DALTON

Synthesis and reactions of novel dipalladium(II) complexes of the type $[\{Pd[PPh_2CH{=}C(R){-}N{-}N{=}C(R)CHPPh_2]\}_2]$ (R = Bu^t or Ph). Crystal structure of the *tert*-butyl complex containing two Pd–C bonds and five fused chelate rings

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Treatment of the neutral chloropalladium(II) complexes $[PdCl\{PPh_2CH{=}C(R){-}N{-}N{=}C(R)CH_2PPh_2\}]$ (R = Bu^t **1a** or Ph **1b**) with two equivalents of $Li[N(SiMe_3)_2]$ gave the novel dipalladium(II) complexes $[\{Pd[PPh_2CH{=}C(R){-}N{-}N{=}C(R)CHPPh_2]\}_2]$ (R = Bu^t **2a** or Ph **2b**) containing two palladium–carbon bonds, five fused chelate rings and enamine type (C=C–N) moieties. Treatment of the chloroplatinum(II) complex $[PtCl\{PPh_2CH{=}C(Bu^t){-}N{-}N{=}C(Bu^t)CH_2PPh_2\}]$ **1c** with an excess of KOBu^t in dimethyl sulfoxide (dmso) gave what was probably the species $[Pt\{PPh_2CH{=}C(Bu^t){-}N{-}N{=}C(Bu^t)CHPPh_2\}(dmso)]$ **3** containing both a co-ordinated and an unco-ordinated phosphine. The dipalladium(II) complex **2a** or **2b** underwent electrophilic attack at the enamine carbon with acids (HX) to give salts of type $[\{Pd[PPh_2CH_2C(R){=}N{-}N{=}C(R)CHPPh_2]\}_2]X_2$ **4** (R = Bu^t or Ph; X = trifluoroacetate, chloride or picrate); these, when treated with sodium methoxide, deprotonated at the methylene carbon to give the neutral complex **2a** or **2b**. Treatment of **2a** with less than 2 equivalents of trifluoroacetic acid gave the monoprotonated complex $[Pd\{PPh_2CH{=}C(Bu^t)N{-}N{=}C(Bu^t)CHPPh_2\}\text{-}\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CHPPh_2\}][O_2CCF_3]$ **5a**, mixed with **2a** and **4a**. Complex **2a** with Br_2 or MeI underwent attack at the enamine carbon *C*=C–N to give the corresponding bromo or methyl derivatives $[\{Pd[PPh_2CH(R)CBu^t{=}N{-}N{=}C(Bu^t)CHPPh_2]\}_2]X_2$ (R = Br, X = Br **6a**; R = Me, X = I **6b**) respectively. When the methyl-substituted salt was treated with KOBu^t it gave the neutral dipalladium(II) complex $[\{PdCl[PPh_2C(Me){=}C(Bu^t){-}N{-}N{=}C(Bu^t)CHPPh_2]\}_2]$ **7**. The crystal structure of **2a** was determined.

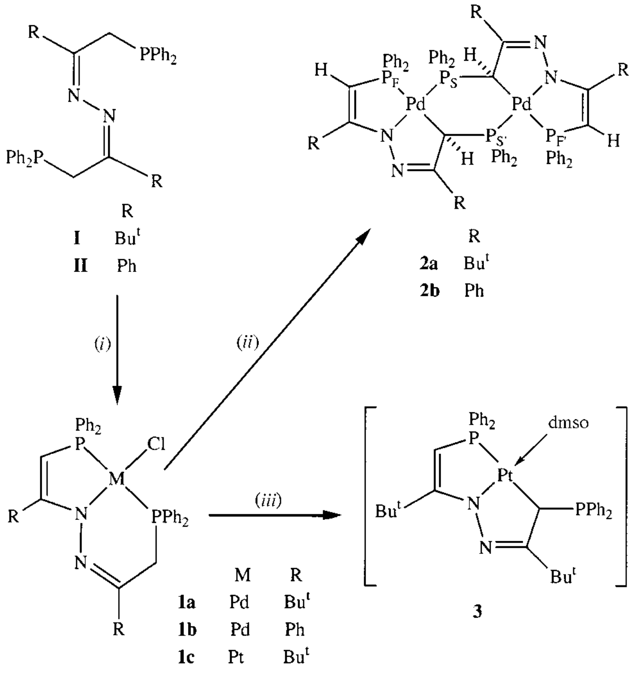
In previous work, we have shown that the azine diphosphine $PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2$ **I** can react in the *Z*,*E* configuration and then act as a terdentate *P*,*N*,*P′* ligand with fused five- and six-membered rings, in square-planar, octahedral or seven-co-ordinate complexes.[1–3] Thus with Group 6 metal carbonyls we prepared complexes of the type *fac*-$[M(CO)_3\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2\}]$ (M = Mo, W or Cr). A recent publication[4] from this laboratory has described completely specific alkylations of the ligand backbone of the molybdenum or tungsten complexes. The proton on the carbon atom α to phosphorus in the metal carbonyl azine diphosphine complexes *fac*-$[M(CO)_3\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2\}]$ is activated and the carbon could be deprotonated by *n*-butyllithium. The complexes were first deprotonated in the five-membered ring chelate and treatment of the resultant carbanions with electrophiles such as an alkyl halide (RX) gave derivatives *fac*-$[M(CO)_3\{PPh_2CH(R)C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2\}]$ (M = Mo or W), exclusively. When treated with a second mole of base the methylene in the six-membered chelate ring of this complex was deprotonated and the carbon alkylated. The alkylations in both five- and six-membered rings were stereospecific; thus dimethylation of the complex with the *A* configuration at the metal gave exclusively the *R*,*R* configurations on the two substituted carbons and the complex with the *C* configuration at the metal gave the *S*,*S* configurations at the carbons. We had earlier shown that in terdentate complexes of type $[MCl\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2\}]X$ (M = Pd or Pt; X = Cl, picrate or formate) the CH_2 hydrogens underwent H/D exchange with acid catalysts, *i.e.* they were activated and that on treatment with a base such as triethylamine the five-membered ring chelate in the cationic complex rapidly loses a proton to give a neutral complex of type $[MCl\{PPh_2CH{=}C(Bu^t){-}N{-}N{=}C(Bu^t)CH_2PPh_2\}]$ (M = Pd or Pt).[3]

It has been shown[5] that alkyl- or aryl-lithium, LiR, reagents or Grignard reagents, MgRX, react with complexes such as $[PdX_2(dppm)]$ or $[PtX_2(dppm)]$ (X = Cl or I; dppm = $Ph_2PCH_2PPh_2$) to give complexes of type $[MR_2(dppm)]$ (M = Pd or Pt, R = alkyl or aryl). However, bulky bases such as lithium bis(trimethylsilyl)amide $Li[N(SiMe_3)_2]$ removed a proton from the methylene of the dppm. Thus treatment of a suspension of $[PtI_2(dppm)]$ with 1 mol equivalent of $Li[N(SiMe_3)_2]$ in tetrahydrofuran, followed by methyl iodide, gave $[PtI_2\{Ph_2PCH(Me)PPh_2\}]$.[6,7]

In the present work we describe how treatment of palladium complexes of type $[PdCl\{PPh_2CH{=}C(R){-}N{-}N{=}C(R)CH_2PPh_2\}]$ (R = Bu^t or Ph) with $Li[N(SiMe_3)_2]$ gives the novel dipalladium complexes $[\{Pd[PPh_2CH{=}C(R){-}N{-}N{=}C(R)CHPPh_2]\}_2]$ containing five fused chelate rings and two palladium–carbon bonds. Some chemistry of these dipalladium complexes is described, in particular electrophilic attack on the ligand backbones. The behaviour of an analogous platinum complex when treated with $Li[N(SiMe_3)_2]$ was also investigated.

