

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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Dimethyl(2,2'-bipyridine)palladium(II) reacted with methyl triflate (CF₃SO₃Me) at -60 °C to form a palladium(IV) complex which reacted with a range of monodentate phosphines [PPh₃, PMePh₂, PMe₂Ph, PCy₃, P(OMe)₃], 1,2-bis(diethylphosphino)ethane (depe), or *syn,syn*-1,5,9-triethyl-1,5,9-triphosphacyclodecane (*syn,syn*-Et₃[12]aneP₃) to form complexes containing octahedral palladium(IV) centres *fac*-[PdMe₃(2,2'-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, [PdMe₃(N–N)(PMe₂Ph)][O₃SCF₃] [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 [PtMe₃(2,2'-bipy)(L)][O₃SCF₃] [L = PPh₃ **8**, PMePh₂ **9** or PMe₂Ph **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–N)(L)]⁺ **1a–7a**; a structural analysis of square-planar [PdMe(2,2'-bipy)(PMe₂Ph)][O₃SCF₃] **3a** is reported. The stability of palladium(IV) complexes decreases in the order PMe₂Ph > PMePh₂ > PPh₃, and for complexes of PMe₂Ph there is a stability order phen > 2,2'-bipy > tmen for [PdMe₃(bidentate ligand)(PMe₂Ph)]⁺.

Introduction

There are several palladium catalysed processes for which the involvement of palladium(IV) intermediates have amply been demonstrated *via* spectroscopic 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 bromine³ and the acetoxylation of arenes in the presence of oxidants such as Cr₂O₇^{2–} and IPh(O₂CMe)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 [PdMe₃(2,2'-bipy)(L)]⁺ (L = PPh₃, PMePh₂ or PMe₂Ph; 2,2'-bipy = 2,2'-bipyridyl) formed in equilibrium with [PdIME₃(2,2'-bipy)] in CD₂Cl₂, and formation of [PdMe₃(2,2'-bipy)(PPh₃)]⁺ on reaction of methyl triflate (CF₃SO₃Me) with [PdMe₂(2,2'-bipy)] followed by addition of PPh₃.⁷ We report here the first isolation and structural determination for an organopalladium(IV) phosphine complex, [PdMe₃(phen)(PMe₂Ph)][O₃SCF₃] (phen = 1,10-phenanthroline), characterisation of several palladium(IV) and

platinum(IV) analogues, a structural analysis of [PdMe(2,2'-bipy)(PMe₂Ph)][O₃SCF₃] 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*-Et₃[12]aneP₃).

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 [PdMe₂(tmen)] (tmen = *N,N,N',N'*-tetramethylethylenediamine) in CD₃CN to form [PdMe₃(tmen)(NCCD₃)]⁺[O₃SCF₃]⁸ and of [PdMe₂(2,2'-bipy)] in (CD₃)₂CO to form [PdMe₃(2,2'-bipy){OC(CD₃)₂}]⁺[O₃SCF₃] or [PdMe₃(O₃SCF₃)(2,2'-bipy)].⁷ In view of the recent structural analysis of [Pt(O₃SCF₃-O)Me₃]{(2,6-Prⁱ₂C₆H₃NCH)₂-N,N}⁹ and solution NMR studies of [Pt(O₃SCF₃-O)Me₃-(tmen-*N,N'*)]¹⁰ it can now be assumed that the triflate ion is co-ordinated to Pd^{IV} in the 2,2'-bipy complex.

