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CYCLOMETALLATION REACTIONS OF *N*-(BENZYLIDENE)-BENZYLAMINES WITH PALLADIUM COMPOUNDS

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Summary

The cyclometallation of p-$RC_6H_4CH{=}NCH_2C_6H_5$ (R = H, Cl, NO_2) by PdX_2 (X = Cl, AcO) has been studied.

In every case the cyclometallation occurs with formation of a five-membered ring containing the methine group. The structure of these compounds $[PdX(p\text{-}RC_6H_3CH{=}NCH_2C_6H_5)]_2$, derived from ^1H NMR spectra, are different from those reported previously. Reaction of these compounds with PEt_3 gives the compounds $[PdX(p\text{-}RC_6H_3CH{=}NCH_2C_6H_5)(PEt_3)_2]$ but with an excess of PPh_3 only the complexes $[PdX(p\text{-}RC_6H_3CH{=}NCH_2C_6H_5)(PPh_3)]$ are formed.

Introduction

Cyclometallation reactions of *N*-donor ligands, in which σ metal–aryl bonds are formed by replacement of *ortho*-hydrogens by metal atoms, have attracted much attention during recent years [1,2].

The complexes so formed have been used in regiospecific organic syntheses [3,4], as well as in the synthesis of carbene complexes [5] and of several new compounds with metal–metal bonds [6].

According to Cope's rules [7], the formation of a five-membered ring is specially favoured with *N*-donor ligands, but some six-membered cyclometallated compounds have been reported recently [8,9]. An electrophilic substitution mechanism has been proposed for the palladiation of many *N*-donors ligands, after the coordination of the ligand to the metal [10], but, on the other hand, reactions in $[Mn(Me)(CO)_5]$ complexes appear to involve nucleophilic substitution [11].

The cyclopalladiation of *N*-(benzylidene)benzylamine ligands could "theoretically" lead to two different palladium(II)-imine complexes having the general structures A or B shown in Fig. 1, both of which contain a five-membered ring.

Thomson and Heck proposed the B structure $[(AcO)Pd(C_6H_4CH_2N{=}C(R)C_6H_5)]_2$ (R = H or Me) for the compounds obtained by the reaction of $Pd(AcO)_2$ with the

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imines [12], while Dehand et al. obtained $[ClPd(C_6H_4C(Me)=NCH_2C_6H_5)]_2$, with structure A, by the treatment of $[PdCl_2(NH_2CH_2C_6H_5)_2]$ with PhCOMe [13].

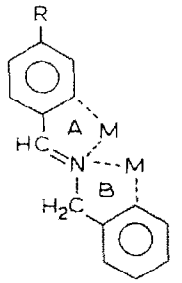
Following our studies on cyclometallation reactions of *N*-donor ligands [14,15], we have investigated the action of PdX_2 (X = Cl or AcO) on the *N*-(benzylidene)benzylamines *p*-$RC_6H_4CH=NCH_2C_6H_5$ (R = H, Cl, NO_2) in order to check which phenyl ring is metallated, and to study the effect of the substituents in the *para*-position on the mechanism of this reaction.

Results and discussion

The action of PdX_2 (X = Cl, AcO) on the imines *p*-$RC_6H_4CH=NCH_2C_6H_5$, where R = H, Cl, NO_2, (Ia,b,c) was examined in anhydrous AcOH under reflux for 20–45 min. The structure $[PdX(p\text{-}RC_6H_3CH=NCH_2C_6H_5)]_2$ (IIa,b,c) is formed with all three imines, but the yields are lower when $PdCl_2$ is used since Pd^0 is also formed. These results agree with the better ability of $Pd(AcO)_2$ to cyclometallated *N*-donor ligands [16].

The ^1H NMR spectra of the compounds II are too complex for use in determining the structure for these compounds, but the mononuclear complexes obtained when the compounds II were treated with phosphines can be easily characterized by ^1H NMR spectroscopy, so it is possible to derive their structures.

The addition of an excess of PEt_3 to acetone solutions of the complexes II in the presence of LiBr gives $[PdBr(p\text{-}RC_6H_3CH=NCH_2C_6H_5)(PEt_3)_2]$ (IIIa,b,c). Decom-



R = H, Cl, NO_2

Fig. 1. Possible structures for palladium(II)-imine complexes.

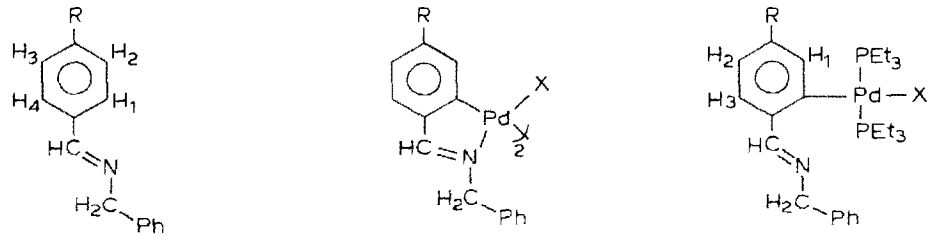


Fig. 2. Structures of compounds I–III.