Results and Discussion

The various complexes and their transformations are shown in Schemes 1–3. Treatment of a solution of the chloropalladium(II) complex **1a**[3] in tetrahydrofuran with 2 equivalents of $Li[N(SiMe_3)_2]$ gave an intensely red solution, from which the complex **2a** was isolated as red prisms, in 80% yield. Complex **2a** was stable in tetrahydrofuran solution in air at ambient temperatures for several days, after which it started to decompose. Preparative details, mass spectral and elemental analytical data are in the Experimental section; phosphorus-31 NMR, infrared, proton and carbon-13 NMR data are in Tables 2–4. The product **2a** was characterised by elemental analysis (C, H and N) and the mass spectrum (FAB) showed a group of peaks at *m*/*z* 1332–1345 for the molecular ion with the maximum of 1338 as expected for the formula $C_{72}H_{80}N_4P_4Pd_2$ and suggests a dinuclear complex. The $^{31}P\text{-}\{^1H\}$ NMR spectrum (Fig. 1) of **2a**



Scheme 1 (*i*) $[PdCl_2(NCPh)_2]$ or $[PtCl_2(cod)]$ (cod = cycloocta-1,5-diene), NEt_3; (*ii*) for **1a** or **1b**, thf, 2 equivalents $Li[N(SiMe_3)_2]$; (*iii*) for **1c**, dmso, $KOBu^t$

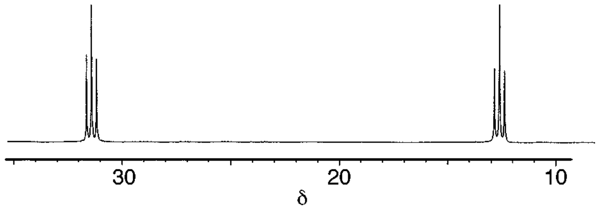


Fig. 1 The $^{31}P-\{^1H\}$ NMR spectrum (101.25 MHz) of complex **2a** in deuteriochloroform showing the 'deceptively simple' triplets of the AA′XX′ spin system with $N = |J(P_FP_S) + J(P_FP_{S'})| = 46$ Hz

shows two 'virtual'[8–10] or 'deceptively simple'[8] 1 : 2 : 1 triplets, at δ 31.5 and 12.4. The four-spin system, which gives rise to this spectrum, is of the AA′XX′ type in which the various coupling constants are of magnitude and relative signs so as to give the observed spectrum. Any 'outer' peaks are of such very low intensity that they are unobserved, hence the use of the expressions 'deceptively simple' or 'virtual', see refs. 8–12 for a discussion of the phenomenon with some examples of how it has been used for studying tertiary phosphine–metal complexes, especially before $^{31}P-\{^1H\}$ NMR spectroscopy became more readily available. It is likely that the weak peaks are overlapped and obscured by the strong peaks in the spectra shown in Figs. 1, 4 and 5 and with the spectra of related compounds discussed in this paper. The structure was determined by a single-crystal X-ray diffraction study which showed the complex to have a binuclear diphosphine-bridged structure **2a** (see Fig. 2). Selected bond lengths and bond angles are in Table 1. The deprotonated azine diphosphine ligand is co-ordinated in a terdentate manner to one palladium, through one nitrogen, one phosphorus and the carbon α to the second phosphorus atom; the second phosphorus acts as a bridge to the other palladium atom. This arrangement gives five fused chelate rings, with the central, six-membered ring, puckered as seen in Fig. 3. There is thus a 'pocket' in the molecule with the six-membered ring involving the sequence of atoms Pd–C–P–Pd–C–P, at the bottom of the pocket. The hydrogen atoms of the two CHPd groups are on the outside of the pocket. The Pd · · · Pd distance is long [3.1598(10) Å, see Table 1] and is indicative of little, if any, bonding interaction between the palladiums. In **2a** we have labelled the two chemically equivalent phosphorus atoms in the central six-membered ring, P_S and $P_{S'}$ and the two chemically equivalent phosphorus atoms in a five-membered ring, P_F and $P_{F'}$.

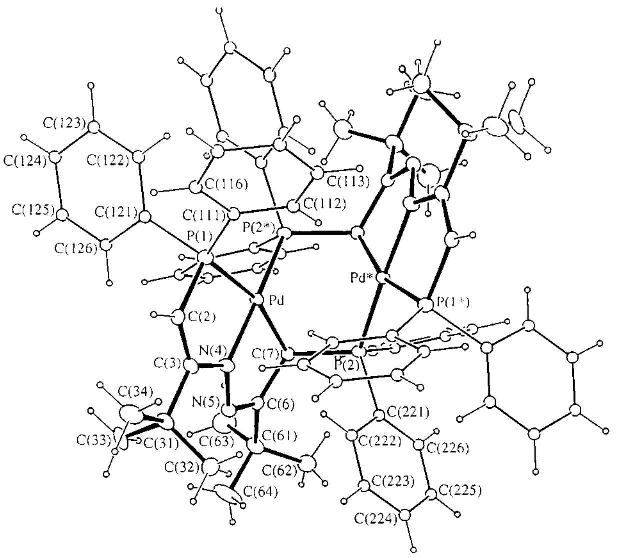


Fig. 2 An ORTEP[13] diagram of the crystal structure of the dipalladium(II) complex **2a** showing the five fused chelate rings and two palladium–carbon bonds

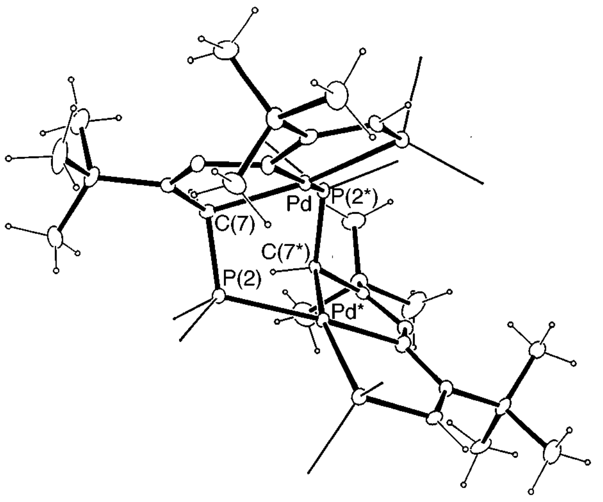


Fig. 3 View of the crystal structure of the dipalladium(II) complex **2a** showing the puckering of the central six-membered chelate ring which forms a 'pocket' in the centre of the molecule. For clarity the phenyl rings have been omitted

The NMR data for complex **2a** and of related species shown in Schemes 1–3 were assigned on the basis of $^{31}P-\{^1H\}$, ^1H, $^1H-\{^{31}P\}$ and $^{13}C-\{^1H\}$ NMR spectroscopy [including attached proton tests (APTs)], some two-dimensional correlation spectroscopy, *e.g.* $^{13}C–^1H$, $^{31}P–^1H$ and $^{31}P–^{31}P$ COSY spectra, and also by arguments based on the chemistry. For **2a** the resonance at δ_P 31.5 is assigned to P_F and that at 12.4 to P_S (these assignments are especially based on the results obtained by the protonation and methylation experiments on **2a**). In the $^1H-\{^{31}P\}$ NMR spectrum of **2a** there are singlets at δ 0.31 and 1.45, each of relative intensity 18 due to the two kinds of *tert*-butyl groups (two of each kind), and singlets at δ 4.21 and 4.65, each of relative intensity two, due to the two different kinds of CH protons. That at δ 4.21, assigned to CHP_F, became a doublet in the ^1H NMR spectrum and a $^{31}P–^1H$ COSY spectrum established that this proton was coupled to P_S and not to P_F; this result may at first sight seem surprising but there are many examples of two-bond (geminal couplings) being very small, or zero, for example in systems such as $C{=}CH_2$; presumably because positive and negative contributions to the *J* value cancel one another out. The resonance at δ 4.65, assigned to CHPd, was a double doublet in the ^{1}H NMR spectrum and the ^{31}P–^{1}H COSY spectrum established that the hydrogen was coupled to both P_F and P_S. A ^{13}C-{^{1}H} NMR spectrum, and ^{13}C–^{1}H and ^{31}P–^{1}H COSY spectra, established that the resonance at δ_C 77.2 (Table 4) was due to CHP_F and that at δ_C 54.3 due to *C*HPd. Other proton and carbon-13 data are in Tables 3 and 4.

