Synthesis and Characterization of Cyclometallated Complexes of Benzalazines. Crystal and Molecular Structure of $[\{Pd(p\text{-}ClC_6H_3CH{=}N^-)Cl(PEt_3)_2\}_2]$ †

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The reaction of benzalazines, $(p\text{-}RC_6H_4CH{=}N^-)_2$ (R = H, Cl, NO_2, or NMe_2), with $PdCl_2$ leads in the the first two cases to the formation of cyclometallated polymeric species that react with phosphines to yield dimetallated compounds $[\{Pd(p\text{-}RC_6H_3CH{=}N^-)Cl(PR'_3)_2\}_2]$ (R' = Et or Ph) and/or $[\{Pd(p\text{-}RC_6H_3CH{=}N^-)Cl(PPh_3)\}_2]$. Phosphine exchange reactions give the complex $[\{Pd(p\text{-}RC_6H_3CH{=}N^-)Cl(PEt_3)(PPh_3)\}_2]$. The molecular structure of $[\{Pd(p\text{-}ClC_6H_3CH{=}N^-)Cl(PEt_3)_2\}_2]$ has been determined by a single-crystal *X*-ray analysis. The crystals are monoclinic, space group $P2_1/n$, $a = 11.124(3)$, $b = 10.062(2)$, $c = 22.566(5)$ Å, $\beta = 102.95(3)$°, and $Z = 2$; $R = 0.052$ for 3 306 reflections. Palladium atoms are five-co-ordinated, the Pd–N distance being 2.743 Å. However, n.m.r. spectra show that, in solution, free rotation around the C(aromatic)–C(azomethine) bonds does occur even at –100 °C.

Cyclometallation reactions, in which aryl metal–carbon σ bonds are formed by replacement of *ortho*-hydrogens by metal atoms,[1] have drawn much attention in the past few years, several reviews having been already published on nitrogen-,[2] phosphorus-,[3] sulphur-,[4] and arsenic-containing[5] cyclometallated complexes. These compounds have been used in regiospecific organic syntheses[6] as well as to obtain carbene complexes,[7] and several new products with metal–metal bonds.[8] Moreover, the existence of this sort of compound has been proposed to explain some catalytic reactions in olefin hydrogenations.[9]

According to Cope and Friedrich,[10] the formation of five-membered rings is specially favoured with N-donor ligands, although a few six-membered cyclometallated compounds have also been recently reported.[11]

In contrast with the cyclometallation of imines[12] and hydrazones,[13] that of benzalazines (benzylidene hydrazones) has been scarcely studied. To the best of our knowledge, only monometallated compounds $[Mn(C_6H_4CH{=}N{-}N{=}CHC_6H_5)(CO)_4]$ and $[\{Pd(C_6H_4CH{=}N{-}N{=}CHC_6H_5)(O_2CMe)\}_2]$, obtained by reaction of benzalazine with $[MnMe(CO)_5]$[14] and $Pd(O_2CMe)_2$,[15] respectively, have been described. Since there are few cyclometallated compounds of any sort containing more than one metal atom per ligand molecule,[16] it is of interest to gain insight into the reaction of $PdCl_2$ with $(p\text{-}RC_6H_4CH{=}N^-)_2$ in order to obtain dimetallated compounds. We report here that such a dimetallation can be performed when R is H or Cl.

Results and Discussion

The action of $PdCl_2$ on the azines $(p\text{-}RC_6H_4CH{=}N^-)_2$, in which R = H (1a), Cl (1b), NO_2 (1c), or NMe_2 (1d), was examined in anhydrous acetic acid under reflux for 24 h. In the cases of (1a) and (1b) very insoluble precipitates, (2a) and (2b) respectively, are formed; by treatment with an excess of PR'_3 (R' = Et or Ph) these precipitates are converted to $[\{Pd(p\text{-}RC_6H_3CH{=}N^-)Cl(PEt_3)_2\}_2]$ (3a),(3b) and $[\{Pd(p\text{-}RC_6H_3CH{=}N^-)Cl(PPh_3)_2\}_2]$ (4a),(4b), respectively. In the case of (1c) a yellow precipitate is obtained, which by further treatment with PEt_3 or PPh_3 gives $[PdCl_2(PR'_3)_2]$ and the free azine, so that it can be suggested that the former precipitate is not a C-metallated compound. The benzalazine derivative (1d) does not afford the desired metallic complex, the reduction of Pd^{II} to Pd^0 occurring instead.

The insoluble products (2a) and (2b) are thought to be polymers, in view of the structure of the starting azines and the nature of the compounds obtained [(3a), (3b); (4a), (4b)] by treatment with phosphines. It is known[2] that N-donor ligands such as azobenzenes, benzylamines, imines, hydrazones, *etc.* react with divalent Pd salts to give dimeric *ortho*-metallated products, which are difficult to characterize because of their insolubility in most common organic solvents. However, soluble monomeric derivatives are formed when those products are treated with amines or phosphines. Phosphines cleave not only the chloro-bridge bonds as amines do but also the N–Pd co-ordinated bond.

