Ligand Exchange Reactions in Cyclopalladated Complexes of Benzylideneanilines. Crystal Structure of $[Pd(C_6H_4CH=NC_6H_5)Br(PPh_3)_2]$†

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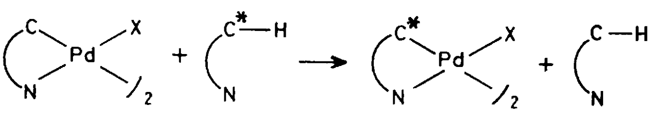
The ligand exchange reactions between $[\{Pd(p\text{-}RC_6H_3CH=NC_6H_5)(O_2CMe)\}_2]$ and the free imines $p\text{-}RC_6H_4CH=NC_6H_5$ (R = H, Cl, NMe_2, or NO_2) ($N^\frown CH$) in acetic acid have been studied. The substitution process is favoured when the incoming ligand contains electron-withdrawing substituents. From the results obtained a new mechanism involving a bis-cyclometallated complex $(N^\frown C^*)Pd(C^\frown N)]$ as intermediate is proposed. The dimeric cyclopalladated compounds are obtained by metallation of the imines by $Pd(O_2CMe)_2$; by reaction with phosphines PR'_3 and LiBr, $[Pd(p\text{-}RC_6H_3CH=NC_6H_5)Br(PR'_3)]$ and $[Pd(p\text{-}RC_6H_3CH=NC_6H_5)Br(PR'_3)_2]$ are formed (R' = Ph or Et). All the compounds have been fully characterized and their ^1H and ^{13}C n.m.r. spectroscopic data recorded. The molecular structure of $[Pd(C_6H_4CH=NC_6H_5)Br(PPh_3)_2]$ has been determined by a single-crystal *X*-ray analysis. The crystals are monoclinic, space group $P2_1/a$, $a = 17.427(3)$, $b = 24.790(4)$, $c = 10.424(2)$ Å, $\beta = 98.91(2)°$, and $Z = 4$; $R = 0.053$ for 6 579 reflections. The palladium atoms are five-co-ordinated, the Pd–N distance being 2.710(6) Å.

Cyclometallated compounds of transition metals have attracted a great deal of attention during recent years. These compounds have been used for the synthesis of carbene complexes, compounds with metal–metal bonds, binuclear hydrido-bridged complexes, and particularly in regiospecific organic syntheses in both stoicheiometric and catalytic reactions.[1–4]

The substitution reactions of ancillary non-metallated ligands and transmetallation reactions between cyclometallated complexes and free metal salts have been widely studied.[5] Ryabov and Yatsimirsky[6] have recently reported a remarkable new ligand exchange reaction between cyclopalladated complexes and the free ligands to afford new metallacycles (see below).



This process has permitted the obtention of cyclopalladated compounds of N-donor ligands containing electron-withdrawing substituents which are difficult to prepare by direct palladation since the process occurs by the electrophilic attack of Pd^{II} on the ligand ring.

It has also been possible to obtain the six-membered cyclometallated complex $[\{PdCl(bzpy)\}_2]$ (Hbzpy = 2-benzylpyridine), by the action of Hbzpy on $[\{PdCl(dmba)\}_2]$ (Hdmba = *N*,*N*-dimethylbenzylamine)[7] despite the fact that the formation of five-membered rings is specially favoured with N-donor ligands according to Cope's rules.[8]

Following our current interest in metallation of N-donor ligands[9] we have obtained compounds of the type $[\{Pd(p\text{-}RC_6H_3CH=NC_6H_5)(O_2CMe)\}_2]$ (R = H, Cl, NMe_2, or NO_2) and studied their ligand exchange reactions with free imines, in order to study the effect of the substituents in the substitution reaction. From the results obtained, a new mechanism involving a bis-cyclometallated complex, $[N^\frown C^*)Pd(C^\frown N)]$, as intermediate is proposed.

Results and Discussion

The action of $Pd(O_2CMe)_2$ on the imines $p\text{-}RC_6H_4CH=NC_6H_5$ [R = H (**1a**), Cl (**1b**), NMe_2 (**1c**), or NO_2 (**1d**)] was examined in anhydrous $MeCO_2H$ under reflux. Cyclopalladation of the imines with formation of dimers $[\{Pd(p\text{-}RC_6H_3CH=NC_6H_5)(O_2CMe)\}_2]$ (**2**) occurs in all the cases studied, even with the imine (**1d**) which contains an electron-withdrawing substituent. Schiff bases containing electron-withdrawing substituents react slowly (R = NO_2, 5 h) as compared with those having electron-donating substituents (R = NMe_2, 15 min), in keeping with literature suggestions on electrophilic attack of Pd^{II} on N-donor ligands.[5]

The addition of PR'_3 (R' = Ph or Et) to acetone solutions of complexes (**2**), in the presence of LiBr, gives the cyclometallated compounds $[Pd(p\text{-}RC_6H_3CH=NC_6H_5)Br(PR'_3)]$ [R' = Ph (**3**) or Et (**4**)]. Decomposition occurs in the absence of LiBr and it is not possible to obtain the compounds $[Pd(p\text{-}RC_6H_3CH=NC_6H_5)(O_2CMe)(PR'_3)]$.

Similarly, the reaction of an excess of PR'_3 with (**2**), in the presence of LiBr, gives the compounds $[Pd(p\text{-}RC_6H_3CH=NC_6H_5)Br(PR'_3)_2]$ [R' = Ph (**5**) or Et (**6**)].

