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Palladium complexes of bridgehead phosphines

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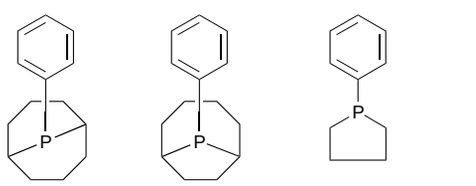
Palladium chloro complexes reacted with 9-phenyl-9-phosphabicyclononanes (PPBN) and 1-phenylphospholane and gave *trans*-chlorobis(phosphine)palladium(II) complexes, 1-phenylphospholane also gave rise to a chloro-bridged dimer. With palladium acetate, the two isomers of PPBN (9-phenyl-9-phosphabicyclo-[3.3.1]nonane and -[4.2.1]nonane, 3,3,1-PPBN and 4,2,1-PPBN respectively) formed *trans* bis(phosphine) complexes exclusively whereas 1-phenylphospholane formed the *cis*-bis(phosphine) complex; examples of both *trans* and *cis* complexes have been structurally characterised. The acetate groups were readily replaced by sulfonic and phosphonic acids to give sulfonato and phosphonato complexes respectively. Reduction of the acetato–4,2,1-PPBN complex to $[Pd^0(4,2,1\text{-PPBN})_3]$ occurred in alcoholic media readily, however the isomeric 3,3,1-PPBN complex was considerably more resistant to reduction. Abstraction of halide from both dichloro–PPBN complexes by $Ag(O_3SCF_3)$ in ethanol resulted in the formation of phosphonium salts.

Ligand derived influences upon transition-metal catalysed reactions are well known to result from electronic and steric properties of the ligand. The chemistry of palladium–phosphine complexes has previously been extensively studied.[1] Complexes of both mono- and bi-dentate phosphine ligands are of particular industrial interest due to their ability to catalyse a wide range of processes such as carbonylation,[2] carboalkoxylation,[3] amidation,[4] vinylic hydrogen substitution,[5] oxidation[6] and polymerisation reactions.[7] In palladium-catalysed carbonylations of alkenes and alkynes, triphenylphosphine complexes of palladium acetate are known to be active. Rates and selectivities in these reactions have been reported to vary as the phosphine ligand substituents vary. Whereas simple dialkylphenylphosphines such as dimethylphenylphosphine are generally poor ligands in these applications giving rise to complexes that are less active than those of PPh_3, a class of bridgehead monoaryl phosphines with strained or constrained alkyl substituents form catalytically more active species than does PPh_3. Such ligands include the 9-phenyl-9-phosphabicyclononanes, 9-phenyl-9-phosphabicyclo-[4.2.1]nonane (4,2,1-PPBN) and -[3.3.1]nonane (3,3,1-PPBN).

Although 9-phosphabicyclononanes have previously been used with $[Co_2(CO)_8]$ in catalytic hydroformylations,[8] no complexes were characterised in these studies and the chemistry of these phosphines is still unexplored; there are no other reports of well characterised PPBN complexes. The crystalline 3,3,1 isomer of PPBN is comprised of two six-membered rings whilst the liquid 4,2,1-PPBN consists of a five- and a seven-membered ring. These subtle variations in structure may have unpredicted influences upon the behaviour of their metal complexes in catalytic reactions; indeed there are significant differences in reactivity observed between complexes of the two PPBN isomers. Thus in some carbonylations, palladium–4,2,1-PPBN complexes are five times more active than those of 3,3,1-PPBN under the same conditions.[9] This activity is enhanced in the presence of a strong acid with weakly co-ordinating anions[10] which can clearly lead to phosphonium salt formation. Phosphonium salts may also be formed by elimination of hydrocarbon functions from metal complexes which constitutes a degradation pathway causing deactivation during catalysis. A more detailed understanding of these ligands and their complexes will be of value in the development of useful applications. For this reason we have chosen to study the co-ordination behaviour of PPBN and related compounds in an attempt to gain insight into the steric and electronic influences these variations in structure may have upon the reactivity of derived complexes. Since the most apparent difference between the two PPBN isomers is in the sizes of the heterocyclic rings, we have investigated a model analogue of 4,2,1-PPBN (which forms the more active carbonylation catalyst), *i.e.* the known five-membered heterocyclic phosphine, 1-phenylphospholane.[11]



3,3,1-PPBN 4,2,1-PPBN 1-Phenylphospholane

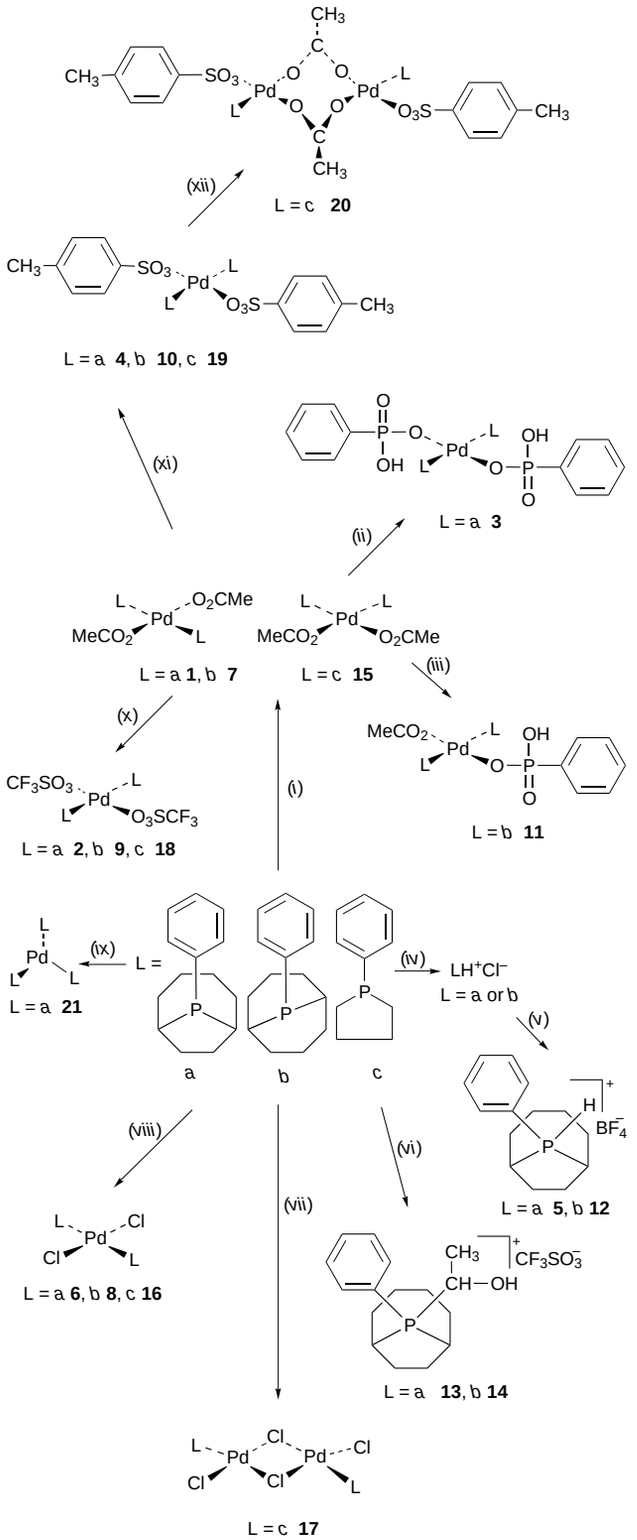
The present study includes the investigation of the co-ordination complexes formed between the phosphines and a series of palladium(II) precursors and the formation of phosphonium salts in the presence of palladium. The reactivity between the bis(acetato)bis(phosphine)palladium(II) complexes isolated and toluene-*p*-sulfonic or phenylphosphonic acid, has been studied. The reduction of the $[Pd(O_2CMe)_2(PPBN)_2]$ complexes for both of the isomers, which may be relevant to the understanding of the different catalytic activities for the two isomers, is also discussed. The new complexes and phosphonium salts are detailed in Scheme 1.

Results and Discussion

9-Phenyl-9-phosphabicyclo[4.2.1]nonane complexes

The synthetic approaches to the palladium 4,2,1-PPBN complexes are all similar *via* common palladium(II) starting materials, NMR data for the palladium complexes discussed below are collected in Table 1.

The addition of 2 mol equivalents of 4,2,1-PPBN to a toluene solution of $[Pd(O_2CMe)_2]$ affords an orange methanol soluble complex **1**. Microanalysis data indicate the formula $[Pd(O_2CMe)_2(4,2,1\text{-PPBN})_2]$. The co-ordination of the tertiary phosphine is indicated in the $^{31}P\text{-}\{^1H\}$ NMR spectrum (δ 37.7) where the co-ordination chemical shift (Δ) from the free phosphine is *ca.* 30 ppm. In the $^{31}C\text{-}\{^1H\}$ NMR spectrum, resonances corresponding to the carbonyl carbons (δ 176.4) and



Scheme 1 Synthesis of palladium complexes and phosphonium salts. (*i*) $[Pd(O_2CMe)_2]$:2L, PhMe; (*ii*) $2PhP(O)(OH)_2$:$1[Pd(O_2CMe)_2L_2]$, MeOH; (*iii*) $2PhP(O)(OH)_2$:$1[Pd(O_2CMe)_2L_2]$, MeOH; (*iv*) 1HCl:0.5L, EtOH; (*v*) $1.5AgBF_4$:1L, thf; (*vi*) $1PdCl_2$:$2Ag(O_3SCF_3)$:2L, EtOH, 80 °C; (*vii*) $1[PdCl_2(NCPh)_2]$:1L, PhMe; (*viii*) $1[PdCl_2(NCPh)_2]$ or $1PdCl_2$:2L, PhMe; (*ix*) $1K_2[PdCl_4]$:2KOH:3.5L, EtOH, reflux 20 min; (*x*) $2CF_3SO_3H$:$1[Pd(O_2CMe)_2L_2]$, PhMe; (*xi*) $2MeC_6H_4SO_3H$:$1[Pd(O_2CMe)_2L_2]$, PhMe; (*xii*) $2MeCO_2H$, $2MeC_6H_4SO_3H$:$1[Pd(O_3SC_6H_4Me)_2L_2]$, PhMe

methyl carbon (δ 25.07) are observed. In the infrared spectrum, two bands assigned to ν(CO) (1623 and 1307 cm^{-1}) confirm unidentate co-ordination of acetate. When a stoichiometric amount of trifluoromethanesulfonic acid is added to a toluene solution of **1** yellow crystals of a new material (**2**) are isolated for which analytical data indicate the formula $[Pd(O_3SCF_3)_2(4,2,1\text{-PPBN})_2]\cdot 2H_2O$. All spectroscopic data clearly confirm the replacement of acetate by trifluoromethanesulfonate; bands attributable to acetate are absent from the infrared spectrum and two absorptions assigned to $\nu_{sym}(SO_3)$ (1040 and 1045 cm^{-1}) are observed; the splitting of $\nu_{sym}(SO_3)$ is indicative of trifluoromethanesulfonate co-ordination.[12] Addition of excess trifluoromethanesulfonic acid to a solution of **1** results in the isolation of **2**, but in poorer yields.