The behaviour shown by the benzalazines studied may be accounted for by the mechanism proposed for the palladation of azobenzene[17] and asymmetrically substituted azobenzenes,[18] *i.e.* co-ordination of the ligand to the metal followed by electrophilic attack of Pd^{II} on the aromatic ring. Thus,

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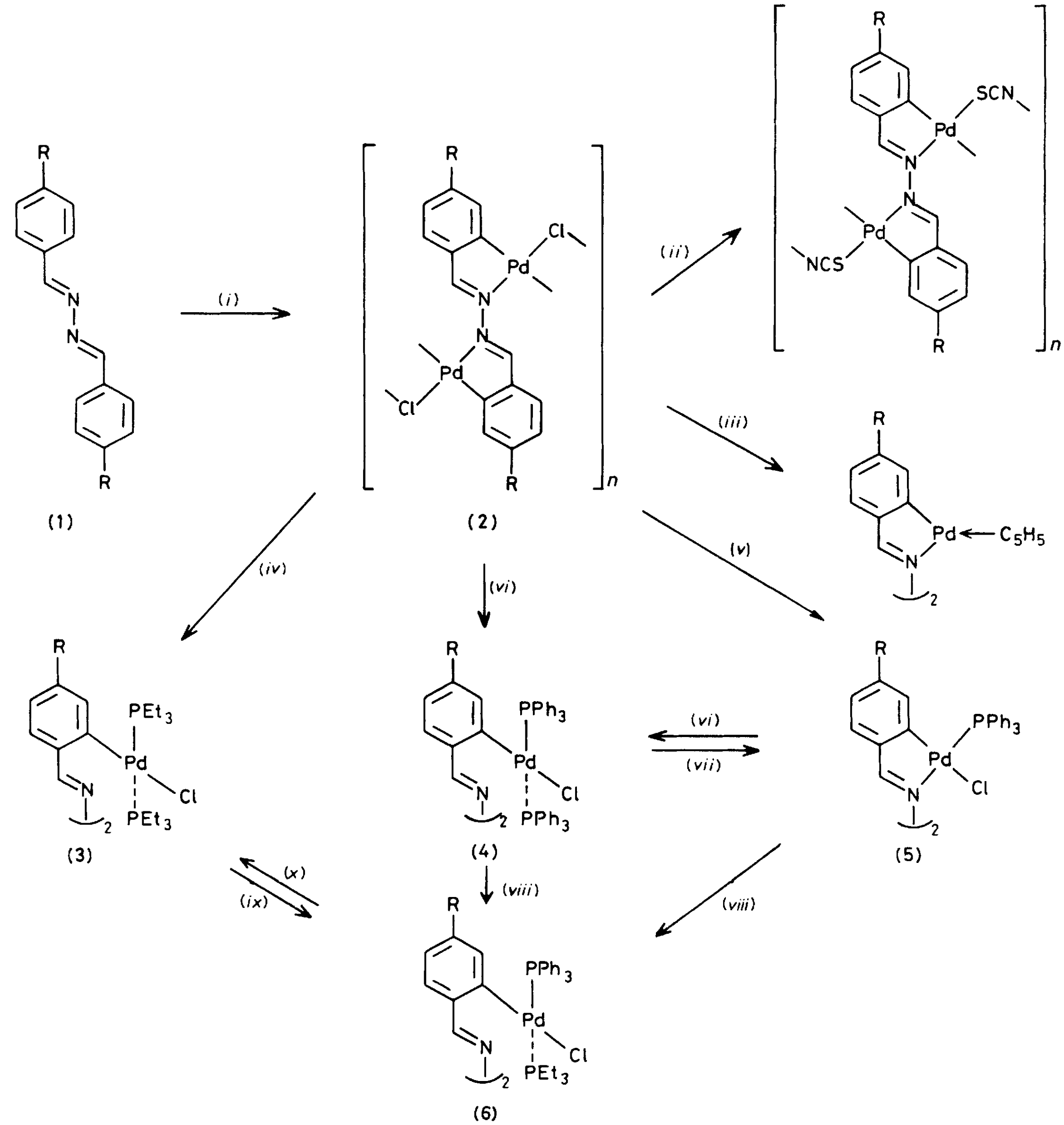
† μ-[2,2'-Azinodi-5-chlorophenyl-C^1,N(Pd^1);$C^{1'}$,N'(Pd^2)]-bis-[chlorobis(triethylphosphine)palladium(II)].