position occurs in absence of LiBr and it is not possible to obtain the complexes $[Pd(AcO)(p\text{-}RC_6H_3CH{=}NCH_2C_6H_5)(PEt_3)_2]$. The use of an excess of PPh_3 gives only the cyclometallated compounds $[PdX(p\text{-}RC_6H_3CH{=}NCH_2C_6H_5)(PPh_3)]$, and this difference in behaviour can be accounted for by the greater basicity and nucleophilic character of PEt_3, relative to PPh_3, which enables it to breaks the Pd–N bond. In the analogous cyclopalladated compounds $[PdX(C_6H_4CH{=}NC_6H_5)]_2$ with the less basic *N*-benzylideneaniline ligand, PPh_3 gives the compounds $[PdX(C_6H_4CH{=}NCH_2C_6H_5)(PPh_3)_2]$ with two phosphine ligands [17].

The ^1H NMR spectra of III (see below) show that the *N*-(benzylidene)benzylamines have been metallated to give a type A ring (see Fig. 1), i.e. the rings which have been formed contain the methine group in every case, contrary to Thomson and Heck's proposal. Even the imine Ic, with an NO_2 substituent which deactivates the aromatic ring to electrophilic attack, give the cyclometallated compound with the A ring.

Since compounds with the B ring are obtained from benzylamines, these results may be explained in terms of the formation of a 5-membered aromatic ring involving the two conjugated double bonds of the (–C=C–C=N–) system and the filled palladium *d* orbitals of appropriate symmetry [18].

The existence of 5-membered aromatic rings had previously been proposed by Crociani et al. [19] to explain the value of ν(Pd–Cl) in the IR spectra of the cyclopalladated compounds $[PdCl(C{-}N)]_2$ where C–N = azobenzene or *N*,*N*-methylbenzylamine.

Similar results have been found in the cyclometallated derivatives of hydrazones (see Fig. 3). With $C_6H_5N(Me)N{=}CHR$ (R = H, Me) B-rings are formed in giving $[PdX(C_6H_4N(Me)N{=}CHR)]_2$ [12], but with $C_6H_5C(Me){=}NNHC_6H_5$ only A-rings are obtained in $[PdX(C_6H_5C(Me){=}NNHC_6H_5)]_2$, although five membered B-rings could also be formed [13].

Characterization of compounds

The new compounds are pale yellow solids which are stable to air. The PPh_3-containing compounds (IV) are sparingly soluble in the common organic solvents, but the PEt_3-containing compounds III are quite soluble in all common organic solvents. The cyclometallated compounds II are quite soluble in chloroform, acetone and benzene, and slightly soluble in ethanol and diethyl ether.

The analytical data and decomposition temperatures are shown in Table 1. The

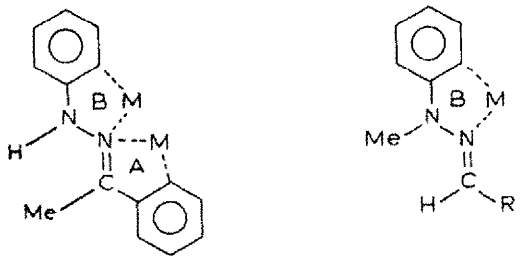


Fig. 3. Possible structures for cyclometallated derivatives of hydrazones.

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 surrounding the palladium atoms.

The IR spectra show the typical bands of co-ordinated phosphines and imines. The compounds II show two bands at 1580 and 1420 cm^{-1} which are characteristic of the bridging acetate ligand. The wavenumbers corresponding to ν_{asym}(C=N) are included in Table 1, these values being smaller than those corresponding to free imines (c.a. 1650 cm^{-1}). It should be noted that ν(C=N) appears at 1630 cm^{-1} in compounds with Pd–N bonds in agreement with the expected bond order decrease due to the nitrogen coordination, whereas in compounds III, in which there are apparently no Pd–N bonds, the analogous signals appear at 1635–40 cm^{-1}, suggesting that there is some degree of interaction between these atoms, as has been found in analogous compounds [14].

The ^{1}H NMR spectra (60 MHz) of the compounds II and III in $CDCl_3$ solution are reported in Table 2. In the ^{1}H NMR spectrum of IIa (200 MHz) the azomethine proton gives a singlet 7.4 ppm downfield of that of the free imine. This shift would result from the expected decrease in bond order due to the nitrogen coordination, and agrees with the shifts reported for analogous cyclometallated compounds [17].

In the spectra of IIa, recorded by Thomson and Heck [12], the peaks of the azomethine and aromatic protons overlap.

The methylene protons are not equivalent because of the Pd–N bond and the fact that free rotation around the N–CH_2 bond is hindered. These protons appear as two doublets at δ 4.0 and 4.6 ppm. Moreover every signal appears as doublet probably due to the coupling with azomethine protons ($^4J(^1H–^1H)$ 1.0 Hz).

The acetate protons are observed as a singlet at 2.1 ppm, indicating that the cyclometallated dimers have a *trans* configuration.