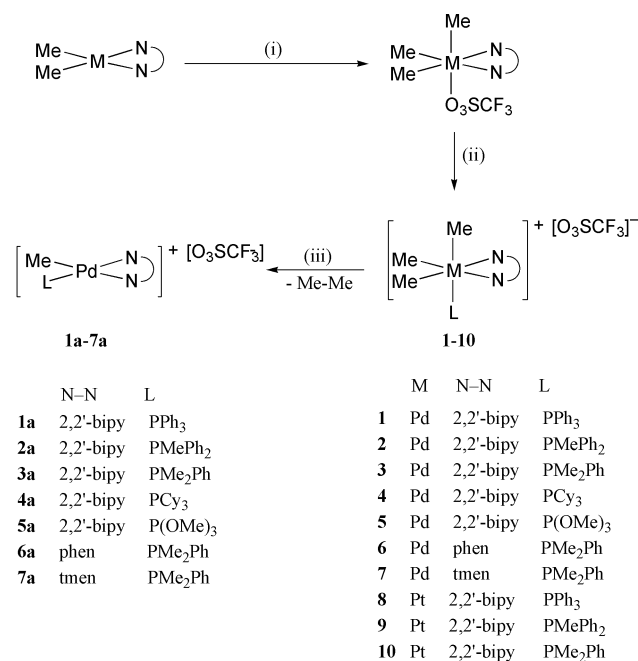
The triflate ligand in [PdMe₃(O₃SCF₃)(bidentate ligand)] is readily displaced by monodentate phosphines (Scheme 1) to form complexes **1–7**, where the oxidation and ligand exchange reactions are performed at -60 to -40 °C to avoid decomposition of unstable palladium(IV) species. Complexes of dimethylphenylphosphine (**3**, **6**) were isolable, and both suf-

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

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

Complex	Decomp./ °C ^d	¹ H NMR ^b				³¹ P NMR ^c		Analysis (%)		
		MMe ₃ <i>trans</i> N		MMe ₃ <i>trans</i> -P		δ	$J(\text{PPt})/\text{Hz}$	C	H	N
		δ	$J(\text{HP})$	δ	$J(\text{HP})$					
1 [PdMe ₃ (2,2'-bipy)(PPh ₃)] [O ₃ SCF ₃] ^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] ^f	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] ^f	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] ^e		1.20	8.4	0.43	7.6	-15.1	998			
10 [PtMe ₃ (2,2'-bipy)(PMe ₂ Ph)] [O ₃ SCF ₃] ^e		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 ^f	0	1.69	8	0.86	8.8	-6.5, -6.0 ^g -44.6, -44.3 ^g -6.7 ^g -35.0 ^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					

^a Required values given in parentheses. ^b In acetone-*d*₆, SiMe₄ as reference. ^c In acetone-*d*₆, H₃PO₄ 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.



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**, **2**, **4**, **5**, **7**), -40 (**3**, **6**), 25 °C (**8**, **9**, **10**); (iii) in acetone, M = Pd, -40 (**7a**), -20 (**1a**, **4a**), 0 (**2a**, **3a**, **5a**), 20 °C (**6a**).

ficiently crystalline for X-ray structural examination. The structure of [PdMe₃(phen)(PMe₂Ph)] [O₃SCF₃] **6** is described below, together with the reductive elimination product [PdMe(2,2'-bipy)(PMe₂Ph)] [O₃SCF₃] **3a** which was present as an impurity in less stable [PdMe₃(2,2'-bipy)(PMe₂Ph)] [O₃SCF₃] **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 ¹H and ³¹P NMR spectra similar to those of palladium(IV) analogues, together with additional features associated with coupling involving the ¹⁹⁵Pt nucleus (Table 1, Fig. 1). Thus, two methylmetal(IV) resonances are observed in 2:1 ratio, with