The action of $PdCl_2$ on (**5**) and (**6**) leads to the cyclometallated compounds (**3**) and (**4**) respectively and eventually, if an excess of $PdCl_2$ is used, the cyclometallated dimeric compounds $[\{Pd(p\text{-}RC_6H_3CH=NC_6H_5)Br\}_2]$ are formed. In both cases $PdCl_2$ traps the phosphine released from the metallated compounds giving $[PdCl_2(PR'_3)_2]$.

The ligand exchange reactions between these cyclopalladated complexes and the free imines have been studied.

The action of the stoicheiometric amount (2:1) of the imines on the complexes $[\{Pd(p\text{-}RC_6H_3CH=NC_6H_5)(O_2CMe)\}_2]$ was examined in anhydrous acetic acid under reflux for 24 h. It is

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† Bromo(*o*-phenyliminomethylphenyl-*C*,*N*)bis(triphenylphosphine)-palladium(II).

Supplementary data available (No. SUP 56529, 2 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii–xx. Structure factors are available from the editorial office.

apparent from the results obtained (Table 1) that the ligand exchange is favoured when the incoming ligand contains electron-withdrawing substituents although it is well known that electron-withdrawing substituents prevent the palladation process.

Thus, the complex $[\{\overline{\mathrm{Pd}(\mathrm{C_6H_4CH{=}N}}\mathrm{C_6H_5})(\mathrm{O_2CMe})\}_2]$ **(2a)** reacts with the imines p-$\mathrm{RC_6H_4CH{=}NC_6H_5}$ [R = Cl **(1b)** or R = $\mathrm{NO_2}$ **(1d)**] giving **(2b)** and **(2d)** in good yields (reactions 1 and 2 in Table 1), while neither **(2b)** nor **(2d)** reacts with the imine **(1a)** (reactions 4 and 7).

The exchange reactions between imines containing substituents with similar electronic properties, **(1b)** and **(1d)** (reactions 5 and 8) show the reversibility of this process, but the imine (**1d**; R = $\mathrm{NO_2}$) replaces the imine (**1b**; R = Cl) of complex **(2b)** with a 55% yield (reaction 5) while the imine (**1b**; R = Cl) replaces the imine (**1d**; R = $\mathrm{NO_2}$) of complex **(2d)** with only a 25% yield (reaction 8), in agreement with the greater electron-withdrawing character of the $\mathrm{NO_2}$ substituent. When the imine (**1c**; R = $\mathrm{NMe_2}$) is involved as a leaving or incoming ligand, decomposition takes place in all the cases (reactions 3, 6, 9, 10, 11, and 12) along with deposition of $\mathrm{Pd^0}$, since neither the complex **(2c)** nor the free imine **(1c)** is stable under the reaction conditions.

The mechanism previously proposed to explain these ligand exchange reactions[7] involves an attack of the incoming ligand on the dimeric cyclopalladated compound to give a monomeric complex **(I)** followed by protonolysis of the Pd–C bond of the palladacycle with formation of **(II)**; the subsequent palladation of the incoming ligand and the dissociation of the leaving ligand accomplish the mechanism (Scheme 1).

Table 1. Exchange of cyclometallated ligands in acetate-bridged palladium(II) complexes *

Reaction	Complex	Free ligand	Product	Yield/%
1	**(2a)**	**(1b)**	**(2b)**	60
2	**(2a)**	**(1d)**	**(2d)**	70
3	**(2a)**	**(1c)**	Decomp.	
4	**(2b)**	**(1a)**	**(2b)**	60
5	**(2b)**	**(1d)**	**(2b)** **(2d)**	25 55
6	**(2b)**	**(1c)**	Decomp.	
7	**(2d)**	**(1a)**	**(2d)**	70
8	**(2d)**	**(1b)**	**(2b)** **(2d)**	25 60
9	**(2d)**	**(1c)**	Decomp.	
10	**(2c)**	**(1a)**	Decomp.	
11	**(2c)**	**(1b)**	Decomp.	
12	**(2c)**	**(1d)**	Decomp.	

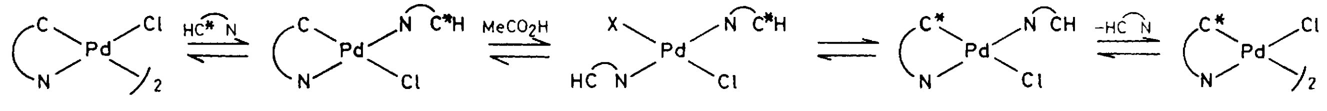
* All the reactions were carried out in refluxing acetic acid for 24 h.

It is difficult to accept that the intermediate **(II)**, which contains the two ligands N-co-ordinated to the metal, undergoes only the metallation of the incoming ligand, especially when the incoming ligands are less activated than the leaving ligands towards the electrophilic attack by $\mathrm{Pd^{II}}$. Thus [PdCl(denba)] is formed from [{PdCl(dmba)}$_2$] and denba (Hdenba = *N,N*-diethyl-*p*-nitrobenzylamine) in acetic acid–benzene in 46% yield, and [{PdCl(azbz)}$_2$] (Hazbz = azobenzene) is obtained from $[\{\mathrm{PdCl[Fe(\eta\text{-}C_5H_5)\ (\eta\text{-}C_5H_3CH_2NMe_2)}\}_2]$ and azobenzene in acetic acid–chloroform (1:1) in 72% yield. Moreover, the ligand exchange reactions occur also between [{PdCl(dmba)}$_2$] and azobenzene in the presence of the leaving ligand.[6]

