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Note

Organopalladium(IV) complexes containing phosphine ligands, and the structure of the platinum(IV) complex $[PtMe_3(bpy)(PPh_3)][O_3SCF_3]$ (bpy = 2,2′-bipyridine)

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Abstract

Solutions containing unstable organopalladium(IV) complexes of phosphines, $[PdMe_3(bpy)(L)]^+$ (L = $PMePh_2$, PMe_2Ph, PPh_3), are generated on reaction of $PdIMe_3(bpy)$ with the phosphines in dichloromethane-d_2. The complex $[PdMe_3(bpy)(PPh_3)]^+$ may also be formed quantitatively on the reaction of $PdMe_2(bpy)$ with methyl triflate and triphenylphosphine in acetone-d_6. A solution of the platinum(IV) analogue $[PtMe_3(bpy)(PPh_3)][O_3SCF_3]$ is formed following a similar procedure and isolated as crystals on reaction of $PtIMe_3(bpy)$ with silver triflate followed by PPh_3. An X-ray structure determination of the platinum(IV) complex shows the *fac*-$PtMe_3$ configuration for octahedral $[PtMe_3(bpy)(PPh_3)]^+$, and supports the assignment of identical structures for the unstable palladium(IV) complexes from comparison of ^{1}H- and ^{13}P-NMR spectra of palladium(IV) and platinum(IV) complexes.

Keywords: Palladium; Platinum; Phosphine complexes; Crystal structure

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1. Introduction

The organometallic chemistry of palladium(IV) has developed rapidly since 1986 to include a wide range of supporting polydentate ligands containing nitrogen [1], sulfur [2], oxygen [3] or silicon [4] donor atoms [5–7]. However, to date there are no reports of the isolation or spectroscopic detection of complexes containing phosphine donor ligands, although there is excellent kinetic evidence in the earlier literature for their transient formation as intermediates [8]. We report here our preliminary results demonstrating the formation of trimethylpalladium(IV) complexes containing a mixed donor set of 2,2′-bipyridine (bpy) and monodentate phosphines as ligands.

2. Results and discussion

The first reported alkylpalladium(IV) complex, $PdIMe_3(bpy)$, has been shown by ^{1}H-NMR spectroscopy to form an equilibrium with $[PdMe_3(bpy)(NCCD_3)]I$ when dissolved in acetonitrile-d_3 [9]. It has also been established that reductive elimination of ethane from this complex in solution proceeds predominantly via dissociation of iodide [10,11]. Thus, it may be possible to take advantage of the lability of the Pd^{IV}–I bond to explore the potential formation of phosphine complexes via competition with the iodide ligand.

Addition of triphenylphosphine to $PdIMe_3(bpy)$ in dichloromethane-d_2 at −40°C results in the detection of ∼10% of the palladium(IV) as $[PdMe_3(bpy)(PPh_3)]^+$ (Table 1, discussed below). At higher temperatures reductive elimination of ethane occurs. The more polar solvent acetone-d_6, expected to enhance dissociation of iodide, is unsuitable for the exchange studies owing to

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Table 1
Selected NMR data for the cations $[MMe_3(bpy)(L)]^+$

M	L	^1H-NMR [a]				^{31}P-NMR [b]		T (°C)
		$\delta(MMe_3)$	$^3J_{HP}$ (Hz)	$^2J_{HPt}$ (Hz)	δ(H6) (bpy)	$\delta(^{31}P)$	$^1J_{PPt}$ (Hz)	
Cations formed on addition of phosphines to $PdIMe_3(bpy)$ in dichloromethane-d_2 [c]								
Pd	PMe_2Ph	1.45 (6H)	9.2		8.50m (2H)	−16.7		0
		0.83 (3H)	9.2					
Pd	$PMePh_2$	1.61 (6H)	8.8		8.72m (2H)	−5.9		0
		1.00 (3H)	8.8					
Pd	PPh_3	1.69 (6H)	8.4		8.61m (2H)	5.6		−40
		1.08 (3H)	8.0					
Cations formed on reaction of $MMe_2(bpy)$ with MeO_3SCF_3 followed by addition of PPh_3 in acetone-d_6								
Pd	PPh_3	1.79 (6H)	8.4		8.59m (2H)	9.1		−20
		1.17 (3H)	8.0					
Pt	PPh_3	1.38 (6H)	7.2	67.6	8.64m (2H)	0.0	998	20
		0.54 (3H)	7.2	59.4				

