Palladium Complexes of Azines, α-Diazines and α-2-Pyridylazines containing (1*R*)-(+)-Camphor or (1*R*)-(−)-Fenchone Groups†

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Mixed monoazines of types $H_2C{=}N{-}N{=}C_{10}H_{16}$ [$C_{10}H_{16}$ is a (1*R*)-(+)-camphor residue (L^1), or a (1*R*)-(−)-fenchone residue (L^2)] or $Me_2C{=}N{-}N{=}C_{10}H_{16}$ [$C_{10}H_{16}$ is a (1*R*)-(+)-camphor residue (L^3)], or α-diazines $C_{10}H_{16}{=}N{-}N{=}CH{-}CH{=}N{-}N{=}C_{10}H_{16}$ [$C_{10}H_{16}$ is a (1*R*)-(+)-camphor residue (L^4) or a (1*R*)-(−)-fenchone residue (L^5)], or α-2-pyridyl azines $C_{10}H_{16}{=}N{-}N{=}CHC_5H_4N$ [$C_{10}H_{16}$ is a (1*R*)-(+)-camphor residue (L^6) or a (1*R*)-(−)-fenchone residue (L^7)] reacted with Na_2PdCl_4 to give compounds of type $[PdCl_2L^n{}_2]$ for L^1, L^2 or L^3 as monodentate nitrogen-donor ligands and chelated mononuclear complexes of the type $[PdCl_2L^n]$ for L^4, L^5, L^6 or L^7. The complexes of the monodentate azines L^1 and L^2 exist in solution as mixtures of isomers differing in the ligating nitrogens. The compounds L^1, L^2 and L^4–L^7 also reacted with $[Pd_2Cl_4(PR_3)_2]$ to give $[PdCl_2(PR_3)L^n]$ ($n = 1$, $R_3 = Me_2Ph$ or $Me_2(C_6H_4OMe\text{-}4)$; $n = 2$, $R_3 = Me_2Ph$, $Me_2(C_6H_4OMe\text{-}4)$ or Ph_3; $n = 4$ or 5, $R_3 = Me_2Ph$; $n = 6$, $R_3 = Bu^n{}_3$; $n = 7$, $R_3 = Bu^n{}_3$ or Me_2Ph), in which the ligands are monodentate, or $[\{PdCl_2(PR_3)\}_2L^n]$ ($L^n = L^4$–L^7, $R_3 = Me_2Ph$), in which the ligands are bidentate bridging. The phosphine complexes were characterised in solution but were isolated only for $[PdCl_2(PR_3)L^n]$ ($L^n = L^6$, $R_3 = Bu^n{}_3$; L^7, $R_3 = Bu^n{}_3$ or Me_2Ph; L^2, $R_3 = Ph_3$). Compounds L^4, L^6 or L^7 reacted with the η^3-methylallylpalladium complex $[\{PdCl(\eta^3\text{-}CH_2CMeCH_2)\}_2]$ and NH_4PF_6 to give $[Pd(\eta^3\text{-}CH_2CMeCH_2)L^n]PF_6$ ($L^n = L^4$, L^6 or L^7). The crystal structure of $[PdCl_2L^6]\cdot 0.5CH_2Cl_2$ was determined by *X*-ray diffraction analysis: the crystals are monoclinic, space group $P2_1$ with $a = 9.5830(13)$, $b = 13.9720(14)$ and $c = 14.726(2)$ Å, $\beta = 97.610(11)°$ and $Z = 4$. It shows two molecules of the complex in the asymmetric unit differing only in the torsion angles around the N–N bond.

The chemistry of palladium complexes containing nitrogen-donor ligands is extensive[1] and includes the use of metal complexes with chiral nitrogen-donor ligands as catalysts to effect asymmetric induction for example with the addition of diethylzinc to aldehydes.[2] Some palladium complexes with nitrogen-donor ligands also show antitumour activity.[3] We have reported the synthesis of some α-diazines (2,3,6,7-tetraazaoctatetraenes) derivatives with bulky and chiral end substituents of type $C_{10}H_{16}{=}N{-}N{=}CH{-}CH{=}N{-}N{=}C_{10}H_{16}$ [$C_{10}H_{16}$ is a (1*R*)-(+)-camphor residue or (1*R*)-(−)-fenchone residue] and the related α-2-pyridyl azines $C_{10}H_{16}{=}N{-}N{=}CH{-}C_5H_4N$. We reported that these azines formed complexes with Group VI metals and found that they acted as chelating ligands forming intensely coloured complexes with five-membered chelate rings, using a N=C–C=N moiety,[4] and akin to complexes of the well known α-diimines. We have now studied the behaviour of these bulky α-diazines and α-pyridyl azines as well as some related unsymmetrical (mixed) azines as ligands for palladium(II) and report our results in this paper.

Results and Discussion

The unsymmetrical mixed azines (1*R*)-(+)-camphor formaldehyde azine, (1*R*)-(−)-fenchone formaldehyde azine and acetone (1*R*)-(+)-camphor azine are, to the best of our knowledge, new and were prepared by condensation of (1*R*)-(+)-camphor hydrazone[5] or (1*R*)-(−)-fenchone hydrazone[6–8] with formaldehyde or acetone using a similar technique to the preparation of the α-diazines and α-2-pyridyl azines:[4] details are given in the Experimental section together with characterising data for these compounds. The new palladium complexes, which were isolated, were characterised by elemental analysis (C, H and N) and IR spectroscopy (details in Table 1) and these and the other palladium complexes which were formed only in solution and not isolated were further characterised by ^1H and $^{31}P\text{-}\{^1H\}$ (Table 2) and $^{13}C\text{-}\{^1H\}$ NMR spectroscopy (Table 3). Only especially noteworthy features of the characterising data will be mentioned in the text.

Reactions with Sodium Tetrachloropalladate(II).—When a solution of sodium tetrachloropalladate(II) in methanol was treated with 2 mole equivalents of (1*R*)-(+)-camphor formaldehyde azine, (1*R*)-(−)-fenchone formaldehyde azine or acetone (1*R*)-(+)-camphor azine, the colour changed from dark red to orange-yellow and in each case a palladium complex was obtained as an orange solid. The elemental analytical figures suggested that these complexes were of formula $[PdCl_2(H_2C{=}N{-}N{=}C_{10}H_{16})_2]$ [$C_{10}H_{16}$ is a (1*R*)-(+)-camphor residue **1**, or a (1*R*)-(−)-fenchone residue **2**] or $[PdCl_2(Me_2C{=}N{-}N{=}C_{10}H_{16})_2]$ **3** [$C_{10}H_{16}$ is a (1*R*)-(+)-camphor residue]. It seemed likely that these complexes were square planar around palladium, but what needed to be established was whether they were of *cis* or *trans* configuration and which of the two azine nitrogens was co-ordinated.

There are two possible co-ordination modes for each of the azines: through the $H_2C{=}N$ nitrogen or through the $C_{10}H_{16}N$ nitrogen. As complexes **1** and **2** each contain two azine ligands there are therefore three possible linkage isomers, two symmetrical and one unsymmetrical. These are shown in Scheme 1 as **a**, **b** and **c**. Additionally, each of these three could

† camphor = 1,7,7-Trimethylbicyclo[2.2.1]heptan-2-one; fenchone = 1,3,3-trimethylbicyclo[2.2.1]heptan-2-one.

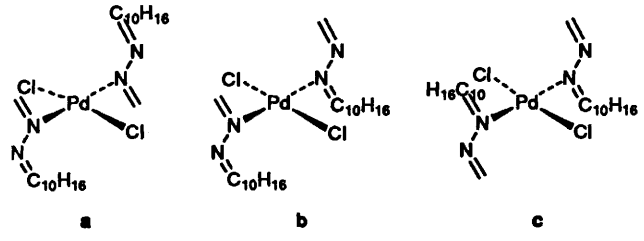
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: mmHg ≈ 133 Pa.

Table 1 Elemental analytical[a] and IR[b] data

Compound	Analysis (%)				IR/cm^{-1}	
	C	H	N	Cl	$\nu_{(Pd-Cl)}$	$\nu_{(C=N)}$
1	49.65 (49.5)	7.05 (6.8)	10.4 (10.5)	13.45 (13.3)	352 (sh), 332[c]	1660[d]
2	49.25 (49.5)	6.65 (6.8)	10.35 (10.5)	13.5 (13.3)	345, 322	1640, 1610
3	52.7 (52.95)	7.55 (7.5)	9.55 (9.5)	12.25 (12.0)	340, 312w[c]	
4	49.5 (49.7)	6.45 (6.45)	10.5 (10.55)	13.25 (13.35)	348 (sh), 338[c]	1660
5	49.65 (49.7)	6.4 (6.45)	10.6 (10.55)	13.35 (13.35)	348, 320m	1650
6	44.5 (44.4)	4.65 (4.9)	9.9 (9.7)	16.35 (16.4)	350, 348 (sh)	1660
7	44.25 (44.4)	4.95 (4.9)	9.75 (9.7)	16.5 (16.4)	350 (br)	1650
12	56.35 (56.35)	5.4 (5.4)	4.55 (4.55)	11.7 (11.5)	350, 340w	1640, 1612
17	50.2 (50.5)	5.55 (5.65)	7.25 (7.35)	12.65 (12.4)	360	1650
18	52.65 (52.95)	7.55 (7.6)	6.55 (6.6)	11.5 (11.15)	355	1660
19	53.1 (52.95)	7.8 (7.6)	6.75 (6.6)	11.35 (11.15)	355	1650
22	47.35 (47.25)	6.55 (6.25)	8.65 (8.5)	17.5 (17.25)[e]	—	
23	42.9 (42.75)	4.95 (5.0)	7.4 (7.5)	20.15 (20.3)[e]	—	
24	42.6 (42.75)	5.15 (5.0)	7.4 (7.5)	20.1 (20.3)[e]	—	

[a] Calculated values in parentheses. [b] Recorded as KBr discs unless stated otherwise. All bands were strong unless stated otherwise; m = medium, w = weak, br = broad, sh = shoulder. [c] In Nujol. [d] In CH_2Cl_2 solution. [e] Analysis for F.