Finally, the formation of the six-membered ring complex [{PdCl(bzpy)}$_2$] from the five-membered ring complex [{PdCl(dmba)}$_2$] and 2-benzylpyridine has been explained by this mechanism also,[7] implying that the intermediate [PdCl(X)(Hdmba)(Hbzpy)]$^+$ (X = solvent molecule or vacant co-ordination site) undergoes metallation of the Hbzpy ligand, even when it is well known that N-donor ligands form five-membered rings much more readily than the six-membered compounds.[8]

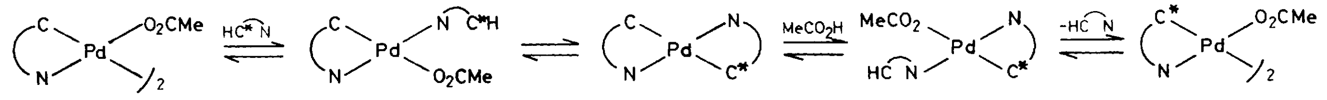
Alternatively, the ligand exchange process could be explained assuming a key intermediate of the type $[\overline{(\mathrm{N}^\frown\mathrm{C}^*)\mathrm{P}}\overline{\mathrm{d}(\mathrm{C}^\frown\mathrm{N})}]$ and the substitution would be related to the different stability of the σ(Pd–C) bonds to the protonolysis. Thus, electron-donating substituents will stabilize the Pd–C bond towards the action of acetic acid. The mechanism we propose consists of the following steps (Scheme 2). (*a*) As in first step of the mechanism proposed by Ryabov,[6,7] an incoming ligand ($\mathrm{HC^*}{}^\frown\mathrm{N}$) splits the dimeric complex leading to a monomeric complex **(I)**. (*b*) The intermediate **(I)** undergoes metallation of the incoming ligand giving the bis-cyclometallated compound **(III)**. (*c*) Protolysis of **(III)** and dissociation of the leaving ligand leads to the cyclometallated complex.

It has not been possible to observe the bis-cyclometallated intermediate **(III)**, but complexes of this type have been reported. Recently, Pregosin and Rüedi,[10] studying the action of CO on cyclometallated compounds $[\{\overline{\mathrm{Pd}(\mathrm{C}^\frown}\mathrm{N})(\mathrm{O_2CMe})\}_2]$ ($\mathrm{C}^\frown\mathrm{N} = \mathrm{RC_6H_3CH{=}NC_6H_4Me}$-$p$) in order to prepare the *ortho*-substituted esters, have obtained the complex $[\overline{(\mathrm{N}^\frown\mathrm{C})\mathrm{P}}\overline{\mathrm{d}(\mathrm{C}^\frown\mathrm{N})}]$ (where $\mathrm{C}^\frown\mathrm{N} = 5\text{-}\mathrm{NO_2C_6H_3CH{=}NC_6H_4Me}$-$p$) but the corresponding complexes with $\mathrm{C}^\frown\mathrm{N}$ = p-$\mathrm{RC_6H_3CH{=}NC_6H_4Me}$-$p$ (R = Cl or $\mathrm{NO_2}$) only could be detected by n.m.r. With imines containing electron-donating substituents R = H, $\mathrm{CH_3}$, or OMe these complexes were not formed. It should be noted also that the exchange ligand



(I) (II)

Scheme 1. X represents a solvent molecule or a vacant co-ordination site



(I) (III)

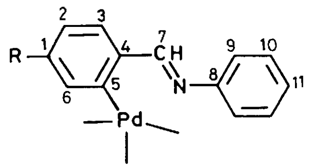
Scheme 2.

Table 2. Analytical data,[a] melting points, and i.r. data

Compound	Analysis (%) C	H	N	M.p. (°C)	ν(C=N)/ cm^{-1}
(2a)[b]	53.5 (52.15)	3.8 (3.75)	4.0 (4.05)	234—236[c]	*d*
(2b)	47.4 (47.4)	3.1 (3.15)	3.7 (3.70)	240—242[c]	*d*
(2c)	53.2 (52.55)	4.6 (4.65)	7.5 (7.20)	224—226[c]	*d*
(2d)	46.2 (46.15)	3.0 (3.05)	7.1 (7.15)	256—258[c]	*d*
(3a)[e]	60.2 (59.25)	4.1 (4.00)	2.4 (2.25)	210—212[c]	1 610
(3b)	57.1 (56.15)	3.8 (3.60)	2.1 (2.10)	202—204[c]	1 600
(3c)	59.2 (59.0)	4.4 (4.45)	4.2 (4.15)	188—190[c]	1 560
(3d)	55.5 (55.3)	3.6 (3.55)	4.1 (4.15)	214—216[c]	1 570
(4c)	47.7 (47.8)	5.6 (5.70)	5.4 (5.30)	162—164	1 580
(4d)	43.3 (43.10)	4.6 (4.55)	5.3 (5.30)	140—142	1 570
(5a)[b]	65.8 (66.05)	4.5 (4.50)	1.6 (1.55)	206—208	1 610
(5b)	63.7 (63.6)	4.2 (4.20)	1.6 (1.50)	208—210	1 615
(5c)	65.4 (65.6)	4.8 (4.80)	3.1 (3.00)	204—206	1 560
(5d)	62.7 (62.9)	4.2 (4.15)	3.0 (3.00)	210—212	1 580
(6a)	49.6 (49.85)	6.7 (6.65)	2.3 (2.30)	132—134	1 620
(6b)	47.0 (47.15)	6.1 (6.10)	2.2 (2.20)	158—160	1 615
(6c)	51.0 (50.25)	7.1 (7.00)	4.3 (4.35)	144—146	1 560
(6d)	45.5 (46.35)	6.1 (6.00)	4.2 (4.30)	156—158	1 565

[a] Calculated values are given in parentheses. [b] Previously reported, see ref. 12. [c] With decomposition. [d] Overlapped by the acetate bands. [e] Previously reported, see P. W. Clark and S. F. Dyke, *J. Organomet. Chem.*, 1984, **276**, 421.

