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FULL PAPER

Trimethyl-palladium(IV) and -platinum(IV) complexes containing phosphine donor ligands, including studies of 1,5,9-triethyl-1,5,9-triphosphacyclodecane and X-ray structural studies of palladium(II) and palladium(IV) complexes †

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Received 13th June 2000, Accepted 10th August 2000
First published as an Advance Article on the web 13th September 2000

Dimethyl(2,2′-bipyridine)palladium(II) reacted with methyl triflate (CF_3SO_3Me) at −60 °C to form a palladium(IV) complex which reacted with a range of monodentate phosphines [PPh_3, $PMePh_2$, PMe_2Ph, PCy_3, $P(OMe)_3$], 1,2-bis(diethylphosphino)ethane (depe), or *syn*,*syn*-1,5,9-triethyl-1,5,9-triphosphacyclodecane (*syn*,*syn*-Et_3[12]aneP_3) to form complexes containing octahedral palladium(IV) centres *fac*-$[PdMe_3(2,2'\text{-bipy})(L)]^+$ **1**–**5**, **11**–**13**. The ligand depe bridges between palladium(IV) centres in a binuclear complex (**11**), the triphosphine forms both mononuclear (**13**) and binuclear species (**12**), and representative complexes of other bidentate nitrogen donor ligands have also been prepared, $[PdMe_3(N\text{–}N)(PMe_2Ph)][O_3SCF_3]$ [N–N = 1,10-phenanthroline (phen) **6** or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmen) **7**]. The first structural analysis of an organopalladium(IV) phosphine complex is reported, and octahedral **6** and platinum(IV) complexes $[PtMe_3(2,2'\text{-bipy})(L)][O_3SCF_3]$ [L = PPh_3 **8**, $PMePh_2$ **9** or PMe_2Ph **10**] have been isolated. All of the palladium(IV) complexes reductively eliminate ethane on decomposition to form palladium(II) species, where the monodentate phosphines form $[PdMe(N\text{–}N)(L)]^+$ **1a**–**7a**; a structural analysis of square-planar $[PdMe(2,2'\text{-bipy})(PMe_2Ph)][O_3SCF_3]$ **3a** is reported. The stability of palladium(IV) complexes decreases in the order $PMe_2Ph > PMePh_2 > PPh_3$, and for complexes of PMe_2Ph there is a stability order phen > 2,2′-bipy > tmen for $[PdMe_3(\text{bidentate ligand})(PMe_2Ph)]^+$.

Introduction

There are several palladium catalysed processes for which the involvement of palladium(IV) intermediates have amply been demonstrated *via* spectrocopic detection of intermediates or well characterised model reactions closely related to steps in the catalytic reactions.[1] Apart from the ring-opening polymerisation of cyclic disilanes,[2] these are restricted to systems in which strong oxidising agents are present,[1] *viz*. the reaction of electrophilic alkynes with tetramethyltin in the presence of bromine[3] and the acetoxylation of arenes in the presence of oxidants such as $Cr_2O_7^{2-}$[4] and $IPh(O_2CMe)_2$.[5,6] In a wide range of reactions for which palladium(IV) intermediates are suggested, usually involving phosphines as ligands, suitable reactions that model all key steps in the processes have not been established.[1]

We have commenced a study of the role of phosphine ligands in palladium(IV) chemistry, and to date have reported the spectroscopic detection of unstable species $[PdMe_3(2,2'\text{-bipy})(L)]^+$ (L = PPh_3, $PMePh_2$ or PMe_2Ph; 2,2′-bipy = 2,2′-bipyridyl) formed in equilibrium with $[PdIMe_3(2,2'\text{-bipy})]$ in CD_2Cl_2, and formation of $[PdMe_3(2,2'\text{-bipy})(PPh_3)]^+$ on reaction of methyl triflate (CF_3SO_3Me) with $[PdMe_2(2,2'\text{-bipy})]$ followed by addition of PPh_3.[7] We report here the first isolation and structural determination for an organopalladium(IV) phosphine complex, $[PdMe_3(phen)(PMe_2Ph)][O_3SCF_3]$ (phen = 1,10-phenanthroline), characterisation of several palladium(IV) and platinum(IV) analogues, a structural analysis of $[PdMe(2,2'\text{-bipy})(PMe_2Ph)][O_3SCF_3]$ formed on reductive elimination of ethane from a palladium(IV) complex, and the further development of this chemistry to include the cyclic phosphine *syn*,*syn*-1,5,9-triethyl-1,5,9-triphosphacyclodecane (*syn*,*syn*-Et_3[12]aneP_3).

† Electronic supplementary information (ESI) available: NMR data for palladium-(II) and -(IV) complexes. See http://www.rsc.org/suppdata/dt/b0/b004741o/

Results and discussion

Synthesis and characterisation of complexes

All organopalladium(IV) complexes detected to date contain a polydentate ligand, although the presence of a single monodentate ligand as part of the co-ordination sphere is commonly observed. Oxidation of diorganopalladium(II) complexes by methyl triflate has been developed by van Koten, and more recently in our laboratory, *e.g.* oxidation of $[PdMe_2(tmen)]$ (tmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) in CD_3CN to form $[PdMe_3(tmen)(NCCD_3)][O_3SCF_3]$[8] and of $[PdMe_2(2,2'\text{-bipy})]$ in $(CD_3)_2CO$ to form $[PdMe_3(2,2'\text{-bipy})\{OC(CD_3)_2\}][O_3SCF_3]$ or $[PdMe_3(O_3SCF_3)(2,2'\text{-bipy})]$.[7] In view of the recent structural analysis of $[Pt(O_3SCF_3\text{-}O)Me_3\{(2,6\text{-}Pr^i_2C_6H_3NCH)_2\text{-}N,N\}]$[9] and solution NMR studies of $[Pt(O_3SCF_3\text{-}O)Me_3(tmen\text{-}N,N')]$[10] it can now be assumed that the triflate ion is co-ordinated to Pd^{IV} in the 2,2′-bipy complex.