Scheme 1 The three different isomers of complexes **1** ($C_{10}H_{16}$ = D-camphor residue) and **2** ($C_{10}H_{16}$ = L-fenchone residue)

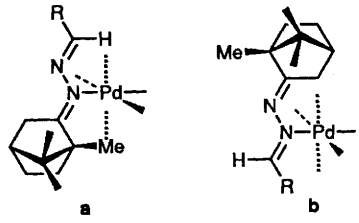


Fig. 1 Approach of one hydrogen from the N=CHR group and the $C^{10}H$ protons to the palladium upon co-ordination of the azine (R = H) or diazine (R = CH=NN=$C_{10}H_{16}$) when co-ordinated through the $C_{10}H_{16}N$ nitrogen (**a**) and not when co-ordinated through the HRC=N group (**b**). The organic group shown is D-camphor but for L-fenchone the situation is the same

be either *cis* or *trans* at the palladium making a total of six possible isomers. In Scheme 1 we have chosen to depict the isomers as *trans* at the palladium centre: this is discussed further below. The types of co-ordination modes adopted by the azines in **1** and **2** were established by NMR spectroscopy. It was clear from the ^1H and ^{13}C-{^1H} NMR spectra of both **1** and **2** that more than one species (isomer) was present in solution and the number of isomers was determined by counting the sets of resonances due to individual $C_{10}H_{16}N$–N=CH_2 units. One would expect each of the isomers of types **a** and **c** to give a single set of resonances for the two equivalent $C_{10}H_{16}N$–N=CH_2 groups but isomers of type **b** to give two sets of resonances of equal intensity, because the co-ordinated azines are inequivalent. In fact the isomer mixtures of types **1** or **2** each showed four sets of resonances from the $C_{10}H_{16}N$–N=CH_2 units in both their ^1H and ^{13}C NMR spectra. For **1** the sets were in an approximate ratio of 0.3:1:1:1 which did not vary with temperature over the range −40 to +60 °C, whilst for **2** the ratio was about 0.1:1:1:2. Four sets of resonances, two of which are in a 1:1 ratio, strongly suggest that both **1** and **2** exist in solution as all three isomers **a**–**c**.

For the camphor formaldehyde azine complexes **1** the three sets of resonances of approximately equal intensity imply that the unsymmetrical isomer **1b** is present to the extent of 60%, that the symmetrical isomer is present to the extent of about 30% and that the other symmetrical isomer is present to the extent of 10%. For the fenchone formaldehyde azine complexes **2** the unsymmetrical isomer **2b** must be present as just less than half the mixture with one of the symmetrical isomers accounting for most of the rest and the third (symmetrical) isomer present in only a small amount. Two-dimensional nuclear Overhauser enhancement spectroscopy (NOESY) experiments showed that in each case the isomers were interconverting, although slowly on the NMR time-scale.

The two possible modes for each ligand would be expected to give rise to different patterns of chemical shifts. In particular the co-ordination of the $C_{10}H_{16}N$ nitrogen brings the three protons in the C^{10} methyl group *and* that hydrogen of the H_2C=N moiety, which is cisoid to the nitrogen, to a position above or below the co-ordination plane of the metal (see Fig. 1). Such an environment leads to a distinct shift to low field in the corresponding resonances in, for example, complexes of monodentate α-diimines with palladium.[9] We have therefore assigned, with some confidence, co-ordination shifts to low field for the C^{10} methyl group and the single H–C=N hydrogen referred to above to a ligand bonded *via* the $C_{10}H_{16}N$ nitrogen.

In the ^1H NMR spectrum of complex **2**, the unsymmetrical isomer did indeed have a HC=N resonance at significantly lower field than the others (δ 9.33) which was coupled to a resonance at δ 7.26 (*cf.* the resonances for the free azine which occur at δ 7.14 and 6.75). The coupling constant was 11 Hz and this was similar to that found for all complexes of this ligand and the corresponding camphor ligand and was rather smaller than that observed for the free azine (14.3 Hz). There was also a resonance due to a methyl group in the fenchone residue at δ 2.89 which was assigned to this isomer by integration. This again represents a significant co-ordination shift as the other methyl groups, again assigned to this isomer by integration, appeared in the region δ 1.62–1.21 (and which were therefore little shifted from those of the free azine).

The resonances in the ^1H NMR spectrum of complex **2** which arose from the more abundant of the symmetrical isomers included a pair of doublets due to the H_2C=N group. The low-field shift of one of these doublets (δ 8.54) and of one of the (three) methyl resonances suggested that this isomer was **2c**. The less abundant of the two symmetrical isomers was therefore

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

	^1H							
		Pyridyl protons				Camphor or fenchone		
Compound	HCNN	H^3	H^4	H^5	H^6	methyls	Others[b]	^{31}P
1a	7.46,[c] 7.01[c]	—	—	—	—	0.96, 0.95, 0.91	—	—
1b	9.25,[c] 7.27[c]	—	—	—	—	2.58, 0.91, 0.86	—	—
	7.42,[c] 6.86[c]	—	—	—	—	0.98, 0.84, 0.81	—	—
1c	8.46,[c] 7.27[c]	—	—	—	—	2.43, 0.94, 0.89	—	—
2b	9.33,[c] 7.26[c]	—	—	—	—	2.89, 1.62, 1.51	—	—
	7.59,[c] 6.76[c]	—	—	—	—	1.21, 1.24, 1.24	—	—
2c	8.54,[c] 7.33[c]	—	—	—	—	2.69, 1.19, 1.14	—	—
3a[d]	2.91, 1.96[e]	—	—	—	—	1.01, 0.88, 0.86	—	—
3b[d]	2.79, 1.92[e]	—	—	—	—	1.04, 0.88, 0.86	—	—
5	7.75–7.65[f]	—	—	—	—	1.31–1.16[f]	—	—
6[g]	7.84	7.72	7.64	8.10	9.22	1.53, 1.06, 0.97	—	—
7[g,h]	7.88	7.77	7.64	8.11	9.21	1.54, 1.06, 0.97	—	—
8a[d]	7.37,[c,i] 7.17[c,j]	—	—	—	—	0.98, 0.88, 0.75	1.85 (PMe)	7.2
8b[d]	8.89,[c,k] 7.25[c,l]	—	—	—	—	1.95, 0.89, 0.81	1.80, 1.79 (PMe)	4.6
9a[d]	7.36,[c,i] 7.16[c,j]	—	—	—	—	0.98, 0.88, 0.77	3.82 (OMe), 1.79 (PMe)	6.5
9b[d]	8.88,[c,k] 7.24[c,l]	—	—	—	—	1.96, 0.89, 0.81	3.82 (OMe), 1.77, 1.76 (PMe)	4.0
10a[d]	7.58,[m] 7.01[c,j]	—	—	—	—	*m*	*m*	9.2
10b[d]	8.91,[c,k] 7.28[c,l]	—	—	—	—	2.27, 1.29, 1.25	1.85, 1.83 (PMe)	5.2
11a[d]	*m*	—	—	—	—	*m*	*m*	8.2
11b[d]	8.87,[c,k] 7.23[c,l]	—	—	—	—	2.25, 1.24, 1.20	3.82 (OMe), 1.78, 1.76 (PMe)	4.2
12a[d]	*m*	—	—	—	—	—	—	30.9
12b[d]	9.04,[c,k] 7.28[c,l]	—	—	—	—	2.47, 1.22, 1.18	—	27.5
13[d]	9.47	—	—	—	—	1.90, 0.89, 0.83	1.88, 1.84 (PMe)	5.2
14[d]	9.50	—	—	—	—	2.24, 1.23, 1.22	1.87, 1.84 (PMe)	6.1
15[d]	9.52,[k,n] 7.96[n]	—	—	—	—	*m*	*m*	5.1
16[d]	9.55,[k,n] 7.98[n]	—	—	—	—	2.30, 1.23, 1.23, 1.22, 1.21, 1.21	1.81, 1.79 (PMe)	6.1
17	9.42	8.16	7.75	7.35[l]	8.82[i]	1.35, 1.27, 1.27	1.88 (PMe)	7.0
18	9.38	8.21	7.78	7.36	8.81[i]	1.11, 0.97, 0.87	1.94, 1.70, 1.52, 0.99 (PBu)	28.1
19	9.45	8.14	7.77	7.35[l]	8.81[i]	1.31, 1.29, 1.27	1.94, 1.71, 1.52, 0.99 (PBu)	28.1
20[d]	10.76	8.20	*m*	*m*	8.84[i]	1.99, 0.92, 0.87	1.92, 1.92, 1.85, 1.82 (PMe)	9.4, 6.8
21[d]	11.04	8.14	*m*	*m*	8.84[i]	2.28, 1.28, 1.24	1.95, 1.92, 1.84, 1.83 (PMe)	9.0, 7.4
22[d]	7.83	—	—	—	—	1.05, 0.97, 0.84	3.88, 3.77, 3.25, 3.22 (CH)	
	7.81					1.05, 0.97, 0.82	2.16 (CH_3)	
23[o]	8.23	8.11	7.98	7.70	8.77	1.04, 0.95, 0.82	4.18, 3.74, 3.37, 3.37 (CH), 2.19 (Me)	
23'[o]	8.21	*m*	*m*	*m*	*m*	1.04, 0.95, 0.84	4.16, 3.65, 3.05, 3.05 (CH), 2.17 (Me)	
24[d,g]	8.07	8.14	7.86	7.68	8.71	1.40–1.05[f]	4.05, 3.31, 2.94, 2.94 (CH), 2.16 (Me)	
24'[d,g]	8.04	*m*	*m*	*m*	*m*	1.40–1.05[f]	4.10, 3.68, 3.37, 3.30 (CH), 2.12 (Me)	

[a] Recorded in $CDCl_3$ solution at 400.13 (^1H) or 36.2 MHz (^{31}P) unless otherwise stated. All resonances are singlets unless otherwise stated exept for those due to the pyridyl protons which were all multiplets as described elsewhere. [b] Phosphine aryl resonances not listed; PMe resonances were doublets $^2J(PH) \approx 12$ Hz, PBu resonances were multiplets. [c] $^2J(HH) = 11.2 \pm 0.4$ Hz. [d] Recorded at 233 K. [e] $H_3CC{=}NN$. [f] Several overlapping resonances. [g] Recorded in CD_2Cl_2 solution. [h] Resonances listed for major conformer only. [i] $^4J(PH) = 3.3 \pm 0.2$ Hz. [j] $^4J(PH) = 9.4 \pm 0.1$ Hz. [k] $^5J(PH) = 2.0 \pm 0.5$ Hz. [l] $^5J(PH) \leqslant 1$ Hz. [m] Obscured by overlapping resonances. [n] $^3J(HH) = 8.5$ Hz. [o] Recorded at 213 K.

assigned as **2a**. The low-field shift expected for the HC=N proton lying above the palladium and the methyl protons on the C^{10} of the $C_{10}H_{16}N$ moiety (Fig. 1) became a consistent feature of those complexes in which the $C_{10}H_{16}N$ nitrogen was assigned as co-ordinated to the palladium.