Supplementary data available (No. SUP 23694, 14 pp.): thermal parameters, observed and calculated structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

when azines (1a) and (1b) are treated with $PdCl_2$ in refluxing acetic acid for 6—7 h, no C-metallated compounds are formed, but after 24 h (2a) and (2b) are eventually obtained, as mentioned. In the case of (1c), although the formation of the initial non-metallated complex seems to occur, the electrophilic attack of co-ordinated Pd^{II} on the aromatic rings, highly deactivated by the strong electron-withdrawing NO_2 groups, does not take place. On the other hand, azine (1d), with the greatest π-electron density, only causes the reduction of Pd^{II} to Pd^0.

The reactivity of the insoluble compounds (2a) and (2b) is summarized in the Scheme. They do not react with $K(O_2CMe)$, but with K(NCS) in refluxing acetone, thiocyanato-bridged polymers are formed. Furthermore, the reaction of (2a) or (2b) with thallium cyclopentadienide in refluxing thf leads to red unstable compounds (i.r., 760 cm^{-1}; ^{1}H n.m.r., δ 5.7 p.p.m.), probably of composition $[\{Pd(p\text{-}RC_6H_3CH{=}N\text{-})(C_5H_5)\}_2]$. With PPh_3 in refluxing chloroform, (2a) and (2b) afford $[\{Pd(p\text{-}RC_6H_3CH{=}N\text{-})Cl(PPh_3)\}_2]$ (5a), (5b), whereas an excess of PPh_3 yields $[\{Pd(p\text{-}RC_6H_3CH{=}N\text{-})Cl(PPh_3)_2\}_2]$ (4a), (4b); however, PEt_3 and (2a) or (2b) give $[\{Pd(p\text{-}RC_6H_3CH{=}N\text{-})Cl(PEt_3)_2\}_2]$ (3a), (3b) in a straightforward reaction. Cyclometallated compounds (5a) and (5b) are also formed when (4a) and (4b) are treated with polymers (2a) and (2b), probably through a mechanism in which the internal nucleophilic attack of the nitrogen atoms promotes the loss of one phosphine ligand.[19] The action of $PdCl_2$ on (4a) and (4b) also leads to (5a) and (5b), $PdCl_2$ trapping the phosphine released from (4a) and (4b) to give $[PdCl_2(PPh_3)_2]$. In the



Scheme. R = H (compounds a) or Cl (compounds b): (*i*) $PdCl_2$ in refluxing $MeCO_2H$; (*ii*) K(SCN) in refluxing acetone; (*iii*) $Tl(C_5H_5)$ in thf; (*iv*) excess of PEt_3 in refluxing $CHCl_3$; (*v*) PPh_3 in refluxing $CHCl_3$; (*vi*) excess of PPh_3 in refluxing $CHCl_3$; (*vii*) $PdCl_2$, or (2a) or (2b), in $MeCO_2H$; (*viii*) PEt_3 in refluxing $CHCl_3$; (*ix*) excess of PPh_3 in refluxing $CHCl_3$ (only if R = Cl); (*x*) excess of PEt_3 in refluxing $CHCl_3$ (only if R = Cl)

Table 1. Analytical data, melting points, and i.r. data for compounds (3)—(6)

	Analysis (%) [a]				I.r. (cm^{-1})	
Compound	C	H	N	M.p. (°C) [b]	$\bar{\nu}_{asym}$(C=N)	$\bar{\nu}$(PdCl) [c]
(3a)	47.2 (47.4)	7.4 (7.25)	2.7 (2.9)	175—176	1 615	265
(3b)	44.4 (44.2)	6.6 (6.6)	3.0 (2.7)	203—205	1 615	260
(4a)	67.3 (67.1)	4.6 (4.55)	1.7 (1.8)	198—200	1 620	280
(4b)	64.1 (64.2)	4.2 (4.25)	1.7 (1.75)	218—221	1 615	280
(5a)	58.9 (59.15)	3.9 (3.95)	2.6 (2.75)	206—207	1 600	295
(5b)	55.5 (55.4)	3.5 (3.5)	2.3 (2.6)	187—189	1 600	295
(6a)	59.3 (59.5)	5.8 (5.6)	2.4 (2.25)	190—191	1 615	260
(6b)	56.3 (56.4)	5.3 (5.15)	2.1 (2.1)	215—217	1 615	265

[a] Calculated values are given in parentheses. [b] With decomposition. [c] Nujol mulls.

cyclometallated compounds (5a) and (5b) the Pd–N bond is easily broken: the addition of an equivalent amount of PEt_3 gives [{Pd(*p*-$RC_6H_3CH{=}N$–)Cl(PEt_3)(PPh_3)}$_2$] (6a), (6b), with two different phosphines, while that of PPh_3 affords (4a) and (4b), as expected.