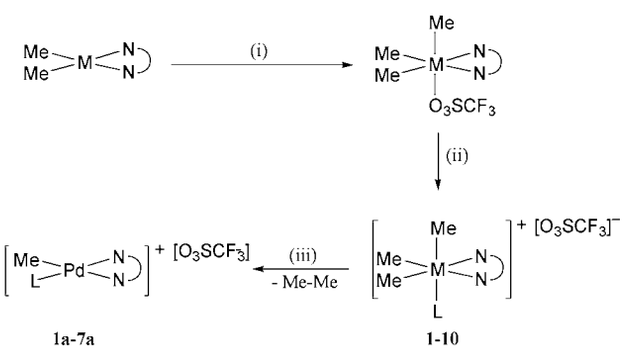
The triflate ligand in $[PdMe_3(O_3SCF_3)(\text{bidentate ligand})]$ is readily displaced by monodentate phosphines (Scheme 1) to form complexes **1**–**7**, where the oxidation and ligand exchange reactions are performed at −60 to −40 °C to avoid decomposition of unstable palladium(IV) species. Complexes of dimethylphenylphosphine (**3**, **6**) were isolable, and both suf-

DOI: 10.1039/b004741o

Table 1 Analytical[a] and physical data for the metal(IV) complexes

Complex	Decomp./ °C[d]	^{1}H NMR[b] MMe$_3$ *trans* N δ	*J*(HP)	MMe$_3$ *trans*-P δ	*J*(HP)	^{31}P NMR[c] δ	*J*(PPt)/Hz	Analysis (%) C	H	N
1 [PdMe$_3$(2,2′-bipy)(PPh$_3$)][O$_3$SCF$_3$][e,f]	−20	1.79	8.4	1.17	8.0	9.1				
2 [PdMe$_3$(2,2′-bipy)(PMePh$_2$)][O$_3$SCF$_3$][f]	0	1.62	8.4	0.97	8.8	−5.5				
3 [PdMe$_3$(2,2′-bipy)(PMe$_2$Ph)][O$_3$SCF$_3$]	20	1.53	8.8	0.79	8.8	−11.3		44.40 (44.42)	4.77 (4.74)	4.62 (4.71)
4 [PdMe$_3$(2,2′-bipy)(PCy$_3$)][O$_3$SCF$_3$][f]	0	1.70	7.2	0.95	7.6	1.5				
5 [PdMe$_3$(2,2′-bipy){P(OMe)$_3$}][O$_3$SCF$_3$][f]	−20	1.64	10.4	0.80	13.6	112.8				
6 [PdMe$_3$(phen)(PMe$_2$Ph)][O$_3$SCF$_3$]	20	1.67	8.8	0.83	8.8	−10.6		46.67 (46.57)	4.53 (4.56)	4.62 (4.53)
7 [PdMe$_3$(tmen)(PMe$_2$Ph)][O$_3$SCF$_3$][f]	−40	1.89	6.4	1.30	6.8	−17.2				
8 [PtMe$_3$(2,2′-bipy)(PPh$_3$)][O$_3$SCF$_3$][e]		1.38	7.2	0.54	7.2	0.0				
9 [PtMe$_3$(2,2′-bipy)(PMePh$_2$)][O$_3$SCF$_3$]		1.20	8.4	0.43	7.6	−15.1	998			
10 [PtMe$_3$(2,2′-bipy)(PMe$_2$Ph][O$_3$SCF$_3$]		1.09	8.0	0.29	8.0	−22.6	1083 1172.6	38.82 (38.66)	3.81 (4.13)	4.21 (4.10)
11 [{PdMe$_3$(2,2′-bipy)}$_2$(depe)][O$_3$SCF$_3$]$_2$[f]	−20	1.52	8.0	0.76	8.4	−3.3				
12 [{PdMe$_3$(2,2′-bipy)}$_2$(Et$_3$[12]aneP$_3$)][O$_3$SCF$_3$]$_2$	0	1.69	8	0.86	8.8	−6.5, −6.0[g]				
		1.70	8.4			−44.6, −44.3[g]				
13 [PdMe$_3$(2,2′-bipy)(Et$_3$[12]aneP$_3$)][O$_3$SCF$_3$][f]	0	1.52	8.4	0.78	8.8	−6.7[g] −35.0[g]				

[a] Required values given in parentheses. [b] In acetone-d_6, SiMe$_4$ as reference. [c] In acetone-d_6, H$_3$PO$_4$ as reference. [d] In acetone-d_6. [e] From ref. 7. [f] Insufficiently stable for isolation as pure complex. [g] Integration low field : high field = 2 : 1.



	N–N	L
1a	2,2′-bipy	PPh$_3$
2a	2,2′-bipy	PMePh$_2$
3a	2,2′-bipy	PMe$_2$Ph
4a	2,2′-bipy	PCy$_3$
5a	2,2′-bipy	P(OMe)$_3$
6a	phen	PMe$_2$Ph
7a	tmen	PMe$_2$Ph

	M	N–N	L
1	Pd	2,2′-bipy	PPh$_3$
2	Pd	2,2′-bipy	PMePh$_2$
3	Pd	2,2′-bipy	PMe$_2$Ph
4	Pd	2,2′-bipy	PCy$_3$
5	Pd	2,2′-bipy	P(OMe)$_3$
6	Pd	phen	PMe$_2$Ph
7	Pd	tmen	PMe$_2$Ph
8	Pt	2,2′-bipy	PPh$_3$
9	Pt	2,2′-bipy	PMePh$_2$
10	Pt	2,2′-bipy	PMe$_2$Ph

Scheme 1 Synthesis of complexes of monodentate phosphines. (i) Methyl triflate in acetone, −60 (M = Pd), 25 °C (Pt); (ii) L in acetone, −60 (**1**,[7] **2**, **4**, **5**, **7**), −40 (**3**, **6**), 25 °C (**8**,[7] **9**, **10**); (iii) in acetone, M = Pd, −40 (**7a**), −20 (**1a**, **4a**), 0 (**2a**, **3a**, **5a**), 20 °C (**6a**).