The ^{13}C-{^1H} NMR spectrum of the mixture of isomers of complex **2** also supported our assignments from the ^1H NMR data. The major symmetric form gave rise to a resonance at δ 193.9 for the C^2 carbons of the fenchone residue whilst the unsymmetrical isomer gave rise to resonances for these carbons at δ 199.7 and 181.5. It therefore appeared as though we had another parameter with which to determine how the ligand co-ordinated to the palladium: *viz.* the co-ordination shift of the C^2 resonance (difference in chemical shift, Δδ, between free and co-ordinated azine). The Δδ values for these carbons are therefore 10.7, 16.5 and −1.8 ppm respectively.

In contrast to the chemical shifts exhibited by the C^2 carbons, those for the $H_2C{=}N$ carbons showed little variation whether they were co-ordinated or not, being in all cases 5–7 ppm downfield of the corresponding resonance for the free azine. The values of $^1J(CH)$ for the $H_2C{=}N$ group in the (1*R*)-(−)-fenchone formaldehyde azine remained at values similar to those of the free azine.

Additionally, the C–H correlation spectrum confirmed that it was the resonances for the C^{10} methyl protons (the carbon resonance of which was also a little downfield of that of the free azine) that were shifted downfield with respect to the other methyl resonances where the C=N in the fenchone residue was co-ordinated, the C^{10} methyl proton resonance in **2c** being at δ 2.69 and in **2b** the corresponding resonances were at δ 2.89 (co-ordinated C=N, see above) and 1.21 (unco-ordinated C=N).

The analysis of the NMR spectra of complex **2**, in which the resonances were easily assigned as belonging to the same isomer by integration, made the assignment of the resonances of **1** that much easier. In the ^1H NMR spectrum of **1** the unsymmetrical isomer again has a resonance at particularly low field for one of

Table 3 Carbon-13 NMR data[a]

	Camphor or fenchone carbons											2-Pyridyl carbons					
Compound	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	C^{11}	C^{12}	C^{13}	C^{14}	C^{15}	C^{16}	Others
1a/b	56.0	195.0	41.4	44.2	26.9	32.2	49.8	19.0	20.0	14.8	155.8[b]						
	54.3	184.8	38.0	44.0	26.9	32.2	48.1	18.6	19.8	10.8	153.9[c]						
	54.0	183.3	36.7	43.4	26.7	32.1	48.1	18.6	19.6	10.8	153.7[d]						
2b	53.6	199.7	50.6	49.0	*e*	34.0	44.9	*e*	*e*	21.6	154.1						
	52.8	181.5	46.0	49.0	*e*	33.9	42.3	*e*	*e*	17.0	152.6						
2c	52.6	193.9	49.0	49.7	24.9	34.1	44.6	24.2	23.3	21.1	154.9						
3a[f]	54.0	182.3	43.3	38.1	26.7	31.7	47.8	18.5	19.6	11.1	170.3						27.8, 21.2 (N=C*Me*)
3b[f]	54.0	182.2	43.3	38.1	26.7	31.7	47.7	18.5	19.5	11.0	169.6						27.7, 21.1 (N=C*Me*)
6[g]	55.2	*h*	34.6	37.2	26.5	30.8	44.5	19.8	18.7	10.9	156.2	153.9	127.7	140.7	126.4	151.5	
8a[f]	53.5	183.7[i]	38.2	43.6	26.5	31.9	47.9	19.4	18.5	10.9	152.8	—	—	—	—	—	13.3, 13.2 (PMe)
8b[f]	55.0	191.7[j]	39.5	42.8	26.5	31.8	49.1	19.8	18.7	14.5	152.9	—	—	—	—	—	13.1, 12.7 (PMe)
9a[f]	53.5	183.5[i]	38.2	43.6	26.6	31.9	47.9	19.5	18.5	10.9	152.7	—	—	—	—	—	55.3 (OMe), 13.7, 13.5 (PMe)
9b[f]	55.0	191.4[k]	39.5	42.8	26.6	31.8	49.2	19.8	18.7	14.5	152.9	—	—	—	—	—	55.2 (OMe), 13.4, 13.0 (PMe)
10a[f]	52.0	180.5	49.0	45.3	24.5	33.8	41.9	23.8	23.6	16.9	150.4[k]	—	—	—	—	—	14.2, 13.4 (PMe)
10b[f]	52.6[l]	194.7[k]	48.8[m]	48.4	24.6	33.4	44.2	23.8	23.6	21.1	152.5	—	—	—	—	—	13.2, 12.8 (PMe)
11b[f]	52.6	194.4[k]	48.7[m]	48.4	24.6	33.4	44.2	23.8	23.6	21.1	152.4	—	—	—	—	—	55.2 (OMe), 13.7, 13.2 (PMe)
12b[f]	52.8	195.0[k]	48.9[m]	48.4	24.5	33.3	44.1	23.8	23.4	21.4	152.5	—	—	—	—	—	—
13[f]	55.3	193.0[j]	39.9	42.8	26.6	32.0	49.4	19.8	18.7	14.3	159.1	—	—	—	—	—	12.9, 12.4 (PMe)
14[f]	52.8	196.0[k]	48.9[m]	48.4	24.6	33.6	44.3	24.1	24.1	20.9	158.9	—	—	—	—	—	13.3, 12.9 (PMe)
15[f]	55.2	192.8[j]	39.7	42.7	26.5	32.0	49.4	19.7	18.7	14.2	159.4	—	—	—		—	12.9, 12.4 (PMe)
	52.7	183.4	35.8	43.1	26.8	32.0	47.8	19.3	18.6	11.1	154.7						
16[f]	52.8	196.0[j]	48.9[m]	48.3	24.8	32.0	44.2	24.1	23.1	21.1	159.4	—	—	—	—	—	13.4, 13.2 (PMe)
	50.9	186.8	45.4	48.0	24.5	32.0	42.5	24.0	23.3	17.0	154.8						
17	51.2	185.1	45.3	48.5	25.1	34.0	43.0	24.3	23.8	17.2	154.6	153.4	125.0	137.8	123.3	150.5	13.8 (PMe)
18	52.8	180.4	35.9	43.9	27.2	32.6	48.0	19.7	18.8	11.1	153.5	153.5	125.0	137.7	123.4	150.4	23.2, 24.2, 26.2, 13.8 (PBu)
19	51.1	184.9	45.3	48.7	25.1	34.0	42.9	24.2	23.9	17.0	154.5	153.5	124.9	137.6	123.0	150.3	23.0, 24.0, 26.1, 13.6 (PBu)
20	54.8	188.7[j]	38.9	43.0	26.5	31.9	49.3	19.8	18.7	14.3	160.3	151.8	126.0	138.2	124.0	150.7	13.8, 13.7, 13.2, 13.0 (PMe)
21	52.5	193.7[k]	48.3	48.3	24.6	33.7	44.0	24.2	23.4	20.8	160.3	151.9	126.1	138.3	123.8	150.6	13.6, 13.6, 13.4, 13.2 (PMe)
22	53.7	183.0	35.6	43.3	26.5	32.1	48.3	19.3	18.4	10.6	153.4	—	—	—	—	—	136.5 (*C*Me), 62.1,
	53.6	183.0	35.4	43.3	26.3	32.0	48.1	19.1	18.4	10.5	153.1						61.8 (CH_2), 23.6 (C*Me*)
23, 23'[f]	53.6	182.5	35.5	43.2	26.5	31.9	48.3	19.3	18.5	10.8	157.2	154.0	129.0	140.9	127.7	151.2	136.1 (*C*Me), 62.9,
											157.0						62.7 (CH_2), 23.7 (Me)
																	135.7 (*C*Me), 59.8 (CH_2)

[a] Spectra recorded in $CDCl_3$ solution at 301 K and an operating frequency of 100.6 MHz unless stated otherwise. All resonances were singlets except where otherwise stated. Carbon atoms are numbered as in complexes **6** and **7**. The PMe resonances were doublets with ^1J(PC) 38–40 Hz, PBu resonances were doublets. [b] ^1J(CH) = 168.4, 179.4 Hz. [c] ^1J(CH) = 166.0, 180.7 Hz. [d] ^1J(CH) = 171.8, 188.1 Hz. [e] Resonance not assigned due to overlapping signals. [f] Spectrum recorded at 233 K. [g] In CD_2Cl_2 solution. [h] Not observed. [i] ^4J(PC) = 1.6 Hz. [j] ^3J(PC) = 3.7 Hz. [k] ^3J(PC) = 2.7 Hz. [l] ^4J(PC) = 1.2 Hz. [m] ^4J(PC) = 3.7 Hz.

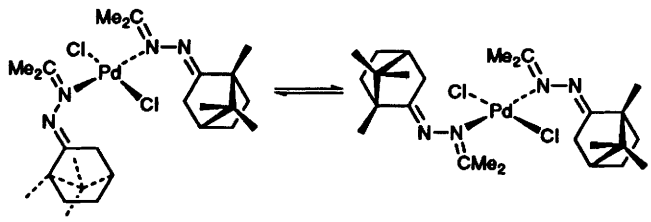
the H_2C=N protons (δ 9.25) which is coupled to another hydrogen resonating at δ 7.27 (*cf.* δ 9.33 and 7.26 for the corresponding complex **2b**) and a methyl group appears at δ 2.58 whereas most of the other methyls in the mixture of isomers appear at δ 1.04–0.87. The other particularly low-field HC=N resonance (δ 8.46) belonged to the least-abundant isomer which also gave rise to a methyl resonance at δ 2.43 and must therefore be **1c** leaving the symmetrical **1a** (δ 7.46 and 7.01 for the H_2C=N protons, *i.e.* no large shift to lower field) as the species present in about 30%.