Pale brown dichloromethane soluble crystals of complex **3** are isolated from the addition of 1 mol equivalent of phenylphosphonic acid to a methanolic solution of **1**. Analytical data for the crystalline product indicate the formula $[Pd\{OP(O)(OH)Ph\}_2(4,2,1\text{-PPBN})_2]\cdot 2H_2O$. The room-temperature $^{31}P\text{-}\{^1H\}$ NMR spectrum exhibits two resonances (δ 53.0 and 22.0) and in the reaction mixture, there is a resonance due to unreacted **1** of approximately equal intensity. These can be assigned to co-ordinated phosphine and co-ordinated phenylphosphonic acid respectively and indicate the formation of one isomer of the palladium(II) complex and that the mineral acid is acting as a monobasic acid. The $^{31}P\text{-}\{^1H\}$ NMR spectrum was temperature invariant (down to −90 °C). The ^1H NMR spectrum, although broad, supports the formulation and includes a resonance assigned to the hydroxy protons (δ 6.55) in exchange with OH from water of crystallisation and which disappears upon addition of D_2O. Again, the ^1H NMR spectrum was temperature invariant upon cooling. As for complex **2**, absorbances due to acetate were absent from the infrared spectrum. The addition of 2 equivalents of toluene-*p*-sulfonic acid to a toluene solution of **1** affords yellow crystals of complex **4**. Analytical data confirm the formula $[Pd(O_3SC_6H_4Me)_2(4,2,1\text{-PPBN})_2]$. Upon displacement of acetate by sulfonate anions, a downfield shift of 7 ppm is observed in the $^{31}P\text{-}\{^1H\}$ NMR spectrum. Two sulfonate absorptions appear in the infrared spectrum [$\nu(SO_3)$ = 1258 and 1026 cm^{-1}] which vary slightly from those observed for the unco-ordinated acid. Once again, absorbances attributable to acetate were not observed. Thus the data are consistent with **4** containing co-ordinated toluene-*p*-sulfonate. Complex **4** is also isolated from the reaction of $[Pd(O_2CMe)_2]$ with 4,2,1-PPBN and toluene-*p*-sulfonic acid. In the presence of less than 2 mol equivalents of acid, a mixture of **4** and unreacted starting material $[Pd(O_2CMe)_2(4,2,1\text{-PPBN})_2]$ was observed in the supernatant solution by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy with **4** precipitating after several hours. Dissolution of **4** in methanol in the absence of acid and under anaerobic conditions leads to the oxidation of the phosphine to its oxide (identified by NMR spectroscopy). Addition of excess mineral acid resulted in a precipitate of **4** as well as a phosphonium salt as indicated by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy (δ 24); an identical chemical shift was observed from the addition of toluene-*p*-sulfonic acid to 4,2,1-PPBN in methanol in the absence of palladium complexes. The phosphonium salt was further characterised as the tetrafluoroborate **5** for which analytical data confirm the formulation $C_{14}H_{19}PH^+BF_4^-$. A smaller difference in chemical shift is observed between the free phosphine and the phosphonium salts (*ca*. 11 ppm), in comparison with the co-ordination complexes (*ca*. 30–35 ppm).

The addition of 2 equivalents of 4,2,1-PPBN to a toluene solution of $[PdCl_2(NCPh)_2]$ yielded yellow crystals of complex **6**. Analytical data indicate the formula $[PdCl_2(4,2,1\text{-PPBN})_2]$. Spectroscopic data support the formation of **6** with resonances attributed to the aliphatic and aromatic protons being observed in the ^1H NMR spectrum. Resonances for the aliphatic and aromatic carbons are present in the $^{13}C\text{-}\{^1H\}$ NMR spectrum. A Δ value of *ca*. 35 ppm downfield from the free phosphine is observed in the $^{31}P\text{-}\{^1H\}$ NMR spectrum, which is slightly larger than for the corresponding bis(acetato) complex **1** and indicates stronger Pd–P bonding in **6**. A single metal–chloride stretch is observed in the infrared spectrum (350 cm^{-1}) indicating the formation of a *trans*-dichloro complex,[13] there was no

Table 1 The NMR spectroscopic data for the palladium complexes[a]

Complex	δ ^{31}P-{^{1}H}	δ ^{1}H	δ ^{13}C-{^{1}H}
1 $[Pd(O_2CMe)_2(4,2,1\text{-PPBN})_2]$	37.7 (s)	7.7 (2 H, m, aryl), 7.4 (3 H, m, aryl), 3.2–1.3 (15 H, m, CH_3, CH_2, CH)	176.4 (s, CO), 131.58 (s, aryl), 129.89 (d, $^{1}J_{PC}$ 9, PC), 128.91 (d, $^{1}J_{PC}$ 11, aryl), 32.87 (s), 32.17 (s), 30.14 (s), 25.87 (d, $^{1}J_{PC}$ 20, PCH_2), 25.07 (s, CH_3CO_2)
2 $[Pd(O_3SCF_3)_2\text{-}(4,2,1\text{-PPBN})_2]\cdot 2H_2O$	48.7 (s)	7.85 (2 H, br s, aryl), 7.6 (3 H, br s, aryl), 3.25 (2 H, br s, CH), 2.0 (12 H, br m, CH_2)	132.4 (s, aryl), 130.4 (d, $^{2}J_{PC}$ 11.3, PC*C*H), 130.0 (d, $^{3}J_{PC}$ 17, PCCH*C*H), 128.1 (d, $^{1}J_{PC}$ 47, PC), 119.9 (q, $^{1}J_{CF}$ 319.0, CF_3), 31.7 (s), 29.7 (s), 28.2 (s), 26.1 (s)
3 $[Pd\{OP(O)(OH)Ph\}_2\text{-}(4,2,1\text{-PPBN})_2]\cdot 2H_2O$	53.0 (br s), 22.0 (br s)	7.85 (br s), 7.55– 7.35 (br m), 6.55 (1 H, br s, OH), 3.0 (2 H, br s, H_2O), 2.0 (br m), 0.85 (m)	*b*
4 $[Pd(O_3SC_6H_4Me)_2(4,2,1\text{-PPBN})_2]$	44.4 (s)	8.1 (2 H, br s, aryl), 7.7 (2 H, d, $^{3}J_{HH}$ 8, aryl), 7.6 (3 H, br s, aryl), 7.0 (2 H, d, $^{3}J_{HH}$ 8, aryl), 3.7 (1 H, br s, CH), 2.8 (3 H, br s, CH_2, CH), 2.3 (3 H, s, CH_3), 2.1 (7 H, br m, CH, CH_2)	141.0 (s, aryl), 140.0 (s, aryl), 131.2 (d, $^{1}J_{PC}$ 17.4, aryl), 129.6 (d, $^{3}J_{PC}$ 7.5, aryl), 129.3 (s, aryl), 128.9 (s, aryl), 128.5 (s, aryl), 126.5 (s, aryl), 32.4 (br s), 29.8 (br s), 26.1 (s), 21.3 (s)
6 $[PdCl_2(4,2,1\text{-PPBN})_2]$	40.6 (s)	7.7 (2 H, m, aryl), 7.35 (3 H, m, aryl), 3.2 (2 H, m, CH_2), 2.6 (2 H, m, CH_2), 2.0 (2 H, m, CH_2), 1.6 (8 H, m, CH_2, CH)	132.1 (s, aryl), 130.2 (s, aryl), 129.3 (s, aryl), 128.5 (s, aryl), 35.0 (s), 32.2 (s), 30.7 (s), 25.8 (s)
7 $[Pd(O_2CMe)_2(3,3,1\text{-PPBN})_2]$	4.3 (s)	7.5 (5 H, br s, aryl), 2.8 (6 H, br s, CH_2), 2.5 (3 H, br s, CH_2, CH), 2.4 (2 H, br s, CH_2), 1.8 (4 H, br s, CH_3, CH), 1.3 (2 H, br s, CH_2)	176.4 (s, CO), 132–125 (m, aryl), 30–20 (m, CH, CH_2, CH_3)
8 $[PdCl_2(3,3,1\text{-PPBN})_2]$	5.7 (s)	7.5 (2 H, m, aryl), 7.4 (3 H, m, aryl), 3.1 (2 H, s, CH_2), 2.6 (2 H, s, CH_2), 1.9 (6 H, m, CH_2), 1.75 (3 H, m, CH_2, CH), 1.3 (1 H, s, CH)	*b*
9 $[Pd(O_3SCF_3)_2(3,3,1\text{-PPBN})_2]$	23.5 (s)	8.1–7.5 (5 H, m, aryl), 2.7 (1 H, br s, CH), 2.1–1.45 (11 H, br m, CH_2, CH), 1.3 (2 H, br m, CH_2)	132.6 (s, aryl), 131.5 (s, aryl), 130.5 (s, aryl), 130.0 (s, aryl), 121.3 (q, $^{1}J_{CF}$ 305, CF_3), 30.1 (s), 28.6 (s), 27.3 (s), 26.1 (s), 22.0 (s)
10 $[Pd(O_3SC_6H_4Me)_2(3,3,1\text{-PPBN})_2]$	19.6 (s)	8.0 (2 H, br s, aryl), 7.7 (2 H, d, $^{2}J_{HH}$ 8, aryl), 7.6 (2 H, br s, aryl), 7.4 (3 H, aryl), 6.9 (2 H, d, $^{2}J_{HH}$ 8, aryl), 2.9 (2 H, br s, CH), 2.3 (3 H, s, CH_3), 2.2–1.8 (12 H, br m, CH_2)	141.3 (s, aryl), 140.0 (s, aryl), 131.7 (s, aryl), 130.3 (d, $^{1}J_{PC}$ 11, PC), 128.5 (s, aryl), 127.3 (s, aryl), 126.3 (s, aryl), 125.3 (s, aryl), 28.6 (s), 26.3 (d, $^{1}J_{PC}$ 27.5, PCH), 21.2 (s), 20.0 (s)
11 $[Pd(O_2CMe)\{OP(O)(OH)Ph\}\text{-}(3,3,1\text{-PPBN})_2]$	33.0 (s), 21.3 (s)	12.2 (1 H, br s, OH), 8.2–7.1 (10 H, m, aryl), 3.0–0.9 (31 H, br m, CH, CH_2, CH_3)	131.5 (s, aryl), 130.9 (s, aryl), 129.3 (s, aryl), 127.4 (s, aryl), 127.3 (s, aryl), 31.9 (s), 29.2 (s), 28.9 (s), 27.6 (s), 22.6 (s), 21.2 (s), 20.2 (s), 14.0 (s, CH_3)
15 $[Pd(O_2CMe)_2(PhPC_4H_8)_2]$	31.6 (s)	7.6–7.36 (5 H, m, aryl), 2.3 (3 H, m, CH_3), 1.9–1.5 (8 H, m, CH_2)	177.2 (s, CO), 131.5 (s, aryl), 130.9 (s, aryl), 128.6 (s, aryl), 25.9 (s, CH_3), 23.6 (s)
16 $[PdCl_2(PhPC_4H_8)_2]$	32.4 (s)	7.8–7.5 (5 H, m, aryl), 2.6–2.4 (4 H, m, CH_2), 1.9 (2 H, m, CH_2), 1.7 (2 H, m, CH_2)	132.3 (s, aryl), 131.88 (d, $^{1}J_{PC}$ 10, PC), 131.2 (s, aryl), 129.2 (d, $^{3}J_{PC}$ 11, PCH_2CH_2), 29.4 (d, $^{1}J_{PC}$ 34, PCH_2), 26.5 (s)
17 $[Pd_2Cl_4(PhPC_4H_8)_2]$	42.7 (s)	7.8 (2 H, m, aryl), 7.5 (3 H, m, aryl), 2.7 (2 H, m, CH_2), 2.4 (2 H, m, CH_2), 2.0 (2 H, m, CH_2), 1.8 (2 H, m, CH_2)	*b*
18 $[Pd(O_3SCF_3)_2(PhPC_4H_8)_2]\cdot 2H_2O$	44.4 (s)	7.6–7.4 (5 H, m, aryl), 2.6 (2 H, m, CH_2), 2.0 (4 H, m, CH_2), 1.7 (2 H, m, CH_2)	132.5 (s, aryl), 131.3 (d, $^{1}J_{PC}$ 10.7, PC), 129.5 (d, $^{3}J_{PC}$ 10.6, PCCH*C*H), 127.5 (s, aryl), 119.9 (q, $^{1}J_{CF}$ 318, CF_3), 26.8 (d, $^{1}J_{PC}$ 35.7, PCH_2), 25.6 (s)
19 $[Pd(O_3SC_6H_4Me)_2(PhPC_4H_8)_2]$	40.6 (s)	7.7–7.0 (9 H, m, aryl), 2.8–1.6 (11 H, m, CH_2, CH_3)	140.6 (s, aryl), 40.1 (s, aryl), 131.7 (s, aryl), 30.6 (s, aryl), 128.9 (s, aryl), 128.3 (s, aryl), 126.5 (s, aryl), 25.1 (s, aryl), 27.4 (s), 23.5 (s), 21.2 (s)
20 $[Pd_2(O_2CMe)_2(O_3SC_6H_4Me)_2\text{-}(PhPC_4H_8)_2]$	42.8 (s)	7.7–7.0 (9 H, m, aryl), 2.8–1.6 (14 H, br m, CH_2, CH_3)	141.0 (s, aryl), 140.3 (s, aryl), 131.8 (s, aryl), 129.6 (s, aryl), 129.1 (s, aryl), 128.6 (s, aryl),126.5 (s, aryl), 26.7 (s), 26.3 (s), 25.7 (s), 21.3 (s)
21 $[Pd(4,2,1\text{-PPBN})_3]$[c]	32.4 (s)	7.30–6.98 (5 H, m, aryl), 2.76 (2 H,br s), 2.18 (2 H, br s), 1.97 (2 H, br s), 1.60 (4 H, br s), 1.41 (2 H, br s)	142.8 (s, aryl), 41.2 (s), 34.8 (s), 32.5 (s), 26.4 (s)