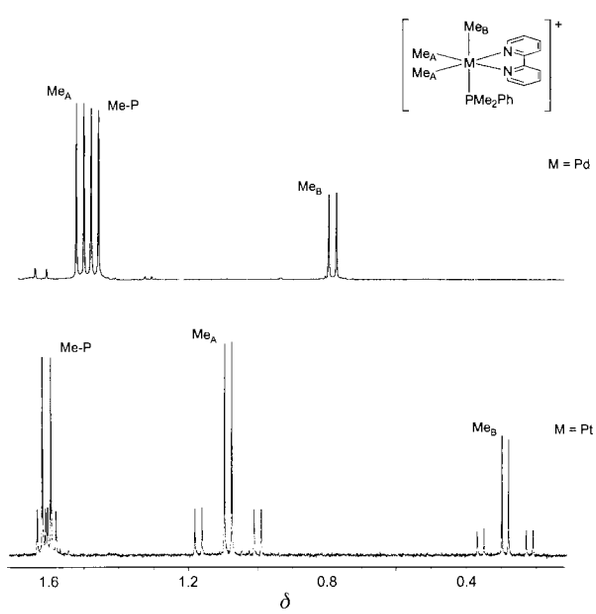


Fig. 1 ^{1}H NMR spectra of [MMe$_3$(2,2′-bipy)(PMe$_2$Ph)][O$_3$SCF$_3$] [M = Pd **3** or Pt **10**] in the region showing methyl groups bonded to the metal and phosphorus atoms. Coupling ^3J(HP) is shown for methylmetal(IV) protons, ^2J(HP) for methylphosphorus(III), and for the platinum complex sidebands associated with ^2J(HPt) and ^3J(HPt) (Table 1).

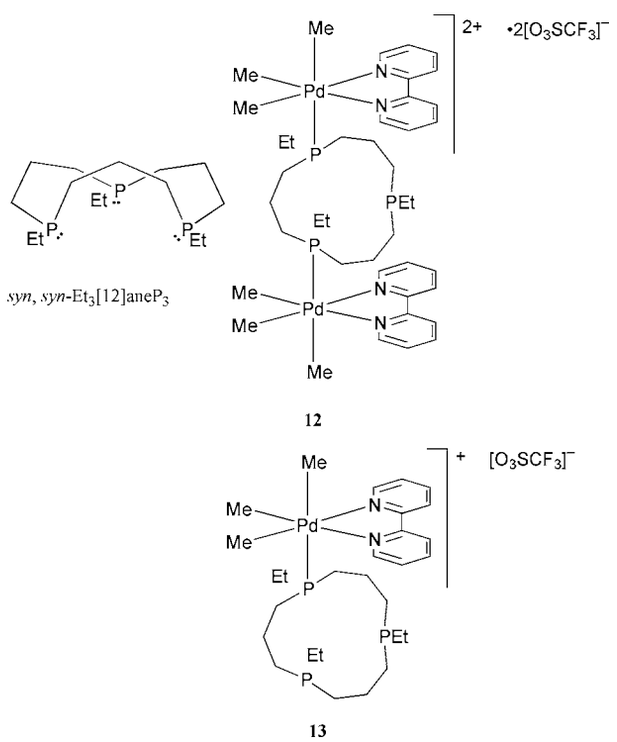
ficiently crystalline for X-ray structural examination. The structure of [PdMe$_3$(phen)(PMe$_2$Ph)][O$_3$SCF$_3$] **6** is described below, together with the reductive elimination product [PdMe(2,2′-bipy)(PMe$_2$Ph)][O$_3$SCF$_3$] **3a** which was present as an impurity in less stable [PdMe$_3$(2,2′-bipy)(PMe$_2$Ph)][O$_3$SCF$_3$] **3**.

Three platinum(IV) complexes were prepared for comparison of spectra with those of palladium(IV) complexes. The platinum(IV) complexes are stable at ambient temperature and exhibit ^{1}H and ^{31}P NMR spectra similar to those of palladium(IV) analogues, together with additional features associated with coupling involving the ^{195}Pt nucleus (Table 1, Fig. 1). Thus, two methylmetal(IV) resonances are observed in 2 : 1 ratio, with resonances for platinum(IV) complexes generally 0.4–0.5 ppm to higher field; and for both Pd^{IV} and Pt^{IV}, at higher field as phenyl groups are replaced by methyl groups in phosphine ligands PMe$_2$Ph > PMePh$_2$ > PPh$_3$. The downfield shift of the ^{31}P resonance on co-ordination of phosphines follows a similar trend, PMe$_2$Ph > PMePh$_2$ > PPh$_3$, reflected also in coupling constants ^1J(PPt).

Reductive elimination of ethane from the palladium(IV) complexes **1**–**7** occurs at −40 to 20 °C, depending on the ligand present. Ethane and the palladium(II) products were characterised by NMR spectroscopy, as well as the isolation and structural analysis of **3a**. The more strongly donating phosphines

enhance stability of the palladium(IV) complexes, and the tmen complex **7** is the least stable consistent with the lower stability of $[PdIMe_3(tmen)]$[8] compared with $[PdIMe_3(2,2'\text{-bipy})]$.[11] The palladium(II) complexes **1a**–**5a** give broad 2,2′-bpy resonances at room temperature in both $(CD_3)_2CO$ and $CDCl_3$, and the isolated complex $[PdMe(2,2'\text{-bipy})(PMe_2Ph)][O_3SCF_3]$ **3a** exhibited well resolved spectra showing two pyridine ring environments when cooled to −30 °C in $(CD_3)_2CO$. These results indicate the presence of exchange, presumably intramolecular and facilitated by triflate co-ordination to give a five-co-ordinate intermediate.