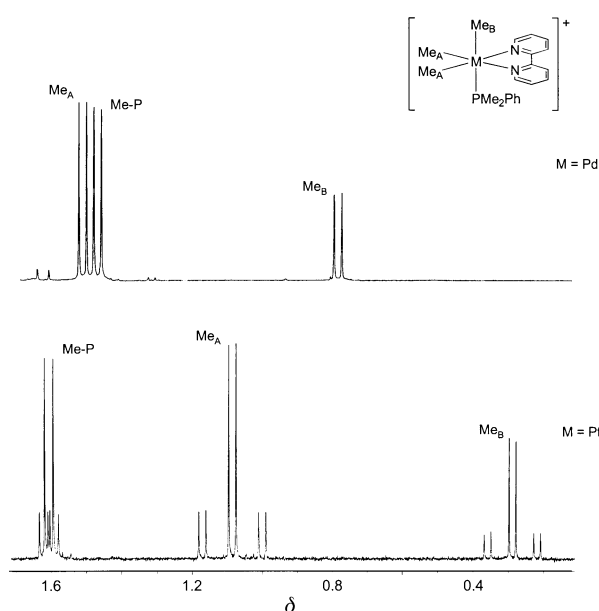


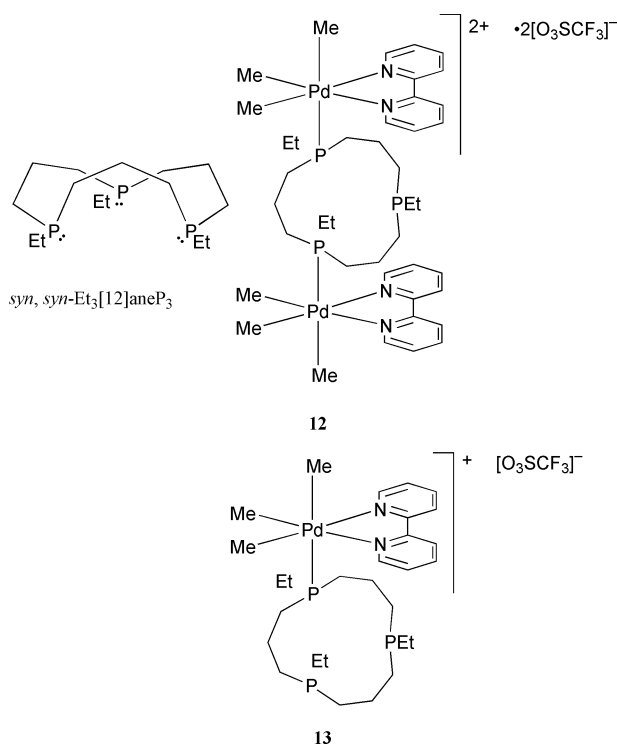
Fig. 1 ¹H NMR spectra of [MMe₃(2,2'-bipy)(PMe₂Ph)] [O₃SCF₃] [M = Pd **3** or Pt **10**] in the region showing methyl groups bonded to the metal and phosphorus atoms. Coupling ³J(HP) is shown for methylmetal(IV) protons, ²J(HP) for methylphosphorus(III), and for the platinum complex sidebands associated with ²J(HPt) and ³J(HPt) (Table 1).

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 PMe₂Ph > PMePh₂ > PPh₃. The downfield shift of the ³¹P resonance on co-ordination of phosphines follows a similar trend, PMe₂Ph > PMePh₂ > PPh₃, 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 $[\text{PdMe}_3(\text{tmen})]^8$ compared with $[\text{PdMe}_3(2,2'\text{-bipy})]$.¹¹ The palladium(II) complexes **1a–5a** give broad 2,2'-bpy resonances at room temperature in both $(\text{CD}_3)_2\text{CO}$ and CDCl_3 , and the isolated complex $[\text{PdMe}_3(2,2'\text{-bipy})(\text{PMe}_2\text{Ph})][\text{O}_3\text{SCF}_3]$ **3a** exhibited well resolved spectra showing two pyridine ring environments when cooled to -30°C in $(\text{CD}_3)_2\text{CO}$. 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. $[\text{PdMe}_3\{\text{CpCo}(\text{PO}(\text{OMe})_3)_3\text{-O}, \text{O}', \text{O}''\}]$ ($[\text{CpCo}(\text{PO}(\text{OEt})_3)_3]^-$ = cyclopentadienyltris(dimethylphosphito-*P*-cobaltate)¹² and $[\text{PdMe}_3(9\text{S3})][\text{NO}_3]$ (9S3 = 1,4,7-trithia-cyclononane).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 $[\text{PdIME}_3(2,2'\text{-bipy})]$ by $[\text{CpCo}(\text{PO}(\text{OEt})_3)_3]^-$ to form $[\text{PdMe}_3\{\text{CpCo}(\text{PO}(\text{OEt})_3)_3\text{-O}, \text{O}', \text{O}''\}]$.¹² If successful, this approach would lead to displacement of 2,2'-bipy and the triflate ligand from $[\text{PdMe}_3(\text{O}_3\text{SCF}_3)(2,2'\text{-bipy})]$ to give $[\text{PdMe}_3\{\text{syn,syn-Et}_3[12]\text{aneP}_3\}][\text{O}_3\text{SCF}_3]$.