We have also made the azine diphosphine **II** by condensing the known keto phosphine $Ph_2PCH_2C(=O)Ph$[14] with hydrazine. Treatment of **II** with [$PdCl_2(NCPh)_2$], followed by triethylamine, gave complex **1b** as a purple solid; see Experimental section for details and Tables 2 and 3 for characterising spectroscopic data. Similar treatment of the chloropalladium(II) complex **1b** with 2 equivalents of Li[$N(SiMe_3)_2$] gave the corresponding dinuclear palladium(II) complex **2b** as an orange solid, in 85% yield. This was characterised in a similar fashion to **2a**. The infrared (KBr disc) spectrum showed a ν(C=N) absorption band at 1485 cm^{-1}. The ^{31}P-{^{1}H} NMR spectrum was an AA′XX′ pattern with two sets of 'deceptively simple' triplets at δ 20.3 and 17.3 with $N = |J_{AX} + J_{AX'}| = 34$ Hz. Proton NMR

Table 1 Selected bond lengths (Å) and angles (°) for compound **2a** with estimated standard deviations (e.s.d.s) in parentheses

Pd–N(4)	2.018(5)	Pd–C(7)	2.102(6)
Pd–P(2*)	2.282(2)	Pd–P(1)	2.298(2)
Pd···Pd*	3.1598(10)	P(1)–C(2)	1.779(6)
P(2)–C(7)	1.839(6)	C(2)–C(3)	1.355(8)
C(3)–N(4)	1.374(7)	C(3)–C(31)	1.545(8)
N(4)–N(5)	1.383(6)	N(5)–C(6)	1.282(7)
C(6)–C(7)	1.527(8)	C(6)–C(61)	1.541(7)
N(4)–Pd–C(7)	79.7(2)	N(4)–Pd–P(2*)	167.68(14)
C(7)–Pd–P(2*)	91.6(2)	N(4)–Pd–P(1)	82.83(14)
C(7)–Pd–P(1)	162.4(2)	P(2)–Pd–P(1)	105.29(6)
N(4)–Pd–Pd*	120.29(14)	C(7)–Pd–Pd*	78.5(2)
P(2*)–Pd–Pd*	65.58(4)	P(1)–Pd–Pd*	112.96(4)
C(2)–P(1)–Pd	98.8(2)	C(7)–P(2)–Pd*	112.1(2)
C(3)–C(2)–P(1)	118.6(4)	C(2)–C(3)–N(4)	117.5(5)
C(2)–C(3)–C(31)	122.4(5)	N(4)–C(3)–C(31)	120.2(5)
C(3)–N(4)–N(5)	118.9(5)	C(3)–N(4)–Pd	122.1(4)
N(5)–N(4)–Pd	116.7(3)	C(6)–N(5)–N(4)	114.4(5)
N(5)–N(6)–C(7)	121.0(5)	N(5)–C(6)–C(61)	116.6(5)
C(7)–C(6)–C(61)	122.3(5)	C(6)–C(7)–P(2)	120.5(4)
C(6)–C(7)–Pd	105.1(4)	P(2)–C(7)–Pd	100.7(3)

* Atoms marked with an asterisk are related to their unmarked equivalents by the operator $\frac{3}{2} - x, \frac{1}{2} - y, z$.

Table 2 ^{31}P-{^{1}H} NMR[a] and infrared[b] data

Compound	$\delta(P_A)$	$\delta(P_B)$	J or N	ν(C=N)
1b	49.4	31.3	453	1615m[c]
2a	31.5	12.4	46	1490m
2b	20.3	17.3	34	1485m
3	23.3	−11.4	*d*	—
4a	51.4	14.8	54	1485m
4b	37.0	22.7	42	1490w
4c	55.1	17.2	56	1495w
4d	50.5	12.6	54	1490m
4e	36.6	22.8	43	1490m
6a	53.8	16.9	54	1485w
6b	49.9	20.6	50	1495m
6c	52.4	18.4	52	1495m
7	56.6	13.9	40	1490m

[a] Recorded at 101.25 MHz, chemical shifts are in ppm relative to 85% H_3PO_4, solvent $CDCl_3$, J values are in Hz; for the monopalladium complexes, $J = J(PP)$; for the dipalladium complexes, $N = J(P_FP_S) + J(P_FP_{S'})$. [b] As KBr disc, m = medium, s = strong, w = weak. [c] ν(Pd–Cl) (Nujol mull between Polythene plates) 330w cm^{-1}. [d] No observable ^3J(PP) coupling; $^1J(PtP_A)$ 2118, $^1J(PtP_B)$ 112 Hz.

Table 3 Proton NMR data[a]

Compound	$\delta(Bu^t)$	$\delta(CH_2P/{=}CHP/CHPd/CH)$
1b	—	3.33 [2 H, dd, ^2J(PH) 10.8, ^4J(PH) 3.9, CH_2P]
		4.65 [2 H, dd, ^2J(PH) 6.4, J(PH) 1.6, =CHP]
2a	0.31 (18 H, s, 2Bu^t)	4.21 [2 H, d, J(PH) 4.1, 2=CHPd]
	1.45 (18 H, s, 2Bu^t)	4.65 [2 H, dd, J(PH) 8.0 and 3.4, 2CHPd]
2b	—	3.73 [2 H, d, ^2J(PH) 6.5, 2CHP]
		5.97 (2 H, m, 2CHP)
4a	0.50 (18 H, s, 2Bu^t)	3.48 [2 H, dd, ^2J(PH) 14, ^2J(HH) 15.8, 2CH_2P]
	1.16 (18 H, s, 2Bu^t)	4.46 [2 H, dd, ^2J(PH) 5.5, ^2J(HH) 15.8, 2CH_2P]
		7.03 (2 H, t,[b] 2CHPd)
4b	—	3.59 [2 H, dd, ^2J(PH) 13.3, ^2J(HH) 17.0, 2CH_2P]
		4.20 [2 H, dd, ^2J(PH) 6.2, ^2J(HH) 17.0, 2CH_2P]
		6.75 (2 H, m, 2CHPd)
4c	0.56 (18 H, s, 2Bu^t)	3.29 [2 H, m, ^2J(HH) 16.6, 2CH_2P]
	1.14 (18 H, s, 2Bu^t)	3.61 [2 H, m, ^2J(HH) 16.6, 2CH_2P]
		6.24 (2 H, t,[b] 2CHPd)
4d	0.59 (18 H, s, 2Bu^t)	3.24 [2 H, dd, ^2J(PH) 14.4, ^2J(HH) 16.2, 2CH_2P]
	1.17 (18 H, s, 2Bu^t)	3.49 [2 H, dd, ^2J(PH) 5.1, ^2J(HH) 16.2, 2CH_2P]
		5.81 (2 H, t,[b] 2CHPd)
4e[c]	—	3.71 [2 H, dd, ^2J(PH) 13.1, ^2J(HH) 17.2, 2CH_2P]
		4.11 [2 H, dd, ^2J(PH) 6.3, ^2J(HH) 17.2, 2CH_2P]
		6.75 (2 H, m, 2CHPd)
6a	0.64 (18 H, s, 2Bu^t)	3.77 [2 H, d, ^2J(PH) 11.2, 2CHBr]
	1.30 (18 H, s, 2Bu^t)	5.28 [2 H, d, ^2J(PH) 9.2, 2CHPd]
6b[d,e]	0.68 (18 H, s, 2Bu^t)	4.08 [2 H, m, ^3J(HH) 6.6, 2C*H*Me]
	1.20 (18 H, s, 2Bu^t)	6.26 (2 H, m, 2CHPd)
6c[d,f]	0.57 (18 H, s, 2Bu^t)	3.99 [2 H, m, ^3J(HH) 6.5, 2C*H*Me]
	1.20 (18 H, s, 2Bu^t)	6.49 (2 H, m, 2CHPd)
7[g]	0.29 (18 H, s, 2Bu^t)	4.04 [2 H, dd, J(PH) 8.5, 7.2, 2CHPd]
	1.53 (18 H, s, 2Bu^t)	

[a] Recorded at 250.13 MHz, chemical shifts (δ) are in ppm relative to $SiMe_4$, J values are in Hz, solvent $CDCl_3$ unless otherwise stated. In all cases, ^{1}H and ^{1}H-{^{31}P} NMR spectra were measured: multiplicities refer to ^{1}H NMR spectra; the CHPd and =CHP resonances in the ^{1}H-{^{31}P} spectra were in all cases singlets. [b] Probably a 'deceptively simple' 1:2:1 triplet with the outer doublet peaks 17 (**4a**), 16 (**4c**) and 14.8 Hz (**4d**) apart; these resonances were singlets in the ^{1}H-{^{31}P} NMR spectra. [c] In CD_2Cl_2. [d] Recorded at 400.13 MHz. [e] δ(Me) 1.61 [6 H, dd, ^3J(HH) 6.6, ^3J(PH) 16.1 Hz, 2CH*Me*]. [f] δ(Me) 1.89 [6 H, dd, ^3J(HH) 6.5, ^3J(PH) 15.4 Hz, 2CH*Me*]. [g] δ(Me) 1.82 [6 H, d, ^3J(PH) 10.7 Hz, 2=CMe].