[a] Chemical shifts in ppm from $SiMe_4$.

[b] Chemical shifts in ppm from H_3PO_4.

[c] $PdIMe_3(bpy)$ in dichloromethane-d_2: 1.83 (6H), 1.14 (3H), 8.87 (2H) at 0°C and 1.79 (6H), 1.13 (3H), 8.72 (2H) at −40°C.

the low solubility of $PdIMe_3(bpy)$ in this solvent. However, for the stronger donor ligands $PMePh_2$ and PMe_2Ph, displacement of iodide from $PdIMe_3(bpy)$ in dichloromethane-d_2 is about 2/3 complete for $PMePh_2$ and quantitative for PMe_2Ph at 0°C.

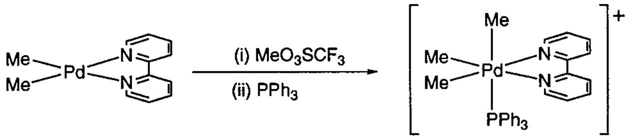
To avoid the presence of iodide as a ligand competing with PPh_3, and noting that methyl triflate reacts with $PdMe_2$(tmeda) (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) in acetone-d_6 at −40°C to form unstable $[PdMe_3(tmeda)(acetone\text{-}d_6)]^+$ [12], we performed a similar reaction with $PdMe_2(bpy)$, followed by immediate addition of PPh_3. This reaction resulted in NMR spectra consistent with exclusive formation of $[PdMe_3(bpy)(PPh_3)]^+$ (Scheme 1).

Alkylplatinum(IV) complexes are far more stable than those of palladium(IV), and thus to confirm the assignment of structure for the unstable palladium(IV) complex the platinum(IV) analogue was synthesised and characterised by X-ray diffraction. A solution of the platinum(IV) complex was obtained, by an identical procedure to that for palladium, and isolated in crystalline form by an alternative synthesis involving the reaction of $PtIMe_3(bpy)$ with silver triflate in acetone, followed by addition of PPh_3.

The cations $[MMe_3(bpy)(PPh_3)]^+$ exhibit appropriate integration in the ^1H-NMR spectra (1:1:1 MMe_3–bpy–PPh_3), where the methylmetal(IV) resonances occur in a 2:1 ratio (*trans* to bpy and PPh_3, respectively) and the $PtMe_3$ moieties exhibit $^2J_{HPt}$ (Table 1). The coupling constants $^3J_{HP}$ are similar for methyl groups both *cis* and *trans* to PPh_3, as documented for $[PtMe_3(py)_2(PMe_2Ph)]^+$ (py = pyridine, 8.4 and 7.2 Hz) [13] and $[PtMe_3(p\text{Tol-BIAN})(PPh_3)]^+$ (*p*Tol-BIAN = bis(*p*-tolylimino)acenaphthene, 8.1 and 6.6 Hz) [14]. Coordinated triphenylphospine is detected by the presence of a ^{31}P resonance at 9.1 for palladium and 0.0 ppm for platinum, where the platinum complex exhibits $^1J_{PPt} =$ 998 Hz, similar to that for the *p*Tol-BIAN complex (0.19 ppm, 1038 Hz).