Facially co-ordinated tridentate ligands are able to stabilise organopalladium(IV) species for both hard and soft donor ligands, *e.g.* $[PdMe_3\{CpCo(PO(OMe)_3)_3\text{-}O,O',O''\}]$ ($[CpCo(PO(OEt)_3)_3]^-$ = cyclopentadienyltris(dimethylphosphito-*P*)-cobaltate)[12] and $[PdMe_3(9S3)][NO_3]$ (9S3 = 1,4.7-trithiacyclononane).[13] The enhanced stability of these complexes has been attributed to the presence of ligands disfavouring formation of five-co-ordinate intermediates that are generally believed to be required for facile reductive elimination of ethane.[1,12,13] Thus, with an appropriate choice of ligand it was considered feasible that organopalladium(IV) complexes with phosphine donor groups as the only ancillary ligand(s) could be detectable. The ligand *syn*,*syn*-1,5,9-triethyl-1,5,9-triphosphacyclodecane (Scheme 2) was chosen to attempt this in view of



Scheme 2 *syn*,*syn*-1,5,9-Triethyl-1,5,9-triphosphacyclodecane and complexes obtained using this ligand.

the high stability of a range of complexes in which it co-ordinates in a facial tridentate mode,[14] with structural analyses of octahedral complexes showing P–M–P angles close to 90°.[14b] A synthetic strategy identical to that of steps (i) and (ii) in Scheme 1 was adopted in view of the facile displacement of iodide and 2,2′-bipy in $[PdIMe_3(2,2'\text{-bipy})]$ by $[CpCo(PO(OEt)_3)_3]^-$ to form $[PdMe_3\{CpCo(PO(OEt)_3)_3\text{-}O,O',O''\}]$.[12] If successful, this approach would lead to displacement of 2,2′-bipy and the triflate ligand from $[PdMe_3(O_3SCF_3)(2,2'\text{-bipy})]$ to give $[PdMe_3\{syn,syn\text{-}Et_3[12]aneP_3\}][O_3SCF_3]$.

^1H and ^{31}P NMR studies similar to those of Scheme 1 indicate that 2,2′-bipy is not displaced from $[PdMe_3(O_3SCF_3)(2,2'\text{-bipy})]$. Instead, spectra show the formation of complexes **12** and **13** (Scheme 2), and a complex containing bridging 1,2-

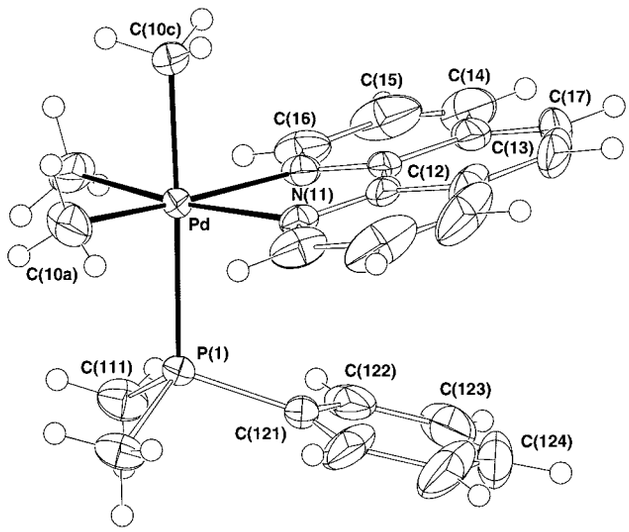


Fig. 2 Projection of the cation of $[PdMe_3(phen)(PMe_2Ph)][O_3SCF_3]$ **6**; thermal ellipsoids (20%) are shown for non-hydrogen atoms, and hydrogen atoms have been given an arbitrary radius of 0.1 Å.

bis(diethylphosphino)ethane (**11**) (Table 1) was generated to assist with interpretation of NMR spectra. Thus, **12**, containing the ligand as a bridge between two palladium(IV) centres, is formed as the dominant product in $(CD_3)_2CO$, in which *syn*,*syn*-$Et_3[12]aneP_3$ has low solubility, and the 1 : 1 complex **13** is the dominant product when the phosphine is added as a $CDCl_3$ solution to $[PdMe_3(O_3SCF_3)(2,2'\text{-bipy})]$ in $(CD_3)_2CO$. ^{31}P NMR spectra show co-ordinated and unco-ordinated phosphorus environments in the anticipated ratios, and both ^1H and ^{31}P NMR spectra are similar to those of **1**–**7** (Table 1) and **11**. More complex spectra are obtained for **12**, where the bridging nature of the ligand generates two centres of chirality at the co-ordinated phosphorus atoms. Thus, the ^{31}P NMR spectra show two sets of resonances for the two possible diastereomers of **12**, whereas in the ^1H NMR spectra two separate doublets for the diastereotopic methyl groups *trans* to 2,2′-bipy are observed. The complexes decompose to form ethane at 0 °C, giving very complex spectra that could not readily be interpreted. In these complexes, and others mentioned here containing the tridentate ligand, the assignment of conformation for the ligand is not attempted since the presence as a monodentate or bidentate ligand with phosphine donor(s) directed away from the metal centre would be more consistent with isomerisation during complex formation.