Phosphine Exchange.—As far as phosphine exchange reactions are concerned, it is known that in organometallic square-planar complexes the more basic and less voluminous phosphines can usually replace those less basic and more voluminous.[20] In the present case, it is found that (4b) reacts with equivalent amounts of PEt_3 to give (6b), and with an excess of PEt_3 to yield (3b). Nevertheless, only (6a) has been obtained from (4a), even using an excess of PEt_3. This difference can be attributed to a decrease of the electron density on Pd due to the σ electron-withdrawing character of the chlorine atoms (in *p*-chlorobenzalazine derivatives). From a mechanistic viewpoint, it appears logical that the substitutions of one phosphine for another are facilitated by the intramolecular nucleophilic attack on the nitrogen atom to Pd, going probably through intermediates such as (5); it is to be noted that the substitution of PPh_3 for PEt_3, more basic and smaller than PPh_3, does take place.

Characterization of Compounds (3)—(6).—Compounds (3)—(6) are yellow [orange in the case of (3b)] solids, stable to air. The PPh_3-containing compounds (4) and (5) are scarcely soluble in the most common organic solvents, but those containing PEt_3, compounds (3), are quite soluble in chloroform, acetone, and benzene, and slightly soluble in ethanol, diethyl ether, and light petroleum. Compounds (3) should not be stored for long periods in chloroform solutions, otherwise they decompose to give [$PdCl_2(PEt_3)_2$] and the starting azines.

The analytical data and decomposition points of (3)—(6) are shown in Table 1. The low values of the molar conductivity in anhydrous acetone (10^{-4} mol dm^{-3} solutions) at 20 °C (1—4 Ω^{-1} cm^2 mol^{-1}) indicate the non-electrolytic character of these compounds. Their diamagnetic behaviour suggests a square-planar arrangement of the ligands surrounding the palladium atoms.

The i.r. spectra of compounds (3)—(6) show the typical bands of the co-ordinated phosphines [21] and benzalazines.[22] The wavenumbers corresponding to $\bar{\nu}_{asym}$(C=N) are included in Table 1, these values being smaller than those corresponding to the free azines (*ca.* 1 630 cm^{-1}). It should be noted that in compounds with Pd–N bonds, (5a) and (5b), $\bar{\nu}_{asym}$(C=N) appear at 1 600 cm^{-1} (in agreement with the expected bond order decrease due to the nitrogen co-ordination). whereas in compounds (3) and (4), in which there are apparently no Pd–N bonds, the analogous signals appear at *ca.* 1 615 cm^{-1} [suggesting, however, some degree of interaction between such atoms, as confirmed by an *X*-ray analysis of (3b)].

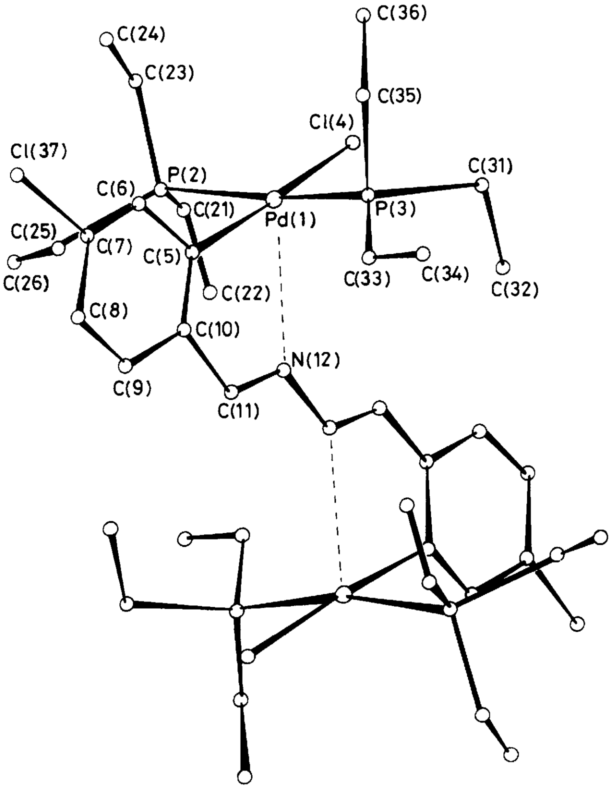


Figure 1. Molecular structure of [{Pd(*p*-$ClC_6H_3CH{=}N$–)Cl(PEt_3)$_2$}$_2$] (3b)

Weak bands at 260—295 cm^{-1} have been assigned to the Pd–Cl stretching vibrations (see Table 1) and point to a *trans* relative position of the chlorine and carbon atoms.[23] The highest $\bar{\nu}$ values for cyclometallated compounds may be explained by the formation of the so-called 'five-membered aromatic ring' [24] constituted by the C=C–C=N system and the *d* orbitals of the palladium atom. No signals at 550 ± 5 cm^{-1} appear for (4a) or (4b), so that a *trans* square-planar configuration may be attributed to these complexes.[25]

The crystal structure of (3b) is composed of discrete molecules separated by van der Waals distances, each molecule being on a inversion centre (see Figure 1). Selected bond lengths and angles are listed in Table 2. The palladium atom