Table 4 ^{13}C-{^{1}H} NMR data[a]

Compound	δ_C
I	29.2 [1 C, d, ^{1}J(PC) 21.3, CH_2P], 161.1 [1 C, d, ^{2}J(PC) 8.2, C=N]
2a	30.7 (6 C, s, 2C*Me*$_3$), 31.2 (6 C, s, 2C*Me*$_3$), 35.8 [2 C, d, ^{3}J(PC) 4.1, 2*C*Me$_3$], 37.6 [2 C, d, ^{3}J(PC) 13.7, 2*C*Me$_3$], 54.3 (2 C, dt,[b] 2CHPd), 77.2 [2 C, d, *J*(PC) 53.0, 2CHP$_F$, 153.4 (2 C, m, 2CN), 182.3 [2 C, d, *J*(PC) 17.9, 2CN]
4a[c]	28.6 (6 C, s, 2C*Me*$_3$), 30.1 (6 C, s, 2C*Me*$_3$), 38.4 [2 C, d, ^{3}J(PC) 3.6, 2*C*Me$_3$], 40.2 [2 C, d, ^{3}J(PC) 1.6, 2*C*Me$_3$], 43.8 [2 C, dd, *J*(PC) 23.8 and ≈2, 2CH$_2$P], 57.3 (2 C, see text, 2CHPd), 185 (4 C, m, 4CN)
4c	28.6 (6 C, s, 2C*Me*$_3$), 30.1 (6 C, s, 2C*Me*$_3$), 38.5 [2 C, d, ^{3}J(PC) 3.9, 2*C*Me$_3$], 40.2 [2 C, d, ^{3}J(PC) 1.8, 2*C*Me$_3$], 44.6 [2 C, d, ^{1}J(PC) 23.3, 2CH$_2$P], 57.4 (2 C, m, 2CHPd), 185 (4 C, m, 4CN)
4d	28.7 (6 C, s, 2C*Me*$_3$), 30.1 (6 C, s, 2C*Me*$_3$), 38.3 [2 C, d, ^{3}J(PC) 3.2, 2*C*Me$_3$], 40.4 (2 C, m, 2*C*Me$_3$), 44.1 [2 C, d, ^{1}J(PC) 23.8, 2CH$_2$P], 57.3 [2 C, dd, ^{1}J(PC) 10.0, ^{2}J(PC) 72.7, 2CHPd], 184.4 (2 C, m, 2CN), 185.5 (2 C, m, 2CN)
6a	30.0 (6 C, s, 2C*Me*$_3$), 30.7 (6 C, s, 2C*Me*$_3$), 35.3 [2 C, d, ^{3}J(PC) 3.0, 2*C*Me$_3$], 37.1 [2 C, d, ^{3}J(PC) 14.4, 2*C*Me$_3$], 54.1 (2 C, m, 2CHBr), 76.2 (2 C, m, 2CHPd), 181.8 [2 C, d, ^{2}J(PC) 16.7, 2CN], 185.5 (2 C, m, 2CN)
6b[c]	21.5 [2 C, d, ^{2}J(PC) 6.3, 2CH*Me*], 28.6 (6 C, s, 2C*Me*$_3$), 30.8 (6 C, s, 2C*Me*$_3$), 39.5 (2 C, s, 2*C*Me$_3$), 40.0 (2 C, s, 2*C*Me$_3$), 51.3 [2 C, d, ^{1}J(PC) 23.4, 2*C*HMe], 60.2 (2 C, m, 2CHPd), 186.5 (2 C, m, 2CN), 190.0 (2 C, m, 2CN)

[a] Recorded at 62.9 MHz, unless shown otherwise, chemical shifts (δ) in ppm relative to $SiMe_4$, *J* values are in Hz, solvent $CDCl_3$ unless otherwise stated. An attached proton test was applied to the carbon resonances to establish whether the carbons were CH_3, CH_2, CH or CN and for complexes **2a** and **4a** ^{13}C–^{1}H COSY experiments were conducted to establish connectivities. [b] The doublet spacing was 80.8 Hz and the separation of the peaks of the 1:2:1 triplets was 14.4 Hz; this pattern was probably a doublet of deceptively simple 1:2:1 triplets, *i.e.* with $N = |^{1}J(P_SC) + {}^{2}J(P_{S'}C)| = 28.8$ Hz. [c] Recorded at 100.6 MHz in CD_2Cl_2.

data are in Table 3 but the complex was rather insoluble and a carbon-13 NMR spectrum was not recorded.

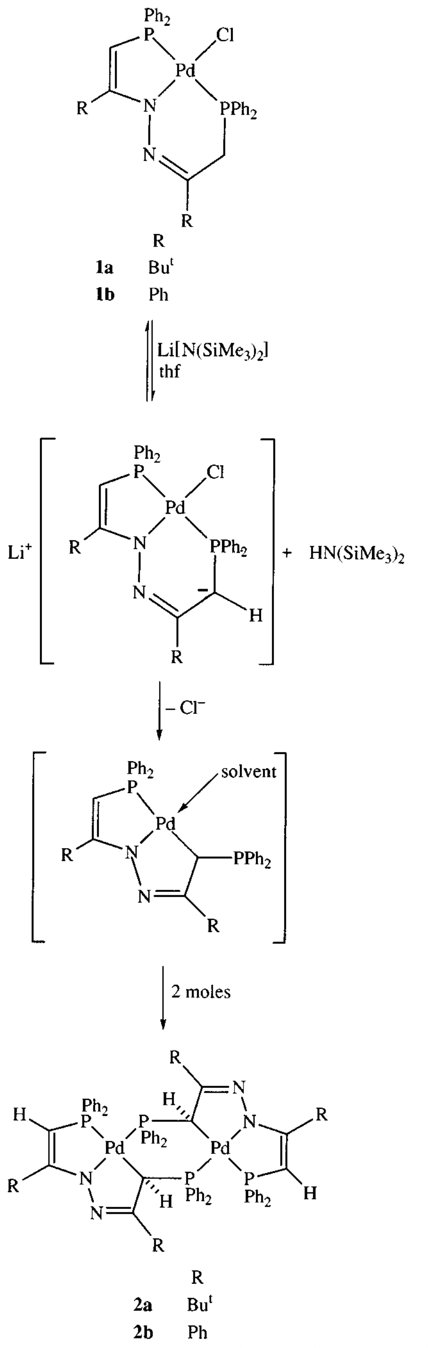
We suggest that the novel and stable dipalladium(II) complexes of type **2** are formed by deprotonation of a complex of type **1** with 1 equivalent of Li[N(SiMe$_3$)$_2$] to give a carbanion which loses a chloride ion and rearranges to give a species containing an unco-ordinated PPh_2 group. This PPh_2 group then rapidly attacks the palladium of another molecule of the same species in an intermolecular reaction to give the five fused-chelate-ring product of type **2**; see Scheme 2.

We attempted to synthesize the analogous diplatinum(II) complex by treating the neutral platinum complex **1c**[3] with 2 equivalents of Li[N(SiMe$_3$)$_2$] in tetrahydrofuran. On adding the base there was an immediate change from orange to dark brown but, after 3 d, no substantial amount of a single product could be observed by ^{31}P-{^{1}H} NMR spectroscopy. However, treatment of **1c** with an excess of potassium *tert*-butoxide in dry dimethyl sulfoxide (dmso) gave a dark solution whose ^{31}P-{^{1}H} NMR spectrum showed two phosphorus singlets, each with satellites, one at δ 23.3, ^{1}J(PtP) = 2118 Hz, and the other at δ −11.4, ^{3}J(PtP) = 112 Hz. The resonance at δ 23.3, indicates a phosphorus directly bonded to platinum and *trans* to carbon, whilst the small value of *J*(PtP) = 112 Hz for the resonance at δ −11.4 and the negative chemical shift is indicative of phosphorus not directly bonded to platinum. We tentatively suggest structure **3** for this complex. There was no observable coupling between the two phosphorus atoms. After 2 d there was no noticeable change in the ^{31}P-{^{1}H} NMR spectrum. The product did not react with either carbon monoxide or triphenylphosphine as evidenced by a ^{31}P-{^{1}H} NMR study. Attempts to isolate **3** gave an orange product whose ^{31}P-{^{1}H} NMR spectrum showed an AB pattern at δ 49.9 and 26.0 [^{2}J(PP) = 394, ^{1}J(PtP$_A$) = 2886 at ^{1}J(PtP$_B$) = 2773 Hz]. However, this decomposed on attempted purification.