Table 3. Proton n.m.r. data[a]



Compound	Methinic protons[b]	Aromatic protons[c]
(2a)[d]	7.63s	7.2—6.6br m
(2b)[d]	7.63s	7.2—7.1m (H^2,H^3), 6.58s (H^6)
(2c)[d,e]	7.42s	6.28dd (8.3, 2.3) (H^2), 7.09d (8.3, –) (H^3), 5.74d (–, 2.3) (H^6)
(2d)[d]	7.83s	7.95dd (8.2, 2.2)(H^2), 7.40d (8.2, –) (H^3), 7.31d (–, 2.2) (H^6)
(3a)	8.25d (6.8)	6.9m (H^2), (H^3),[f] 6.5m (H^1,H^6)
(3b)	8.23d (6.4)	6.96dd (8.0, 1.7) (H^2), (H^3),[f] 6.35dd (–, 1.7) [*J*(PH) = 5.3] (H^6)
(3c)[e]	8.03s	6.2dd (8.5, 2.2) (H^2), (H^3),[f] 5.8d (–, 2.2) (H^6)
(3d)	8.37d (6.7)	*f*
(4c)[e]	7.97d (6.6)	6.40d (8.3, –) (H^2), (H^3),[f] 6.56d [*J*(P–H) = 5.9] (H^6)
(4d)	8.33d (6.1)	8.03d (8.2, –) (H^2), 7.59 (8.2, –) (H^3), 8.17d [*J*(P–H) = 5.9] (H^6)
(5a)	8.18s	6.5br m (H^2, H^3, H^1), (H^6)[f]
(5b)	8.37s	6.54d (8.0, –) (H^2), 6.82d (8.0, –) (H^3), 6.77s (H^6)
(5c)[e]	8.02s	6.12dd (8.6, 2.1) (H^2), (H^3),[f] 5.95d (–, 2.1) (H^6)
(5d)	8.76s	*f*
(6a)	9.17s	7.0m (H^1,H^2), 7.9m (H^3), 7.4m (H^6)
(6b)	9.12s	7.03d (8.3, –) (H^2), 7.89d (8.3, –) (H^3), 7.46s (H^6)
(6c)[e]	9.04s	6.45d (8.6, –) (H^2), 7.88d (8.6, –) (H^3), 6.82s (H^6)
(6d)	9.26s	8.12d (8.6, –) (H^2), 7.86d (8.6, –) (H^3), 8.33s (H^6)

[a] In $CDCl_3$; chemical shifts (δ/p.p.m.) with respect to internal $SiMe_4$. [b] ^4J(P–H) are given in parentheses (Hz). [c] Assignments are given in parentheses: see above for numbering scheme. ^3J(H–H), ^4J(H–H) are given in parentheses. See text for assignment of C_6H_5N protons. [d] δ(CH_3COO); 1.80, 1.74, 1.84, 1.94 for compounds **(2a)**, **(2b)**, **(2c)**, and **(2d)** respectively. [e] δ(NMe_2): 2.86, 2.38, 3.06, 2.41, 2.99 for compounds **(2c)**, **(3c)**, **(4c)**, **(5c)**, and **(6c)** respectively. [f] Not visible: resonance under PPh_3 protons.

reactions need the presence of acetic acid, a solvent in which the cyclometallations preferentially take place.

The σ(Pd–C) bonds of intermediate **(III)** will be more easily hydrolysed by acetic acid and the less electronegative the co-ordinated imines are. If the incoming imines contain more electron-withdrawing substituents than the leaving imines, as in reactions 1 and 2 (Table 1), the $\underline{Pd\text{–}C_6H_4CH{=}NC_6H_5}$ bond of the bis-C$\frown$N complex $[(C_6H_5\overline{N{=}C_6H_3R\text{-}p)Pd}\,\overline{(C_6H_4CH{=}N}C_6H_5)]$ will undergo hydrolysis preferentially and the substitution will take place. In the reverse reactions 4 and 7 (Table 1) the intermediate **(III)** would be the same as above but no substitution occurs since in this case the Pd–C bond of the incoming ligand is broken. In the cases where the imines involved have substituents of similar character (R = Cl or NO_2; reactions 5 and 8) the two Pd–C bonds can be hydrolysed in a similar way, and a mixture of the two cyclometallated complexes will be obtained. But since imine (**1d**; R = NO_2) is more electronegative than imine (**1b**; R = Cl) the Pd–C bond of the *p*-$ClC_6H_4CH{=}NC_6H_5$ derivative will be more easily broken, and the complex **(2d)** will be the major component of the mixture in both reactions (reactions 5 and 8).

The results reported by Ryabov[6,7] could also be explained by this mechanism, since the leaving ligand has, in general, greater electron density in the metallated ring.

Characterization of Compounds.—The new compounds are yellow, **(3)**—**(6)**, or orange, **(2)**, air-stable solids. All compounds are quite soluble in chloroform, acetone, ethanol, or hot acetic acid [**(2c)** decomposes in the last solvent with formation of Pd^0], and slightly soluble in diethyl ether and alkanes.

Analytical data and decomposition temperatures are shown in Table 2. The low values of the molar conductivity in anhydrous acetone (10^{-4} mol dm^{-3} solution) at 20 °C show the non-electrolytic character of these compounds. Their diamagnetic behaviour suggests a square-planar arrangement of the ligands around the palladium atoms.