The structure of the cation in $[PtMe_3(bpy)(PPh_3)][O_3SCF_3]$ is shown in Fig. 1. The crystals have two independent cations and anions, the platinum environments exhibiting differences in bond lengths $< 2\sigma$ and in angles < 2°. Fig. 1 illustrates the facial configuration of the $PtMe_3$ group, the distorted octahedral geometry for platinum (angles at platinum 77.7(1)–95.8(2)°). The Pt–C distances *trans* to triphenylphosphine (2.086(4), 2.088(4) Å) are longer than those *trans* to 2,2′-bipyridine (2.055(4)–2.073(4) Å), reflecting the higher *trans* influence of PPh_3 and/or the small 'bite' of the bpy ligand. The platinum atoms lie close to the mean planes of the pyridine rings (0.032(6)–0.212(5) Å), and the pyridine rings form dihedral angles of 4.4(1) and 4.9(1)° within the 2,2′-bipyridine ligands. The trifluoromethanesulfonate groups are regular and do not exhibit disorder.

This work is currently being extended to include other phosphine donors and other classes of organo groups bonded to palladium(IV), with the eventual goal



Scheme 1.

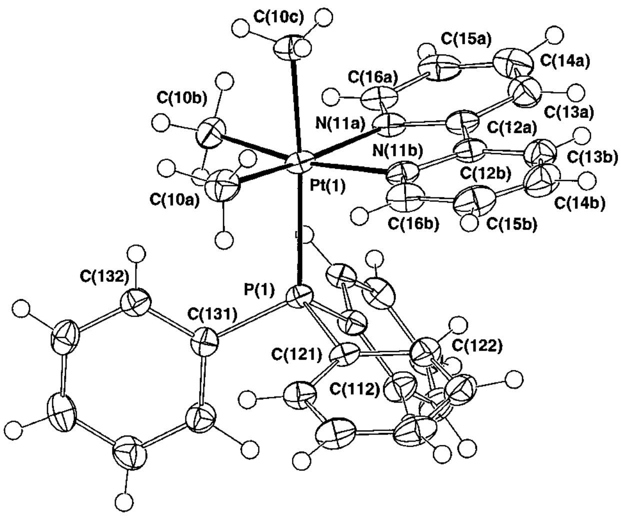


Fig. 1. Projection of cation **1** of the two similar independent cations in $[PtMe_3(bpy)(PPh_3)][O_3SCF_3]$, showing 50% thermal ellipsoids for the non-hydrogen atoms, hydrogen atoms having an arbitrary radius of 0.1 Å. Selected bond lengths (Å) and angles (°) for cations **1** ($n = 1$) and **2** ($n = 2$), respectively: Pt(n)–C(n0a) 2.073(4), 2.067(4); Pt(n)–C(n0b) 2.055(4), 2.059(4); Pt(n)–C(n0c) 2.086(4), 2.088(4); Pt(n)–N(n1a) 2.149(3), 2.143(3); Pt(n)–N(n1b) 2.137(3), 2.131(3); Pt(n)–P(n) 2.418(1), 2.4179(9); C(n0a)–Pt(n)–C(n0b) 91.3(2), 91.4(2); C(n0a)–Pt(n)–C(n0c) 84.4(2), 86.0(2); C(n0b)–Pt(n)–C(n0c) 85.4(2), 85.9(2); C(n0a)–Pt(n)–N(n1a) 170.4(2), 170.7(2); C(n0a)–Pt(n)–N(n1b) 95.8(2), 95.2(1); C(n0a)–Pt(n)–P(n) 90.0(1), 89.1(1); C(n0b)–Pt(n)–N(n1a) 94.3(1), 94.5(1); C(n0b)–Pt(n)–N(n1b) 169.6(1), 169.0(2); C(n0b)–Pt(n)–P(n) 94.4(1), 95.6(1); C(n0c)–Pt(n)–N(n1a) 88.3(1), 87.4(1); C(n0c)–Pt(n)–N(n1b) 87.7(2), 85.8(2); C(n0c)–Pt(n)–P(n) 174.3(1), 174.9(1); N(n1a)–Pt(n)–N(n1b) 77.7(1), 78.0(1); N(n1a)–Pt(n)–P(n) 97.34(9), 97.39(8); N(n1b)–Pt(n)–P(n) 93.17(8), 93.26(8); Pt(n)–P(n)–C(n11) 117.2(1), 117.2(1); Pt(n)–P(n)–C(n21) 110.5(1), 109.8(1); Pt(n)–P(n)–C(n31) 117.2(1), 117.0(1).