¹H and ³¹P NMR studies similar to those of Scheme 1 indicate that 2,2'-bipy is not displaced from $[\text{PdMe}_3(\text{O}_3\text{SCF}_3)(2,2'\text{-bipy})]$. Instead, spectra show the formation of complexes **12** and **13** (Scheme 2), and a complex containing bridging 1,2-

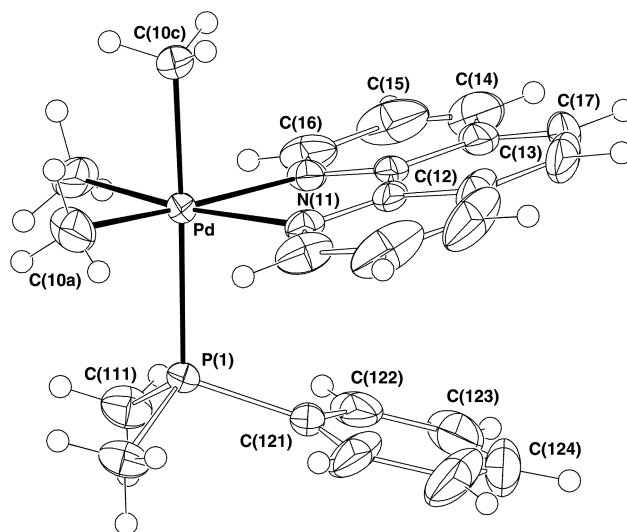


Fig. 2 Projection of the cation of $[\text{PdMe}_3(\text{phen})(\text{PMe}_2\text{Ph})][\text{O}_3\text{SCF}_3]$ **6**; thermal ellipsoids (20%) are shown for non-hydrogen atoms, and hydrogen atoms have been given an arbitrary radius of 0.1 Å.

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 $(\text{CD}_3)_2\text{CO}$, in which *syn,syn*- $\text{Et}_3[12]\text{aneP}_3$ has low solubility, and the 1 : 1 complex **13** is the dominant product when the phosphine is added as a CDCl_3 solution to $[\text{PdMe}_3(\text{O}_3\text{SCF}_3)(2,2'\text{-bipy})]$ in $(\text{CD}_3)_2\text{CO}$. ³¹P NMR spectra show co-ordinated and unco-ordinated phosphorus environments in the anticipated ratios, and both ¹H and ³¹P 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 ³¹P 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, $[\text{PdMe}_3(\text{O}_3\text{SCF}_3)(\text{tmen})]$ was generated at low temperature (Scheme 1) and treated with *syn,syn*- $\text{Et}_3[12]\text{aneP}_3$. 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 $[\text{PdMe}_3(\text{phen})(\text{PMe}_2\text{Ph})][\text{O}_3\text{SCF}_3]$ **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*-PdC₃ 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 [PdMe₃(phen)(PMe₂Ph)][O₃SCF₃]**6**^a

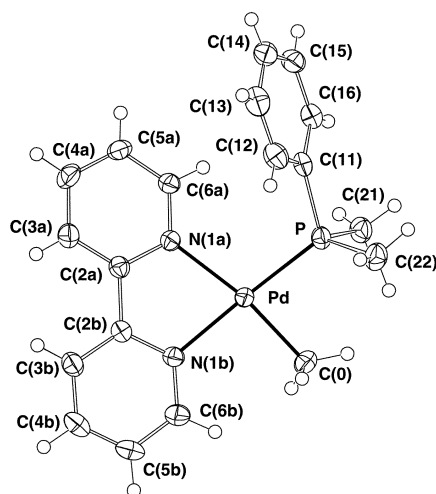
Pd–C(10a, 10c)	2.045(3), 2.082(4)	S(1)–C(0)	1.828(6)
Pd–N(11)	2.193(2)	S(1)–O(11, 13)	1.418(2), 1.426(3)
Pd–P(1)	2.422(1)	C(0)–F(1, 2)	1.330(4), 1.321(6)
C(10a)–Pd–C(10a ⁱ , 10c)	87.0(1), 86.6(1)	Pd–P(1)–C(111, 121)	116.0(1), 109.7(1)
C(10a)–Pd–N(11, 11 ⁱ)	173.2(1), 98.0(1)	C(0)–S(1)–O(11, 13)	103.8(1), 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 ⁱⁱ , 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 C₁₂N₂ 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'-bipy)(PMe₂Ph)][O₃SCF₃]**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 CN₂P 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'-bipy)(PMe₂Ph)][O₃SCF₃]**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 PMe₂Ph ligand is oriented with the phenyl group adjacent to the phen ligand, similar to the arrangement found in [PdBrMe₂(CH₂C₆H₄Br-*p*)(phen)]¹⁵ and [PdBrMe₂(CH₂COPh)(2,2'-bipy)]¹⁶.