[a] δ in ppm, *J* in Hz, in $CDCl_3$ unless otherwise stated. [b] Poorly soluble. [c] In C_6D_6.

indication of the *cis* isomer by NMR spectroscopy. The bis(phosphine) complex **6** and unreacted starting material are observed (^{31}P NMR spectroscopy) if only 1 mol equivalent of 4,2,1-PPBN is added to $[PdCl_2(NCPh)_2]$.

9-Phenyl-9-phosphabicyclo[3.3.1]nonane complexes

The reactions of 3,3,1-PPBN with $[Pd(O_2CMe)_2]$, $[PdCl_2(NCPh)_2]$ and $PdCl_2$ all yield products similar to those obtained from reactions of 4,2,1-PPBN, *i.e.* $[Pd(O_2CMe)_2L_2]$ **7** and $[PdCl_2L_2]$ **8**. The ^{31}P-{^{1}H} NMR spectra exhibit sharp singlets (δ 4.3 and 5.7 respectively); the co-ordination chemical shifts are similar to those observed for the 4,2,1-PPBN complexes (for 3,3,1-PPBN ^{31}P δ −37). Spectroscopic data are collected in Table 1. The *trans* co-ordination of the chloro ligands in complex **8** is verified by the infrared spectrum, in which a single palladium–chloride stretching frequency is observed (340 cm^{-1}), in good agreement with the data for previously reported analogues.[13] Again, as for the behaviour of 4,2,1-PPBN with

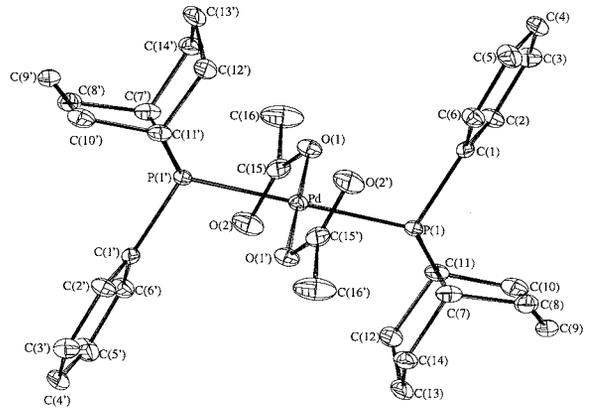


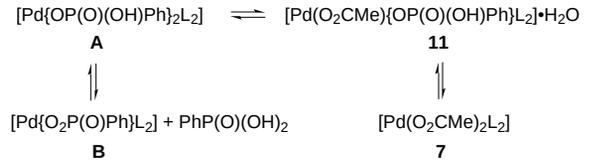
Fig. 1 The solid-state structure of $[Pd(O_2CMe)_2(3,3,1\text{-PPBN})_2]$ **7**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd–P(1), 2.3483(13), Pd–O(1) 2.064(13), P(1)–C(1) 1.849(4); P(1)–Pd–P(1′) 180.0, P(1)–Pd–O(1) 85.12(7), P(1)–Pd–O(1′) 94.88(7), O(1)–Pd–O(1′) 180.0, C(7)–P(1)–C(11) 96.7(2)

$[Pd(O_2CMe)_2]$, complex **8** and unreacted starting material result if a deficiency (*i.e.* less than 2 mol equivalents) of 3,3,1-PPBN is added to $[PdCl_2(PhCN)_2]$ as determined by ^{31}P NMR spectroscopy.

The crystal structure of complex **7** reveals that the solution and solid-state structures are consistent (Fig. 1). The co-ordination around the d^8 palladium centre is approximately square planar with *trans* phosphine groups. The structure is centrosymmetric and thus the PdO_2P_2 framework is exactly planar. The O(1′)–Pd–P(1) angle however, is slightly enlarged at 94.88(7)° and the O(1)–Pd–P(1) angle is compressed to 85.12(7)°. This distortion may be due to the proximity of the cyclic alkyl group of the phosphine ligand to the acetate C–O(2) fragment leading to steric hindrance and/or electronic repulsion. The Pd–P bond length [2.3483(13) Å] is slightly shorter than that previously reported for $[PdCl_2(Bu^t_2PPh)_2]$ [2.398(3) Å],[14] although it is similar to that observed in *trans*-$[PdI_2(PPhMe_2)_2]$ [2.333(2) Å].[15] It is also considerably longer than the bonds in the 1-phenylphospholane–acetato complex **15** [average 2.257 Å] (see below); similar variations in bond lengths between *cis* and *trans* isomers have been previously reported for palladium complexes.[16]

Reactions of trifluoromethanesulfonic acid and toluene-*p*-sulfonic acid with the acetate **7** also yield the analogous yellow complexes **9** and **10** respectively. Analytical data are consistent with the formulae $[Pd(O_3SCF_3)_2(3,3,1\text{-PPBN})_2]$ and $[Pd(O_3SC_6H_4Me)_2(3,3,1\text{-PPBN})_2]$ respectively. The solid toluenesulfonato complex **10** may be isolated from methanol, whereas with **4** under similar acidic conditions, the phosphonium salt of 4,2,1-PPBN is formed. The difference in behaviour between the 4,2,1-PPBN and 3,3,1-PPBN toluenesulfonato complexes may be related to relative differences in lability, as was observed for the phenylphosphonato complexes (see below). This is more likely due to differences in kinetic properties, rather than thermodynamic stabilities between complexes of the two phosphines.

Addition of 1 mol equivalent of phenylphosphonic acid to a methanolic solution of **7** led to the isolation of a yellow complex **11** shown by analysis to be $[Pd\{PhP(O)_2OH\}(O_2CMe)(3,3,1\text{-PPBN})_2]\cdot H_2O$ as opposed to $[Pd\{PhP(O)_2OH\}_2(4,2,1\text{-PPBN})_2]\cdot 2H_2O$ **3**, which is isolated from the corresponding reaction with 4,2,1-PPBN. The room-temperature ^{31}P-$\{^1H\}$ NMR spectrum exhibits two resonances (δ 33.0 and 21.3). Variable-temperature ^{31}P-$\{^1H\}$ NMR spectroscopy indicates that complex **11** is labile, at −64 °C, resonances assigned to **11** are observed (δ 35.1 and 23.4) as well as resonances at δ 48.0, 19.6, 13.8 and 4.5; the spectrum does not change significantly upon further cooling (−90 °C). The last two resonances are assigned to free phenylphosphonic acid and unreacted **7**



Scheme 2 Possible equilibria proposed for $[Pd(O_2CMe)OP(O)(OH)Ph\}(3,3,1\text{-PPBN})_2\cdot H_2O$ **14**, where L = 3,3,1-PPBN

respectively. The room-temperature ^1H NMR spectrum shows resonances due to co-ordinated ligands as well as a broad singlet corresponding to an acidic proton (δ 12.2) which supports the formation of **11**. The ambient temperature ^{13}C-$\{^1H\}$ NMR spectrum exhibits a resonance assigned to acetate methyl carbons (δ 14.0), other resonances observed are broad. Acetate is observed in the infrared spectrum [ν(CO) 1640 and 1306 cm^{-1}] as well as peaks corresponding to phenylphosphonate (1490, 1026, 752, 716 and 695 cm^{-1}).