As tmen is expected to be more easily displaced than 2,2′-bipy, $[PdMe_3(O_3SCF_3)(tmen)]$ was generated at low temperature (Scheme 1) and treated with *syn*,*syn*-$Et_3[12]aneP_3$. The NMR spectra at −60 °C show free tmen as well as resonances attributable to the phosphine co-ordinated to palladium. As reductive elimination of ethane occurs at the same temperature, the palladium(IV) complex(es) could not be identified.

X-Ray structural studies

The results of the single crystal X-ray studies are consistent in stoichiometry, connectivity and stereochemistry with the formulations as given above, and as presented in Figs. 2 and 3 and Tables 2 and 3 subject to caveats concerning **6** mentioned in the Experimental section.

As modelled in space group $P2_1/m$, both the cation and anion for $[PdMe_3(phen)(PMe_2Ph)][O_3SCF_3]$ **6** are disposed about a crystallographic mirror plane which, in the cation, passes through Pd–P,C(121, 124) and the midpoints of the central bonds of the phen ligand, and in the anion through S,C and one each of oxygen and fluorine, staggered about the S–C bond. The cation shows the *fac*-PdC_3 configuration in an octahedral geometry consistent with Pd^{IV}, where the Pd–C bond *trans* to

Table 2 Selected bond distance (Å) and angles (°) for $[PdMe_3(phen)(PMe_2Ph)][O_3SCF_3]$ **6**[a]

Pd–C(10a, 10c)	2.045(3), 2.082(4)	S(1)–C(0)	1.828(6)
Pd–N(11)	2.193(2)	S(1)–O(11, 13)	1.418(2), 1.426(3)
Pd–P(1)	2.422(1)	C(0)–F(1, 2)	1.330(4), 1.321(6)
C(10a)–Pd–C(10a^{i}, 10c)	87.0(1), 86.6(1)	Pd–P(1)–C(111, 121)	116.0(1), 109.7(1)
C(10a)–Pd–N(11, 11^{i})	173.2(1), 98.0(1)	C(0)–S(1)–O(11, 13)	103.8(1), 102.0(2)
N(11)–Pd–N(11^{i})	76.69(8)	O(11)–S(1)–O(11^{ii}, 13)	115.6(1), 114.6(1)
P(1)–Pd–C(10a, 10c)	92.0(1), 178.1(1)	S(1)–C(0)–F(1, 2)	111.2(3), 112.3(3)
P(1)–Pd–N(11)	92.43(7)	F(1)–C(0)–F(1″, 2)	107.5(4), 107.2(3)
Pd–N(11)–C(12, 16)	112.9(2), 128.5(2)		

[a] Deviation (Å) of palladium from the phen $C_{12}N_2$ mean plane ($\chi^2 = 195$) is 0.288(3) Å. Transformations of the asymmetric unit: i x, y, $\frac{1}{2} - z$; ii x, $y - 1$, $\frac{1}{2} - z$.

Table 3 Selected bond distance (Å) and angles (°) for $[PdMe(2,2'\text{-bipy})(PMe_2Ph)][O_3SCF_3]$ **3a**[a]

Pd–C(0)	2.048(3)	Pd–P	2.2363(6)
Pd–N(1a, 1b)	2.141(2), 2.128(2)	S–C	1.820(3)
S–O(1, 2)	1.446(2), 1.440(2)	C–F(1, 2)	1.338(3), 1.331(3)
S–O(3)	1.439(2)	C–F(3)	1.340(3)
C(0)–Pd–N(1a, 1b)	170.5(1), 93.4(1)	N(1a)–Pd–N(1b, P)	77.60(8), 104.76(5)
C(0)–Pd–P	84.57(8)	N(1b)–Pd–P	172.17(5)
Pd–N(1a)–C(2a, 6a)	114.1(2), 128.0(2)	Pd–P–C(11, 21)	113.83(8), 114.04(9)
Pd–N(1b)–C(2b, 6b)	114.4(1), 126.3(2)	Pd–P–C(22)	116.1(1)
C–S–O(1, 2)	102.9(1), 103.3(1)	S–C–F(1, 2)	111.5(2), 111.9(2)
C–S–O(3)	102.6(1)	S–C–F(3)	111.1(2)
O(1)–S–O(2, 3)	114.5(1), 115.5(1)	F(1)–C–F(2, 3)	107.6(2), 107.2(2)
O(2)–S–O(3)	115.4(1)	F(2)–C–F(3)	107.4(2)

[a] Deviation (Å) of atoms from the CN_2P mean co-ordination plane ($\chi^2 = 4842$) are 0.093(1) (Pd), 0.193(4) [C(0)], 0.071(3) [N(1a)], −0.079(4) [N(1b)] and −0.017(1) (P). Deviations of Pd from mean planes of pyridine rings a and b are 0.178(4) and 0.302(3) Å, respectively. Interplanar dihedral angles (°) are 16.54(7) [co-ord., py(a)], 14.67(7)] [co-ord., py(b)] and 6.69(9) [py(a), py(b)].

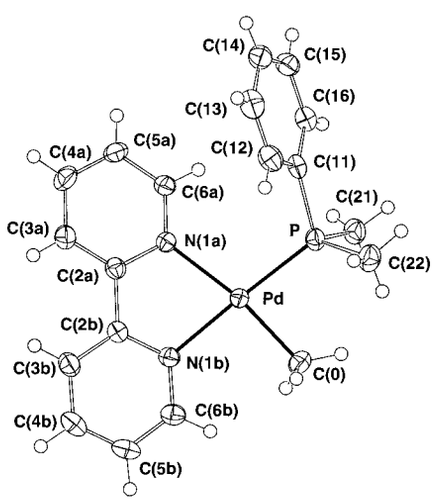


Fig. 3 Projection of the cation of $[PdMe(2,2'\text{-bipy})(PMe_2Ph)][O_3SCF_3]$ **3a** normal to the co-ordination plane. Other details as in Fig. 2.

the phosphine donor is lengthened by *ca*. 0.04 Å compared to Pd–C *trans* to phen. The PMe_2Ph ligand is oriented with the phenyl group adjacent to the phen ligand, similar to the arrangement found in $[PdBrMe_2(CH_2C_6H_4Br\text{-}p)(phen)]$[15] and $[PdBrMe_2(CH_2COPh)(2,2'\text{-bipy})]$.[16]

The palladium(II) complex $[PdMe(2,2'\text{-bipy})(PMe_2Ph)][O_3SCF_3]$ **3a** has the usual quasi-planar four-co-ordinate metal environment, the Pd–N bond *trans* to the methyl group being marginally longer than that *trans* to the phosphine donor. Some wrinkling of the plane may be due to tight packing within it, notably H(6b)···H(0a) 2.16(4) Å.