The ^{13}C-{^1H} NMR spectrum of complex **1** again backed up these assignments. The azine carbons all showed a downfield shift relative to those of the free azine: the resonances due to the three C^2 carbons in the camphor residues of the unsymmetrical and more abundant symmetrical isomers had Δδ values of 14.4, 4.2 and 3.7 ppm. The resonance with the largest co-ordination shift was assigned to co-ordinated C^2=N of the unsymmetrical isomer **1b**. One of the other C^2 resonances (at δ 184.8 or 183.3) must therefore be due to the symmetrical isomer and its relatively low shift confirmed that this must be **1a**. The resonances from the isomer present in only small amounts in solution, **1c**, were too weak to observe.

The NMR data therefore show that complexes **1** and **2** exist in solution as just three of the six possible isomers, one each of types **a**–**c**, and there remained the problem of assigning the stereochemistry at the palladium centre as either *cis* or *trans*.

The IR spectra of complexes **1** and **2** both showed two bands in the region expected for ν(Pd–Cl) which might indicate that the complexes were *cis* and that individual bands for each isomer were not resolved in the solid state. However it is also possible that **1** and **2** are, in fact, *trans* and that some differences in the ν(Pd–Cl) bands for each isomer **a**–**c** were being observed. It seems to us unreasonable that the linkage isomers adopt different geometries at the metal centre, *e.g.* that **1a** and **1c** be *cis* and **1b** be *trans*, *etc.* In Scheme 1 we have chosen to depict all the complexes **1a**–**2c** as *trans*. This is based upon analogy with complexes of hydrazones and similar derivatives, some of which have been characterised crystallographically.[9,10] It should be borne in mind however that the possibility of *cis* stereochemistries cannot be dismissed.

Complex **3**, in contrast to **1** and **2**, showed only one species in solution at ambient temperature but cooling the solution to −40 °C revealed that in fact the complex existed as two forms **3a** and **3b** (in the ratio 2.5:1) which interconverted rapidly on the NMR time-scale. As each form of the complex exhibited only one set of resonances from a camphor residue the two interconverting forms must themselves be symmetric and additionally as the two sets of resonances were so close together (with no more than 0.7 ppm between any of the corresponding ^{13}C resonances in the two forms) we concluded that **3a** and **3b** are not linkage isomers akin to those suggested for **1** and **2**. The IR spectrum of the mixture of **3a** and **3b** in the region expected for ν(Pd–Cl) showed an intense peak at 340 cm^{-1} but also a weaker peak at 312 cm^{-1}. Natile *et al.*[10] suggested that in the related hydrazone complexes $[PdCl_2(Me_2C{=}N{-}NMeR)_2]$ two rotational isomers were observed due to restricted rotation around the Pd–N bonds. These authors formulated their complexes as *trans* and showed that the related complex $[PdCl_2\{Me(Ph)C{=}N{-}NMe_2\}_2]$ is *trans* by a crystal-structure determination. Clearly, **3a** and **3b** could be related as rotamers or conformers of this type, as shown in Scheme 2 (and could *not* be similarly related rotamers of a *cis* isomer, one of which would be less symmetrical) and this seems more likely than the alternative possibility that the two complexes are *cis*/*trans* isomers. As the resonances for the C^{10} methyl protons and C^2 carbons were not shifted to low field in either **3a** or **3b** we propose that it is the acetone azine nitrogen which is the ligating atom. It is perhaps a little surprising that in compounds **1** and **2**, where the two possible nitrogen donors differ more in both steric and electronic properties, that the palladium is less selective about which nitrogen it bonds to than in **3**, where

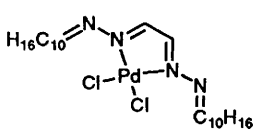


Scheme 2 Interconversion of two conformers of complex **3**

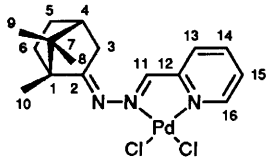
the two possible nitrogens are more similar. The explanation possibly lies in the lack of electron-donating substituents on the formaldehyde azine group making this a less-attractive ligating nitrogen for the metal than an acetone azine nitrogen but having the advantage of little steric crowding.

When a solution of sodium tetrachloropalladate(II) in methanol was treated with bis-[(1*R*)-(+)-camphor] glyoxal diazine $C_{10}H_{16}$=N–N=CH–CH=N–N=$C_{10}H_{16}$ the red solution lightened in colour immediately and a yellow-orange solid was precipitated. The solid had microanalytical figures consistent with it being a complex of the diazine and was assigned the formula $[PdCl_2(C_{10}H_{16}N{-}N{=}CH{-}CH{=}N{-}N{=}C_{10}H_{16}]$, **4**. It proved to be too insoluble to record its NMR spectra but the IR spectrum confirmed the presence of the C=N groups by an absorption at 1660 cm^{-1} and suggested a *cis* arrangement of the palladium–chlorine bonds with a band due to ν(Pd–Cl) at 338 cm^{-1} and a shoulder at 348 cm^{-1}. A similar reaction between sodium tetrachloropalladate(II) and bis[(1*R*)-(−)-fenchone] glyoxal diazine gave an isomeric complex **5**. It had a similar IR spectrum to that of **4** but with two clearly separated bands for ν(Pd–Cl), at 348 and 320 cm^{-1}, again confirming their *cis* orientation. Complex **5** was soluble in $CDCl_3$ but ^1H NMR spectroscopy revealed that it exists in solution in many different forms: several resonances were observed in the region between δ 7.75 and 7.65 for the azine protons. A similar situation is observed for complexes of this ligand with Group VI metal carbonyls[4] and we have ascribed this to restricted rotation around the N–N bonds due to steric interactions between the metal centre and the geminal methyl groups [C(8) and C(9)] in the fenchone residue; clearly the same sort of phenomenon may be in operation in **5**.

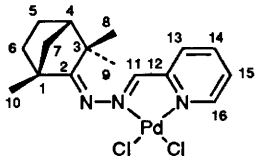
The reaction of sodium tetrachloropalladate(II) with (1*R*)-(+)-camphor pyridine-2-carbaldehyde azine in methanol produced a complex **6** in which the ligand appeared to be bound to the palladium by the pyridine nitrogen and the carbaldehyde azine nitrogen. This complex, like **4**, was insoluble in most organic solvents although a very dilute solution could be obtained in CH_2Cl_2. The ^1H NMR spectrum of **6** in CD_2Cl_2 solution showed a pattern of resonances similar to that observed for complexes of the same ligand with the Group VI metal carbonyls, *viz.* three singlet resonances for the methyls in the camphor residue, multiplets for each of the pyridyl protons and a slightly broad singlet for the azine proton. The coupling constants between the pyridyl protons are not listed in Table 2 for any of the complexes of the pyridyl azine ligands but these were within 0.2 Hz of those found in the complexes of the Group VI metals.[4] The ^{13}C-{^1H} NMR spectrum was also similar to those of other complexes of this ligand, but due to the weakness of the solution we were unable to observe the resonance due to the C^2 carbon in the camphor residue. Surprisingly the IR spectrum of **6** showed the two Pd–Cl stretches to be almost coincident and to be certain that the complex was indeed mononuclear with a genuinely *cis* arrangement of chloride ligands; we obtained the crystal structure of the complex by X-ray diffraction and this is shown in Fig. 2, with fractional non-hydrogen atomic coordinates in Table 4. The structure confirms that in **6** the pyridine nitrogen and the closest azine nitrogen are bonded in a five-membered



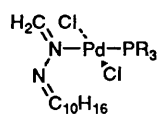
4 $C_{10}H_{16}$ = D-camphor
5 $C_{10}H_{16}$ = L-fenchone



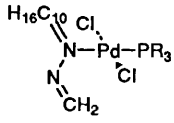
6



7

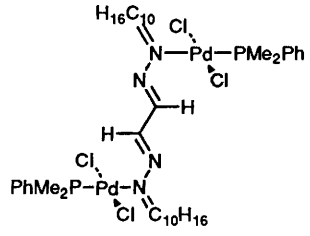


a

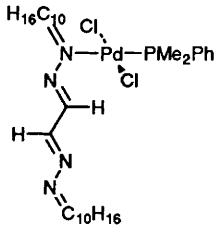


b

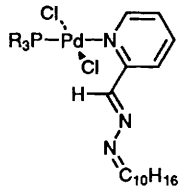
	R_3	$C_{10}H_{16}$
8	Me_2Ph	D-camphor
9	$Me_2(C_6H_4OMe\text{-}4)$	D-camphor
10	Me_2Ph	L-fenchone
11	$Me_2(C_6H_4OMe\text{-}4)$	L-fenchone
12	Ph_3	L-fenchone



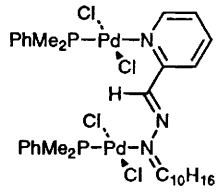
13 $C_{10}H_{16}$ = D-camphor
14 $C_{10}H_{16}$ = L-fenchone