Addition of 2 mol equivalents of phenylphosphonic acid to **7** in methanol gives rise to solutions which show two equally intense resonances in their ^{31}P-$\{^1H\}$ NMR spectra at δ 49.4 and 19.1. These are assigned to $[Pd\{OP(O)(OH)Ph\}_2(3,3,1\text{-PPBN})_2]$, the latter resonance corresponding to co-ordinated phenylphosphonic acid by comparison with the spectrum of **3**. The Pd-containing products isolated from these solutions were oily and pure materials could not be further identified. The data are consistent with equilibria such as those in Scheme 2 with the addition of 2 equivalents of phenylphosphonic acid to **7** in methanol or dichloromethane resulting initially in the formation of compound **11** followed by complex **A**. Other resonances observed at low temperature (see above) may be due to further equilibria such as that between complexes **A** and **B** which would also give rise to free phenylphosphonic acid. Resonances due to **A** are also observed when excess phenylphosphonic acid is added to **7**. Both 3,3,1-PPBN and 4,2,1-PPBN phenylphosphonate systems are labile, however the absence of any evidence for the monosubstituted 4,2,1-PPBN complex suggests that those complexes are more labile than the 3,3,1-PPBN analogues. The compound 4,2,1-PPBN is relatively more sterically demanding and we speculate that this difference in observed behaviour is an interesting and possibly significant consequence.

Addition of HCl to 3,3,1-PPBN followed by $AgBF_4$ led to formation of the phosphonium salt **12** which was isolated as white crystals. Analytical data confirm the formula $Ph(H)PC_8H_{14}BF_4$. A singlet was observed in the ^{13}P-$\{^1H\}$ NMR spectrum (δ 8) and a P–H stretch [ν(PH) 2362 cm^{-1}] was observed in the infrared spectrum. Attempts to form cationic Pd^{II} PPBN complexes by briefly heating an ethanolic solution of $PdCl_2$, AgO_3SCF_3 and 3,3,1-PPBN under reflux, followed by cooling, afforded a water soluble white salt in good yield and for which analytical data indicate the formula $[Ph(MeCHOH)PC_8H_{14}][O_3SCF_3]$, **13** ($^{31}P$, δ 2.4). The analogous 4,2,1-PPBN phosphonium salt **14** is formed in a similar manner. The formulation of **14** is confirmed by analytical data; a singlet is observed in the ^{31}P-$\{^1H\}$ NMR spectrum (δ 22.9) and the presence of trifluoromethanesulfonate is confirmed in the infrared spectra of both the 3,3,1 and 4,2,1 isomers (1223, 1159, 1033 and 639 cm^{-1}; 1230, 1159, 1026 and 639 cm^{-1} respectively). Reduction of $PdCl_2$ by ethanol to give ethanal and HCl could account for the formation of these quaternary salts by insertion of ethanal into a phosphonium P–H function, a black precipitate observed in both cases is consistent with the deposition of palladium. The structure of **13** was confirmed by X-ray crystallography (Fig. 2).

1-Phenylphospholane complexes

A reaction analogous to that for 4,2,1-PPBN occurs between 1-phenylphospholane and $[Pd(O_2CMe)_2]$ resulting in the formation of yellow crystals of complex **15**. Analytical data confirm the formulation $[Pd(O_2CMe)_2(PhPC_4H_8)_2]$, as do NMR data;

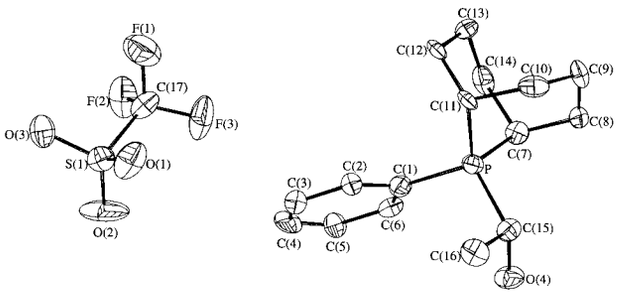


Fig. 2 The solid-state structure of 9-(1-hydroxyethyl)-9-phenyl-9-phosphoniabicyclo[3.3.1]nonane trifluoromethanesulfonate **13**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P–C(1) 1.782(6), P–C(7) 1.788(5), P–C(11) 1.801(5), P–C(15) 1.843(5), C(15)–C(16) 1.518(7); C(1)–P–C(7) 113.1, C(1)–P–C(11) 110.4(3), C(1)–P–C(15) 107.9(2), C(7)–P–C(15) 111.7(3), C(7)–P–C(11) 99.7(2)

cis phosphines are indicated in solution by ^{31}P-{^{1}H} NMR spectroscopy, in which the co-ordination chemical shift (Δ) is *ca*. 50 ppm. This value is high in comparison to the related *trans* PPBN complexes (Δ = 33.6 and 29.7 ppm for 4,2,1- and 3,3,1-PPBN respectively), higher values of Δ are expected for *cis* co-ordination of two phosphine ligands rather than for a *trans* arrangement.[17] The IR spectrum indicates unidentate acetate groups (1569 and 1306 cm^{-1}) and the molecular ion is observed in the mass spectrum (*m*/*z* 552, 1%). The crystal structure of **15** (Fig. 3) shows the solid and solution-state structures to be consistent. The co-ordination of the phosphine ligands around the metal centre is *cis* implying that 1-phenylphospholane is sterically less bulky than 3,3,1-PPBN. The geometry about the palladium atom is distorted square planar. The O(1)–Pd–O(3) bond angle is 86.2(2)° exhibiting a significant compression from the ideal square-planar geometry. This compression can be attributed to the steric effect of the two *cis* phosphines forcing the P(2)–Pd–P(1) angle to open [92.01(7)°], at the expense of the O(3)–Pd–O(1) angle. Less distortion from square-planar geometry is observed for complex **15** than for previously published *cis* palladium complexes.[15] Comparison with [PdCl$_2$(PPhMe$_2$)$_2$] is informative where a 2° compression of the Cl–Pd–Cl angle and an 8° opening of the P–Pd–P angle is observed[17] indicating that PPhMe$_2$ is somewhat bulkier than 1-phenylphospholane. The palladium–phosphorus bond lengths of 2.257(2) and 2.258(2) Å in **15** correlate closely to the value of 2.260(2) Å observed in [PdCl$_2$(PPhMe$_2$)$_2$]. The average Pd–O bond length [2.07(5) Å] is similar to that in complex **7** and slightly shorter than that observed for the related *trans* acetato methoxcarbonyl complex [Pd(O$_2$CMe)(CO$_2$Me)(PPh$_3$)$_3$] [2.116(3) Å].[18]

The reaction between 1-phenylphospholane and [PdCl$_2$(NCPh)$_2$] varies significantly from those previously discussed for 4,2,1- and 3,3,1-PPBN. Whereas the addition of 2 mol equivalents of phosphine to a toluene solution of the palladium(II) starting material yields the analogous white complex [PdCl$_2$(PhPC$_4$H$_8$)$_2$] **16**, in the presence of 1 mol equivalent of phosphine per Pd a yellow dimer **17** is isolated for which analytical data confirm the formulation [Pd$_2$Cl$_4$(PhPC$_4$H$_8$)$_2$]. A singlet is observed in the ^{31}P-{^{1}H} NMR spectrum due to co-ordinated phosphine, this chemical shift is *ca*. 10 ppm downfield from that observed for the monomer. Infrared spectroscopy indicates the presence of Pd–Cl bonds (300 cm^{-1}). Thus formation of monomer **16** or dimer **17** can be controlled by varying the palladium : phosphine ratio and **16** can be formed from the dimer by addition of phosphine, suggesting a relationship between the two as in equation (1). This behaviour is not observed with the

$$[Pd_2Cl_4L_2] + 2L \longrightarrow 2[PdCl_2L_2] \qquad (1)$$

chloride complexes of either PPBN isomer. For **16** two metal–chloride stretching frequencies are observed in the infrared

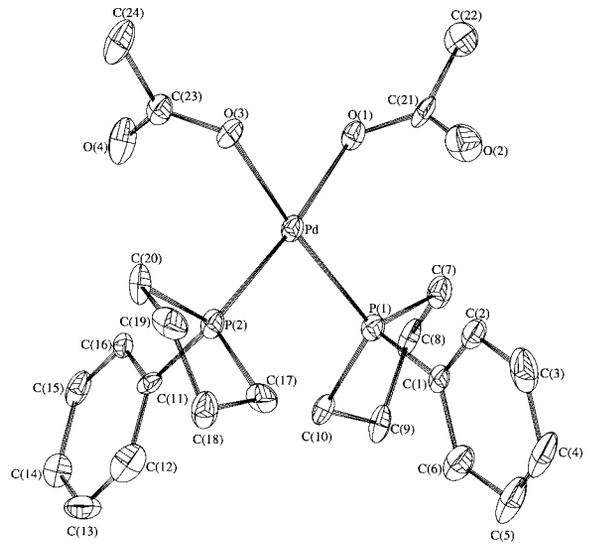


Fig. 3 The solid-state structure of [Pd(O$_2$CMe)$_2$(PhPC$_4$H$_8$)$_2$] **15**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd–P(1) 2.258(2), Pd–P(2) 2.257(2), Pd–O(1) 2.072(5), Pd–O(3) 2.068(4), P(1)–C(1) 1.811(7), P(2)–C(11) 1.822(7); P(1)–Pd–P(2) 92.01(7), P(1)–Pd–O(1) 91.76(13), P(1)–Pd–O(3) 173.7(2), P(2)–Pd–O(1) 173.4(2); P(2)–Pd–O(3) 90.61(14), O(1)–Pd–O(3) 86.2(2), C(7)–P(1)–C(10) 94.1(3), C(17)–P(2)–C(20) 94.1(3)

spectrum (280 and 260 cm^{-1}) indicating *cis* co-ordination of the phosphine ligands.[19]