Concluding remarks

Dimethylpalladium(IV) complexes containing one phosphine donor interaction are stabilised in the co-ordination geometry *fac*-$[PdMe_3(N\text{–}N)(L)]^+$ (L = phosphine), and are sufficiently stable for isolation and structural analysis. Facile reductive elimination of ethane occurs in solution to from monomethylpalladium(II) complexes. The application of the triphosphine *syn*,*syn*-Et_3[12]aneP_3 to this chemistry confirms these observations, but the detection of species containing only phosphine donor groups to support the organopalladium(IV) kernel has continued to be elusive.

Experimental

The reagents $[PdMe_2(2,2'\text{-bipy})]$,[17,18] $[PdMe_2(phen)]$,[17] $[PdMe_2(tmen)]$,[8,18] $[PtMe_2(2,2'\text{-bipy})]$[19] and *syn*,*syn*-1,5,9-triethyl-1,5,9-triphosphacyclododecane[14a] were prepared as described. Solvents were dried, distilled, stored under nitrogen and freshly distilled immediately before use, and all procedures were carried out under nitrogen. NMR spectra were recorded on a Varian Unity Inova 400 WB spectrometer operating at 399.71 (^{1}H) or 161.80 MHz (^{31}P) at room temperature unless otherwise indicated. Chemical shifts are given in ppm relative to $SiMe_4$ or H_3PO_4 (85%). Microanalyses were performed by the Central Science Laboratory, University of Tasmania.

Synthesis of metal(IV) complexes of monodentate phosphines and 1,2-bis(diphenylphosphino)ethane

$[PdMe_3(2,2'\text{-bipy})(PMe_2Ph)][O_3SCF_3]$ 3. Methyl triflate (5.8 μL, 0.052 mmol) was added to a solution of $[PdMe_2(2,2'\text{-bipy})]$ (15 mg, 0.052 mmol) in tetrahydrofuran (3 mL) at −60 °C and the solution warmed and stirred at −40 °C until reaction was essentially complete and the solution had changed from bright orange to pale yellow; PMe_2Ph (7.3 μL, 0.052 mmol) was added at this temperature and the solution stirred for 15 min and cooled pentane (5 mL) at −40 °C added. The solution was left overnight at −20 °C after which time the product had precipitated as a colourless oil. The oil was separated, dried in a vacuum and dissolved in the minimum amount of dichloromethane. Upon slow diffusion of diethyl ether into the solution

at −20 °C the product crystallised over 48 h as a colourless solid. Yield: 23 mg, 74%.

[$PdMe_3$(phen)(PMe_2Ph)][O_3SCF_3] 6. Methyl triflate (7.9 μL, 0.069 mmol) was added to a solution of [$PdMe_2$(phen)] (22 mg, 0.069 mmol) in dichloromethane at (4 mL) −60 °C. The solution was warmed to −40 °C and stirred for 15 min during which time it changed from bright orange to yellow; PMe_2Ph (9.9 μL, 0.069 mmol) was added and the solution concentrated to ≈2 mL below 0 °C. The product was obtained as colourless crystals, suitable for X-ray crystallography, by slow diffusion of diethyl ether into the solution at −20 °C. Yield: 29 mg, 68%.

[$PtMe_3$(2,2′-bipy)($PMePh_2$)][O_3SCF_3] 9. This complex was isolated as a yellow oil by a similar procedure to that for the dimethylphenylphosphine analogue above using methyl triflate (5.9 μL, 0.052 mmol), [$PtMe_2$(2,2′-bipy)] (20 mg, 0.052 mmol) and $PMePh_2$ (9.8 μL, 0.052 mmol). Several attempts to purify the product by crystallisation were unsuccessful. Yield: 28 mg, 72%.

[$PtMe_3$(2,2′-bipy)(PMe_2Ph)][O_3SCF_3] 10. Methyl triflate (5.6 μL, 0.050 mmol) was added to a solution of $PtMe_2$(2,2′-bipy) (19 mg, 0.050 mmol) in tetrahydrofuran (5 mL) at room temperature. The resulting yellow solution was stirred for 30 min, PMe_2Ph (7.1 μL, 0.050 mmol) added and the mixture stirred for 30 min. The solvent was removed in a vacuum, the oily residue washed with pentane and diethyl ether (3 mL) and dissolved in tetrahydrofuran (3 mL). Pentane was added until the solution became cloudy and the mixture stored at −20 °C overnight, after which time the product had precipitated as a pale yellow, crystalline solid. Yield: 21 mg, 61%.