The dinuclear palladium(II) complexes **2a** and **2b** contain enamine type (C=C−N), *i.e.* ene–hydrazone, moieties. Enamines react with electrophiles in what is a very useful and selective synthetic method in organic chemistry,[15–19] and we have reported that platinum complexes of type **1** react with a proton or with methyl iodide or bromine with electrophilic attack at an ene–hydrazone carbon (*C*=C−N−N) on the ligand backbone.[3] We have since studied electrophilic substitution reactions on the backbone of palladium complexes of type **1**.[20] We have now investigated the action of electrophiles on complexes **2a** and **2b**. Treatment of a deuteriochloroform solution of **2a** with 2 mol of trifluoroacetic acid (one per Pd atom) at *ca.* 20 °C gave an immediate reaction, with a change from deep red to yellow. The ^{31}P-{^{1}H} NMR spectrum of the resultant solution was of the AA′XX′ type with the two chemical shifts at δ 51.4 and 14.8 with $N = |J_{AX} + J_{AX'}| = 54$ Hz, as shown in Fig. 4. The protonation was reversible, and on addition of a solution of sodium methoxide the deep red neutral species **2a** was reformed (NMR evidence). The diprotonated complex was isolated as the trifluoroacetate **4a** as yellow microcrystals, by evaporation and addition of diethyl ether to the residue but the product contained solvent of crystallisation (chloroform). Similarly the phenyl analogue **2b** reacted with trifluoroacetic acid to give the diprotonated derivative **4b**. Treatment of **2a** with hydrochloric acid gave the cationic dichloride **4c** and treatment of **2a** or **2b** with picric acid gave the corresponding dipicrate salts **4d** and **4e**, respectively. Further details are in the Experimental section with elemental analytical and mass spectral data, and NMR data in Tables 2–4.

We studied complex **4a** in some detail by NMR spectroscopy. The ^{31}P-{^{1}H} data are in Table 1. The ^{1}H-{^{31}P} NMR spectrum of **4a** showed two *tert*-butyl resonances at δ 0.50 and 1.16, an AB pattern due to the non-equivalent methylene protons at δ 3.48 and 4.46, ^{3}J(HH) = 15.8 Hz, and a singlet at δ 7.03 due to the PCH= protons. In the ^{1}H NMR spectrum the methylene hydrogens were further coupled to one phosphorus giving an ABX pattern; for δ_H 3.48, *J*(PH) = 14.0 Hz and for δ_H 4.46, *J*(PH) = 5.5 Hz. A selective decoupling experiment established that the methylene hydrogens were coupled to the phosphorus, δ_P 51.4, *i.e.* P_F. The =CHPd protons were coupled to both P_F and P_S and gave an apparent triplet (a deceptively simple 1:2:1 triplet). Carbon-13, APT and heteronuclear COSY experiments established that the protons of the *tert*-butyls absorbing at δ 0.50 were attached to the carbons absorbing at δ 28.6 and those absorbing at δ 1.16 were attached to the carbons absorbing at δ 30.1. The methylene carbons absorbed at δ 43.8 as a doublet of doublets with *J*(PC) = 23.8 Hz and ≈2 Hz; such a chemical shift (δ *ca.* 44) is typical of a methylene carbon in a five-membered chelate ring.[1–4] The PCH= carbons absorbed at δ 57.3 as a second-order quartet with a doublet separation of *N* 73.5 Hz and two equally intense outer peaks 95.3 Hz apart.

The protonations of complexes **2a** and **2b** were reversible. In the presence of sodium methoxide **4a**–**4e** were deprotonated readily at the methylene carbon to give the neutral dipalladium(II) complexes **2a** or **2b**, as indicated by the discharge of the yellow colour to red (or orange) and subsequently confirmed by NMR studies. Although **4a**, **4c** and **4d** contain the same dipalladium dications the chemical shifts of the CH_2P and the =CHPd protons differ a lot between the three species, *e.g.* for the CH_2P protons δ 3.48 and 4.46 (**4a**), 3.29 and 3.61 (**4c**) and 3.24 and 3.49 (**4d**), and for the PdCH proton δ 7.03 (**4a**), 6.24 (**4c**) and 5.81 (**4d**), *i.e.* ion-pair interaction has a considerable effect on chemical shifts.



Scheme 2 A possible mechanism for the formation of a dinuclear palladium(II) complex of type **2**; thf = tetrahydrofuran

We have also investigated the action of less than 2 mol of an acid on complex **2a** in attempts to identify the formation of a monoprotonated species. Treatment of a deuteriochloroform solution of **2a** with 1 mol equivalent of trifluoroacetic acid (*i.e.* 0.5 mol equivalent per palladium atom) gave a dark green solution which soon faded to a pale green-yellow, exhibiting the ^{31}P-{^{1}H} NMR spectrum shown in Fig. 5. The green species was presumably due to an unstable intermediate, present in small amount. The peaks marked n and n′ in Fig. 5 are due to the starting complex **2a**, d and d′ to the diprotonated species **4a** and the other three peaks, m, m′ and m″, with relative intensities in the ratio 1:1:2, are assigned to the monoprotonated species **5a**. A ^{31}P–^{31}P COSY experiment established that the phosphorus atoms causing m, m′ and m″ were coupled together giving a deceptively simple spectral pattern. Thus P_S and $P_{S'}$ must resonate with virtually the same chemical shifts. In the ^{1}H NMR spectra of this protonated mixture we could identify the patterns due to **2a** and **4a** and the methylene hydrogens, CH_2P, of **5a** as resonating at δ ≈3.4 and 3.13, J(HH) = 15.2 Hz, and two singlets

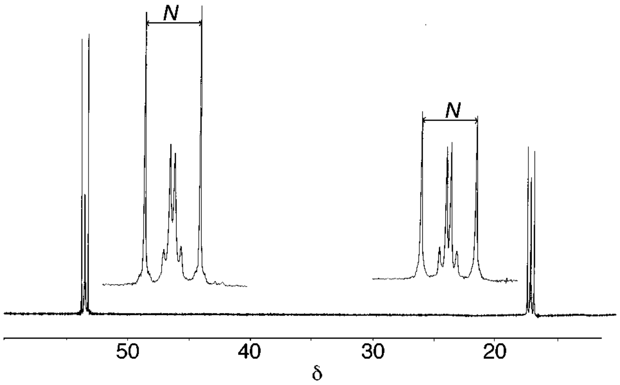
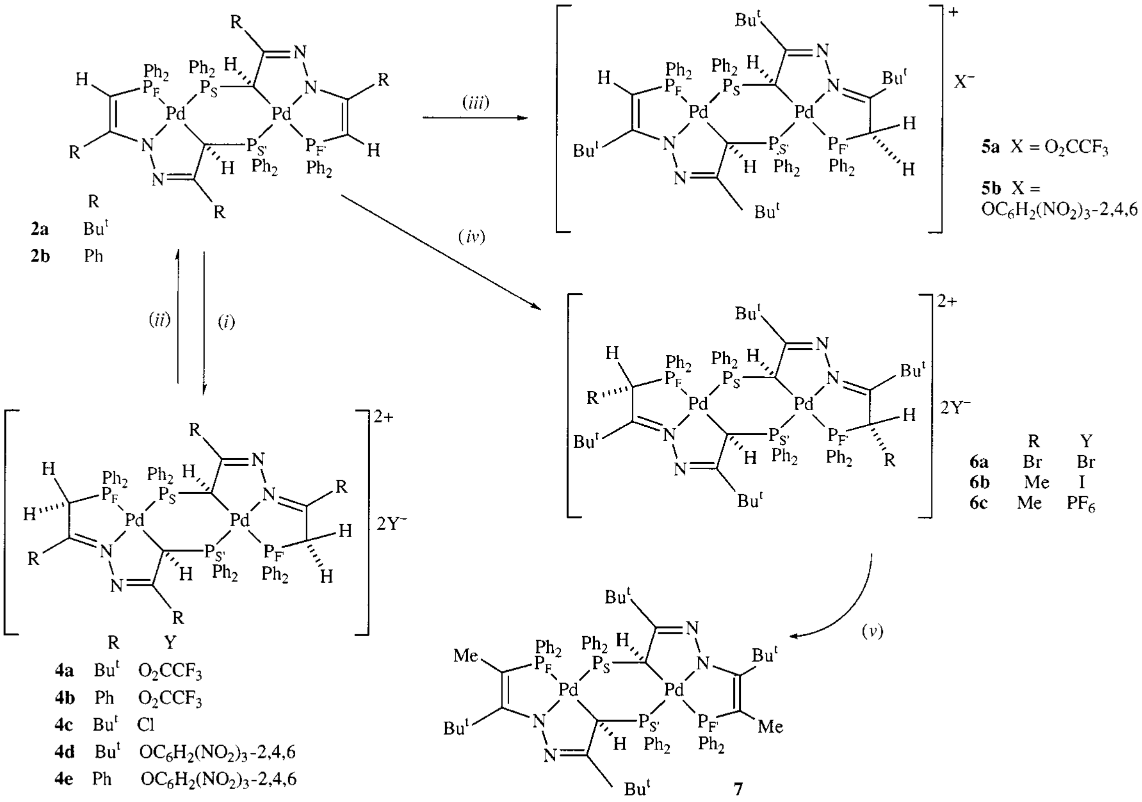