The palladium(II) complex [PdMe(2,2'-bipy)(PMe₂Ph)][O₃SCF₃]**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-[PdMe₃(N–N)(L)]⁺ (L = phosphine), and are sufficiently stable for isolation and structural analysis. Facile reductive elimination of ethane occurs in solution to form monomethylpalladium(II) complexes. The application of the triphosphine *syn,syn*-Et₃[12]aneP₃ 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 [PdMe₂(2,2'-bipy)],^{17,18} [PdMe₂(phen)],¹⁷ [PdMe₂(tmen)],^{8,18} [PtMe₂(2,2'-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 (¹H) or 161.80 MHz (³¹P) at room temperature unless otherwise indicated. Chemical shifts are given in ppm relative to SiMe₄ or H₃PO₄ (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

[PdMe₃(2,2'-bipy)(PMe₂Ph)][O₃SCF₃]3**.** Methyl triflate (5.8 μL, 0.052 mmol) was added to a solution of [PdMe₂(2,2'-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; PMe₂Ph (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 $-20\text{ }^{\circ}\text{C}$ the product crystallised over 48 h as a colourless solid. Yield: 23 mg, 74%.

[PdMe₃(phen)(PMe₂Ph)][O₃SCF₃] 6. Methyl triflate (7.9 μL , 0.069 mmol) was added to a solution of [PdMe₂(phen)] (22 mg, 0.069 mmol) in dichloromethane at (4 mL) $-60\text{ }^{\circ}\text{C}$. The solution was warmed to $-40\text{ }^{\circ}\text{C}$ and stirred for 15 min during which time it changed from bright orange to yellow; PMe₂Ph (9.9 μL , 0.069 mmol) was added and the solution concentrated to $\approx 2\text{ mL}$ below $0\text{ }^{\circ}\text{C}$. The product was obtained as colourless crystals, suitable for X-ray crystallography, by slow diffusion of diethyl ether into the solution at $-20\text{ }^{\circ}\text{C}$. Yield: 29 mg, 68%.

[PtMe₃(2,2'-bipy)(PMePh₂)][O₃SCF₃] 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), [PtMe₂(2,2'-bipy)] (20 mg, 0.052 mmol) and PMePh₂ (9.8 μL , 0.052 mmol). Several attempts to purify the product by crystallisation were unsuccessful. Yield: 28 mg, 72%.

[PtMe₃(2,2'-bipy)(PMe₂Ph)][O₃SCF₃] 10. Methyl triflate (5.6 μL , 0.050 mmol) was added to a solution of PtMe₂(2,2'-bipy) (19 mg, 0.050 mmol) in tetrahydrofuran (5 mL) at room temperature. The resulting yellow solution was stirred for 30 min, PMe₂Ph (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 $-20\text{ }^{\circ}\text{C}$ 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)(PMe₂-Ph)][O₃SCF₃] 3a

Methyl triflate (6.8 μL , 0.060 mmol) was added to a solution of [PdMe₂(2,2'-bipy)] (18 mg, 0.060 mmol) in tetrahydrofuran (4 mL) at $-60\text{ }^{\circ}\text{C}$ and the solution warmed and stirred at $-40\text{ }^{\circ}\text{C}$ for 30 min giving a pale yellow solution; PMe₂Ph (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 $-20\text{ }^{\circ}\text{C}$ over 48 h. Yield: 30 mg, 89%. ¹H NMR (CDCl₃, $-30\text{ }^{\circ}\text{C}$): 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, PCH₃) and 0.91 (d, ³J(HP) = 3.2 Hz, 3 H, PdCH₃). ³¹P-{¹H} NMR (CDCl₃, $-30\text{ }^{\circ}\text{C}$): δ 10.5 (Found: C, 42.58; H, 4.00; N, 5.00. C₂₀H₂₂F₃N₂PPdS 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 $-20\text{ }^{\circ}\text{C}$. As the solutions were warmed to room temperature, decomposition was monitored by ¹H NMR spectroscopy. In both cases reductive elimination of ethane was observed at $20\text{ }^{\circ}\text{C}$. [PdMe(phen)(PMe₂Ph)][O₃SCF₃] **6a**: ¹H NMR (acetone-*d*₆, $20\text{ }^{\circ}\text{C}$) 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, PCH₃) and 1.14 (d, ³J(HP) = 2.9 Hz, 3 H, PdCH₃); ³¹P-{¹H} NMR (acetone-*d*₆, $20\text{ }^{\circ}\text{C}$) δ 10.4.