15 $C_{10}H_{16}$ = D-camphor
16 $C_{10}H_{16}$ = L-fenchone



	R_3	$C_{10}H_{16}$
17	Me_2Ph	L-fenchone
18	Bu^n_3	D-camphor
19	Bu^n_3	L-fenchone



20 $C_{10}H_{16}$ = D-camphor
21 $C_{10}H_{16}$ = L-fenchone

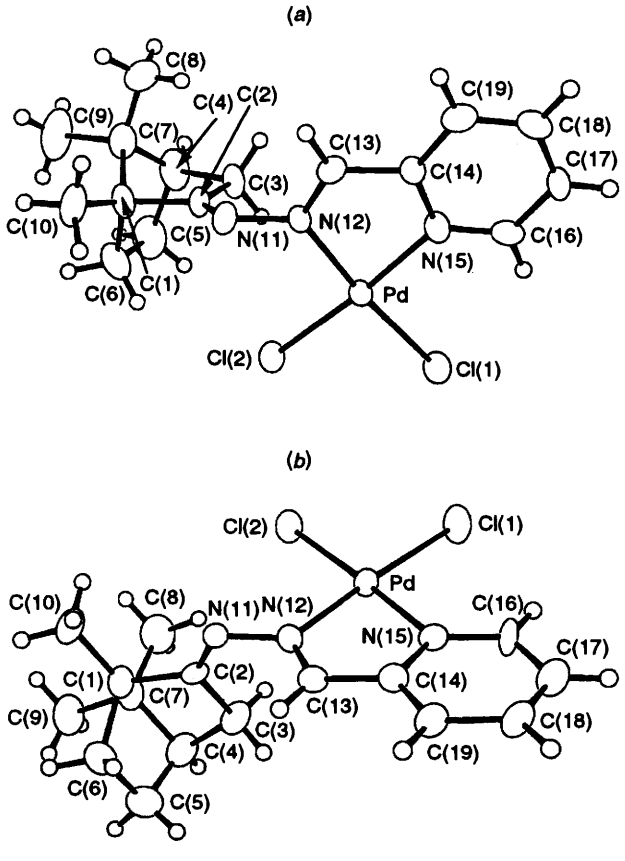


Fig. 2 An ORTEP representation of (*a*) molecule 1 and (*b*) molecule 2 of compound **6**. Thermal ellipsoids are drawn at the 50% probability level whilst, for clarity, hydrogen atoms are drawn as circles with a small arbitrary radius

chelated ring to a *cis*-$PdCl_2$ moiety. The structure contains two independent molecules of **6** in the asymmetric part of the cell together with a disordered CH_2Cl_2 solvate molecule. The two molecules are almost related to one another by a centre of symmetry. Only atoms C(5)–C(10) of the chiral (1*R*)-(+)-camphor fragments of the two molecules are not related by this false centre of symmetry and this led to considerable problems with pseudo-symmetry during structure solution and refinement. These problems which were aggravated by disorder of the solvent molecule (see Experimental section for more details) led to relatively high estimated standard deviations in the derived bond lengths and angles listed in Table 5. The major difference between the two molecules is in the orientation of their (1*R*)-(+)-camphor residues relative to the palladium co-ordination plane such that the torsion angle C(2)–N(11)–N(12)–C(13) is 111.6(9)° for molecule 1 and −103.0(9)° for 2. A detailed comparison between the two molecules is precluded as most of the apparent differences between them are not significant. The Pd–Cl and Pd–N bond lengths are similar to those found for a range of complexes containing sp^2-hybridised nitrogen(s) as donor atom(s).[10–15] There is no evidence for any interaction between the (1*R*)-(+)-camphor residue and the palladium atom. The bond lengths in the co-ordinated 2-pyridyl azine ligand were similar to those found in free (1*R*)-(−)-fenchone pyridine-2-carbaldehyde azine.[4]

Treatment of sodium tetrachloropalladate(II) with (1*R*)-(−)-fenchone pyridine-2-carbaldehyde azine gave complex **7** which was analogous to **6** although, as with other complexes of this ligand,[4] the ^1H NMR spectrum showed the presence in solution of three species. These we assign as conformational isomers related by rotation around the N–N bond. The ^{13}C-{^1H} NMR spectrum of **7**, recorded at 100.6 MHz, proved too complex to interpret fully due to overlapping signals.

Reactions with Bridged Complexes of Type [$Pd_2Cl_4(PR_3)_2$].—Treatment of [$Pd_2Cl_4(PMe_2R)_2$] (R = Ph or C_6H_4OMe-4) suspended in $CDCl_3$ solution with an equi-

Table 4 Fractional non-hydrogen atomic coordinates ($\times 10^4$) for complex **6** with estimated standard deviations (e.s.d.s) in parentheses

	Molecule 1			Molecule 2		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Pd	11 431.8(6)	9 999.8(3)	11 806.3(4)	11 430.4(6)	9 421.9(2)	16 797.8(4)
Cl(1)	10 307(3)	10 547(2)	12 976.6(15)	12 583(2)	10 568(2)	17 716.7(15)
Cl(2)	12 668(3)	8 911(2)	12 737.5(15)	10 288(3)	8 880(2)	17 970.0(15)
C(1)	15 683(9)	8 326(7)	10 908(6)	15 713(9)	11 016(7)	15 718(6)
C(2)	14 515(9)	9 055(7)	10 911(6)	14 500(9)	10 358(6)	15 816(5)
C(3)	15 119(8)	9 982(9)	11 284(6)	15 174(9)	9 419(9)	16 181(7)
C(4)	16 709(9)	9 709(7)	11 481(7)	16 715(9)	9 605(7)	16 198(6)
C(5)	16 838(9)	9 065(7)	12 353(5)	16 995(8)	9 653(6)	15 201(6)
C(6)	16 104(8)	8 129(5)	11 958(5)	16 304(7)	10 606(5)	14 841(5)
C(7)	16 880(6)	9 014(5)	10 697(5)	16 847(6)	10 680(5)	16 500(4)
C(8)	16 597(10)	9 467(7)	9 761(6)	16 419(8)	10 874(7)	17 441(5)
C(9)	18 326(8)	8 525(7)	10 796(8)	18 302(7)	11 115(6)	16 462(6)
C(10)	15 363(10)	7 433(8)	10 371(7)	15 306(9)	12 067(7)	15 617(6)
N(11)	13 241(8)	8 846(6)	10 600(5)	13 225(7)	10 573(6)	15 589(4)
N(12)	12 264(6)	9 594(6)	10 681(4)	12 253(7)	9 829(6)	15 667(4)
C(13)	11 710(8)	9 975(9)	9 943(5)	11 720(7)	9 407(8)	14 906(5)
C(14)	10 648(8)	10 737(7)	9 998(6)	10 677(9)	8 693(7)	14 996(6)
N(15)	10 386(7)	10 894(6)	10 865(5)	10 418(7)	8 493(6)	15 870(4)
C(16)	9 465(9)	11 574(7)	11 002(6)	9 520(9)	7 798(7)	16 012(6)
C(17)	8 755(8)	12 102(7)	10 282(6)	8 840(10)	7 269(8)	15 288(6)
C(18)	9 013(9)	11 907(8)	9 393(6)	9 041(9)	7 464(8)	14 415(6)
C(19)	9 972(9)	11 229(8)	9 255(6)	10 002(9)	8 204(8)	14 249(6)

Table 5 Selected bond lengths (Å), angles (°) and torsion angles (°) for complex **6** with e.s.d.s in parentheses

	Molecule 1	Molecule 2
Pd–N(12)	2.013(6)	2.017(6)
Pd–N(15)	2.029(7)	2.035(7)
Pd–Cl(2)	2.274(2)	2.285(2)
Pd–Cl(1)	2.282(2)	2.292(2)
C(1)–C(2)	1.514(12)	1.505(13)
C(1)–C(7)	1.559(11)	1.548(10)
C(1)–C(6)	1.569(11)	1.584(11)
C(2)–N(11)	1.279(11)	1.260(10)
C(2)–C(3)	1.494(14)	1.528(13)
C(3)–C(4)	1.560(11)	1.496(13)
C(4)–C(7)	1.533(12)	1.567(12)
C(4)–C(5)	1.559(13)	1.528(12)
C(5)–C(6)	1.560(11)	1.549(10)
N(11)–N(12)	1.419(10)	1.410(10)
N(12)–C(13)	1.263(11)	1.309(10)
C(13)–C(14)	1.483(13)	1.430(13)
C(14)–N(15)	1.351(11)	1.371(10)
N(12)–Pd–N(15)	79.9(3)	80.2(3)
N(12)–Pd–Cl(2)	94.4(2)	94.6(2)
N(15)–Pd–Cl(2)	174.1(2)	174.1(2)
N(12)–Pd–Cl(1)	173.8(2)	173.4(2)
N(15)–Pd–Cl(1)	94.0(2)	93.6(2)
Cl(2)–Pd–Cl(1)	91.67(9)	91.55(9)
N(11)–C(2)–C(3)	129.4(8)	130.4(8)
N(11)–C(2)–C(1)	121.1(9)	124.3(8)
C(3)–C(2)–C(1)	109.5(7)	105.2(7)
C(2)–N(11)–N(12)	114.3(8)	115.5(7)
C(13)–N(12)–N(11)	116.5(7)	116.8(6)
C(13)–N(12)–Pd	115.0(6)	115.3(6)
N(11)–N(12)–Pd	127.9(5)	127.6(5)
N(12)–C(13)–C(14)	118.0(7)	115.7(7)
N(15)–C(14)–C(13)	112.5(7)	116.4(8)
C(2)–N(11)–N(12)–C(13)	111.6(9)	−103.0(9)

molar amount of either (1*R*)-(+)-camphor formaldehyde azine or (1*R*)-(−)-fenchone formaldehyde azine caused complete dissolution of the binuclear palladium complex and the formation of complexes of the type $[PdCl_2(PMe_2R)(H_2C{=}N{-}N{=}C_{10}H_{16})]$ [R = Ph **8**, or C_6H_4OMe-4 **9**, $C_{10}H_{16}$ is a (1*R*)-(+)-camphor residue; R = Ph **10** or C_6H_4OMe-4 **11**, $C_{10}H_{16}$ is a (1*R*)-(−)-fenchone residue] which were characterised by ^1H, ^{13}C and ^{31}P NMR spectroscopy. The ^1H and ^{31}P-{^1H} NMR spectra of each solution showed that the resonances were broad at ambient temperature but upon cooling to −30 °C the spectra sharpened to reveal the presence in solution of two complexes for each reaction mixture. For example, in the ^{31}P NMR spectrum of **8** at −30 °C and 36.2 MHz, two singlet resonances, present in an approximate ratio of 2:1, were observed which we assigned to two species, **8a** and **8b**. In the ^1H NMR spectrum at −30 °C and 400 MHz, **8a**, the more abundant of the two forms, gave rise to one doublet resonance for the phosphine methyl protons and three singlets for the methyl groups in the camphor residues. In addition there appeared two doublets of doublets for the $H_2C{=}N$ protons (at δ 7.37 and 7.17) which in the ^1H-{^{31}P} NMR spectrum became doublets [^2J(HH) = 11.4 Hz]; the coupling of the protons to ^{31}P was 3.3 and 9.4 Hz for the resonances at δ 7.37 and 7.17, respectively. Isomer **8b**, the less abundant of the two forms, gave rise to a similar pattern of resonances in the ^1H NMR spectrum but the couplings of the $H_2C{=}N$ protons to ^{31}P were both smaller. Additionally one of these resonances and one of those from a methyl group in the camphor residue of **8b** were at much lower field (δ 8.88 and 1.94, respectively) than the other corresponding resonances. Further information as to the structure of these isomers came from the low-temperature ^{13}C-{^1H} NMR spectrum. This showed that the resonances for the C^2 carbons in the camphor residue appeared as doublets with that for **8b** at δ 191.7 [J(PC) = 3.7 Hz] and that for **8a** at 183.7 [J(PC) = 1.6 Hz]. In contrast the resonances for the $H_2C{=}N$ carbons appeared as slightly broad singlets which, as with the corresponding resonances of **1**, had similar chemical shifts for the two forms. We concluded that **8a** and **8b** are linkage isomers: the low field shift of one $H_2C{=}N$ proton, one CH_3 and the C^2 carbon indicate that in **8b** the Pd is bound to the $C_{10}H_{16}N$ unit (*cf.* **1c**) whilst the larger J(PH) values imply that in **8a** the Pd is bound to the $H_2C{=}N$ group.