Synthesis of the palladium(II) complex [PdMe(2,2′-bipy)(PMe_2Ph)][O_3SCF_3] 3a

Methyl triflate (6.8 μL, 0.060 mmol) was added to a solution of [$PdMe_2$(2,2′-bipy)] (18 mg, 0.060 mmol) in tetrahydrofuran (4 mL) at −60 °C and the solution warmed and stirred at −40 °C for 30 min giving a pale yellow solution; PMe_2Ph (8.6 μL, 0.060 mmol) was added at this temperature and the solution warmed to room temperature and stirred at this temperature for 2 h. The solvent was removed in a vacuum, the residue dissolved in the minimum amount of dichloromethane, and the product crystallised on slow diffusion of diethyl ether into the solution at −20 °C over 48 h. Yield: 30 mg, 89%. ^{1}H NMR ($CDCl_3$, −30 °C): δ 8.64 (m, 1 H, H6A bipy), 8.62 (m, 1 H, H3A bipy), 8.55 (m, 1 H, H3B bipy), 8.28 (m, 1 H, H4A bipy), 8.08 (m, 1 H, H4B bipy), 7.81 (m, 2 H, Ph), 7.71 (m, 1 H, H5A bipy), 7.55 (m, 3 H, Ph), 7.37 (m, 1 H, H6B bipy), 7.20 (m, 1 H, H5B bipy), 1.89 (d, ^2J(HP) = 10.0, 6 H, PCH_3) and 0.91 (d, ^3J(HP) = 3.2 Hz, 3 H, $PdCH_3$). ^{31}P-{^{1}H} NMR ($CDCl_3$, −30 °C): δ 10.5 (Found: C, 42.58; H, 4.00; N, 5.00. $C_{20}H_{22}F_3N_2PPdS$ requires C, 42.53; H, 3.93; N, 4.96%).

Decomposition of the isolated palladium(IV) complexes 3 and 6

The complexes were dissolved in acetone-d_6 at −20 °C. As the solutions were warmed to room temperature, decomposition was monitored by ^{1}H NMR spectroscopy. In both cases reductive elimination of ethane was observed at 20 °C. [PdMe(phen)(PMe_2Ph)][O_3SCF_3] **6a**: ^{1}H NMR (acetone-d_6, 20 °C) very broad resonances for phen, δ 8.10 (m, 2 H, Ph), 7.61 (m, 3 H, Ph), 2.11 (d, ^2J(HP) = 10.4, 6 H, PCH_3) and 1.14 (d, ^3J(HP) = 2.9 Hz, 3 H, $PdCH_3$); ^{31}P-{^{1}H} NMR (acetone-d_6, 20 °C) δ 10.4.

^{1}H NMR studies of the formation of palladium(IV) complexes of monodentate phosphine and depe in solution at low temperatures: general procedure

[$PdMe_2$(2,2′-bipy)] (7.0 mg, 0.024 mmol) in acetone-d_6 (0.3 mL) was cooled to −60 °C and methyl triflate (2.7 μL, 0.024 mmol) added. The mixture was warmed to −40 °C and stirred for about 30 min until a clear yellow solution was obtained. It was then again cooled to −60 °C, an equimolar amount of the phosphine added, the mixture transferred to a NMR tube and placed in a precooled NMR spectrometer (−60 °C). The reaction was monitored by ^{1}H NMR spectroscopy starting at −60 °C and warming the solution to room temperature in 20 °C intervals. In all cases quantitative formation of the palladium(IV) complexes [$PdMe_3$(2,2′-bipy)(phosphine)][O_3SCF_3] was observed at −60 °C; decomposition of the complexes *via* reductive elimination of ethane and formation of [PdMe(2,2′-bipy)(phosphine)][O_3SCF_3] took place at different temperatures indicated below.

[$PdMe_3$(2,2′-bipy)(PPh_3)][O_3SCF_3] 1. Decomposition starts at −20 °C. [PdMe(2,2′-bipy)(PPh_3)][O_3SCF_3] **1a**: ^{1}H NMR (acetone-d_6) very broad resonances for 2,2′-bipy, δ 7.86 (m, 6 H, Ph), 7.67 (m, 3 H, Ph), 7.60 (m, 6 H, Ph) and 0.85 (s, 3 H, $PdCH_3$); ^{31}P-{^{1}H} NMR (acetone-d_6) δ 40.7.

[$PdMe_3$(2,2′-bipy)($PMePh_2$)][O_3SCF_3] 2. Decomposition starts at 0 °C. [PdMe(2,2′-bipy)($PMePh_2$)][O_3SCF_3] **2a**: ^{1}H NMR (acetone-d_6) very broad resonances for 2,2′-bipy, δ 7.86 (m, 4 H, Ph), 7.60 (m, 6 H, Ph), 2.38 (d, ^2J(HP) = 10.0, 3 H PCH_3) and 0.91 (d, ^3J(HP) = 2.8 Hz, 3 H, $PdCH_3$); ^{31}P-{^{1}H} NMR (acetone-d_6) δ 25.4.

[$PdMe_3$(2,2′-bipy)(PCy_3)][O_3SCF_3] 4. Decomposition starts at 0 °C. [PdMe(2,2′-bipy)(PCy_3)][O_3SCF_3] **4a**: ^{1}H NMR (acetone-d_6) very broad resonances, could not be assigned; ^{31}P-{^{1}H} NMR (acetone-d_6) δ 28.9.

[$PdMe_3$(2,2′-bipy){$P(OMe)_3$}][O_3SCF_3] 5. Decomposition starts at −20 °C. [PdMe(2,2′-bipy){$P(OMe)_3$}][O_3SCF_3] **5a**: ^{1}H NMR (acetone-d_6) very broad resonances for 2,2′-bipy, δ 3.93 (d, ^3J(HP) = 13.2 Hz, 9 H $POCH_3$) and 1.02 (s, 3 H, $PdCH_3$); ^{31}P-{^{1}H} NMR (acetone-d_6) δ 122.9.