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

[PdMe₂(2,2'-bipy)] (7.0 mg, 0.024 mmol) in acetone-*d*₆ (0.3 mL)

was cooled to $-60\text{ }^{\circ}\text{C}$ and methyl triflate (2.7 μL , 0.024 mmol) added. The mixture was warmed to $-40\text{ }^{\circ}\text{C}$ and stirred for about 30 min until a clear yellow solution was obtained. It was then again cooled to $-60\text{ }^{\circ}\text{C}$, an equimolar amount of the phosphine added, the mixture transferred to a NMR tube and placed in a precooled NMR spectrometer ($-60\text{ }^{\circ}\text{C}$). The reaction was monitored by ¹H NMR spectroscopy starting at $-60\text{ }^{\circ}\text{C}$ and warming the solution to room temperature in $20\text{ }^{\circ}\text{C}$ intervals. In all cases quantitative formation of the palladium(IV) complexes [PdMe₃(2,2'-bipy)(phosphine)][O₃SCF₃] was observed at $-60\text{ }^{\circ}\text{C}$; decomposition of the complexes *via* reductive elimination of ethane and formation of [PdMe(2,2'-bipy)(phosphine)][O₃SCF₃] took place at different temperatures indicated below.

[PdMe₃(2,2'-bipy)(PPh₃)][O₃SCF₃] 1. Decomposition starts at $-20\text{ }^{\circ}\text{C}$. [PdMe(2,2'-bipy)(PPh₃)][O₃SCF₃] **1a**: ¹H 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, PdCH₃); ³¹P-{¹H} NMR (acetone-*d*₆) δ 40.7.

[PdMe₃(2,2'-bipy)(PMePh₂)][O₃SCF₃] 2. Decomposition starts at $0\text{ }^{\circ}\text{C}$. [PdMe(2,2'-bipy)(PMePh₂)][O₃SCF₃] **2a**: ¹H 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 PCH₃) and 0.91 (d, ³J(HP) = 2.8 Hz, 3 H, PdCH₃); ³¹P-{¹H} NMR (acetone-*d*₆) δ 25.4.

[PdMe₃(2,2'-bipy)(PCy₃)][O₃SCF₃] 4. Decomposition starts at $0\text{ }^{\circ}\text{C}$. [PdMe(2,2'-bipy)(PCy₃)][O₃SCF₃] **4a**: ¹H NMR (acetone-*d*₆) very broad resonances, could not be assigned; ³¹P-{¹H} NMR (acetone-*d*₆) δ 28.9.

[PdMe₃(2,2'-bipy){P(OMe)₃}[O₃SCF₃] 5. Decomposition starts at $-20\text{ }^{\circ}\text{C}$. [PdMe(2,2'-bipy){P(OMe)₃}[O₃SCF₃] **5a**: ¹H NMR (acetone-*d*₆) very broad resonances for 2,2'-bipy, δ 3.93 (d, ³J(HP) = 13.2 Hz, 9 H POCH₃) and 1.02 (s, 3 H, PdCH₃); ³¹P-{¹H} NMR (acetone-*d*₆) δ 122.9.

[PdMe₃(tmen)(PMe₂Ph)][O₃SCF₃] 7. Methyl triflate (3.6 μL , 0.032 mmol) was added to a solution of [PdMe₂(tmen)] (8.1 mg, 0.032 mmol) in acetone-*d*₆ (0.3 mL) at $-60\text{ }^{\circ}\text{C}$. After stirring for 20 min PMe₂Ph (4.6 μL , 0.032 mmol) was added and the solution transferred to a NMR tube. The reaction was monitored by ¹H NMR from $-60\text{ }^{\circ}\text{C}$ to room temperature in $20\text{ }^{\circ}\text{C}$ intervals. Decomposition starts at $-40\text{ }^{\circ}\text{C}$. [PdMe(tmen)-(PMe₂Ph)][O₃SCF₃] **7a**: ¹H NMR (acetone-*d*₆, $0\text{ }^{\circ}\text{C}$) δ 7.92 (m, 2 H, Ph), 7.56 (m, 3 H, Ph), 2.95 (broad, 2 H, NCH₂), 2.81 (broad, 2 H, NCH₂), 2.66 (d, ⁴J(HP) = 2.0, 6 H, NCH₃), 2.49 (s, 6 H, NCH₃), 1.83 (d, ²J(HP) = 10.0, 6 H, PCH₃) and 0.31 (d, ³J(HP) = 3.6 Hz, 3 H, PdCH₃); ³¹P-{¹H} NMR (acetone-*d*₆, $0\text{ }^{\circ}\text{C}$) δ 8.0.