The low-temperature ^1H, ^{31}P and ^{13}C NMR spectra of complex **9** showed a similar set of resonances to those of **8** but for **10** and **11** the spectra indicated that the ratio of the two forms was rather different. Isomer **10a** (the species with resonances most closely corresponding to those of **8a**) was present as no more than 10% of the reaction mixture and whilst

the amount of **11a** was again *ca.* 10% of the mixture (^{31}P evidence), the ^{1}H and ^{13}C resonances for this species were obscured by those for the **b** isomer. Whilst much of the spectroscopic data for **10** and **11** were similar to those of **8** and **9**, one difference worthy of note occurred in the ^{13}C spectra where, for **10b** and **11b**, the resonances for C^1 and C^3 were coupled to ^{31}P. Previously we commented on the low-field shift of the C^2 resonance indicating co-ordination by the $C_{10}H_{16}N$ nitrogen (*e.g.* in **1** and **2**) and the phosphorus–carbon coupling in **10b** and **11b** reinforces our assignments of the connectivity in these compounds.

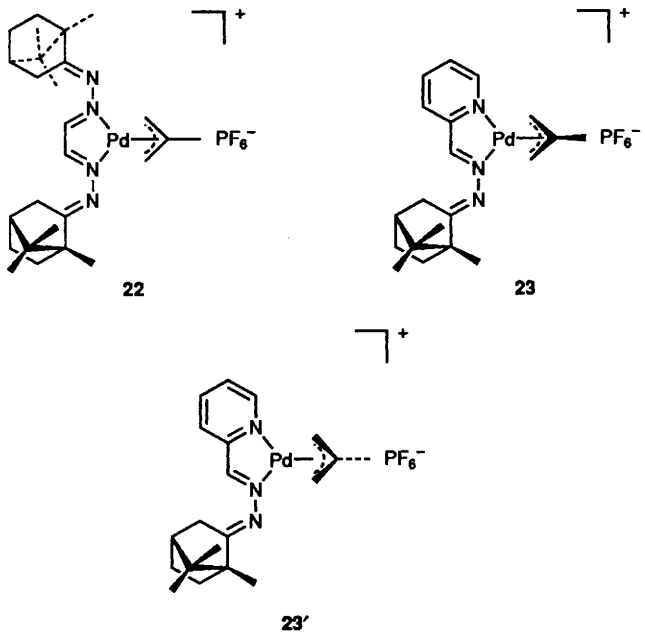
Our attempts to observe similar behaviour between the azines and $[Pd_2Cl_4(PPh_3)_2]$ were frustrated by the relative insolubility of the binuclear palladium compound. Treatment of suspensions of $[Pd_2Cl_4(PPh_3)_2]$ with 1 mole equivalent of $C_{10}H_{16}$-N–N=CR_2 [$C_{10}H_{16}$ = (1*R*)-(−)-camphor residue, R = H or Me] in dichloromethane caused partial dissolution of the binuclear palladium complex but an excess of the azine was required to cause complete dissolution to give yellow-orange solutions, which presumably contained complexes of the azines but were difficult to characterise, and we were unable to isolate any complex in a pure form. Treatment of $[Pd_2Cl_4(PPh_3)_2]$ with (1*R*)-(−)-fenchone formaldehyde azine in CH_2Cl_2 solution caused partial dissolution of the palladium complex, in a similar way to that observed with the mixed (1*R*)-(+)-camphor azines above, and addition of a large excess of the azine was again required to cause the palladium to react completely. When followed by addition of light petroleum to the reaction solution, orange crystals of a compound **12** were precipitated which microanalytical data suggested had incorporated the azine and was $[PdCl_2(PPh_3)(H_2C{=}N{-}N{=}C_{10}H_{16})]$. The IR spectrum showed a strong peak at 350 cm^{-1} and a much weaker peak at 340 cm^{-1} (and so we assumed that the principal species precipitated from the solution had a *trans* configuration at the metal centre) and also two strong peaks at 1640 and 1612 cm^{-1} due to the two ν(C=N) stretches. The compound was sparingly soluble in benzene but more readily soluble in $CDCl_3$ and CD_2Cl_2. Unfortunately, solutions of the complex which did not contain a large excess of the azine quite rapidly decomposed with $[Pd_2Cl_4(PPh_3)_2]$ precipitating within a few minutes from $CDCl_3$ or CD_2Cl_2. The ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR spectroscopic data for **12** were obtained in $CDCl_3$ solution at −30 °C, in the presence of an excess (*ca.* eight fold) of the (1*R*)-(−)-fenchone formaldehyde azine. The ^{31}P-{^{1}H} spectrum showed two species in a ratio of *ca.* 8:1 which were assigned by analogy with **10** and **11** as **12a** and **12b**. Isomer **12b**, the more abundant, gave rise to patterns of resonances in both the ^{1}H and ^{13}C-{^{1}H} spectra similar to those of **10b** and **11b**, whilst the resonances due to **12a** were obscured by the PPh_3 resonances and those of the free azine. We concluded that **12** exists as isomers in the same way as **10** and **11** and that the **b** forms of these complexes at least have the *trans* configuration. Very probably, **10a**, **11a** and **12a** together with complexes **8** and **9** are also *trans* at the metal centre and in the diagrams that is how we have chosen to draw them.

The reaction of $[Pd_2Cl_4(PMe_2Ph)_2]$ with the α-diazines was more complex than that between this binuclear complex and the mixed monoazines. When an equimolar amount of the palladium binuclear complex and either bis[(1*R*)-(+)-camphor]- or bis[(1*R*)-(−)-fenchone]-glyoxal diazine were dissolved in $CDCl_3$ the ambient-temperature spectra were broad but when the solution was cooled to −30 °C the spectra sharpened revealing that only one product was present in the solution in each case. These products were symmetrical, the two camphor or fenchone residues giving rise to one set of resonances in the ^{1}H and ^{13}C NMR spectra, and the occurrence at relatively low field of both the glyoxal azine protons (which, in contrast to the monoazine complexes, did not couple to ^{31}P) and one of the $C_{10}H_{16}$ methyl groups suggests that in solution the reaction products have the formula $[(PhMe_2Ph)Cl_2Pd(C_{10}H_{16}N{-}N{=}CH{-}CH{=}N{-}NC_{10}H_{16})PdCl_2(PMe_2Ph)]$ [$C_{10}H_{16}$ is a (1*R*)-(+)-camphor residue **13** or a (1*R*)-(−)-fenchone residue **14**] with a palladium atom bonded to the $C_{10}H_{16}N$ nitrogen at each end of the diazine. Our formulation of these complexes was corroborated by the ^{13}C NMR spectra, also recorded at −30 °C, which showed the C^2 resonance at low field. Van Koten and co-workers[15] reported complexes where an α-diimine group bridged two palladiums. Although an analogous co-ordination mode using the glyoxal azine nitrogens can be envisaged, and this mode would be expected to lead to the glyoxal protons resonating at low field (as found), it would not explain the low-field shift of the $C_{10}H_{16}$ $C^{10}H_3$ protons and of the C^2 carbons. The crystal structure of a monodentate α-diimine complex, *viz.* *trans*-$[PdCl_2(PPh_3)(Bu^t{-}N{=}CH{-}CH{=}NBu^t)]$, has been reported.[16]

When the binuclear palladium complex was mixed with 2 mole equivalents of either of the diazines (*i.e.* Pd:diazine = 1:1) in $CDCl_3$ the ambient-temperature spectra were again broad but cooling the solution to −30 °C revealed that the solution contained either **13** or **14** plus free diazine plus a new complex. We formulate this complex as $[PdCl_2(PMe_2Ph)(C_{10}H_{16}{=}N{-}N{=}CH{-}CH{=}N{-}N{=}C_{10}H_{16})]$ [$C_{10}H_{16}$ is a (1*R*)-(+)-camphor residue **15** or a (1*R*)-(−)-fenchone residue **16**] in which the two ends of the diazine are inequivalent. In both cases one of the glyoxal azine protons and one of the six methyl groups were shifted to low field signifying co-ordination of the diazine ligand to the palladium *via* one of the $C_{10}H_{16}N$ nitrogens. In the ^{1}H NMR spectrum, for example, the glyoxal azine protons gave rise to two resonances (at δ 9.55 and 7.98) coupled to each other by 8.5 Hz: the resonance at δ 9.55 also showed a coupling to ^{31}P of 1.6 Hz. We have assumed in the diagrams that the metal in **13**–**16** has the *trans* configuration. This is based on the complexes of the monoazines, particularly **12** above, on diimine complexes reported by van Koten and co-workers[15,16] and the complexes reported below of the pyridine-2-carbaldehyde azines.