The i.r. spectra show the typical bands of co-ordinated phosphines[11] and imines.[12] The compounds $[\{\overline{Pd(p\text{-}RC_6H_3CH{=}N}C_6H_5)(O_2CMe)\}_2]$ show two bands at 1 580 and 1 420 cm^{-1} which are characteristic of bridging acetate ligand. The wavenumbers corresponding to ν(C=N) are included in Table 2. It should be noted that these values are smaller than those corresponding to free imines, even in compounds **(5)** and **(6)** in which there are apparently no Pd–N bonds; this suggests some degree of interaction between these atoms, as confirmed by *X*-ray analysis of **(5a)**.

Proton n.m.r. spectra of the compounds are reported in Table 3. The methinic protons in compounds **(2)** appear at *ca.* 7.4—7.8 p.p.m., shifted to high field by 0.7 p.p.m. relative

Table 4. $^{13}C-\{^1H\}$ N.m.r. data[a]

Compound	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	C^{11}
(2a)	130.3	123.9	127.4	147.5[b]	155.3	132.6	172.7	147.7[b]	123.2	128.0	127.4
(2b)	136.0	124.5	128.4	145.8	156.2	132.1	171.8	146.8	122.9	128.4	127.7
(2c)[c]	150.1	106.1	129.1	133.4	156.9	114.5	170.1	148.3	123.0	127.4	125.3
(2d)	147.1	119.6	126.3	150.4	155.7	127.4	171.2	146.7	122.5	128.3	128.9
(5b)[d]	135.0	122.7	131.1	136.0	168.0	139.2	164.0	152.3	121.5	128.9	125.6
(5d)[d]	146.8	117.5	127.5	130.6	169.5	144.9	162.7	151.6	121.4	129.1	126.4
(6a)	127.7[b]	123.3	129.6[b]	140.4	162.4	136.7	165.1	151.9	120.9	129.0	125.7
(6b)	135.7	123.6	128.3	138.1	164.5	135.6	163.7	151.7	120.9	129.1	125.9
(6c)[c]	151.4[b]	108.4	*e*	*e*	163.9	*f*	164.6	151.7[b]	120.9	128.9	124.8
(6d)	147.5	118.5	127.5	146.0	164.4	130.5	162.6	151.1	121.0	129.3	126.8

[a] In $CDCl_3$, room temperature: see Table 3 for numbering scheme. [b] Not unambiguously assigned. [c] $\delta(NMe_2)$ at 39.7 and 40.2 for compounds **(2c)** and **(6c)** respectively. [d] PPh_3 at C_i: 131.4, 131.8; C_o: 134.7, 134.5; C_m: 127.9, 128.1; C_p: 130.0, 130.1 for compounds **(5b)** and **(5d)** respectively. [e] Resonance under C^{10}. [f] Resonance under C^9.

Table 5. Principal bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

Br–Pd	2.542(1)	C(7)–N	1.281(9)	C(6)–C(1)	1.413(10)	C(4)–C(3)	1.408(10)
C(2)–Pd	2.008(6)	C(8)–N	1.433(7)	C(7)–C(1)	1.483(8)	C(5)–C(4)	1.397(12)
P(1)–Pd	2.351(1)	C(2)–C(1)	1.414(9)	C(3)–C(2)	1.379(8)	C(6)–C(5)	1.389(10)
P(2)–Pd	2.322(1)						
C(2)–Pd–Br	117.6(2)	P(2)–Pd–P(1)	161.3(1)	C(1)–C(2)–Pd	118.2(4)	C(6)–C(5)–C(4)	120.3(7)
P(1)–Pd–Br	95.2(0)	C(8)–N–C(7)	119.4(6)	C(3)–C(2)–Pd	123.6(5)	C(5)–C(6)–C(1)	119.9(7)
P(1)–Pd–C(2)	86.9(2)	C(6)–C(1)–C(2)	120.3(5)	C(3)–C(2)–C(1)	118.2(6)	C(1)–C(7)–N	121.0(6)
P(2)–Pd–Br	89.6(1)	C(7)–C(1)–C(2)	123.4(6)	C(4)–C(3)–C(2)	122.2(6)	C(9)–C(8)–N	122.3(6)
P(2)–Pd–C(2)	88.8(2)	C(7)–C(1)–C(6)	116.2(6)	C(5)–C(4)–C(3)	118.9(6)	C(13)–C(8)–N	116.7(6)

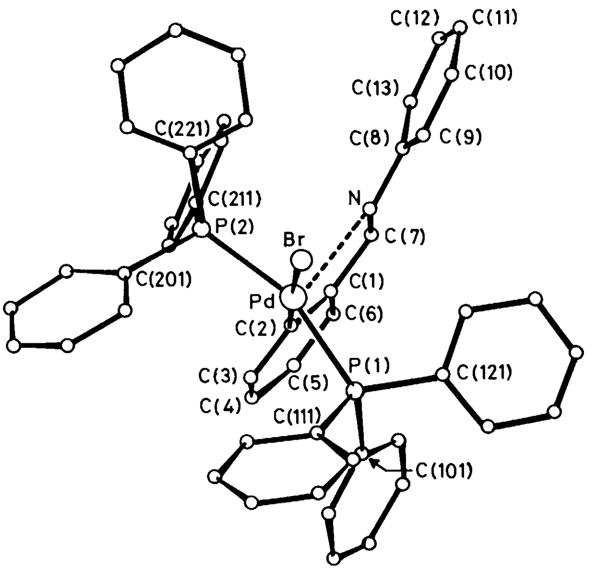


Figure. Molecular structure of $[Pd(C_6H_4CH=NC_6H_5)Br(PPh_3)_2]$

to the free imines. For the compounds containing phosphines $[Pd(p-RC_6H_3CH=NC_6H_5)Br(PR'_3)]$, this signal appears at 8.0—8.3 p.p.m. as a doublet by coupling with ^{31}P, $^4J(P-H)$ = 6—7 Hz. The spectra of compounds $[Pd(p-RC_6H_3CH=NC_6H_5)Br(PR'_3)_2]$ show the methinic protons shifted by 0.8 p.p.m. downfield relative to free imines if R′ = Et, but in the PPh_3-containing compounds this large downfield shift is not observed.