[$PdMe_3$(tmen)(PMe_2Ph)][O_3SCF_3] 7. Methyl triflate (3.6 μL, 0.032 mmol) was added to a solution of [$PdMe_2$(tmen)] (8.1 mg, 0.032 mmol) in acetone-d_6 (0.3 mL) at −60 °C. After stirring for 20 min PMe_2Ph (4.6 μL, 0.032 mmol) was added and the solution transferred to a NMR tube. The reaction was monitored by ^{1}H NMR from −60 °C to room temperature in 20 °C intervals. Decomposition starts at −40 °C. [PdMe(tmen)(PMe_2Ph)][O_3SCF_3] **7a**: ^{1}H NMR (acetone-d_6, 0 °C) δ 7.92 (m, 2 H, Ph), 7.56 (m, 3 H, Ph), 2.95 (broad, 2 H, NCH_2), 2.81 (broad, 2 H, NCH_2), 2.66 (d, ^4J(HP) = 2.0, 6 H, NCH_3), 2.49 (s, 6 H, NCH_3), 1.83 (d, ^2J(HP) = 10.0, 6 H, PCH_3) and 0.31 (d, ^3J(HP) = 3.6 Hz, 3 H, $PdCH_3$); ^{31}P-{^{1}H} NMR (acetone-d_6, 0 °C) δ 8.0.

[{$PdMe_3$(2,2′-bipy)}$_2$(depe)][O_3SCF_3]$_2$ 11. Decomposition starts at −20 °C giving a complex mixture of products.

[{$PdMe_3$(2,2′-bipy)}$_2$(Et_3[12]aneP_3)][O_3SCF_3]$_2$ 12 and [$PdMe_3$(2,2′-bipy)(Et_3[12]aneP_3)][O_3SCF_3] 13. The ligand (7.6 mg, 0.025 mmol) was added to a solution of [$PdMe_3$(2,2′-bipy)(O_3SCF_3)] in acetone-d_6 (0.3 mL) at −60 °C. The phosphine has low solubility and was partly precipitated. Complex ^{1}H NMR spectra were obtained, containing several 2,2′-bipy and Et_3[12]aneP_3 environments. Minor products included **13**, and the major product was **12**. When this reaction was repeated, with addition of Et_3[12]aneP_3 in chloroform-d_3 to retain solubility for the ligand, **12** was formed as a minor product with **13** being the major product. The mixture of complexes decomposes above 0 °C to give ethane and complex ^{1}H NMR spectra.

Crystal structure determinations

Full spheres of CCD area-detector diffractometer data were measured ($2\theta_{max} = 58°$, ω scan mode, monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å, *T ca.* 153 K) yielding N_t total reflections, these being merged to N_r unique (R_{int} quoted) after 'empirical'/multiscan absorption correction, N_o with $F > 4\sigma(F)$ being considered 'observed' and used in the full matrix least squares refinements. Anisotropic thermal parameters were refined for the non-hydrogen atoms. Conventional residuals R, R_w on $|F|$ are quoted at convergence, reflection weights being $(\sigma^2(F) + 0.0004F^2)^{-1}$. Neutral atom complex scattering factors were employed, computation using the XTAL 3.4 program system.[20]

Crystal/refinement data. *Complex* ***3a***. $C_{20}H_{22}F_3N_2O_3PPdS$, $M = 564.9$, monoclinic, space group $P2_1/n$ (C_{2h}^5, no. 14 (variant)), $a = 9.6042(9)$, $b = 11.532(1)$, $c = 20.241(2)$ Å, $\beta = 98.652(1)°$, $V = 2216.4(8)$ Å^3, D_c ($Z = 4$) $= 1.69_3$ g cm^{-3}, $\mu_{Mo} = 10.5$ cm^{-1}, specimen $0.25 \times 0.15 \times 0.13$ mm, '$T_{min,max}$' = 0.71, 0.83, $N_t = 21967$, $N = 5635$ ($R_{int} = 0.027$), $N_o = 4590$, $R = 0.030$, $R_w = 0.035$, $|\Delta\rho_{max}| = 1.0(1)$ e Å^{-3}; (x, y, z, U_{iso})$_H$ refined.

Complex ***6***. $C_{24}H_{28}F_3N_2O_3PPdS$, $M = 619.0$, monoclinic, space group $P2_1/m$ (C_{2h}^2, no. 11), $a = 8.364(1)$, $b = 11.493(2)$, $c = 13.860(2)$ Å, $\beta = 105.812(2)°$, $V = 1281.9(4)$ Å^3, D_c ($Z = 2$) $= 1.60_3$ g cm^{-3}, $\mu_{Mo} = 9.2$ cm^{-1}, specimen $0.20 \times 0.14 \times 0.12$ mm, '$T_{min,max}$' = 0.78, 0.89, $N_t = 12745$, $N = 3424$ ($R_{int} = 0.024$), $N_o = 2905$, $R = 0.034$, $R_w = 0.042$, $|\Delta\rho_{max}| = 0.99(6)$ e Å^{-3}; (x, y, z, U_{iso})$_H$ constrained at estimates.

Despite acceptable residuals, the model presents elements of doubt associated with possible disorder or choice of space group. As modelled in space group $P2_1/m$, displacement amplitudes at the periphery of the aromatic moieties are abnormally high, suggesting that they are displaced to either side of the crystallographic mirror plane which passes through the molecule, indicative of disorder, superlattice, or lower symmetry space group effects, no meaningful refinement accommodating such variations being achieved. Geometrical parameters about the molecular periphery are thus unreliable. Although also subject to considerations of the above type, the anions are otherwise well ordered in both structures.

CCDC reference number 186/2142.

See http://www.rsc.org/suppdata/dt/b0/b004741o/ for crystallographic files in .cif format.

Acknowledgements

We thank the Australian Research Council (A. J. C.) and the UK Engineering and Physical Sciences Research Council (P. G. E.) for financial support, and Dr D. J. Jones (Cardiff) for the synthesis of *syn*,*syn*-Et$_3$[12]aneP$_3$.

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