The reaction between $[Pd_2Cl_4(PMe_2Ph)_2]$ and (1*R*)-(+)-camphor pyridine-2-carbaldehyde azine (Pd:azine 1:1) gave a mixture of products when conducted in dichloromethane or benzene solution. When the reaction was carried out in $CHCl_3$ solution a crystalline product was obtained which was insoluble in common organic solvents but which had an IR spectrum almost identical to that of **6** and an elemental analysis in good agreement with **6**·$CHCl_3$. This, however, appeared to be an atypical example: the reactions between $[Pd_2Cl_4(PMe_2Ph)_2]$ and (1*R*)-(−)-fenchone pyridine-2-carbaldehyde azine or $[Pd_2Cl_4(PBu^n{}_3)_2]$ and either of the pyridine-2-carbaldehyde azines each gave a single product, isolated as a yellow solid. These complexes were formulated as $[PdCl_2(PR_3)(NC_5H_4{-}CH{=}N{-}N{=}C_{10}H_{16})]$ [R_3 = Me_2Ph **17** or $Bu^n{}_3$ **19**, $C_{10}H_{16}$ is a (1*R*)-(−)-fenchone residue; R_3 = $Bu^n{}_3$ **18**, $C_{10}H_{16}$ is a (1*R*)-(+)-camphor residue] and in each case a sizeable coupling between the pyridine H^6 and ^{31}P was observed, whilst the carbaldehyde azine protons remained as singlets, indicating that the ligand was bound to the palladium *via* the pyridine nitrogen, the low-field shift of the carbaldehyde azine protons can again be ascribed to their being brought close to the metal. The IR spectra of **17**–**19** each showed a single strong band due to ν(Pd–Cl) and so we assign these complexes *trans* configurations at the metal centre.

The reaction between $[Pd_2Cl_4(PMe_2Ph)_2]$ and either of the two pyridinecarbaldehyde azines in a 1:1 ratio (*i.e.* Pd:azine 2:1) gave a solution which had broad resonances in the ^{1}H NMR spectrum, but on cooling the solution to −30 °C a sharp spectrum was obtained in which a methyl group in a camphor or fenchone residue appeared at relatively low field and the HC=N proton appeared at very low field (*ca.* δ 11). The HC=N protons did not couple to ^{31}P in either case but the pyridine H^6 protons showed a coupling at low temperature, which was lost at ambient temperature, and so clearly pyridinecarbaldehyde azine is exchanged between different $PdCl_2(PMe_2Ph)$ units. The products were formulated as $[\{PdCl_2(PMe_2Ph)\}_2(\mu{-}NC_5H_4{-}$



CH=N-$NC_{10}H_{16}$)] [$C_{10}H_{16}$ is a (1*R*)-(+)-camphor residue **20** or a (1*R*)-(−)-fenchone residue **21**] with the low-field shift of the HC=N proton arising from a double deshielding by the two palladiums. The formulation was backed up by low-temperature ^{13}C and ^{31}P NMR spectroscopy. The ^{31}P-{^1H} NMR spectra both contained two singlet resonances and the ^{13}C spectra showed the $C_{10}H_{16}$ C^2 carbons at relatively low field. The broadness of the resonances observed for **8–16** and **20** and **21** at ambient temperature presumably all have the same cause. Given that the ambient-temperature spectra of **20** and **21** show a loss of coupling to ^{31}P and our attempts to obtain these species in a solid form resulted in the precipitation of $[Pd_2Cl_4(PR_3)_2]$ we suggest that at temperatures much above −30 °C the equilibrium $2[PdCl_2L(PR_3)] \rightleftharpoons [\{PdCl_2(PR_3)\}_2] + 2L$ is established.

Reactions with $[\{PdCl(\eta^3\text{-}H_2CCMeCH_2)\}_2]$.—When a suspension of the η^3-methylallylpalladium complex $[\{PdCl(\eta^3\text{-}H_2CCMeCH_2)\}_2]$ in methanol was treated with bis[(1*R*)-(+)-camphor] glyoxal diazine and the resultant mixture was warmed gently the palladium complex dissolved. Addition of an excess of NH_4PF_6 solution in methanol followed by cooling to −20 °C produced an off-white solid which was isolated and identified as $[Pd(\eta^3\text{-}H_2CCMeCH_2)\{(C_{10}H_{16}N\text{-}N{=}CH)_2\}]PF_6$ **22**. In the ^1H NMR spectrum of **22** in $CDCl_3$ solution at ambient temperature the two camphor residues appeared to be equivalent although the four allyl protons were each inequivalent. On cooling the solution to −30 °C, however, two sets of resonances for the camphor residues and separate resonances for the two glyoxal azine protons (which did not appear to couple) appeared and demonstrated that the camphor units were in fact inequivalent and rapidly interconverting at room temperature. The ^{13}C-{^1H} NMR spectrum recorded at both ambient temperature and −30 °C mirrored the changes in the ^1H spectrum: two inequivalent ends of the diazine at low temperature coalesced to one set of resonances at ambient whilst the two ends of the methylallyl ligand remained equivalent. Presumably the scrambling of the ends of the diazine ligand is caused by rotation of the allyl moiety around the axis joining it to the palladium.

Our attempts to make a corresponding complex of bis[(1*R*)-(−)-fenchone] glyoxal diazine were unsuccessful, but 2-methylallyl complexes containing the pyridine-2-carbaldehyde azines were prepared in a similar way to **22** and formulated as $[Pd(\eta^3\text{-}H_2CCMeCH_2)(NC_5H_4CH{=}N\text{-}N{=}C_{10}H_{16})]PF_6$ [$C_{10}H_{16}$ is a (1*R*)-(+)-camphor residue **23** or a (1*R*)-(−)-fenchone residue **24**]. These complexes were also fluxional and on cooling the solution to −60 °C the presence of two sets of resonances for each complex were observed, which we formulate as arising from the two isomers shown [**23** and **23'** and **24** and **24'** (L-fenchone replaces D-camphor)].

Conclusion

The (1*R*)-(+)-camphor or (1*R*)-(−)-fenchone monoazines with formaldehyde can bond to palladium using either nitrogen as in complexes **1**, **2** and **8–12**: the (1*R*)-(+)-camphor formaldehyde azine is less likely to bond through the $C_{10}H_{16}N$ than is the corresponding azine of (1*R*)-(−)-fenchone. In **8–12** the ratio of the two bonding modes appears to be largely independent of the phosphine. The diazines of glyoxal use the glyoxal azine nitrogens to chelate (**4**, **5** and **22**) but the $C_{10}H_{16}N$ nitrogens when bonded to palladium in a monodentate or bridging fashion (**13–16**). The pyridinecarbaldehyde azines with (1*R*)-(+)-camphor or (1*R*)-(−)-fenchone use the pyridine and CH=N nitrogens to chelate (**6**, **7**, **23** and **24**), the pyridine nitrogen to bind in a monodentate fashion (**17–19**) and the pyridine and $C_{10}H_{16}N$ nitrogens to bind in a bridging and monodentate fashion (**20** and **21**).

Experimental

General methods and spectroscopic techniques were the same as reported in previous papers from this laboratory.[17] Bis[(1*R*)-(+)-camphor] glyoxal diazine, bis[(1*R*)-(−)-fenchone] glyoxal diazine, (1*R*)-(+)-camphor azine pyridine-2-carbaldehyde and (1*R*)-(−)-fenchone pyridine-2-carbaldehyde azine were prepared as described previously.[4]

Preparations.—(1R)-(+)-*Camphor formaldehyde azine.* Formaldehyde (1.1 cm^3 of a 38% solution in water) was added to a suspension of Na_2SO_4 (20 g) in dichloromethane (25 cm^3) and the mixture stirred vigorously for 5 min until the solution above the Na_2SO_4 was homogenous. (1*R*)-(+)-camphor hydrazone (2.357 g, 14.2 mmol) and HCO_2H (0.3 cm^3) were then added and stirring continued for 1 h. The resultant yellow solution was diluted with diethyl ether (20 cm^3) and washed first with 10% NaOH in saturated NaCl solution and then with saturated NaCl solution. The solution was then dried over $MgSO_4$ before the solvent was removed using a Dufton column and the residue distilled using a Kugelrohr apparatus; the required product distilled as a very pale yellow oil at *ca.* 90 °C (2 mmHg). Upon cooling, the product solidified and could be recrystallised from pentane at −20 °C. Yield 1.72 g, 68% (Found: C, 73.85; H, 10.3; N, 15.55. $C_{11}H_{18}N_2$ requires C, 74.1; H, 10.2; N, 15.7%). NMR ($CDCl_3$): ^1H (99.5 MHz), δ 7.05 [d, 1, ^2J(HH) = 14.1, HC=N], 6.65 [d, 1, ^2J(HH) = 14.1, HC=N], 2.30 (m, 1, *exo*-H^3), 1.80 [d, 1, [^2J(HH) = 18.2 Hz, *endo*-H^3], 0.83 (s, 3), 0.74 (s, 3) and 0.60 (s, 3) (Me); ^{13}C-{^1H} (22.5 MHz), δ 180.6 (C^2), 146.2 (H_2C=N), 52.0 (C^1), 47.3 (C^7), 43.4 (C^4), 35.1 (C^3), 32.0 (C^5), 26.9 (C^6), 19.1/18.4 (C^8/C^9) and 10.8 (C^{10}). IR (CH_2Cl_2 solution): 1665 cm^{-1} [ν(C=N)]. Mass spectrum: *m*/*z* 178 (95 *M*) and 163 (100%, *M* − Me).

(1R)-(−)-*Fenchone formaldehyde azine.* This compound was prepared in the same way but using (1*R*)-(−)-fenchone hydrazone. The compound was distilled at *ca.* 65 °C (2 mmHg) and obtained as a colourless oil. Yield 2.01 g, 79% (Found: C, 74.3; H, 9.95, N, 15.85. $C_{11}H_{18}N_2$ requires C, 74.1; H, 10.2; N, 15.7%). NMR ($CDCl_3$): ^1H (99.5 MHz), δ 7.14 [d, 1, ^2J(HH) = 14.3, HC=N], 6.75 [d, 1, ^2J(HH) = 14.3 Hz, HC=N] and 1.15 (s, 9, Me); ^{13}C-{^1H} (22.5 MHz), δ 183.2 (C^2), 146.1 [^1J(CH) = 162.4, 177.0 Hz in fully coupled spectrum, H_2C=N], 50.5 (C^1), 48.4 (C^4), 45.0 (C^3), 42.5 (C^7), 33.7 (C^6), 24.9 (C^5), 23.6/23.2 (C^8/C^9) and 16.9 (C^{10}). IR (CH_2Cl_2 solution): 1645 cm^{-1} [ν(C=N)]. Mass spectrum: *m*/*z* 178 (64, *M*), 163 (62, *M* − Me), 149 (55, 163 − CH_2) and 135 (54%, 149 − N).