of determining whether organopalladium(IV) groups can be stabilised by a donor set containing phosphorus donor atoms only. Possible roles for palladium(IV) in catalysis may involve the presence of phosphine donor ligands, although definitive evidence is generally lacking to date [5–7], and it is anticipated that development of a palladium(IV) chemistry supported by phosphine ligands will assist in resolving these issues.

3. Experimental

The reagents $PdMe_2(bpy)$ [15,16], $PtMe_2(bpy)$ [17], $PdIMe_3(bpy)$ [9] and $PtIMe_3(bpy)$ [18] were synthesised as reported. Microanalyses were performed by the Central Science Laboratory, University of Tasmania, and NMR spectra were recorded with a Varian Unity Innova 400 MHz wide-bore instrument, with chemical shifts given in ppm relative to $SiMe_4$ or H_3PO_4.

3.1. Generation of solutions containing $[MMe_3(bpy)(L)]^+$

3.1.1. $[PdMe_3(bpy)(PMePh_2)]^+$

Methyldiphenylphosphine (3.2 μl, 0.017 mmol) was added to a solution of $PdIMe_3(bpy)$ (0.0074 g, 0.017 mmol) in dichloromethane-d_2 (0.3 ml) at −60°C in an NMR tube. The reaction was monitored by ^{1}H-NMR spectroscopy and the solution warmed in 20°C intervals until reaction was observed (~ −40°C). After 10 min at 0°C further displacement of iodide did not occur, with ~2/3 of the iodide displaced. At higher temperatures reductive elimination of ethane is observed. ^{1}H-NMR for the cation: δ 8.72 (m, 2, H6), 8.53 (m, 2, H3), 8.22 (m, 2, H4), 7.76 (m, 2, H5), 7.33 (m, 2, Ph), 7.22 (m, 4, Ph), 7.01 (m, 4, Ph), 1.67 (m, $^2J_{HP} = 6.8$ Hz, 3, PCH_3), 1.61 (d, $^3J_{HP} = 8.8$ Hz, 6, $PdCH_3$), 1.00 (d, $^3J_{HP} = 8.8$ Hz, 3H, $PdCH_3$).

3.1.2. $[PdMe_3(bpy)(PMe_2Ph)]^+$

Following a similar procedure the cation was formed quantitatively at 0°C. ^{1}H-NMR for the cation: δ 8.50 (m, 2, H6), 8.42 (m, 2, H3), 8.17 (m, 2, H4), 7.62 (m, 2, H5), 7.20 (m, 1, Ph), 7.06 (m, 2, Ph), 6.58 (m, 2, Ph), 1.45 (m, $^3J_{HP} = 9.2$ Hz, 6, $PdCH_3$), 1.31 (d, $^2J_{HP} = 8.0$ Hz, 6, PCH_3), 0.83 (d, $^3J_{HP} = 9.2$ Hz, 3H, $PdCH_3$).