Table 2. Principal bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

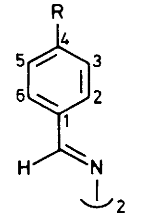
(*a*) Bond lengths

Pd(1)–C(5)	1.998(5)	C(5)–C(10)	1.414(8)	C(8)–C(9)	1.370(11)	N(12)–N(12′)	1.402(11)
Pd(1)–P(2)	2.308(2)	C(5)–C(6)	1.420(9)	C(9)–C(10)	1.377(9)	C(7)–Cl(37)	1.754(7)
Pd(1)–P(3)	2.312(2)	C(6)–C(7)	1.383(10)	C(10)–C(11)	1.458(9)	P(3)–C(31)	1.800(9)
Pd(1)–Cl(4)	2.386(2)	C(7)–C(8)	1.342(10)	C(11)–N(12)	1.264(8)	C(31)–C(32)	1.490(1)
Pd(1)–N(12)	2.743(5)						

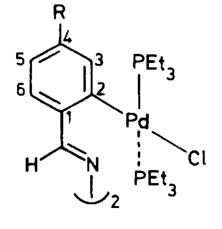
(*b*) Bond angles

P(3)–Pd(1)–P(2)	169.0(1)	C(11)–C(10)–C(5)	120.5(5)	C(5)–C(10)–C(9)	119.5(6)
Cl(4)–Pd(1)–P(2)	88.7(1)	N(12)–C(11)–C(10)	124.0(6)	Pd(1)–P(3)–C(31)	117.6(4)
Cl(4)–Pd(1)–P(3)	91.7(1)	C(11)–N(12)–Pd(1)	100.8(4)	Pd(1)–P(3)–C(33)	116.4(3)
C(5)–Pd(1)–P(2)	90.5(2)	C(10)–C(9)–C(8)	123.4(7)	Pd(1)–P(3)–C(35)	110.6(4)
C(5)–Pd(1)–P(3)	89.1(2)	C(9)–C(8)–C(7)	117.9(6)	P(3)–C(31)–C(32)	112.4(8)
C(5)–Pd(1)–Cl(4)	179.0(2)	C(8)–C(7)–C(6)	122.1(7)	P(3)–C(33)–C(34)	116.4(9)
C(6)–C(5)–Pd(1)	122.4(5)	C(7)–C(6)–C(5)	121.0(7)	P(3)–C(35)–C(36)	114.5(8)
C(10)–C(5)–Pd(1)	121.5(4)	C(6)–C(5)–C(10)	116.1(6)		

Table 3. Proton and ^{13}C-{^1H} n.m.r. data [a] of compounds (1) and (3)



(1a) R = H; (1b) R = Cl



(3a) R = H; (3b) R = Cl

	^1H				^{13}C			
Compound	Azomethine	Aromatic protons [b]	CH_2	CH_3	Azomethine	Aromatic carbons [b]	CH_2	CH_3
(1a)	8.55s	7.80m (H^2, H^6), 7.35m (H^3, H^4, H^5)			162.0	134.0 (C^1), 131.2 (C^4), 128.8 (C^3, C^5), 128.5 (C^2, C^6)		
(1b)	8.60s	7.80d (H^2, H^6),[c] 7.45d (H^3, H^5) [c]			161.1	137.3 (C^1), 132.2 (C^4), 129.7 (C^2, C^6), 129.1 (C^3, C^5)		
(3a)	9.35s	7.85m (H^6), 7.40m (H^3), 7.00m (H^4, H^5)	1.55m	1.05q	166.0	160.0 (C^2), 138.4 (C^1), 136.4 (C^3), 129.2 (C^4), 127.5 (C^6), 123.2 (C^5)	8.0	14.3t
(3b)	9.31s	7.79d (H^6),[d] 7.43br s (H^3), 6.99br d (H^5) [d]	1.54m	1.06q	166.0	162.0 (C^2), 137.5 (C^1), 136.2 (C^3), 135.3 (C^4), 128.3 (C^6), 123.9 (C^5)	8.3	14.8t

[a] In $CDCl_3$; chemical shifts in p.p.m. with respect to internal $SiMe_4$. [b] Assignments are given in parentheses. [c] $^3J(HH) = 8.4$ Hz. [d] $^3J(HH) = 8.0$ Hz.

