pyridazine)]$^+$. At high ion source energies the Pd^{IV} cation undergoes collisionally activated decomposition with solvent molecules in the gas phase to lose ethane and form [PdMe(py$_3$COH)]$^+$, as found for related triorganopalladium(IV) cationic complexes [5].

Correspondence to: Professor A.J. Canty.

* Reference number with an asterisk indicates a note in the list of references.

0022-328X/94/$7.00
SSDI 0022-328X(94)24431-H

Reactions of [$PdMe_2$(pyridazine)] or [PdMePh(tmeda)] with potassium tris(pyrazol-1-yl)borate in $(CD_3)_2CO$ give ^1H NMR resonances attributable to $[PdMeR\{(pz)_3BH\}]^-$ (R = Me, Ph). In preparative procedures, addition of water to acetone solutions of the anions followed by partial evaporation of solvent gives white solids. For $[PdMe_2\{(pz)_3BH\}]^-$ as reagent, the solid was identified by ^1H and ^{13}C NMR as $[PdMe_3\{(pz)_3BH\}]$ [7] *, and the filtrate from this reaction gives $[PdMe\{(pz)_3BH\}(PPh_3)]$ on addition of triphenylphosphine. For $[PdMePh\{(pz)_3BH\}]^-$ as reagent, the solid was identified as a mixture of $[PdMe_2Ph\{(pz)_3BH\}]$ [7] and "$PdPh\{(pz)_3BH\}$", and the latter forms $[PdPh\{(pz)_3BH\}(PPh_3)]$ on addition of PPh_3. When the reaction of $[PdMePh\{(pz)_3BH\}]^-$ with water is carried out at a higher temperature (35°C for 6 h), decomposition of the Pd^{II} product occurs during the reaction, allowing isolation of pure $[PdMe_2Ph\{(pz)_3BH\}]$ after filtration.

The Pd^{II} products may be synthesised independently by addition of $K[(pz)_3BH]$ and PPh_3 to $[PdMe(SMe_2)(\mu\text{-}I)]_2$ or [PdIPh(tmeda)], and the $Pd^{IV}Me_2R$ (R = Me, Ph) and related complexes may be synthesized by oxidative addition of organohalides (R′X) to $[PdMeR\{(pz)_3BH\}]^-$ in dry acetone, *e.g.* $[PdMe_3\{(pz)_3BH\}]$ (R = Me, R′X = MeI) and $[PdMePhR'\{(pz)_3BH\}]$ (R = Ph, R′X = MeI, $PhCH_2Br$). The structure of $[PdMe_3\{(pz)_3BH\}]$ is shown in Fig. 1 [8] *.

Thus, $[PdMe_2\{(py)_3COH\}]$ and $[PdMeR\{(pz)_3BH\}]^-$ react with water to give a mixture of Pd^{IV} and Pd^{II} species (eqn. (1) and (2)), and transfer of a methyl group must occur in addition to oxidation.

$$2[PdMe_2\{(py)_3COH\}] \rightarrow [PdMe_3\{(py)_3COH\}]^+ + \text{“}[PdMe\{(py)_3COH\}]^+\text{”} \quad (1)$$

$$2[PdMeR\{(pz)_3BH\}]^- \rightarrow [PdMe_2R\{(pz)_3BH\}] + \text{“}PdR\{(pz)_3BH\}\text{”}$$

$$(R = Me, Ph) \quad (2)$$

Transfer of a methyl group from Pd^{IV} to Pt^{II} or Pd^{II} centres has been reported recently [9,10,12], *e.g.* in the reaction of $[PdIMe_2Ph(bipy)]$ with $[PdMe_2(bipy)]$ to give [PdMePh(bipy)] and $[PdIMe_3(bipy)]$. Kinetic [11] and NMR [9,11,12] studies suggest that reactions of this type occur *via* dissociation of halide from the Pd^{IV} centre to give a cationic species in which the methyl groups are activated toward nucleophilic attack by the Pd^{II} reagent. Thus, the reactions of $[PdMe_2\{(py)_3COH\}]$ and $[PdMeR\{(pz)_3BH\}]^-$ with water are assumed to involve slow oxidation to give undetected intermediates similar to the platinum(IV) species $[PtPh_2\{(py)_3COH\}(OH)]^+$ and $[PtPh_2\{(py)_3COH\}(OH_2)]^{2+}$, *e.g.* "$[PdMe_2\{(py)_3COH\}(OH)]^+$" in equilibrium with "$[PdMe_2\{(py)_3COH\}(OH)_2)]^{2+}$" or "$[PdMeR\{(pz)_3BH\}(OH)]$" in equilibrium with "$[PdMeR\{(pz)_3BH\}(OH_2)]^+$". Subsequent fast nucleophilic attack on a methyl group of the cations by $[PdMe_2\{(py)_2COH\}]$ or $[PdMeR\{(pz)_3BH\}]^-$ may then occur, resulting in methyl group transfer from Pd^{IV} to Pd^{II} to give $[PdMe_3\{(py)_3COH\}]^+$ and $[PdMe_2R\{(pz)_3BH\}]$, respectively, with some monoorganopalladium(II) species as by-products.