[{PdMe₃(2,2'-bipy)}₂(depe)][O₃SCF₃]₂ 11. Decomposition starts at $-20\text{ }^{\circ}\text{C}$ giving a complex mixture of products.

[{PdMe₃(2,2'-bipy)}₂(Et₃[12]aneP₃)][O₃SCF₃]₂ 12 and [PdMe₃(2,2'-bipy)(Et₃[12]aneP₃)][O₃SCF₃] 13. The ligand (7.6 mg, 0.025 mmol) was added to a solution of [PdMe₃(2,2'-bipy)(O₃SCF₃)] in acetone-*d*₆ (0.3 mL) at $-60\text{ }^{\circ}\text{C}$. The phosphine has low solubility and was partly precipitated. Complex ¹H NMR spectra were obtained, containing several 2,2'-bipy and Et₃[12]aneP₃ environments. Minor products included **13**, and the major product was **12**. When this reaction was repeated, with addition of Et₃[12]aneP₃ 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 $0\text{ }^{\circ}\text{C}$ to give ethane and complex ¹H NMR spectra.

Crystal structure determinations

Full spheres of CCD area-detector diffractometer data were measured ($2\theta_{\max} = 58^\circ$, ω scan mode, monochromatic Mo-K α radiation, $\lambda = 0.71073 \text{ \AA}$, $T \text{ ca. } 153 \text{ K}$) 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**. $\text{C}_{20}\text{H}_{22}\text{F}_3\text{N}_2\text{O}_3\text{PPdS}$, $M = 564.9$, monoclinic, space group $P2_1/n$ (C_{2h}^5 , no. 14 (variant)), $a = 9.6042(9)$, $b = 11.532(1)$, $c = 20.241(2) \text{ \AA}$, $\beta = 98.652(1)^\circ$, $V = 2216.4(8) \text{ \AA}^3$, D_c ($Z = 4$) = 1.69_3 g cm^{-3} , $\mu_{\text{Mo}} = 10.5 \text{ cm}^{-1}$, specimen $0.25 \times 0.15 \times 0.13 \text{ mm}$, ' $T_{\text{min,max}}$ ' = $0.71, 0.83$, $N_t = 21967$, $N = 5635$ ($R_{\text{int}} = 0.027$), $N_o = 4590$, $R = 0.030$, $R_w = 0.035$, $|\Delta\rho_{\max}| = 1.0(1) \text{ e \AA}^{-3}$; ($x, y, z, U_{\text{iso}}\text{H}$) refined.

Complex **6**. $\text{C}_{24}\text{H}_{28}\text{F}_3\text{N}_2\text{O}_3\text{PPdS}$, $M = 619.0$, monoclinic, space group $P2_1/m$ (C_{2h}^2 , no. 11), $a = 8.364(1)$, $b = 11.493(2)$, $c = 13.860(2) \text{ \AA}$, $\beta = 105.812(2)^\circ$, $V = 1281.9(4) \text{ \AA}^3$, D_c ($Z = 2$) = 1.60_3 g cm^{-3} , $\mu_{\text{Mo}} = 9.2 \text{ cm}^{-1}$, specimen $0.20 \times 0.14 \times 0.12 \text{ mm}$, ' $T_{\text{min,max}}$ ' = $0.78, 0.89$, $N_t = 12745$, $N = 3424$ ($R_{\text{int}} = 0.024$), $N_o = 2905$, $R = 0.034$, $R_w = 0.042$, $|\Delta\rho_{\max}| = 0.99(6) \text{ e \AA}^{-3}$; ($x, y, z, U_{\text{iso}}\text{H}$) 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.

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