is directly co-ordinated to five atoms: P(2), P(3), Cl(4), C(5), and N(12). The five atoms, Pd(1), P(2), P(3), Cl(4), and C(5), are not coplanar, the largest deviation from the mean plane reaching 0.29 Å for C(5). The Pd–P, Pd–Cl, and Pd–C distances and related angles are similar to those found in analogous compounds.[26] However, it is remarkable that the Pd–N(12) distance (2.743 Å) is shorter than the sum of the van der Waals radii and than that observed for similar compounds without Pd–N bonds (about 3.1 Å),[26] but is larger than the value found in compounds with Pd–N bonds (2.0 Å).[26] This suggests a significant Pd(1)–N(12) interaction, which is also reflected by the value of 120.5° for the C(5)–C(10)–C(11) angle, lower than that found for the free benzalazine (122.5°). The angle between the Pd(1)–N(12) bond and the mean plane is 83.6°, while the dihedral angle between the phenyl ring and the C–C=N–N=C moiety is 3.4°. The remaining bond distances and angles of the azine ligand are equal within one standard deviation to those obtained for the free, non-metallated benzalazine.[27]

Proton n.m.r. spectra of compounds (3a) and (3b) in $CDCl_3$ solution are reported in Table 3. First of all, it is to be noted that the appearance of only one azomethine signal for each compound as well as the presence of four and three aromatic protons in (3a) and (3b), respectively, support the symmetrical and dipalladated structure of these compounds. Moreover, the unequivocal assignment (based on the observed coupling constants) of the aromatic protons of (3b) affords conclusive evidence about the palladation position, as independently shown by the *X*-ray analysis. The spectrum of (3a) agrees similarly with the depicted structure. The most remarkable effect of the $PdCl(PEt_3)_2$ substituent is in both cases a shielding of the *para*-hydrogen atoms (H^5) with regard to the corresponding protons of the starting azines. As far as the $PdCl(PEt_3)_2$ group itself is concerned, the methyl signals appear in both cases as quintuplets, which is characteristic[28] of a *trans* arrangement of the two phosphines (due to the so-called ' virtual coupling ').

The chemical shifts of the azomethine protons of (3a) and (3b) also deserve attention, because these protons lie at lower field than those of the starting, non-metallated azines, in spite of the fact that: (*i*) the δ values for azomethine protons of $[Mn(C_6H_4CH{=}N{-}N{=}CH{-}C_6H_5)(CO)_4]$ are reported[14] to be 8.54 p.p.m. (N-metallated azomethine) and 8.43 p.p.m.

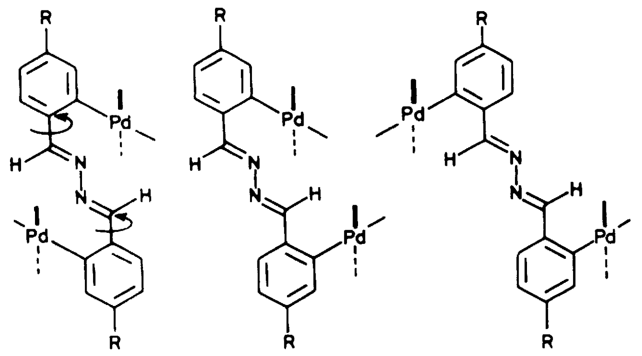


Figure 2. Expected main conformations of compounds (3a) and (3b)

(non-metallated azomethine); (*ii*) the most downfield shifted signals reported[15] for $[\{\overline{Pd(C_6H_4CH{=}N}{-}N{=}CHC_6H_5)(O_2CMe)\}_2]$ are found at δ 8.75 and 8.65 p.p.m. As it is well established that the close vicinity of hydrogen and metal atoms gives rise to a large paramagnetic shift of such protons[28] (*e.g.*, $\Delta\delta = 1.55$ p.p.m. for the *o*-methyl substituents of *trans*-$[Pd(NMe_2C_6H_4Me\text{-}o)_2(O_2CCF_3)_2]$), it must be concluded that the chemical shifts observed for the azomethine protons of (3a) and (3b) are approximately mean values among those corresponding to the planar or almost planar conformers shown in Figure 2. In other words, a relatively fast rotation around C_{sp^2}(aromatic)–C(azomethine)$_{sp^2}$ bonds and an equilibrium position not too much shifted to any of those conformers appear to occur in solution, as would be expected. Thus, although the ' frozen ', *crystalline structure* of (3b), as already mentioned, agrees with the first conformer shown in Figure 2, in chloroform solution at room temperature rotation is not hindered around the (essentially) single bonds.

In an attempt to detect splittings of signals or changes in the population of conformers, 200-MHz ^1H n.m.r. spectra of (3b) were recorded at 25, −50, and −100 °C in diluted CD_3COCD_3 solution; for the sake of comparison, spectra of starting azine (1b) were registered under the same conditions. Since no significant variations are observed, in going from room temperature to −100 °C, for azomethine (from δ 9.38 to 9.35 p.p.m.), H^6 (from 7.81 to 7.79), and H^5 (from 7.05 to 7.07) protons of (3b), as well as for all protons of (1b), it should be concluded that free rotation around C–C bonds linking aryl and azomethine groups is held even at the lowest temperature allowed in practice by the solubility of (3b). On the other hand, small but significant upfield shifts are clearly observed for protons H^3 (from δ 7.52 to 7.39 p.p.m.), and for the methylene (from 1.61 to 1.50) and methyl (from 1.10 to 1.02) protons of the PEt_3 groups. These changes, localised at such a specific part of the molecule, suggest the existence of a certain rotational barrier involving the $PdCl(PEt_3)_2$ substituents.