The reactions between **15** and trifluoromethanesulfonic acid and toluene-*p*-sulfonic acid in toluene result in similar products to those observed from similar reactions of the 4,2,1-PPBN complex **1**, thus [Pd(O$_3$SCF$_3$)$_2$(C$_{10}$H$_{13}$P)$_2$] **18** and [Pd(O$_3$SC$_6$H$_4$Me)$_2$(C$_{10}$H$_{13}$P)$_2$] **19** may be isolated respectively. As with 3,3,1-PPBN, the reaction between the phosphine and toluene-*p*-sulfonic acid in methanol proceeds to yield complex **18** and not a phosphonium salt as for 4,2,1-PPBN. The addition of toluene-*p*-sulfonic acid and acetic acid to a toluene solution of **15** affords dichloromethane soluble green crystals of complex **20**, analytical data confirm the formulation as [Pd$_2$(O$_3$SC$_6$H$_4$Me)$_2$(O$_2$CMe)$_2$(PhPC$_4$H$_8$)$_2$]. Spectroscopic data are consistent with the isolation of **20**, the infrared spectrum exhibits two carboxylate carbonyl bands [ν(CO) 1580 and 1420 cm^{-1}], these absorbances and the absence of a strong absorbance at 540 cm^{-1}, are indicative of bridging acetate groups.[20,21]

Palladium(0) complexes

Although the bis(acetate) **1** may be prepared in toluene from which it may be precipitated, it is slightly soluble and dilute solutions can be slowly reduced to form a complex mixture of compounds (as evidenced by ^{31}P NMR spectroscopy), presumably by sacrificial oxidation of phosphine (*cf*. the reduction of **4**). The reduction occurs more rapidly in aqueous/alcoholic media as would be expected, **1** being reduced more rapidly in ethanol than in methanol to give the co-ordinatively unsaturated complex [Pd(4,2,1-PPBN)$_3$] **21**. All spectroscopic data support the formation of compound **21**, with a sharp singlet observed in the ^{31}P-{^{1}H} NMR spectrum (δ 32.4) showing an upfield shift of *ca*. 5 ppm from palladium(II) complexes. The infrared spectrum exhibits stretching frequencies for the phosphine, if exposed to air for *ca*. 1 h, bands assigned to phosphine oxide [ν(PO) 1180 cm^{-1}] and hydroxyl groups (1660, 1628 cm^{-1}) are subsequently observed. Compound **21** could also be prepared directly from potassium tetrachloropalladium(II) in the presence of potassium hydroxide, although with 2 mol equivalents of KOH it was found that the reduction was sometimes incomplete, resulting in the isolation of a mixture of products including **6** identified by ^{31}P-{^{1}H} NMR spectroscopy. Further reduction to form **21** was achieved by adding a large

excess of KOH under continued reflux, in which event the compound was obtained and recrystallised in good yield as a hydrate. Analytical data for these crystals support the formulation $[Pd(4,2,1\text{-PPBN})_3]\cdot 3H_2O$. Attempts to prepare **21** *via* the reduction of the dimer $[Pd_2Cl_2(\eta^3\text{-}C_4H_7)_2]$[22] were unsuccessful. A mixture of complexes was formed in which **6** predominates, again identified by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy.

A variable-temperature $^{31}P\text{-}\{^1H\}$ NMR spectroscopic study of **21** shows no phosphine dissociation in solution over a wide temperature range (30 to −90 °C) suggesting either no or extremely rapid ligand exchange. It has been shown for $[Pd(PPh_3)_4]$ that dissociation into the tris-complex readily occurs in solution, however further dissociation to discrete complexes {*e.g.* $[Pd(PPh_3)_2]$} is contentious.[23,24] A difference between the two PPBN isomers (3,3,1- and 4,2,1-PPBN) could be their ability to dissociate in solution, which in turn could affect the catalytic activity. The extent of ligand dissociation is believed to be dependent on the steric bulk and basicity of the co-ordinating phosphines. Tertiary phosphines with smaller cone angles are more likely to support higher co-ordination numbers than more bulky ligands (*e.g.* PMe_3, $\theta = 118°$ *versus* PPh_3, $\theta = 145°$)[25] and the more basic PMe_3 may also be expected to be more capable of stabilising higher oxidation states than the aryl phosphines. The cone angle of 4,2,1-PPBN ($\theta = 120°$) compares closely to that for trimethylphosphine, on which basis a stable tetrahedral $[Pd^0(4,2,1\text{-PPBN})_4]$ complex might be expected. However, cone angles do not take into account the ability of ligand substituents to interlock (in a cog-wheel fashion). For PMe_3, this opportunity is clearly available whereas for the PPBN ligands, the cycloalkyl substituent restricts this feature causing a reduced ability of the ligands to pack efficiently. We presume that this feature disallows the formation of tetrakis palladium(0) complexes with the PPBN ligands.

The reactions of compound **21** with toluene-*p*-sulfonic acid and phenylphosphonic acid in ethanol were investigated. In both cases no reactions were observed at room temperature. Warming the ethanolic phenylphosphonic reaction mixture (55–60 °C) for 18 h resulted in decomposition of **21** to phosphine oxide and palladium black. The formation of palladium hydride compounds, by oxidative addition of acids to tris- or tetrakis-(phosphine)palladium(0) complexes, has previously been reported.[26,27] In these cases the hydride compounds formed were reported to be unstable with decomposition to palladium black occurring rapidly, they were also prepared using fluorinated acids whose p*K*a values are significantly lower than the acids employed in our study {*e.g.* p*K*a $(CF_3CO_2H) = 0.6$ and p*K*a $[PhP(O)(OH)_2] = 10.5$}.[28,29] If hydride species are being formed in the reaction of **21** with weak acids, we have been unable to isolate them.

The solid-state structure of **21** (Fig. 4) is consistent with the analytical and spectroscopic data. Despite an increasing number of reports of palladium(0) complexes in the literature, this is the first reported structure of one containing tris(aryldialkylphosphine). The Pd and three P atoms are virtually coplanar, the maximum deviation from the least-squares plane is 0.045(2)°. There is some distortion from trigonal-planar geometry with a compression of the P(1)–Pd–P(2) bond angle by 7° to 113.44(6)° whilst the P(1)–Pd–P(3) angle is slightly increased at 128.05(7)°. In the structural determination of $[Pt(PPh_3)_3]$ a compression of 5° is observed in one of the P–Pt–P angles which was attributed to the packing of two of the phenyl rings.[30] In **21** this effect may be explained by inter-ligand interactions $[H(13_A)\cdots H(42_A)\ 2.50(2)$ Å]. The palladium–phosphorus bond lengths are all similar (*ca.* 2.29 Å). A comparison of the structures of the Pd^{II}–3,3,1-PPBN complex **7** with the Pd^0–4,2,1-PPBN complex **21** is of interest in so far as it shows that the average C–P–C angles to the bridgehead carbons vary significantly [96.7(2) *vs.* 90.3(3)°], in the phosphonium salt **13** (derived from 3,3,1-PPBN) this angle is larger at 99.7(2)°. In the relatively sterically unrestricted phospholane complex **15** the

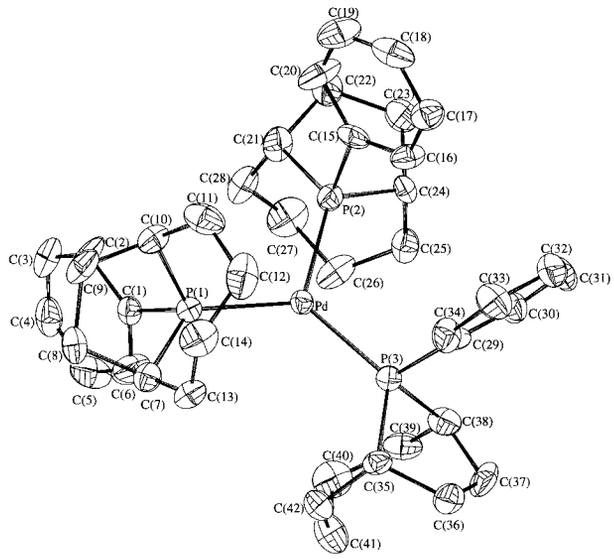


Fig. 4 The solid-state structure of $[Pd(4,2,1\text{-PPBN})_3]$ **21**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd–P(1) 2.297(2), Pd–P(2) 2.292(2), Pd–P(3) 2.284(2), P(1)–C(1) 1.851(4), P(2)–C(15) 1.853(4), P(3)–C(29) 1.857(4); P(1)–Pd–P(2) 113.44(6), P(1)–Pd–P(3) 128.05(7), P(2)–Pd–P(3) 117.87(6), C(7)–P(1)–C(10) 91.1(3), C(21)–P(1)–C(24) 90.1(3), C(35)–P(1)–C(38) 89.6(3)

equivalent angle between phosphorus and the heterocyclic α-carbons is 94.1(3)°. It is unclear how this distortion may differentially influence the behaviour of PPBN complexes; this feature is under further investigation.

When complex **7** is dissolved in toluene, no reduction is observed over prolonged time periods as confirmed by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. In alcoholic media, however, the palladium(II) complex is reduced, initially to a single phosphorus-containing species (causing a deepening of the solution colour to red), and subsequently to a mixture of compounds (indicated by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy). It is postulated that the initial product, which is stable for several days at room temperature in methanol, is a palladium(I) dimeric species (as has been observed for pyridyl phosphines[31]) and is an intermediate in the formation of palladium(0) compounds. Attempts at further characterisation have failed although the infrared spectrum indicates the presence of a co-ordinated acetate anion [ν(CO) 1630 and 1305 cm^{-1}]. In comparison with compounds containing 4,2,1-PPBN, $^{31}P\text{-}\{^1H\}$ NMR spectroscopic studies indicate that the reduction of **7** in methanol proceeds at a considerably slower rate. This could have major implications for the carbonylation catalysis in which 4,2,1-PPBN complexes exhibit greater catalytic activity than those of 3,3,1-PPBN, and it is postulated that the active catalyst is a palladium(0) entity.

It has previously been shown that the reduction of bis(acetato)bis(phosphine)palladium(II) complexes to palladium(0) entities is dependent upon steric and electronic effects.[32] Whilst the two isomeric forms of PPBN may be expected to be electronically similar, sterically there may be some variations between the two due to ring strain within the molecules; this effect may be important in explaining the different reduction rates observed for the 3,3,1- and 4,2,1-PPBN isomers. At present it is not clear whether electronic differences between the two PPBN isomers are significant although recent calculations indicate that they have higher gas-phase basicities as well as higher P–C (phenyl) bond elipticities (implying greater P–C multiple bond character) than either the more simple dialkylphenylphosphine analogue, PMe_2Ph or triphenylphosphine. This effect appears to be caused by the steric influence of the bicyclic ring structure restricting the conformation of the phenyl substituent.[33] These properties are under further investigation.