3.1.3. $[PdMe_3(bpy)(PPh_3)]^+$

Methyl triflate (2.4 μl, 0.022 mmol) was added to a solution of $PdMe_2(bpy)$ (0.0062 g, 0.022 mmol) in acetone-d_6 (0.3 ml) at −60°C and the solution warmed until reaction was essentially complete at −40°C. A cooled solution (−40°C) of PPh_3 (0.0056 g) in acetone-d_6 (0.1 ml) was added. The spectra show the presence of minor quantities of reactant and *cis*-$PdMe_2(PPh_3)_2$. ^{1}H-NMR for the cation: δ 8.78 (m, 2, H3), 8.59 (m, 2, H6), 8.29 (m, 2, H4), 7.79 (m, 2, H5), 7.45 (m, 3, Ph), 7.32 (m, 6, Ph), 7.05 (m, 6, Ph), 1.79 (d, $^3J_{HP} = 8.4$ Hz, 6, CH_3), 1.17 (d, $^3J_{HP} = 8.0$ Hz, 3H, CH_3).

3.1.4. $[PtMe_3(bpy)(PPh_3)]^+$

A similar experiment to that for palladium gave a spectrum identical to that reported below for the isolated complex.

3.1.5. $[PtMe_3(bpy)(PPh_3)][O_3SCF_3]$

A solution of silver triflate (0.0222 g, 0.087 mmol) in acetone (2 ml) was added to a solution of $PtIMe_3(bpy)$ (0.0455 g, 0.087 mmol) in acetone (5 ml) at room temperature. After 10 min the precipitate of AgI was removed and PPh_3 (0.0228 g, 0.087 mmol) was added to the filtrate. The resulting clear solution was stirred for 30 min and the solvent removed in a vacuum. The residue was extracted with acetone (2 ml) and the solution filtered through Celite. The product crystallised on slow diffusion of pentane into the solution

(0.053 g, 75%). ^{1}H-NMR (acetone-d_6): δ 8.66 (m, 2, H3), 8.64 (m, 2, H6), 8.34 (m, 2, H4), 7.79 (m, 2, H5), 7.46 (m, 3, Ph), 7.36 (m, 6, Ph), 7.12 (m, 6, Ph), 1.38 (d, $^3J_{HP} = 7.2$, $^2J_{HPt} = 67.6$ Hz, 6, CH_3), 0.54 (d, $^3J_{HP} = 7.2$, $^2J_{HPt} = 59.4$ Hz, 3, CH_3). ^{31}P-NMR (acetone-d_6): δ 0.0 ($^1J_{PPt} = 998$ Hz). Anal. Calc. for $C_{32}H_{32}F_3N_2O_3PPtS$: C, 47.58; H, 3.99; N, 3.47; S, 3.97. Found: C, 47.43; H, 3.73; N, 3.33; S, 3.80%.

3.2. X-ray structure determination for [PtMe$_3$(bpy)(PPh$_3$)][O$_3$SCF$_3$]

$C_{32}H_{32}F_3N_2O_3PPtS$, $M = 807.33$, triclinic, space group $P\bar{1}$, $a = 9.4497(9)$, $b = 16.759(1)$, $c = 20.050(2)$ Å, $\alpha = 81.962(1)$, $\beta = 89.241(1)$, $\gamma = 80.720(1)°$, $V = 3102.7(8)$ Å^3, $D_{calc.}$ $(Z = 4) = 1.729$ g cm^{-3}; $F(000) = 1592$, $\mu_{Mo} = 46.95$ cm^{-1}; specimen: $0.35 \times 0.30 \times 0.07$ mm; $T_{min,\ max}$ 0.498, 0.831 (‘empirical’ correction), ω scan mode, $2\theta_{max} = 58°$, monochromatic Mo–K$_\alpha$ radiation, $\lambda = 0.7107_3$ Å, temperature = 153 K. A full sphere of absorption corrected area-detector diffractometer data (Bruker CCD instrument) (36 148 reflections) were merged to give 15 103 unique ($R_{int} = 0.032$), 12 050 with $F > 4\sigma(F)$ being considered ‘observed’ and used in the full-matrix least-squares refinement (anisotropic thermal parameter refinement for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ included constrained). Conventional R, R_w (statistical weights) on $|F|$ 0.028, 0.033.

4. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (deposition no. 137496). Copies of the information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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