Finally, we shall briefly comment on the ^{13}C n.m.r. spectra of (3a) and (3b) summarized in Table 3, which obviously confirm the structures proposed for these compounds. Both spectra are characterized by two very downfield shifted signals in relation to the normal range of δ values for aromatic carbons; one peak corresponds, of course, to the azomethine carbons whereas the other one can be only attributed to the palladated carbon atom, taking into account the large deshielding undergone by aromatic carbon nuclei as a consequence of the *ipso*-palladation.[29] The assignment of carbon atoms C^3—C^6 of (3a) and C^3, C^5, and C^6 of (3b) is not, however, so straightforward, but it has been accomplished after calculating the shifts induced by the $PdBr(PEt_3)_2$ substituent on the benzene carbons {*i.e.*, in $[PdBr(C_6H_5)(PEt_3)_2]$}, namely $\Delta\delta_{ipso} = 25.7$, $\Delta\delta_{ortho} = 8.0$, $\Delta\delta_{meta} = -0.8$, and $\Delta\delta_{para} = -6.2$ p.p.m., and assuming, as usually done, that these parameters, when added to the $\delta(^{13}C)$ values for the aromatic carbon atoms of starting azines (1a) and (1b), can very approximately afford the $\delta(^{13}C)$ values for all the aromatic carbon atoms of (3a) and (3b).

Experimental

N.m.r. spectra were obtained on Hitachi-Perkin-Elmer R-24B (^1H, 60 MHz) and Varian XL (^1H, 200 MHz; ^{13}C, 50.3 MHz) spectrometers. I.r. spectra were recorded on a Beckman IR-20A as KBr discs or Nujol mulls. Microanalyses were performed by the Institut de Química Bio-orgànica de Barcelona.

Crystal Data for $[\{Pd(p\text{-}ClC_6H_3CH{=}N{-})Cl(PEt_3)_2\}_2]$ (3b).—$C_{38}H_{68}Cl_4N_2P_4Pd_2$, Monoclinic, space group $P2_1/n$, $a = 11.124(3)$, $b = 10.062(2)$, $c = 22.566(5)$ Å, $\beta = 102.95(3)°$, $U = 2\,462(1)$ Å^3, $Z = 2$, $F(000) = 1\,060$, Cu-K_α radiation, $\lambda = 1.540\,51$ Å, $\mu = 91.6$ cm^{-1}.

Data Collection.—A small crystal was selected for *X*-ray crystal analysis, and mounted on a Syntex four-circle diffractometer, using the ω-scan technique and Cu-K_α radiation. The unit-cell parameters were measured by centring 15 independent reflections, and refining the orientation matrix and unit-cell parameters by least-squares methods. 3 306 Independent reflections were measured up to $2\theta \leqslant 114°$, 2 746 of which were considered as observed applying the condition $I > 2.5\sigma(I)$. Lorentz-polarization, but not absorption, corrections were made.

Structure Solution and Refinement.—The structure was solved by direct methods, using the MULTAN system of computer programs.[30] An *E*-map computed from the set of phases with the highest combined figure of merit revealed peaks for all non-hydrogen atoms. Isotropic and anisotropic refinements were carried out by full-matrix least-squares methods using the SHELX 76 computer program.[31] The effects of anomalous dispersion were included for all atoms. A difference synthesis revealed the positions of 10 hydrogen atoms, which were refined with an overall isotropic temperature factor, and anisotropically for the remaining atoms. The refinement was terminated at $R = 0.052$. A subsequent difference map did not reveal the remaining hydrogen atoms. Final atomic parameters are listed in Table 4. A view of the molecule is shown in Figure 1.

Materials and Syntheses.—Solvents were dried and distilled before use. Benzalazines, $(p\text{-}RC_6H_4CH{=}N{-})_2$ (R = H, Cl NO_2, or NMe_2), were prepared according to published methods.[32]

A stirred suspension of $PdCl_2$ (0.35 g, 2 mmol) in anhydrous acetic acid (30 cm^3) was treated with an excess of azine (2.5 mmol) and refluxed for 24 h. The suspension was cooled, and the precipitate filtered off and washed with ethanol and chloroform. The solids obtained, (2a) and (2b), were used in the following reactions without further purification.

$[\{Pd(p\text{-}RC_6H_3CH{=}N{-})Cl(PEt_3)_2\}_2]$ (3a), (3b). A stirred suspension of (2a) or (2b) (0.5 g) in chloroform (50 cm^3) was treated with PEt_3 (1.1 g, 9 mmol); the mixture was refluxed for 45 min under nitrogen. After filtering off the solid, the filtrate was concentrated *in vacuo*. The yellow solid residue was purified by column chromatography over silica gel, with $CHCl_3$–MeOH (15 : 1) as the eluant, to afford (3a) or (3b) in 35—40% yield.