Fig. 4 The ^{31}P-{^{1}H} NMR spectrum (101.25 MHz) of complex **4a**, formed *in situ* by treating a deuteriochloroform solution of **2a** with 2 mol equivalents of CF_3CO_2H. The spectrum is of the AA′XX′ type and deceptively simple. The doublet of separations $N = |J(P_FP_S) + J(P_FP_{S'})|$ are shown

at δ 5.62 and 5.66 due to the CHPd proton. We could also identify the two *tert*-butyl resonances of **2a** (δ 0.31 and 1.45) and the two *tert*-butyl resonances of **4a** (δ 0.50 and 1.16) in the mixture and also see four equally intense *tert*-butyl resonances of the monoprotonated species **5a** (δ 0.72, 0.96, 1.00 and 1.03), *i.e.* although P_S and $P_{S'}$ have virtually the same chemical shift the hydrogens of the four *tert*-butyl groups do not. Treatment of **2a** with 0.5 mol equivalent of trifluoroacetic acid, *i.e.* 0.25 mol of acid per Pd atom, gave a ^{31}P-{^{1}H} NMR spectrum corresponding to a mixture of **2a**, **4a** and **5a** but with peaks d and d′ of very low intensity, s and s′ of high intensity and m, m′ and m″ of medium intensity. From the spectrum shown in Fig. 5 and from the chemical shifts given above, a phosphorus of type P_S absorbs within the range δ 10.2–17, a phosphorus P_F adjacent to a CH absorbs at δ 28.6–31.7 and a phosphorus P_F adjacent to a CH_2, *i.e.* adjacent to a protonated carbon, absorbs at δ 50–53.6. We also studied the action of increasing proportions of 2,4,6-trinitrophenol (picric acid) on **2a** in chloroform and observed the intermediate monoprotonated species **5b**. On adding 1 mol equivalent of picric acid to **2b** in chloroform the ^{31}P-{^{1}H} NMR spectrum showed the almost exclusive formation of **5b**, with second-order patterns very similar to the ones marked m″, m′ and m in Fig. 5, at δ 11.1, 28.8 and 49.9 in the intensity ratios 2:1:1; very little of **2a** and **4d** were present in the solution.

Treatment of complex **2a** with 2 mol equivalents of bromine in carbon tetrachloride at *ca.* 20 °C gave the brominated salt **6a**. The ^{31}P-{^{1}H} NMR spectrum of **6a** showed an AA′XX′ pattern, at δ 53.8 and 16.9 with $N = |J_{AX} + J_{AX'}| = 54$ Hz. In the ^{1}H NMR spectrum the doublet at δ 3.77, ^{2}J(PH) = 11.2 Hz, is assigned to CHBr. Bromination also resulted in a shift of the CHPd hydrogen to the higher value of δ 5.28 as a doublet, ^{2}J(PH) = 9.2 Hz. Electrophilic attack at the enamine type carbon, *C*=C–N, by Br would generate a chiral centre at carbon. One might therefore expect to get *R* and *S* isomers at both enamine carbons and therefore produce dibrominated products with chemically inequivalent bromines. However, a careful study of the reaction mixture by ^{31}P-{^{1}H} NMR spectroscopy showed only one product. Examination of the crystal structure of **2a**, particularly the view shown in Fig. 3, suggests that attack on the enamine carbon would be much more likely to occur exterior to the 'pocket', *i.e.* the racemic mixture (*RR* + *SS*) would preferentially be formed. Since we could detect only one product we suggest that no attack on C=CH from the side within the pocket occurred.

When a solution of complex **2a** in chloroform was treated with an excess of methyl iodide at *ca.* 20 °C it slowly turned green and finally yellow. After putting the reaction mixture aside for 5 d at *ca.* 20 °C the dimethylated palladium(II) salt **6b** was isolated as a yellow solid, in 79% yield. Complex **6b** was also obtained nearly quantitatively (92%) by heating the neutral



Scheme 3 (*i*) At least 2 mol equivalents of CF_3CO_2H, HCl or 2,4,6-$(O_2N)_3C_6H_2OH$; (*ii*) NaOMe; (*iii*) 1 equivalent of CF_3CO_2H; (*iv*) Br_2–CCl_4 or MeI, with NH_4PF_6 added for **6c**; (*v*) KOBu^t

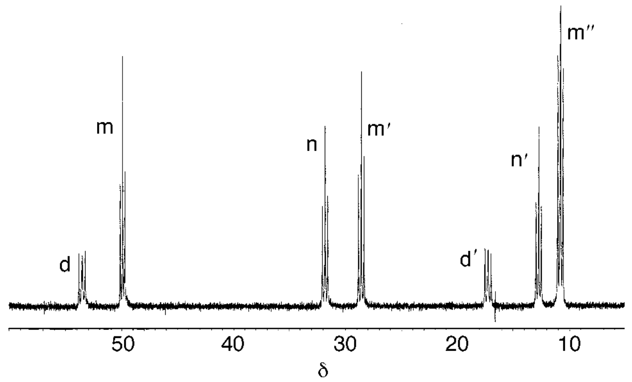


Fig. 5 The ^{31}P-{^{1}H} NMR spectrum (101.25 MHz) of the mixture of complexes **2a**, **4a** and **5a**, formed by treating **2a** with 1 mol equivalent of CF_3CO_2H. The resonances are identified as follows: n and n′ for the neutral complex **2a**, m, m′ and m″ for the monoprotonated complex **5a** and d and d′ for the diprotonated complex **4a**; the linkages were established by a ^{31}P–^{31}P COSY experiment. The chemical shifts of the phosphorus atoms of **5a** with the separation of the outer peaks of the three 'deceptively simple' patterns are as follows: m, δ 49.9(t), separation 42.5 Hz; m′ δ 28.6(t), separation 49.5 Hz; m″, δ ≈10.9(q), separation 46 Hz

dipalladium(II) complex **2a** with methyl iodide in chloroform at *ca.* 61 °C for 11 h, *i.e.* as with the bromination (above) only the *racemic* and none of the *meso* isomer was formed. The ^{31}P-{^{1}H} NMR spectrum of **6b** showed an AA′XX′ pattern with triplets at δ 49.9 and 20.6, $N = |J_{AX} + J_{AX'}| = 50$ Hz. In the ^{1}H NMR spectrum the doublet of doublets resonance at δ 1.61, ^3J(PH) = 16.1 Hz and ^3J(HH) = 6.6 Hz, was assigned to the methyl CH*Me* hydrogens, the multiplet at δ 4.08, ^3J(HH) = 6.6 Hz, to the methine C*H*Me hydrogen and the multiplet at δ 6.26 to the CHPd hydrogen. The ^{13}C-{^{1}H} NMR spectrum showed a doublet at δ 51.3, ^1J(PC) = 23.4 Hz, for the *C*HMe carbon and a multiplet at δ 60.2 for the CHPd carbon. The corresponding PF_6^- salt **6c** was prepared by the addition of ammonium hexafluorophosphate to a solution of **6b** in methanol. The ^{31}P-{^{1}H} NMR spectrum of **6c** confirmed the replacement of Cl^- with PF_6^-.

The dimethylated complex **6b** was resistant to deprotonation by sodium methoxide. However, treatment with an excess of potassium *tert*-butoxide in dry dimethyl sulfoxide gave the neutral dimethyldipalladium(II) complex **7** as a brown solid, in 88% yield. The ^{31}P-{^{1}H} NMR spectrum of this neutral complex showed two triplets at δ 56.6 and 13.9 with $|J_{AX} + J_{AX'}| = 40$ Hz. In the ^{1}H NMR spectrum, the methyl =C*Me* hydrogens gave a doublet at δ 1.82, ^3J(PH) = 10.7 Hz whilst the CHPd hydrogen gave a doublet of doublets at δ 4.04, *J*(PH) = 8.5 and 7.2 Hz and a singlet in the ^{1}H-{^{31}P} NMR spectrum.