Attempts to isolate [Pd^0(3,3,1-PPBN)$_3$] from palladium chloro complexes *via* a number of routes have failed,[21,34] resulting in the isolation of **8**, again highlighting the inherent relative stability of the palladium(II) complexes of 3,3,1-PPBN in comparison to the palladium(0) oxidation state.

Conclusion

A range of palladium(II) complexes has been successfully isolated and characterised for the three tertiary phosphines, 3,3,1-PPBN, 4,2,1-PPBN and 1-phenylphospholane, including those involving the weak acids, toluene-*p*-sulfonic and phenylphosphonic acid, which both support the catalytic carbonylation of propyne.

The reduction of [$Pd^{II}(O_2CMe)_2$(4,2,1-PPBN)$_2$] **1** to [Pd^0(4,2,1-PPBN)$_3$] in methanolic solutions proceeds significantly faster than the corresponding reduction of the 3,3,1 analogue **7** which may have important implications in catalytic reactions. Systematic structural comparisons of PPBN complexes indicate that there may be distortions in 4,2,1-PPBN complexes that are less severe in the 3,3,1-PPBN analogues.

Experimental

All syntheses described were carried out under strictly anaerobic conditions using a Halco Engineering 140 FF glove box, or using standard vacuum-line techniques. All solvents were refluxed under N_2 over sodium–benzophenone and were distilled immediately prior to use with the exception of ethanol, methanol and dichloromethane which were dried over CaH_2 and toluene which was refluxed over sodium. Light petroleum had a b.p. range 40–60 °C. Recrystallisation of air stable compounds was by conventional techniques in air.

The compounds 1-phenylphospholane and both 9-phenyl-9-phosphabicyclononane isomers were prepared according to literature preparations.[8,35] Unless otherwise stated, ^{31}P and ^{13}C NMR spectroscopic data were collected on a JEOL FX90Q spectrometer (^{31}P at 36.23 and ^{13}C at 22.49 MHz), or on a Bruker WM360 spectrometer (^{13}C at 90.56 MHz). Proton NMR spectroscopic data were collected on a Bruker WM360 spectrometer (^{1}H at 360.13 MHz) or a Bruker DPX400 spectrometer (^{1}H at 400 MHz). Spectra were referenced externally to 85% H_3PO_4 (^{31}P); $SiMe_4$ or internally to residual protic impurity (C_6D_6, δ 7.15; $CDCl_3$, δ 7.27) (^{1}H) or solvent carbons (C_6D_6, δ 128.0; $CDCl_3$, δ 76.9) (^{13}C). Infrared data were obtained on a Perkin-Elmer 577 Grating Infrared spectrophotometer or a Nicolet 510 FT-IR in conjunction with a Nicolet 620 processor. All elemental analyses were performed on a Perkin-Elmer 240C elemental analyser. Mass spectrometry data were collected on a Platform II Fisons VG machine. Melting points were measured in capillaries and are uncorrected. Palladium(II) acetate, trifluoromethanesulfonic acid, phenylphosphonic acid, toluene-*p*-sulfonic acid, silver trifluoromethanesulfonate, silver tetrafluoroborate and potassium tetrachloropalladium(IV) were all used as supplied (Aldrich). Bis(benzonitrile)dichloropalladium(II) was prepared as previously described.[36]

Syntheses

Bis(acetato)bis(9-phenyl-9-phosphabicyclo[4.2.1]nonane)palladium(II) 1. The compound [$Pd(O_2CMe)_2$] (0.1 g, 0.45 mmol) was dissolved in toluene (30 cm^3), addition of 4,2,1-PPBN (0.2 g, 0.9 mmol) caused the solution to darken from orange to brown. An orange precipitate formed after 12 h at room temperature. The crude complex was isolated by filtration and orange crystals were obtained from chloroform (151 mg, 51%), m.p. 160 °C (decomp.) (Found: C, 57.7; H, 6.9. $C_{32}H_{44}O_2P_2Pd$ requires C, 58.2; H, 6.8%). IR (Nujol) $\tilde{\nu}_{max}$/cm^{-1}: 1320w, 1260w, 1210w, 1180w, 1120w, 1020w, 920w, 905w, 870w, 800s, 740m, 723m, 700s, 620m, 580m, 510s, 495w, 465w, 420w and 370w (4,2,1-PPBN), 1623 (C=O) and 1307m (C–O). Electron impact (EI) mass spectrum: *m*/*z* 218 (84%, L^+), 201 (40, $[L - CH_2]^+$), 188 {22, $[L - (CH_2)_2]^+$}, 174 {28, $[L - (CH_2)_3]^+$}, 160 {20, $[L - (CH_2)_4]^+$}, 108 (57, $[M - PhP]^+$) and 77 (100, Ph^+).

Bis(trifluoromethanesulfonato)-9-phenyl-9-phosphabicyclo-[4.2.1]nonanepalladium(II) dihydrate 2. Trifluoromethanesulfonic acid (0.3 cm^3, 0.30 mmol, 1 mol dm^{-3} solution) was added to a pale orange solution of [$Pd(O_2CMe)_2$(4,2,1-PPBN)$_2$] (100 mg, 0.15 mmol) in toluene (30 cm^3). A deep orange solution formed which became cloudy after stirring (1 h). A yellow solid **2** (93 mg, 85%) was isolated from the orange supernatant after 20 h, m.p. 214 °C (Found: C, 41.3; H, 4.9. $C_{30}H_{38}F_6O_6P_2PdS_2\cdot 2H_2O$ requires C, 41.1; H, 4.7%). IR (KBr) $\tilde{\nu}_{max}$/cm^{-1}: as for complex **1** and 1258s [$\nu_{asym}(CF_3)$], 1173m [$\nu_{sym}(SO_3)$] and 1040, 1045m [$\nu_{asym}(SO_3)$] and 639m [ν(CS)].

Bis(9-phenyl-9-phosphabicyclo[4.2.1]nonane)bis(phenylphosphonato)palladium(II) dihydrate 3. Phenylphosphonic acid (24 mg, 0.51 mmol) was added to an orange solution of **1** (100 mg, 0.15 mmol) in methanol (20 cm^3). After 20 h the solvent was removed *in vacuo* and the solid recrystallised from CH_2Cl_2–octane (1:3, 20 cm^3) resulting in pale brown crystals of **3** (93 mg, 69%) (Found: C, 54.0; H, 6.1. $C_{40}H_{50}O_6P_4Pd\cdot 2H_2O$ requires C, 53.8; H, 5.8%). IR (KBr) $\tilde{\nu}_{max}$/cm^{-1}: as for **1** and 1131s, 927m, 759s, 695s, 555m and 527s [$PhP(O)(OH)_2$]. EI mass spectrum: *m*/*z* 697 (1%, $M^+ - C_6H_5PO_3H$), 324 (1, $[M - LC_{12}H_{10}P_2O_6H_2]^+$), 218 (80, L^+), 156 (3, $[M - L_2C_{12}H_{10}P_2O_3]^+$), 109 {66, $[M - Pd(C_6H_5PO_6H_2L_2]^+$}, 107 {57, $[M - (C_6H_5PO_3H)_2L_2]^+$} and 77{78, $[M - Pd(C_6H_5P_2O_6H)L_2]^+$}.

Bis(9-phenyl-9-phosphabicyclo[4.2.1]nonane)bis(tolyl-*p*-sulfonato)palladium(II) 4. Toluene-*p*-sulfonic acid (57 mg, 0.3 mmol) was added to a yellow solution of [$Pd(O_2CMe)_2$(4,2,1-PPBN)$_2$] (100 mg, 0.15 mmol) in toluene (30 cm^3), after 1 h the solution became cloudy. A yellow air stable solid **4** (113 mg, 82%) was isolated by filtration and dried *in vacuo*, m.p. 210 °C (Found: C, 55.3; H, 5.9. $C_{42}H_{52}O_6P_2PdS_2$ requires C, 54.8; H, 5.7%). IR (Nujol) $\tilde{\nu}_{max}$/cm^{-1}: as for **1** and 1258m [$\nu_{asym}(SO_3)$] and 1026m [$\nu_{sym}(SO_3)$]. EI mass spectrum: *m*/*z* 218 (7%, $[C_{14}H_{19}P]^+$) and 217 (35, $[C_{14}H_{19}P - H]^+$).

9-Hydrido-9-phenyl-9-phosphoniabicyclo[4.2.1]nonane tetrafluoroborate 5. Hydrochloric acid (5 cm^3) was added to a solution of 4,2,1-PPBN (0.25 g, 1.15 mmol) in ethanol (10 cm^3). After 15 h the solvents were removed *in vacuo* yielding the white chloride salt of **7** which was redissolved in ethanol (10 cm^3). Addition of an aliquot of the chloride salt solution (2.5 cm^3) to a solution of $AgBF_4$ (0.26 g, 1.38 mmol) in tetrahydrofuran (thf) (20 cm^3) resulted in a white precipitate of AgCl being formed which was removed by filtration. Removal of the solvent *in vacuo* followed by dissolution in dichloromethane and filtration removed any unreacted $AgBF_4$. Diethyl ether (60 cm^3) was added to the clear filtrate. The crude product **5** was formed after 15 h at room temperature as a white precipitate. After filtration the salt was recrystallised from thf as white prisms (179 mg, 51%) (Found: C, 54.8; H, 6.7. $C_{14}H_{20}BF_4P$ requires C, 54.9; H, 6.5%). IR (Nujol) $\tilde{\nu}_{max}$/cm^{-1}: 2360w, (P–H), 1320w, 1260w, 1210w, 1180w, 1120w, 1020w, 920w, 905w, 870w, 800s, 740m, 723m, 700s, 620m, 580m, 510s, 495w, 465w, 420w and 370w (4,2,1-PPBN). NMR, ^{31}P-{^{1}H}: δ 20.0 (s).

Dichlorobis(9-phenyl-9-phosphabicyclo[4.2.1]nonane)-palladium(II) 6. To an orange suspension of [$PdCl_2(CNPh)_2$] (0.2 g, 0.52 mmol) in toluene (30 cm^3) 4,2,1-PPBN (0.28 g, 1.3 mmol) was added *via* a syringe, resulting in an immediate change to yellow. Concentration of the yellow solution to *ca*. 20

cm^3 and cooling to −20 °C (12 h) afforded crude complex **6** in moderate yield. Recrystallisation from dichloromethane yielded yellow crystals of **6** (217 mg, 68%), m.p. 230 °C (decomp.) (Found: C, 55.1; H, 6.3. $C_{28}H_{38}Cl_2P_2Pd$ requires C, 54.8; H, 6.2%). IR (Nujol) $\tilde{\nu}_{max}/cm^{-1}$: as for **1** and 350s (PdCl). EI mass spectrum: *m*/*z* 395 (1%, $[M - C_{14}H_{19}P]^+$), 361 (1, $[M - C_{14}H_{19}PCl]^+$), 325 (3, $[M - C_{14}H_{19}PCl_2]$), 218 (5, $[C_{14}H_{19}P]^+$), 142 {6, $[M - (C_{14}H_{19}P)_2Cl]^+$} and 72 (3, Cl_2).