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

Atom	*X/a*	*Y/b*	*Z/c*
Pd(1)	531(0)	511(0)	3 613(0)
P(2)	2 134(2)	−986(2)	3 706(1)
P(3)	−953(2)	2 147(2)	3 354(1)
Cl(4)	−812(2)	−1 123(2)	3 051(1)
C(5)	1 670(5)	1 855(6)	4 093(3)
C(6)	2 454(7)	2 667(7)	3 828(3)
C(7)	3 266(6)	3 552(6)	4 177(4)
C(8)	3 328(7)	3 717(7)	4 774(4)
C(9)	2 587(7)	2 936(7)	5 040(3)
C(10)	1 760(5)	2 029(6)	4 723(3)
C(11)	1 030(6)	1 210(7)	5 044(3)
N(12)	294(6)	313(6)	4 794(2)
C(21)	1 769(12)	−2 735(10)	3 829(6)
C(22)	1 386(19)	−2 966(15)	4 444(9)
C(23)	2 505(11)	−1 223(11)	2 942(5)
C(24)	2 913(14)	16(13)	2 689(6)
C(25)	3 525(11)	−626(10)	4 267(6)
C(26)	4 411(17)	−1 687(15)	4 452(11)
C(31)	−2 544(8)	1 635(12)	3 175(5)
C(32)	−2 938(14)	1 061(20)	3 710(6)
C(33)	−861(11)	3 561(12)	3 902(6)
C(34)	−1 762(16)	4 698(15)	3 706(8)
C(35)	−797(11)	3 034(12)	2 627(6)
C(36)	−862(12)	2 148(16)	2 098(5)
Cl(37)	4 251(2)	4 458(2)	3 820(1)

[{Pd(*p*-RC$_6$H$_3$CH=N$^-$)Cl(PPh$_3$)$_2$}$_2$] (4a), (4b). To a suspension of (2a) or (2b) (0.5 g) in chloroform (50 cm^3) was added PPh$_3$ (2.3 g, 9 mmol), and the mixture refluxed for 45 min. The precipitate was filtered off and recrystallized from CH$_2$Cl$_2$–MeOH to give (4a) or (4b) in 60—65% yield.

[{Pd(*p*-RC$_6$H$_3$CH=N$^-$)Cl(PPh$_3$)}$_2$] (5a), (5b). A mixture of (2a) or (2b) (0.5 g) and PPh$_3$ (0.4 g) in chloroform (30 cm^3) was refluxed for 30 min. The precipitate which formed was filtered off and recrystallized from Me$_2$CO–EtOH to give (5a) or (5b) in 45% yield.

Reaction of (4a) *and* (4b) *with* (2a) *and* (2b), *or with* PdCl$_2$. Compound (2a) (0.1 g) or PdCl$_2$ (0.05 g, 0.3 mmol) was added to a suspension of (4a) (0.2 mmol) in acetic acid (30 cm^3). After stirring for 24 h at room temperature, the precipitate was collected and recrystallized from CHCl$_3$–EtOH to afford (5a) in 60% yield. Compound (4b) reacts similarly with (2b) or with PdCl$_2$ to give (5b).

[{Pd(*p*-RC$_6$H$_3$CH=N$^-$)Cl(PEt$_3$)(PPh$_3$)}$_2$] (6a), (6b). Triethylphosphine (0.24 g, 2 mmol) was added under nitrogen to a suspension of (4a) or (4b) (1 mmol), or (5a) or (5b) (1 mmol); the mixture was refluxed for 3 h and then filtered. The filtrate was concentrated *in vacuo*, and the residue recrystallized from CH$_2$Cl$_2$–MeOH to give (6a) or (6b) in 75—80% yield. Compound (6b) can also be obtained from (3b) and PPh$_3$ under similar conditions.

Reaction of (2a) *and* (2b) *with* Tl(C$_5$H$_5$). To a suspension of (2a) or (2b) (0.5 g) in tetrahydrofuran (thf) (50 cm^3) was added Tl(C$_5$H$_5$) (0.37 g, 1.4 mmol), the mixture being refluxed for 45 min. The resulting red solution was filtered and concentrated *in vacuo*, until a red precipitate appeared. These solids are unstable, decomposing when recrystallization is attempted, and no reproducible microanalyses could be obtained. However, these materials exhibit bands at 760 cm^{-1} (in KBr) and ^{1}H n.m.r. signals at δ 5.7 p.p.m. (in CDCl$_3$) which agree with the formulation [{Pd(*p*-RC$_6$H$_3$CH=N$^-$)(C$_5$H$_5$)}$_2$].

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