We attempted to prepare salts from complex **2a** using electrophiles more bulky than methyl iodide, such as allyl bromide, benzyl bromide, *p*-toluenediazonium hexafluorophosphate or dimethyl acetylenedicarboxylate. These attempts all failed. Products showing AA′XX′ patterns were observed by ^{31}P-{^{1}H} NMR spectroscopy but these could not be isolated due to their extreme solubility in most organic solvents. For example the ^{31}P-{^{1}H} NMR spectrum of the dark solution obtained from the prolonged treatment (at *ca.* 20 °C for 3 weeks) of a solution of **2a** in chloroform with an excess of *p*-toluenediazonium hexafluorophosphate showed triplets at δ 48.1 and 12.8, $N = |J_{AX} + J_{AX'}| = 42$ Hz.

Experimental

All the reactions were carried out in a dry atmosphere of nitrogen or argon using degassed solvents. Tetrahydrofuran and benzene were distilled from sodium and benzophenone under argon immediately before use. The chloropalladium(II) and chloroplatinum(II) complexes **1a** and **1c** were prepared according to our published procedure.[3] Infrared spectra were recorded on a Perkin-Elmer model 257 grating spectrometer (4000–600 cm^{-1}), NMR spectra using a JEOL FX-90Q (operating frequencies for ^{1}H and ^{31}P were 89.5 and 36.2 MHz, respectively), a JEOL FX-100 (operating frequencies for ^{1}H and ^{31}P of 99.5

MHz and 40.25 MHz, respectively), a Bruker ARX-250 (operating frequencies for ^{1}H, ^{31}P and ^{13}C of 250.13, 101.25 and 62.9 MHz, respectively) or a Bruker AM-400 spectrometer (operating frequencies for ^{1}H, ^{31}P and ^{13}C of 400.13, 161.9 and 100.6 MHz, respectively). Proton and ^{13}C shifts are relative to tetramethylsilane and ^{31}P shifts to 85% phosphoric acid. Fast atom bombardment (FAB) mass spectra were recorded using a VG Autospec instrument with 8 kV acceleration. For the metal complexes *m*/*z* values are quoted for ^{106}Pd.

Preparations

***Z*,*Z*-PPh$_2$CH$_2$C(Ph)=N–N=C(Ph)CH$_2$PPh$_2$ II.** A solution containing the keto phosphine Ph$_2$PCH$_2$C(=O)Ph[9] with (19.3 g, 63.3 mmol) and hydrazine monohydrate (1.5 cm^3, 31.7 mmol) and acetic acid (3.0 cm^3) in ethanol (150 cm^3) was heated at *ca.* 78 °C for 22 h. The resultant solution was concentrated to low volume under reduced pressure and the product was isolated as yellow needles. Yield (14.2 g, 74%) (Found: C, 79.3; H, 5.75; N, 4.5. $C_{40}H_{34}N_2P_2$ requires C, 79.45; H, 5.65; N, 4.65%). Electron-impact (EI) mass spectrum: *m*/*z*: 604 (*M*).

[PdCl{PPh$_2$CH=C(Ph)–N–N=C(Ph)CH$_2$PPh$_2$}] 1b. A solution containing [PdCl$_2$(NCPh)$_2$] (0.60 g, 0.26 mmol) and the azine diphosphine **II** (0.16 g, 0.26 mmol) in chloroform (5 cm^3) was heated at *ca.* 61 °C for 3 h. An excess of triethylamine (0.3 cm^3) was then added and the resultant purple solution was concentrated to low volume under reduced pressure. Addition of methanol to the residue gave the required product **1b** as a purple solid. Yield 0.84 g, 72% (Found: C, 64.6; H, 4.65; Cl, 4.65; N, 3.8. $C_{40}H_{33}ClN_2P_2Pd$ requires C, 64.45; H, 4.45; Cl, 4.75; N, 3.75%). Mass spectrum (FAB): *m*/*z* 745 (*M* + 1).

[{Pd[PPh$_2$CH=C(Bu^t)–N–N=C(Bu^t)CHPPh$_2$]}$_2$] 2a. A solution of lithium bis(trimethylsilyl)amide Li[N(SiMe$_3$)$_2$] (0.1 mol dm^{-3} in thf, 0.45 cm^3, 0.45 mmol) was added to a solution of complex **1a** (0.16 g, 0.22 mmol) in tetrahydrofuran (5 cm^3). After 15 min the solution was concentrated to low volume (*ca.* 1 cm^3) under reduced pressure after which addition of methanol gave complex **2a** as red crystals. Yield 0.12 g, 80%. A sample was recrystallised from dichloromethane–methanol for analysis (Found: C, 62.0; H, 6.0; N, 3.8. $C_{72}H_{80}N_4P_4Pd_2\cdot 2CH_2Cl_2$ requires C, 61.6; H, 5.8; N, 3.9%). Mass spectrum (FAB): *m*/*z* 1338 (*M*).

[{Pd[PPh$_2$CH=C(Ph)–N–N=C(Ph)CHPPh$_2$]}$_2$] 2b. A solution of Li[N(SiMe$_3$)$_2$] (0.1 mol dm^{-3} in thf, 1.90 cm^3, 1.90 mmol) was added to a solution of complex **1b** (0.70 g, 0.095 mmol) in tetrahydrofuran (10 cm^3). After 15 min the resultant solution was concentrated to low volume (*ca.* 1 cm^3) under reduced pressure; addition of methanol then gave complex **2b** as an orange solid. Yield 0.57 g, 85% [Found: (*i*) C, 64.95; H, 3.75; N, 3.05. (*ii*) C, 65.25; H, 4.05; N, 3.25. $C_{80}H_{64}N_4P_4Pd_2$ requires C, 67.75; H, 4.55; N, 3.95%]. Mass spectrum (FAB): *m*/*z* 1418 (*M*).

[Pt{PPh$_2$CH=C(Bu^t)–N–N=C(Bu^t)CHPPh$_2$}(dmso)] 3. An excess of KOBu^t (*ca.* 0.06 g, 0.50 mmol) was added to a solution of complex **1c** (0.10 g, 0.13 mmol) in dry dimethyl sulfoxide (3 cm^3). The NMR spectrum was recorded, see Discussion. Attempts to isolate the complex by removing the solvent under reduced pressure and trituration of the residue with *n*-hexane gave an orange solid which decomposed on attempted recrystallisation.

[{Pd[PPh$_2$CH$_2$C(Bu^t)=N–N=C(Bu^t)CHPPh$_2$]}$_2$][O$_2$CCF$_3$]$_2$ 4a. An excess of CF_3CO_2H (0.05 cm^3) was added to a solution of complex **2a** (0.10 g, 0.074 mmol) in chloroform (3 cm^3). The resultant yellow solution was evaporated to dryness under reduced pressure after which addition of diethyl ether to the residue gave the protonated complex **5a** as a yellow solid. Yield 0.10 g, 80% [Found: (*i*) C, 53.15; H, 4.6; N, 2.9. (*ii*) C, 53.25; H, 4.75; N, 3.2. $C_{76}H_{82}F_6N_4O_4P_4Pd_2\cdot 1.5CHCl_3$ requires C, 53.3; H, 4.8; N, 3.2%]. Mass spectrum (FAB): *m*/*z* 1338 (*M* − 2CF$_3$CO$_2$H).