The downfield shift observed in the compounds containing PEt_3 can be explained by the paramagnetic anisotropy of the metal, indicating the close vicinity of methinic proton and the palladium atom, in agreement with previously reported results.[13] Taking into account the crystal structure of the similar complex $[\{Pd(p-ClC_6H_3CH=N-)Cl(PEt_3)_2\}_2]$ which shows some interaction between the nitrogen and palladium atoms,[14] it has been proposed that the rotation around the C(aromatic)–C(methinic) bond, in solution at room temperature, is not hindered and that a conformation in which this proton is near the palladium atom has an important contribution.

For the compounds containing the bulkier PPh_3 the rotation around the C(aromatic)–C(methinic) bond is hindered; as a result, the more important conformation in solution will be the same as that in the solid state with a significant palladium–nitrogen interaction (see *X*-ray analysis).

The unequivocal assignment of the $p-RC_6H_4CH=N$ aromatic protons affords conclusive evidence on the palladation position. The C_6H_5N aromatic protons appear as broad multiplet at 7.5—7.2 p.p.m. As far as the $[PdCl(PEt_3)_2]$ group is concerned, the methyl signals appear as quintuplets which are characteristic of a *trans* arrangement of the two phosphines due to the so-called 'virtual coupling', at 1.05 p.p.m. The acetate protons are observed as a singlet at 1.7—1.9 p.p.m., indicating that the cyclometallated dimers have a *trans* configuration.

The $^{13}C-\{^1H\}$ spectra of the compounds are reported in Table 4. The signal for the palladium-bound carbon is shifted greatly downfield compared with the normal range of δ values for aromatic protons, confirming that metallation has occurred. The assignment of the other aromatic carbons has been accomplished from the values of $\delta(^{13}C)$ of the free imines and by calculating the shifts induced by the *trans*-$PdX(PR'_3)_2$ 'substituent' on the benzene carbon atoms. However, for some carbon atoms, the proposed assignment is not unambiguous (see Table 4). The methinic carbons appear as a singlet shifted downfield by 10 p.p.m. relative to free imines. The methyl acetate carbons are observed as a singlet (δ 24.5—24.0) confirming that the cyclometallated dimers have a *trans* configuration. The methylenic carbons of PEt_3 appear as a triplet at δ 14.5—15.0 confirming the *trans* arrangement of the two phosphines.

Crystal Structure of $[Pd(C_6H_4CH=NC_6H_5)Br(PPh_3)_2]\cdot C_3H_6O$.—The crystal structure of $[Pd(C_6H_4CH=NC_6H_5)Br(PPh_3)_2]$ (**5a**) consists of discrete molecules, separated by van der Waals distances (Figure), and one acetone molecule of crystallization per molecule of complex. Selected bond lengths and angles are listed in Table 5. The palladium atom is co-ordinated to five atoms: P(1), P(2), Br, C(2), and N. The Pd, P(1), P(2), Br, and C(2) atoms are not coplanar, the largest deviation from the mean plane reaching 0.370 Å for the two P atoms. The metallated phenyl ring C(1)—C(6) forms a dihedral angle with the latter plane of 84.1(6)°. The steric hindrance between the triphenylphosphine and the imine ligands causes the deviation of the P atoms out of the plane of the complex. The Pd–C(2), Pd–P, and Pd–Br distances and related angles are similar to those found in analogous compounds.[14,15]

The Pd–N distance of 2.710(6) Å is shorter than the sum of the van der Waals radii, and also shorter than the distance observed for similar compounds without Pd–N bonds (*ca.* 3.1 Å),[15] but it is larger than the value found in compounds with a Pd–N bond (*ca.* 2.0 Å).[15] This suggests a significant Pd ··· N interaction as has been found in $[\{Pd(p\text{-}ClC_6H_3CH=N\text{-})Cl(PEt_3)_2\}_2]$.[14] The C(7)=N bond is lengthened upon co-ordination [1.281(9) Å] in relation to the free imine (1.237 Å)[16] and is nearly equal to that in $[Mn(C_6H_4CH=NC_6H_5)(CO)_4]$ [1.285(10) Å],[17] in agreement with a strong Pd ··· N interaction. The C(1)–C(7)–N–C(8) grouping is not planar, the C(7) atom deviates −0.055(8) Å and the other atoms deviate ±0.054 Å, the torsion angle is equal to −170.7(6)°. This group is planar in $[Mn(C_6H_4CH=NC_6H_5)(CO)_4]$. The aniline phenyl ring C(8)–C(13) is twisted 28.7(9)° from the imine C=N–C moiety in the complex; the corresponding twists in $[Mn(C_6H_4CH=NC_6H_5)(CO)_4]$ and in the free ligand are 57.0 and 55.2° respectively.