Acetone (1R)-(+)-*camphor azine*. This compound was prepared in the same way as (1*R*)-(+)-camphor formaldehyde azine but using acetone instead of formaldehyde solution. The compound was distilled at 70 °C (2 mmHg) and isolated as a pale yellow liquid. Yield 1.78 g, 73% (Found: C, 75.55; H, 10.9; N, 13.8. $C_{13}H_{22}N_2$ requires C, 75.7; H, 10.75; N, 13.6%). NMR ($CDCl_3$): ^1H (99.5 MHz), δ 1.94 (s, 3, MeC=N), 1.79 (s, 3, MeC=N), 0.96 (s, 3), 0.85 (s, 3) and 0.71 (s, 3) (Me); ^{13}C-{^1H} (22.5 MHz), δ 172.8 (C^2), 158.0 (Me_2C=N), 52.5 (C^1), 46.2 (C^7), 42.7 (C^4), 33.9 (C^3), 31.5 (C^5), 26.1 (C^6), 23.5 (*Me*C=N), 18.2/17.5 (C^8/C^9), 16.1 (*Me*C=N) and 9.9 (C^{10}). Mass spectrum: *m*/*z* 206 (66, *M*) and 191 (100%, *M* − Me).

$[PdCl_2(H_2C{=}N{-}N{=}C_{10}H_{16})_2]$ **1**. (1*R*)-(+)-Camphor formaldehyde azine (354 mg, 1.99 mmol) was added to a solution of sodium tetrachloropalladate(II) (283 mg, 0.96 mmol) in methanol (5 cm^3) causing the red solution to become yellow-orange. The reaction mixture was then filtered through a Celite plug and the solvent removed under reduced pressure to give a yellow-orange microcrystalline solid which was washed with n-pentane–ethanol (5:1) and then water. Yield 353 mg, 69%.

$[PdCl_2(H_2C{=}N{-}N{=}C_{10}H_{16})_2]$ **2** *and* $[PdCl_2(Me_2C{=}N{-}N{=}C_{10}H_{16})_2]$ **3**. These complexes were prepared in a fashion analogous to that of **1** but using (1*R*)-(−)-fenchone formaldehyde azine and acetone (1*R*)-(+)-camphor azine, respectively. Yields: **2** 51; **3** 74%.

$[PdCl_2\{(C_{10}H_{16}NN{=}CH)_2\}]$ **4**. Sodium tetrachloropalladate(II) (160 mg, 0.54 mmol) in methanol (2 cm^3) was added to a solution of bis[(1*R*)-(+)-camphor] glyoxal diazine (200 mg, 0.564 mmol), also in methanol. This resulted in the immediate formation of an orange-yellow precipitate which, after the reaction mixture was cooled, was filtered off and washed with methanol and then with water. The precipitate was dried over P_4O_{10}. Yield 272 mg, 91%.

$[PdCl_2\{(C_{10}H_{16}NN{=}CH)_2\}]$ **5**. $[PdCl_2(NC_5H_4CH{=}N{-}N{=}C_{10}H_{16})]$ **6** and **7**. These compounds were prepared in the same fashion as **4** but using the corresponding azine or diazine. Yields: **5**, 79; **6**, 77 and **7**, 90%.

$[PdCl_2(PPh_3)(H_2C{=}N{-}N{=}C_{10}H_{16})]$ **12**. (1*R*)-(−)-Fenchone formaldehyde azine (*ca.* 15 fold excess) was added to a suspension of $[\{PdCl_2(PPh_3)\}_2]$ (86 mg, 0.098 mmol) in dichloromethane (5 cm^3). When all the palladium complex had dissolved the reaction mixture was filtered through a Celite plug and the product was precipitated as orange crystals by addition of pentane. It was then washed with pentane and dried *in vacuo*. Yield 97 mg, 80%

$[PdCl_2(PBu^n_3)(NC_5H_4CH{=}N{-}N{=}C_{10}H_{16})]$ **18**. (1*R*)-(+)-Camphor pyridine-2-carbaldehyde azine (102 mg, 0.40 mmol) was added to a solution of $[\{PdCl_2(PBu^n_3)\}_2]$ (148 mg, 0.195 mmol) in dichloromethane (3 cm^3). The solution, initially orange-red, became yellow immediately and was then filtered through a Celite plug before the solvent was evaporated to give a yellow solid residue. This residue was washed with ethanol and then methanol before being dried *in vacuo*. Yield 103 mg, 42%.

$[PdCl_2(PMe_2Ph)(NC_5H_4CH{=}N{-}N{=}C_{10}H_{16})]$ **17** *and* $[PdCl_2(PBu^n_3)(NC_5H_4CH{=}N{-}N{=}C_{10}H_{16})]$ **19**. These complexes were prepared as for **18** but using (1*R*)-(−)-fenchone pyridine-2-carbaldehyde azine and the appropriate palladium phosphine dimer. Yields: **17**, 71; **19**, 87%.

$[Pd(\eta^3\text{-}CH_2CMeCH_2)\{(C_{10}H_{16}NN{=}CH)_2\}]PF_6$ **22**. Bis-[(1*R*)-(+)-camphor] glyoxal diazine (188 mg, 0.53 mmol) was added to a suspension of $[\{PdCl(\eta^3\text{-}CH_2CMeCH_2)\}_2]$ (100 mg, 0.26 mmol) in methanol (10 cm^3). The mixture was stirred until all the palladium complex had dissolved (*ca.* 5 min) and then a solution of NH_4PF_6 in methanol (excess) was added. The solution was then filtered through a Celite plug and cooled to −20 °C whereupon off-white microcrystals were deposited. The product was filtered off and washed with copious amounts of water followed by a little ether and dried *in vacuo*. Yield 260 mg, 77%.

$[Pd(\eta^3\text{-}CH_2CMeCH_2)(NC_5H_4CH{=}N{-}N{=}C_{10}H_{16})]PF_6$ **23** and **24**.These complexes were prepared in a similar fashion to **22** but using the appropriate azine of pyridine-2-carbaldehyde. Yields: **23** 96; **24**, 85%.

Reactions between $[\{PdCl_2(PR_3)\}_2]$ *and* $C_{10}H_{16}NN{=}CH_2$, $(C_{10}H_{16}NN{=}CH)_2$ *or* $NC_5H_4CH{=}NNC_{10}H_{16}$.—In a typical experiment, the binuclear palladium complex (50 mg) was suspended in $CDCl_3$ (*ca.* 0.3 cm^3) in an NMR tube and the required amount of azine or diazine was added. The addition caused complete dissolution of the palladium complex and the NMR spectra were taken of the reaction mixture at +28 and −30 °C.

Single-crystal X-Ray Diffraction Analysis of Complex **6**.—All crystallographic measurements were carried out on a Stoe STADI4 diffractometer operating in the ω–θ scan mode using graphite-monochromated Mo-Kα radiation (λ = 71.069 pm) and an on-line profile-fitting method.[18] The data set was corrected for absorption using azimuthal ψ scans (minimum and maximum transmission factors 0.7439 and 0.8349 respectively).

The structure was determined by direct methods using SHELXS 86[19] and was refined by full-matrix least squares (based on F^2) using SHELXL 93.[20] All data were used in the refinement. The solution gave two molecules in the asymmetric unit which differ principally by a 160° rotation of the camphor molecule relative to the square co-ordination plane of the palladium atom (see Table 5). All non-hydrogen atoms of both molecules were refined with anisotropic thermal parameters. All hydrogen atoms were constrained to calculated positions (C–H 0.93, 0.97, 0.96 and 0.99 Å for phenyl, methylene, methyl and methine hydrogen atoms respectively) with fixed isotropic thermal parameters of $n(U_{eq})$ of the parent carbon atom where *n* was 1.5 for methyl hydrogens and 1.2 for all others. The two molecules are very nearly related to one another by a centre of symmetry and this caused problems with pseudo-symmetry throughout solution and refinement. These problems were considerably aggravated by the presence of a dichloromethane solvate molecule which was unequally disordered over two positions. The close proximity of these two positions and the unequal occupancy meant that the disorder could not be fully characterised and was dealt with as two sets of chlorine atoms with isotropic thermal parameters and respective occupancy factors of 0.7 and 0.3. The weighting scheme was $w = [\sigma^2(F_o^2) + (0.0282P)^2 + 4.8628P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$. The final Fourier-difference synthesis showed some small ripples close to the chlorine atoms of the solvate molecule but was otherwise flat and showed no features of chemical significance (maximum and minimum residual densities 1.198 and −0.414 e $Å^{-3}$). The absolute configuration of the molecule was based initially on the known configuration of the (1*R*)-(+)-camphor starting material and was later confirmed by refinement of a Flack[21] enantiopole parameter to 0.05(5). Final non-hydrogen atomic coordinates are given in Table 4. It should be noted that the disorder and pseudo-symmetry have led to high estimated standard deviations in the derived bond lengths and angles listed in Table 5 so that any apparent differences between the two independent molecules are not significant. The ORTEP[22] diagrams of the two independent molecules are given in Fig. 2.

Crystal data. $C_{16}H_{21}Cl_2N_3Pd{\cdot}0.5CH_2Cl_2$, 0.6 × 0.4 × 0.2 mm, M = 475.12 (includes solvate molecule), monoclinic, space group $P2_1$, a = 9.5830(13), b = 13.9720(14), c = 14.726(2) Å, β = 97.610(11)°, U = 1954.4(4) $Å^3$, Z = 4, D_c = 1.615 Mg m^{-3}, μ = 1.362 mm^{-1}, $F(000)$ = 956.

Data collection. 3.0 < 2θ < 50.0°; each scan divided into 30 steps, scan widths and step sizes calculated from a learnt profile; scan speeds 1.0–8.0° min^{-1} (subject to a fast pre-scan). Number of data collected = 7216; number of unique data, n = 6908; number with $F_o > 4.0\ \sigma(F_o)$ = 5944; $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma(F_o^2)$ = 0.0160; $R_{sig} = \Sigma\sigma(F_o^2)/\Sigma(F_o^2)$ = 0.0251; T = 200 K.

Structure refinement. Number of parameters, $p = 421$; $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.0416$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}} = 0.0842$; goodness of fit $s = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{\frac{1}{2}} = 1.106$; maximum $\Delta/\sigma = -0.599$ [in U_{11} of C(19) of molecule 2], mean $\Delta/\sigma = 0.105$.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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