The following four compounds were prepared in a similar manner to that described for **4a**: [{Pd[PPh$_2$CH$_2$C(Ph)=N–N=C(Ph)CHPPh$_2$]}$_2$][O$_2$CCF$_3$]$_2$ **4b**, by addition of CF_3CO_2H to **2b**, yield 76%, sample for microanalysis recrystallised from chloroform–methanol (Found: C, 57.55; H, 3.5; N, 2.95. $C_{84}H_{66}F_6N_4O_4P_4Pd_2\cdot CHCl_3$ requires C, 57.8; H, 3.8; N, 3.15%), mass spectrum (FAB): *m*/*z* 1418 (*M* − 2CF$_3$CO$_2$H); [{Pd[PPh$_2$CH$_2$C(Bu^t)=N–N=C(Bu^t)CHPPh$_2$]}$_2$]Cl$_2$ **4c**, by the addition of concentrated HCl (0.05 cm^3) to **2a** (60 mg) in chloroform (2 cm^3), yield 59 mg (93%) (Found: C, 61.1; H, 5.8; Cl, 5.25; N, 3.9. $C_{72}H_{82}Cl_2N_4P_4Pd_2$ requires C, 61.3; H, 5.85; Cl, 5.05; N, 3.95%), mass spectrum (FAB): *m*/*z* 1338 [(*M* − 2) − 2Cl]; [{Pd[PPh$_2$CH$_2$C(Bu^t)=N–N=C(Bu^t)CHPPh$_2$]}$_2$][OC$_6$H$_2$(NO$_2$)$_3$]$_2$ **4d**, as yellow microcrystals by the addition of 2 equivalents of picric acid to **2a** in chloroform solution and evaporation of the resultant solution to low volume and addition of hexane, yield 90%, sample for analysis recrystallised from dichloromethane–hexane (Found: C, 55.25; H, 4.5; N, 7.9. $C_{84}H_{86}N_{10}O_{14}P_4Pd_2\cdot 0.5CH_2Cl_2$ requires C, 55.1; H, 4.75; N, 7.6%), mass spectrum (FAB): *m*/*z* 1568 [*M* − (NO$_2$)$_3$C$_6$H$_2$O] and 1338 [(*M* − 2) − 2(NO$_2$)$_3$C$_6$H$_2$O]; and [{Pd[PPh$_2$CH$_2$C(Ph)=N–N=C(Ph)CHPPh$_2$]}$_2$][OC$_6$H$_2$(NO$_2$)$_3$]$_2$ **4e**, by the addition of picric acid to **2b**, yield 90%, sample for analysis recrystallised from dichloromethane–diethyl ether (Found: C, 57.5; H, 3.7; N, 6.95. $C_{92}H_{70}N_{10}O_{14}P_4Pd_2\cdot 0.5CH_2Cl_2$ requires C, 57.4; H, 3.7; N, 7.2%), mass spectrum (FAB): *m*/*z* 1418 [(*M* − 2) − 2(NO$_2$)$_3$C$_6$H$_2$O].

[{Pd[PPh$_2$CH(Br)C(Bu^t)=N–N=C(Bu^t)CHPPh$_2$]}$_2$]Br$_2$ 6a. Solutions of complex **2a** (0.24 g, 0.18 mmol) in chloroform (4 cm^3) and bromine (0.36 mmol) in tetrachloromethane (0.46 cm^3) were stirred together at *ca.* 20 °C for 30 min. The resultant yellow solution was evaporated to dryness under reduced pressure when addition of diethyl ether to the residue gave complex **6a** as a yellow solid. Yield 0.28 g, 94% (Found: C, 51.55; H, 4.8; N, 3.15. $C_{72}H_{80}Br_4N_4P_4Pd_2\cdot 0.25CHCl_3$ requires C, 51.45; H, 4.8; N, 3.35%). Mass spectrum (FAB): *m*/*z* 1578 (*M* − Br), 1498 (*M* − 2Br), 1418 (*M* − 3Br) and 1338 (*M* − 4Br).

[{Pd[PPh$_2$CH(Me)C(Bu^t)=N–N=C(Bu^t)CHPPh$_2$]}$_2$]I$_2$ 6b. (*i*) A solution containing an excess of methyl iodide (0.1 cm^3) and complex **2a** (0.40 g, 0.30 mmol) in chloroform (10 cm^3) was heated at *ca.* 61 °C for 11 h. The resultant yellow solution was evaporated to dryness under reduced pressure and the residue recrystallised from dichloromethane–hexane to give complex **6b** as yellow microcrystals. Yield 0.45 g, 92% (Found: C, 52.65; H, 4.9; N, 3.3. $C_{74}H_{84}I_2N_4P_4Pd_2\cdot CH_2Cl_2$ requires C, 52.8; H, 5.2; N, 3.3%). Mass spectrum (FAB): *m*/*z* 1494 (*M* + 1 − I) and 1367 (*M* + 1 − 2I).

(*ii*) A solution of complex **2a** (0.40 g, 0.30 mmol) and an excess of methyl iodide (0.1 cm^3) was stirred in chloroform (5 cm^3) at *ca.* 20 °C for 5 d. The product was isolated as above. Yield 0.38 g, 79%.

[{Pd[PPh$_2$CH(Me)C(Bu^t)=N–N=C(Bu^t)CHPPh$_2$]}$_2$][PF$_6$]$_2$ 6c. A mixture of ammonium hexafluorophosphate (15 mg, 0.09 mmol) in methanol (1 cm^3) and complex **6b** (0.10 mg, 0.06 mmol) in methanol (3 cm^3) was set aside at *ca.* 20 °C for 1 h. The required product **6c** was obtained as a yellow solid which was filtered off and recrystallised from chloroform–methanol. Yield 0.10 g, 95% (Found: C, 52.3; H, 4.9; N, 3.25. $C_{74}H_{86}F_{12}N_4P_6Pd_2\cdot 0.5CHCl_3$ requires C, 52.1; H, 5.1; N, 3.25%). Mass spectrum (FAB): *m*/*z* 1513 (*M* − PF$_6$) and 1368 (*M* + 2 − 2PF$_6$).

Table 5 Crystallographic data for compound **2a**

Empirical formula	$(C_{36}H_{40}N_2P_2Pd)_2\cdot 2CH_2Cl_2$
T/K	200
λ/Å	0.710 73
Crystal system	Orthorhombic
Space group	*Pccn*
a/Å	13.839(2)
b/Å	20.696(4)
c/Å	25.069(5)
U/Å^3	7180(2)
Z	4
D_c/Mg m^{-3}	1.395
μ/mm^{-1}	0.783
F(000)	3104
Crystal size/mm	0.19 × 0.15 × 0.12
θ_{min}, θ_{max}/°	2.0, 25.0
hkl Ranges	0–16; −5 to 24; −29 to 29
Reflections collected	6616
Independent reflections, p	6326
Reflections with $F_o^2 > 2\sigma F_o^2$	3226
Weighting scheme parameters a, b[a]	0.0377, 6.8967
Data, restraints, parameters (n)	6326, 203, 403
Goodness of fit on F^2, S[b]	1.017
$R1$[c]	0.0499
$wR2$[d]	0.1126
Largest difference map peak and hole/e Å^{-3}	0.998, −0.620

[a] $w = 1/[\sigma^2(F_o^2) + aP^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. [b] $S = \{\Sigma w(F_o^2 - F_c^2)^2/(n - p)\}^{\frac{1}{2}}$. [c] $R1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$. [d] $wR2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2\}^{\frac{1}{2}}$.

[{Pd[PPh$_2$C(Me)=C(Bu^t)–N–N=C(Bu^t)CHPPh$_2$]}$_2$] 7. A mixture of an excess of KOBu^t (0.2 g) and complex **6b** (0.40 g, 0.25 mmol) in dry dimethyl sulfoxide (2 cm^3) was set aside at *ca.* 20 °C for 1 h. The solvent was removed under reduced pressure and addition of methanol (*ca.* 5 cm^3) to the residue gave **7** as a brown solid, which was filtered off, washed with methanol and dried *in vacuo.* Yield 0.30 g, 88% (Found: C, 61.45; H, 6.15; N, 3.6. $C_{74}H_{84}N_4P_4Pd_2\cdot$2dmso requires C, 61.5; H, 6.35; N, 3.6%). Mass spectrum (FAB): m/z 1367 (M + 1).

Crystallography

All crystallographic measurements were made on a Stoe STADI4 diffractometer operating in the ω–θ scan mode using graphite monochromated Mo-Kα radiation (λ = 0.710 73 Å). Crystal data are given in Table 5 together with refinement details. Cell dimensions were refined from the values of 40 selected reflections (together with their Friedel opposites) measured at ±2θ in order to minimise systematic errors.

The structure was solved by heavy-atom methods using SHELXS 86[21] and developed by full-matrix least-squares refinement (on F^2) using SHELXL 93.[22] The dimer possesses crystallographic C_2 symmetry and there is also a CH_2Cl_2 solvate molecule in the asymmetric part of the unit cell. All non-hydrogen atoms (including those of the solvate molecule) were refined with anisotropic displacement parameters. Restraints were applied to the phenyl rings so that they remained flat with overall C_{2v} symmetry. All hydrogen atoms were constrained to idealised positions with a riding model including free rotation of methyl groups.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/530.

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