The phenyl ring C(1)–C(6) and imine moiety form a dihedral angle of 6.7(9)°, larger than that observed in the manganese complex (3.0°) and smaller than that observed in the free imine (10.3°). The two phenyl rings form a dihedral angle of 30.4(9)° that is significantly smaller than the corresponding angle in the above manganese complex (59.9°).[17]

Non-bonded interactions involving the imine CH group and an *ortho* CH group of the aniline phenyl ring have been proposed to explain the non-planar conformation of free benzylideneaniline.[16] The significant Pd ··· N interactions observed in the palladium complex cause the lack of planarity of the C–C=N–C moiety. As a result the imine can assume a more planar geometry than in the free state.

Experimental

N.m.r. spectra were obtained on Varian XL200 (^{13}C, 50.3 MHz) and Bruker WP80 (^1H, 80.13 MHz) spectrometers. I.r. spectra were recorded on a Beckman IR-20A spectrometer as KBr discs. Microanalyses were performed by the Institut de Química Bio-Orgànica de Barcelona (C.S.I.C.).

Crystal Data.—$C_{49}H_{40}BrNP_2Pd\cdot C_3H_6O$, $M = 949.2$, monoclinic, $a = 17.427(3)$, $b = 24.790(4)$, $c = 10.424(2)$ Å, $\beta = 98.91(2)°$, $U = 4\,449(2)$ Å^3, $D_c = 1.42$ g cm^{-3}, $Z = 4$, space group $P2_1/a$, $\mu(\text{Mo-}K_\alpha) = 14.77$ cm^{-1}.

Data Collection.—A small crystal was selected and mounted on a Philips PW-1100 four-circle diffractometer, the unit-cell parameters were determined by refinement of the setting angles for 25 reflections ($5 \leqslant \theta \leqslant 9°$). Intensities were collected with graphite-monochromatized Mo-K_α radiation, using the ω-scan technique (scan width 1°, scan speed 0.03° s^{-1}). 6 579 Reflections were measured in the range $2 \leqslant \theta \leqslant 30°$, 6 339 of which were assumed to be 'observed' by applying the condition $I \geqslant 2.5\sigma(I)$. Lorentz-polarization, but no absorption corrections were made.

Structure Solution and Refinement.—The structure was solved by direct methods using the MULTAN system of computer programs.[18] The *E*-map from the set of phases with the highest combined figure of merit revealed the position of 22 heaviest atoms, a subsequent weighted *F*-synthesis revealed the position of the remaining non-hydrogen atoms. The solvate molecule was observed in a difference synthesis after three isotropic cycles.

The isotropic and anisotropic cycles of refinements were carried out by full-matrix least-squares methods, using SHELX 76.[19] The function minimized was $w||F_o| - |F_c||^2$, where $w = [\sigma^2(F_o) + 0.0023|F_o|^2]^{-2}$, f, f', and f'' were taken from International Tables.[20] Refinements were terminated at $R = 0.053$ ($R' = 0.061$) with all observed reflections; a final difference synthesis revealed the position of 36 (of 46) hydrogen atoms, which were not included due to CPU time computer limitations.

Materials and Syntheses.—Solvents were dried and distilled before use. Benzylideneanilines were prepared according to published methods.[21]

$[\{Pd(p\text{-}RC_6H_3CH=NC_6H_5)(O_2CMe)\}_2]$ [R = H (**2a**), Cl (**2b**), NMe_2 (**2c**), *or* NO_2 (**2d**)].—A stirred suspension of $Pd(O_2CMe)_2$ (1 g, 4.5 mmol) in anhydrous acetic acid (30 cm^3) was treated with an excess of the imine (5 mmol) and refluxed for 15 min (R = NMe_2), 30 min (R = Cl or H), or 5 h (R = NO_2) and then filtered. The filtrate was concentrated *in vacuo*. Compounds (**2**) were precipitated by adding diethyl ether. Yield 70—80%.

$[Pd(p\text{-}RC_6H_3CH=NC_6H_5)Br(PPh_3)]$ [R = H (**3a**), Cl (**3b**), NMe_2 (**3c**) *or* NO_2 (**3d**)].—A stirred mixture of $[\{Pd(p\text{-}RC_6H_3CH=NC_6H_5)(O_2CMe)\}_2]$ (0.5 mmol), PPh_3 (0.26 g, 1 mmol), and LiBr (0.086 g, 1 mmol) in acetone (30 cm^3) was refluxed for 30 min and then filtered. The filtrate was concentrated *in vacuo* and the solid residue obtained was recrystallized from $CHCl_3$ to give (**3**) in 70% yield.

$[Pd(p\text{-}RC_6H_3CH=NC_6H_5)Br(PEt_3)]$ [R = NMe_2 (**4c**) *or* NO_2 (**4d**)].—A mixture of $[\{Pd(p\text{-}RC_6H_3CH=NC_6H_5)(O_2CMe)\}_2]$ (R = NMe_2 or NO_2) (0.5 mmol), PEt_3 (1 mmol), and LiBr (0.086 g, 1 mmol) in acetone (30 cm^3) was refluxed under nitrogen for 30 min and then filtered. The filtrate was concentrated *in vacuo* and the solid obtained, after addition of ethanol, was recrystallized from $CHCl_3$ to give (**4**) in 70% yield.

$[Pd(p\text{-}RC_6H_3CH=NC_6H_5)Br(PPh_3)_2]$ [R = H (**5a**), Cl (**5b**), NMe_2 (**5c**), *or* NO_2 (**5d**)].—A stirred mixture of compounds (**2**) (0.5 mmol), PPh_3 (0.52 g, 2 mmol), and LiBr (0.086 g, 1 mmol) in acetone (30 cm^3) was refluxed for 30 min. The precipitate which formed was filtered off, washed with water, ethanol, and ether, and recrystallized from $CHCl_3$ to afford (**5**) in 70% yield.