Bis(acetato)bis(9-phenyl-9-phosphabicyclo[3.3.1]nonane)-palladium(II) 7. A procedure similar to that for the preparation of **1** was followed. After stirring at room temperature for 16 h a yellow precipitate formed which was isolated by filtration. Recrystallisation from chloroform afforded yellow needles of **7** (190 mg, 64%), m.p. 160 °C (decomp.) (Found: C, 58.0; H,6.7. $C_{32}H_{44}O_4P_2Pd$ requires C, 58.2; H, 6.7%). IR (Nujol) $\tilde{\nu}_{max}/cm^{-1}$: 1320w, 1250w, 1205w, 1160w, 1105m, 1080w, 1015w, 905s, 860w, 800w, 775w, 745m, 725m, 695m, 630w, 620w, 540m, 505w, 495w, 460w, 420w, 360w and 330w (3,3,1-PPBN) and 1623m (C=O) and 1307m (C−O). EI mass spectrum: *m*/*z* 218 (8%, $[C_{14}H_{19}P - H]^+$), 109 (54, $[PhP]^+$) and 77 (90, Ph^+).

Dichlorobis(9-phenyl-9-phosphabicyclo[3.3.1]nonane)-palladium(II) 8. A procedure similar to that for the preparation of **5** was followed. After 15 min stirring the solution became cloudy. A yellow solid **8** (131 mg, 82%) was isolated by filtration, m.p. 160 °C (decomp.) (Found: C, 54.6; H, 6.4. $C_{28}H_{38}Cl_2P_2Pd$ requires C, 54.8; H, 6.2%). IR (Nujol) $\tilde{\nu}_{max}/cm^{-1}$: as for **7** and 350s (PdCl). EI mass spectrum: *m*/*z* 614 (0.4%, M^+), 362 (7, $[M - ClC_{14}H_{19}P]^+$), 326 {1, $[M - Cl(C_{14}H_{19}P)_2]^+$}, 218 (20, $C_{14}H_{18}P$), 176 {13, $[M - (C_{14}H_{19}P)_2 2H^+]$} and 107 {41, $[M - Cl_2(C_{14}H_{19}P)_2]^+$}.

Bis(trifluoromethanesulfonato)bis(9-phenyl-9-phosphabicyclo-[3.3.1]nonane)palladium(II) 9. A procedure similar to that for the preparation of **2** was followed. A yellow solid **9** (83 mg, 89%) was isolated by filtration after 20 h, m.p. 215 °C (Found: C, 42.6; H, 4.3. $C_{30}H_{38}F_6O_6P_2PdS_2$ requires 42.9: H, 4.5%). IR (KBr) $\tilde{\nu}_{max}/cm^{-1}$: as for **7** and 1265s [$\nu_{asym}(CF_3)$], 1230m [$\nu_{sym}(CF_3)$], 1195m [$\nu_{sym}(SO_3)$], 1033s [$\nu_{asym}(SO_3)$] and 639m [ν(CS)]. EI mass spectrum: *m*/*z* 839 (0.4%, M^+), 405 {2, $[M - (C_{14}H_{19}P)_2]^+$} and 218 (3, $[C_{14}H_{19}P]^+$).

Bis(9-phenyl-9-phosphabicyclo[3.3.1]nonane)bis(tolyl-*p*-sulfonato)palladium(II) 10. A procedure similar to that for the preparation of **4** was followed. After stirring for 18 h the yellow solid **10** (106 mg, 77%) was isolated by filtration, m.p. 249 °C (Found: C, 55.6; H, 6.2. $C_{42}H_{52}O_6P_2PdS_2$ requires C, 54.8; H, 5.7%). IR (KBr) $\tilde{\nu}_{max}/cm^{-1}$: as for **7** and 1047m [$\nu_{asym}(SO_3)$]. EI mass spectrum: *m*/*z* 884 (20%, $[M - H]^+$) and 449 {20, $[M - (C_{14}H_{19}P)_2]^+$}.

Acetatobis(9-phenyl-9-phosphabicyclo[3.3.1]nonane)-(phenylphosphonato)palladium(II) monohydrate 11. Addition of phenylphosphonic acid (24 mg, 0.15 mmol) to a solution of **8** (100 mg, 0.15 mmol) in methanol (20 cm^3) resulted in the formation of an orange solution. After 4 d the solution was filtered to remove palladium black and the solvent evaporated. Recrystallisation from CH_2Cl_2–octane (1:4, 25 cm^3) yielded a pale orange solid **11** (68 mg, 58%), m.p. 180 °C (Found: C, 55.4; H, 6.2. $C_{36}H_{47}O_5P_3Pd \cdot H_2O$ requires C, 55.7; H, 6.3%). IR (KBr) $\tilde{\nu}_{max}/cm^{-1}$: as for **7** and 1490m, 1026m, 752m, 716m and 695m [OP(O)(OH)Ph].

9-Hydrido-9-phenyl-9-phosphoniabicyclo[3.3.1]nonane tetrafluoroborate 12. A procedure similar to that for the preparation of **5** was followed. Recrystallisation from thf yielded **13** (215 mg, 61%) as clear needles, m.p. 157 °C (Found: C, 54.9; H, 6.5. $C_{14}H_{20}BF_4P$ requires C, 54.9; H, 6.5%). IR (Nujol) $\tilde{\nu}_{max}/cm^{-1}$: as for **7** and 2362m (PH). NMR, ^1H: δ 7.5 (5 H, m, aryl), 3.0 (1 H, d, $^1J_{PH}$ 401.9, PH), 2.7 (2 H, s, CH_2), 2.4 (3 H, s, CH_2, CH), 2.0 (4 H, m, CH_2), 1.85 (3 H, m, CH_2, CH), 1.3 (2 H, s, CH_2); ^{13}C-{^1H}: δ 130.4 (s, aryl),130.3 (s, aryl), 129.7 (s, aryl), 129.5 (d, $^1J_{PC}$ 9, PC), 32.0 (d, $^1J_{PC}$ 7, PCH), 25.2 (d, $^1J_{PC}$ 6 Hz, PCH), 25.0 (s), 22.1 (s), 21.3 (s), 21.2 (s); ^{31}P-{^1H}: δ 8.0 (s).

9-(1-Hydroxyethyl)-9-phenyl-9-phosphoniabicyclo[3.3.1]-nonanetrifluoromethanesulfonate 13. The compound AgO_3SCF_3 (0.3 g, 1.14 mmol) was added to a warmed (80 °C) suspension of $PdCl_2$ (0.1 g, 0.56 mmol) in ethanol (70 cm^3). After stirring in the absence of light for several hours a black suspension formed which was filtered. The phosphine 3,3,1-PPBN (0.25 g, 1.14 mmol) was added *via* a syringe to the pale brown filtrate which immediately changed to yellow. White air-stable crystals of **13** (489 mg, 70% based on 3,3,1-PPBN) were isolated after concentration and cooling (−20 °C, 1 h), m.p. 215 °C (subl.) (Found: C, 49.5; H, 5.9. $C_{17}H_{24}F_3O_4PS$ requires C, 49.5; H, 5.8%). IR (Nujol) $\tilde{\nu}_{max}/cm^{-1}$: as for **7** and 1715m, 1223w [$\nu_{sym}(CF_3)$], 1159s [$\nu_{sym}(SO_3)$], 1033s [$\nu_{asym}(SO_3)$] and 639s [ν(CS)]. NMR, ^1H: δ 7.6 (5 H, m, aryl), 5.4 (1 H, m, OH), 3.3 (1 H, m, *H*COH), 2.5 (2 H, m, CH), 1.6 (6 H, m, CH_2), 1.4 (6 H, m, CH_2), 1.3 (3 H, m, CH_3); ^{31}P-{^1H}: δ 2.4 (s).

9-(1-Hydroxyethyl)-9-phenyl-9-phosphoniabicyclo[4.2.1]-nonane trifluoromethanesulfonate 14. A procedure similar to that for the preparation of **13** was followed. Compound **14** (291 mg, 62%) was obtained from 4,2,1-PPBN (0.25 g, 1.14 mmol) and recrystallised as air-stable white prisms and needles, m.p. 110 °C (Found: C, 49.2; H, 6.0. $C_{17}H_{24}F_3O_4PS$ requires C, 49.5; H, 5.8%). IR (Nujol) $\tilde{\nu}_{max}/cm^{-1}$: as for **1** and 2362m (PH), 1265s [$\nu_{sym}(CF_3)$], 1230m [$\nu_{sym}(CF_3)$], 1159m [$\nu_{sym}(SO_3)$], 1026s [ν_{asym}-(SO_3)] and 639m [ν(CS)]. NMR, ^{31}P-{^1H}: δ 22.9 (s).

Bis(acetato)bis(1-phenylphospholane)palladium(II) 15. A procedure similar to the preparation of **1** was followed. Upon removing the solvents *in vacuo* a white solid formed in poor yield. The crude product **15** was recrystallised from chloroform yielding clear prisms (119 mg, 48%), m.p. 160 °C (decomp.) (Found: C, 48.1; H, 5.0. $C_{24}H_{32}O_4P_2Pd$ requires C, 48.5; H, 4.8%). IR (Nujol) $\tilde{\nu}_{max}/cm^{-1}$: 1315m, 1281m, 1180w, 1160w, 1120m, 1065m,1039w, 855m, 805m, 760m, 735m, 705s, 695s, 650s, 562s, 515s, 495w, 410m (1-phenylphospholane), 1569w (C=O) and 1306w (C=O). EI mass spectrum: *m*/*z* 552 (1%, M^+) and 164 (40, $[C_{10}H_{13}P]^+$).

Dichlorobis(1-phenylphospholane)palladium(II) 16. The compound $[PdCl_2(NCPh)_2]$ (0.1 g, 0.26 mmol) was dissolved in toluene (30 cm^3). After filtration the solution was cooled to −78 °C, 1-phenylphospholane (0.09 g, 0.52 mmol) was added slowly *via* syringe and the reaction mixture allowed to warm to room temperature with stirring. A white precipitate formed which was isolated by filtration then washed with light petroleum (10 cm^3). Recrystallisation from dichloromethane–light petroleum yielded **16** (91 mg, 69%) as clear crystals, m.p. 176–180 °C (Found: C, 47.6; H, 5.4. $C_{20}H_{26}Cl_2P_2Pd$ requires C, 47.5; H, 5.2%). IR (Nujol) $\tilde{\nu}_{max}/cm^{-1}$: as for **15** and 280w and 260w (PdCl). EI mass spectrum: *m*/*z* 506 (5%, M^+), 164 (14, $[C_{10}H_{13}P]^+$) and 77 (52, Ph^+).