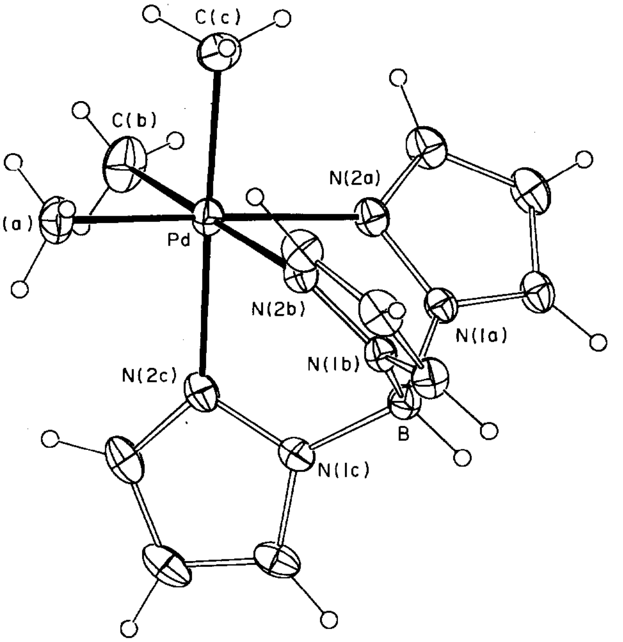


Fig. 1. Projection of the complex $[PdMe_3\{(pz)_3BH\}]$ showing selected atom numbering; 20% thermal ellipsoids are shown for the non-hydrogen atoms. Selected bond distances (Å) and angles (°): Pd–C(a, b, c) 2.034(4), 2.032(7), 2.024(4), Pd–N(2a, 2b, 2c) 2.174(3), 2.178(4), 2.177(3) Å, C(a)–Pd–C(b, c) 87.3(2), 87.5(2), C(b)–Pd–C(c) 87.1(2), C(a)–Pd–N(2a, 2b, 2c) 178.4(2), 93.9(2), 94.0(2), C(b)–Pd–N(2a, 2b, 2c) 94.0(2), 178.5(1), 93.8(2), C(c)–Pd–N(2a, 2b, 2c) 93.4(1), 93.7(2), 178.3(1), N(2a)–Pd–N(2b, 2c) 84.7(1), 85.1(1), N(2b)–Pd–N(2c) 85.4(1)°.

Acknowledgments

We thank the Australian Research Council for support and the Commonwealth Government for a Postgraduate Research Award (to R.T.H.).

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* Tables of atom coordinates bond lengths and angles, and thermal parameters have been deposited in the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Structure factors are available from the authors.

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7 [PdMe$_3$(pz$_3$BH)] (in CDCl$_3$), ^{1}H NMR: 7.64 [3H, pz], 7.54 [3H, pz], 6.20 [3H, pz], 1.38 [3H, s, PdMe]; ^{13}C NMR: 138.3 [pz], 135.4 [pz], 105.5 [pz], 12.8 [PdMe]. [PdMe$_2$Ph{(pz)$_3$BH}] (in CDCl$_3$), ^{1}H NMR: 7.70 [3H, m, pz], 7.62 [1H, s, pz], 7.24 [2H, s, pz], 6.25 [1H, s, pz], 6.15 [2H, s, pz], 7.03 and 6.97 [5H, b, Ph], 1.82 [6H, s, Me]; ^{13}C NMR: 140 [pz], 138.7 [Ph], 136.7 [Ph], 135.6 [pz], 135.2 [pz], 128 [Ph], 124.7 [Ph], 105.9 [pz], 105.7 [pz], 19.07 [PdMe].

8 Crystal data: [PdMe$_3${(pz)$_3$BH}], $C_{12}H_{19}BN_6Pd$, $M = 364.5$, monoclinic, space group $P2_1/c$ (No. 14), $Z = 4$, $a = 16.559(16)$, $b = 7.859(4), c = 13.774(15)$ Å, $\beta = 118.88(8)^0$, $U = 1570$ Å^3, $D_c = 1.54$ g cm^{-3}, $F(000) = 736$, $2\theta_{max} = 55°$, crystal size 0.22×0.40×0.55 mm, $R = 0.032$, $R_w = 0.043$ for 3086 'observed' reflections with $I > 3\sigma(I)$. The structure was determined from diffractometer data (Mo-Kα radiation, $\lambda = 0.7107_3$ Å, $\mu = 10.7$ 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 gaussian absorption correction and solution of the structure by vector methods.

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