$[Pd(p\text{-}RC_6H_3CH=NC_6H_5)Br(PEt_3)_2]$ [R = H (**6a**), Cl (**6b**), NMe_2 (**6c**), *or* NO_2 (**6d**)].—A mixture of compounds (**2**) (0.5 mmol), PEt_3 (2 mmol), and LiBr (0.086 g, 1 mmol) in acetone (30 cm^3) was refluxed for 30 min under nitrogen and then filtered. The filtrate was concentrated *in vacuo* and the

Table 6. Positional parameters of non-hydrogen atoms (× 10^4) with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pd	7 946(0)	1 185(0)	1 664(0)	C(121)	9 342(3)	1 913(2)	3 990(6)
Br	7 901(0)	782(0)	3 893(1)	C(122)	9 717(4)	1 431(3)	4 323(7)
N	9 276(3)	786(2)	10 993(6)	C(123)	10 290(4)	1 413(3)	5 468(8)
C(1)	8 582(4)	1 293(2)	9 211(6)	C(124)	10 455(4)	1 867(3)	6 225(8)
C(2)	7 980(3)	1 473(2)	9 872(6)	C(125)	10 060(5)	2 346(3)	5 873(7)
C(3)	7 437(4)	1 826(2)	−760(7)	C(126)	9 502(4)	2 375(3)	4 754(7)
C(4)	7 456(4)	2 001(3)	7 960(7)	P(2)	6 913(1)	637(1)	800(2)
C(5)	8 049(5)	1 814(3)	7 312(7)	C(201)	6 455(3)	747(2)	−883(6)
C(6)	8 602(4)	1 456(3)	7 917(7)	C(202)	5 706(4)	984(3)	−1 174(7)
C(7)	9 224(4)	937(3)	9 808(7)	C(203)	5 417(5)	1 093(3)	−2 487(8)
C(8)	9 961(3)	511(2)	11 594(7)	C(204)	5 849(5)	979(3)	−3 455(8)
C(9)	10 684(4)	592(3)	11 211(8)	C(205)	6 580(5)	743(3)	−3 167(7)
C(10)	11 341(4)	324(3)	11 902(8)	C(206)	6 864(4)	628(3)	−1 895(7)
C(11)	11 264(4)	−8(3)	12 964(8)	C(211)	7 123(3)	−88(2)	748(6)
C(12)	10 548(4)	−87(3)	13 340(7)	C(212)	6 574(4)	−442(2)	99(7)
C(13)	9 886(4)	181(3)	12 678(7)	C(213)	6 791(5)	−995(3)	41(9)
P(1)	8 668(1)	1 950(1)	2 448(2)	C(214)	7 492(6)	−1 168(3)	548(9)
C(101)	9 284(3)	2 245(2)	1 341(6)	C(215)	8 059(5)	−816(3)	1 161(8)
C(102)	8 972(4)	2 568(2)	277(6)	C(216)	7 854(4)	−264(3)	1 276(7)
C(103)	9 457(4)	2 739(3)	−596(7)	C(221)	6 110(3)	721(2)	1 728(6)
C(104)	10 251(5)	2 595(3)	−431(7)	C(222)	5 679(4)	306(3)	2 114(7)
C(105)	10 551(4)	2 262(3)	598(8)	C(223)	5 055(4)	420(4)	2 790(8)
C(106)	10 069(4)	2 096(3)	1 511(7)	C(224)	4 870(4)	956(4)	3 027(8)
C(111)	7 988(3)	2 470(2)	2 787(6)	C(225)	5 293(4)	1 369(3)	2 645(7)
C(112)	7 356(4)	2 299(3)	3 394(7)	C(226)	5 919(4)	1 255(3)	1 985(7)
C(113)	6 808(4)	2 693(4)	3 675(9)	O	8 883(4)	3 688(3)	5 376(8)
C(114)	6 883(5)	3 211(4)	3 357(9)	C	8 294(7)	3 875(6)	5 689(11)
C(115)	7 522(5)	3 398(3)	2 792(8)	C	7 902(9)	3 407(7)	6 464(14)
C(116)	8 083(4)	3 022(3)	2 519(7)	C	7 985(10)	4 386(6)	5 393(17)

solid obtained was recrystallized from $CHCl_3$ to give (**6**) in 60% yield.

Reaction of (**3**)—(**6**) *with* $PdCl_2$.—These reactions were all carried out in an identical fashion by the same general procedure as illustrated below for $[Pd(C_6H_4CH=NC_6H_5)Br(PPh_3)_2]$ (**5a**).

Compound (**5a**) (0.15 mmol) was added to a suspension of $PdCl_2$ (0.027 g, 0.15 mmol) in acetone (30 cm^3), and the mixture was refluxed for 3 h and then filtered. The filtrate was concentrated *in vacuo* and compound (**3a**) was precipitated by adding ethanol. Yield 70%.

Ligand Exchange Reactions.—Reactions of compound (**2**) with free imines (**1**) were carried out in an identical fashion by the same general procedure as illustrated below for $[\{\overline{Pd(C_6H_4CH=N}C_6H_5)(O_2CMe)\}_2]$ (**2a**) and *p*-$NO_2C_6H_4$-$CH=NC_6H_5$ (**1d**).

A mixture of (**2a**) (0.5 mmol) and (**1d**) (1 mmol) was refluxed for 24 h in acetic acid (30 cm^3). The solution was cooled and then filtered. The filtrate was concentrated *in vacuo*. Compound (**2d**) was precipitated by adding diethyl ether. Yield 70%.

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