Tetrachlorobis(1-phenylphospholane)dipalladium(II) 17. Addition of 1-phenylphospholane (0.045 g, 0.26 mmol) to a cooled (−78 °C) solution of $[PdCl_2(NCPh)_2]$ (0.1 g, 0.26 mmol) in toluene (30 cm^3) afforded an orange precipitate. After filtration the orange solid was washed with light petroleum (10 cm^3), and **17** (103 mg, 58%) was recrystallised from dichloromethane–light petroleum as orange crystals, m.p. 84 °C (Found: C, 35.4; H, 4.3. $C_{20}H_{26}Cl_4P_2Pd_2$ requires C, 35.2; H, 3.8%). IR (Nujol) $\tilde{\nu}_{max}/cm^{-1}$: as for **15** and 300w (PdCl).

Table 2 Crystal data and structure refinement for compounds **7**, **13**, **15** and **21**

	7	**13**	**15**	**21**
Empirical formula	$C_{32}H_{44}O_4P_2Pd$	$C_{17}H_{24}F_3O_4PS$	$C_{24}H_{32}O_4P_2Pd$	$C_{42}H_{57}P_3Pd$
M	899.75	412.39	552.84	761.19
T/K	120(2)	120(2)	150(2)	150(2)
Crystal system	Monoclinic	Orthorhombic	Triclinic	Orthorhombic
Space group	$P2_2/n$	$Pcan$	$P\bar{1}$	$P2_12_12$
a/Å	9.832(4)	14.052(4)	9.199(2)	18.061(2)
b/Å	18.241(6)	10.705(6)	10.103(2)	18.707(2)
c/Å	12.123(2)	25.026(9)	14.0760(9)	10.993(2)
α/°			95.734(8)	
β/°	112.51(3)		107.221(8)	
γ/°			104.469(10)	
U/Å^3	2008.6(11)	3765(3)	1188.3(3)	3714.3(8)
Z	4	8	2	4
D_c/Mg m^{-3}	1.488	1.455	1.545	1.361
μ/mm^{-1}	0.976	0.305	0.944	0.658
F(000)	920	1728	568	1600
Crystal size/mm	0.18 × 0.18 × 0.215	0.145 × 0.2 × 0.11	0.14 × 0.14 × 0.21	0.45 × 0.07 × 0.145
θ range/°	2.28–24.88	1.63–22.77	2.12–24.97	1.85–25.02
Index ranges	$-10 \leqslant h \leqslant 8$	$-14 \leqslant h \leqslant 13$	$-10 \leqslant h \leqslant 10$	$-19 \leqslant h \leqslant 20$
	$-19 \leqslant k \leqslant 14$	$-10 \leqslant k \leqslant 7$	$-9 \leqslant k \leqslant 11$	$-2 \leqslant k \leqslant 14$
	$-14 \leqslant l \leqslant 14$	$-25 \leqslant l \leqslant 25$	$-14 \leqslant l \leqslant 14$	$-12 \leqslant l \leqslant 11$
Reflections collected	7503	9654	4148	15 833
Independent reflections	2869	2250	3174	5653
R_{int}	0.055	0.0927	0.0534	0.1181
Absorption correction factors	0.917/1.806	0.816/1.248	0.898/1.074	0.831/1.318
Data/parameters	2866/238	2245/230	3169/282	5653/379
Goodness of fit on F^2	0.939	0.727	0.76	0.596
Final R indices [$I > 2\sigma(I)$] $R1$, $wR2$	0.0361, 0.0848	0.0456, 0.0781	0.0432, 0.084	0.0379, 0.0687
	(2189 reflections)	(1481 reflections)	(2109 reflections)	(3274 reflections)
R indices (all data) $R1$, $wR2$	0.0538, 0.1083	0.1320, 0.0916	0.0681, 0.0924	0.0775, 0.0770
ρ max, min/e Å^{-3}	1.076, −0.446	0.354, −0.397	0.646, −0.533	0.693, −0.825

Bis(trifluoromethanesulfonato)bis(1-phenylphospholane)-palladium(II) dihydrate 18. A procedure similar to that for the preparation of **2** was followed. The solid immediately dissolved and a deep orange solution formed which became cloudy after 10 min. A white solid **18** (86 mg, 62%) was isolated by filtration after 20 h and triturated with diethyl ether (50 cm^3) (Found: C, 34.7; H, 3.8. $C_{22}H_{26}F_6O_6P_2Pd\cdot 2H_2O$ requires C, 34.6; H, 3.4%). IR (KBr) $\tilde{\nu}_{max}$/cm^{-1}: as for **15** and 1245w [$\nu_{sym}(CF_3)$], 1237m [$\nu_{sym}(CF_3)$], 1175, 1165, 1160m [$\nu_{sym}(SO_3)$], 1005m (br) [ν_{asym}-(SO_3)] and [ν(CS)]. EI mass spectrum: m/z 732 (0.5%, M^+).

Bis(1-phenylphospholane)bis(tolyl-*p*-sulfonato)palladium(II) 19. A procedure similar to that for the preparation of **4** was followed. A yellow solid **19** (123 mg, 84%) was isolated, m.p. 233 °C (Found: C, 52.7; H, 5.5. $C_{34}H_{40}O_6P_2PdS_2$ requires C, 52.6; H, 5.2%). IR (KBr) $\tilde{\nu}_{max}$/cm^{-1}: as for **15** and 1652w, 1455w, 1040m, 1005m, 850s, 815s and 695s ($O_3SC_6H_4Me$). EI mass spectrum: 776 (1%, M^+), 164 (80, $[C_{10}H_{13}P]^+$) and 109 {25, $[M - Pd(CH_3C_6H_5S_2O_6)L_2]^+$}.

Bis(acetato)bis(1-phenylphospholane)bis(tolyl-*p*-sulfonato)-dipalladium(II) 20. Acetic acid (1.1 ml, 0.36 mmol, 0.33 mol dm^{-3} solution) and toluene-*p*-sulfonic acid (69 mg, 0.36 mmol) were added to a suspension of **19** (100 mg, 0.12 mmol) in toluene (30 cm). After 4 d a green solid formed in the yellow supernatant. The oily solid was triturated with diethyl ether (50 cm^3) and the green powder **20** (56 mg, 46%) isolated was recrystallised from CH_2Cl_2–light petroleum (1:4, 50 cm^3), m.p. 205 °C (Found: C, 44.3; H, 4.7. $C_{38}H_{46}O_{10}P_2Pd_2S_2$ requires C, 44.0; H, 5.0%). IR (KBr) $\tilde{\nu}_{max}$/cm^{-1}: as for **15** and 1580w (C=O), 1420w (C=O), 1652w, 1645w (H_2O), 1602w (OH), 1497w, 1005m, 850m, 815s and 695s ($O_3SC_6H_4Me$). EI mass spectrum: m/z 1041 (2%, M^+), 686 (5, $[M - C_{14}H_{19}PCH_3C_6H_4SO_3]^+$), 521 (12, $[M - PdO_2CMeCH_3C_6H_4SO_3C_{14}H_{19}P]^+$), 463 {35, $[PdO_2$-$CMeCH_3C_6H_4SO_3(C_{14}H_{19}P)_2]^+$}, 436 {38, $[C_{14}H_{19}PO_2CMe$-$(CH_3C_6H_4SO_3)_2]^+$} and 164 (15, $[C_{14}H_{19}P]^+$).

Tris(9-phenyl-9-phosphabicyclo[4.2.1]nonane)palladium(0) trihydrate 21. An aqueous solution of potassium tetrachloropalladate (0.8 g, 2.5 mmol, 8 cm^3 H_2O) was added to refluxing ethanol (20 cm^3) containing potassium hydroxide (0.27 g, 4.9 mmol) and over 3 equivalents of 4,2,1-PPBN (1.87 g, 8.56 mmol). After 20 min refluxing the solution was cooled to room temperature. A yellow solid **21** (962 mg, 52%) formed which was isolated by filtration. Further recrystallisation was not required, m.p. 210 °C (decomp.) (Found: C, 61.5; H, 8.2. $C_{42}H_{57}P_3Pd\cdot 3H_2O$ requires C, 61.9; H, 7.7%). IR (Nujol) $\tilde{\nu}_{max}$/cm^{-1}: as for **1**. EI mass spectrum: m/z 234 (40%, $[C_{14}H_{19}PO]^+$), 218 (12, $[C_{14}H_{19}P]^+$), 143 (7, $[C_{14}H_{19}P - C_6H_4]^+$) and 77 (92, Ph^+).

Crystallography

Crystals of compounds **7**, **13**, **15** and **21** were mounted on glass fibres using the oil drop technique and intensity data collected. A summary of crystal data, data collection parameters and model refinement parameters is given in Table 2. Data for these compounds were recorded on a FAST TV Area detector diffractometer, with a molybdenum target ($\lambda_{Mo\text{-}K\alpha}$ = 0.710 69 Å), equipped with an Oxford Cryosystems cryostat and driven by MADNES[37] software operating on a MicroVax 3200, following previously described procedures.[38] The structures were solved *via* direct methods (SHELXS 86),[39] and then subjected to full-matrix least-squares refinement on F_o^2 (SHELX 93).[40] Non-hydrogen atoms were made anisotropic, with hydrogens in calculated positions (C–H = 0.96 Å, with U_{iso} tied to U_{eq} of the parent atoms) whilst the phenyl rings in **21** were constrained to be regular hexagons (C–C = 1.39 Å). Compound **21** crystallises in the chiral space group $P2_12_12$, however a Flack parameter of −0.21(4) confirms the correct absolute structure. Absorption corrections were applied using DIFABS.[41] The weighting scheme used was $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ where $P = \max[(F_o^2) + (2F_c)^2]/3$ and a = 0.0438, 0.0166, 0, 0 for **7**, **13**, **15** and **21**

respectively. Sources of scattering factor data are given in ref. 38. Diagrams were drawn with SNOOPI.[42]

Atomic co-ordinates, 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 186/488.

Acknowledgements

This paper is dedicated to the late Professor Sir Geoffrey Wilkinson whose influence and guidance has enriched so many. We thank the EPSRC and ICI Acrylics for a CASE Studentship (to J. L. T.) and the EPSRC for support for the crystallography facilities.

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Received 22*nd January* 1997; *Paper* 7/00505I