In the spectra of PEt_3-containing compounds III, the azomethine protons are shifted downfield relative to the free imines because of the paramagnetic anisotropy of the metal, indicating the close vicinity of the azomethine proton and the

TABLE 1

ANALYTICAL DATA, MELTING POINTS AND IR DATA FOR COMPLEXES II–IV

Compound	X	Analysis (Found(calcd.)(%))			M.p. (°C)	IR
		C	H	N		ν_{asym}(C=N) (cm^{-1})
IIa	AcO	53.5(53.42)	4.2(4.17)	3.8(3.89)	190–204 [a]	
IIb	AcO	48.9(48.74)	3.5(3.55)	3.5(3.55)	202–204 [a]	
IIc	AcO	47.7(47.50)	3.4(3.46)	6.8(6.92)		
IIc	Cl	44.6(44.11)	2.9(2.89)	7.3(7.35)	260–264 [a]	1620
IIIa	Br	51.4(50.62)	7.0(6.81)	2.1(2.27)	88	1635
IIIb	Cl	50.6(51.45)	6.6(6.72)	2.2(2.31)	100–105	1640
IIIc	Cl	50.8(50.57)	6.5(6.65)	4.3(4.34)	72– 82	1630
IVa	Br	60.0(59.78)	4.3(4.20)	2.2(2.18)	214–216 [a]	1630
IVb	Cl	60.9(60.72)	4.1(4.11)	2.5(2.21)	220–221 [a]	1640
IVb	Br	56.8(56.74)	3.9(3.84)	2.1(2.07)	242–244 [a]	1630
IVC	Br	54.5(55.87)	3.7(3.78)	3.8(4.07)	244–246 [a]	1630

[a] With decomposition.

TABLE 2

^{1}H NMR DATA [a] FOR THE COMPOUNDS I, II AND III IN $CDCl_3$

Compound	X	HC=N	Aromatic protons		CH_3COO	CH_2-N	CH_2-P	CH_3
			Ph-CH=N	Ph-CH_2				
Ia		8.2(s)	7.6(m), 7.3(m)	7.2(s)		4.7(s)		
Ib		8.2(s)	7.6(d)(H_1,H_4) [b], 7.2(d)(H_2,H_3) [b]	7.2(s)		4.7(s)		
Ic		8.2(s)	8.1(d)(H_2,H_3) [b], 7'8(d)(H_1,H_4) [b]	7.2(s)		4.7(s)		
IIa [c]	AcO		6.8–7.4(br.m)		2.0(s)	4.0(d),4.6(d)		
IIb	AcO		6.8–7.3(br.m)		2.1(s)	4.0(d),4.6(d)		
IIIa	Br	9.1(s)	7.3–6.8(br.m)	7.2(s)		4.7(s)	1.6(m)	1.0(q)
IIIb	Cl	9.0(s)	7.8(d)(H_3) [b],7.3(s)(H_1), 6.8(d)(H_2) [b]	7.2(s)		4.7(s)	1.6(m)	1.0(q)
IIIc	Cl	9.1(s)	8.1(s)(H_1), 7.9(d)(H_3) [b], 7.6(d)(H_2) [b]	7.2(s)		4.7(s)	1.6(m)	1.0(q)

[a] In $CDCl_3$, chemical shifts in ppm with respect to internal $SiMe_4$. Recorded with a 60 MHz spectrometer. [b] $^3J(^1H-^1H)$ 8.0 Hz. [c] For 200 MHz spectrum, see text.

palladium and confirming that the metallation has occurred in the A-ring.

The metallation of this ring is also confirmed by the unequivocal assignments of the aromatic protons of the compounds [PdX(*p*-$RC_6H_3CH{=}NCH_2C_6H_5$)$(PEt_3)_2$] where R = Cl, NO_2 (see Table 2).

The formation of ring A has also been confirmed by the signal at δ 7.2 due to the five aromatics protons of the $C_6H_5CH_2$ group, and by the fact that the aromatic regions of the spectra are identical with those reported for [PdX(*p*-$RC_6H_3CH{=}NC_6H_5$)$(PEt_3)_2$] [20]. The methylene protons appear as singlets at δ 4.7 in accordance with the free rotation around the CH_2–N bond in these compounds.

As far as the $PdCl(PEt_3)_2$ group itself is concerned, the methyl signals appear as quintuplets which is characteristic of a *trans* arrangement of the two phosphines, due to so-called "virtual coupling" [21].

Experimental

The NMR spectra were obtained on Hitachi-Perkin Elmer R-24B (^{1}H, 60 MHz) and Varian XL (^{1}H, 200 MHz) spectrometers. The IR spectra were recorded on a Beckman IR-20A, using KBr discs. Microanalyses were performed by the Institut de Química Bio-Orgànica de Barcelona (C.S.I.C.).

Materials and syntheses

Solvents were dried and destilled before use. The imines *p*-$RC_6H_4CH{=}NCH_2C_6H_5$ (R = H, Cl, NO_2) were prepared according to published methods [22].

[Pd(AcO)(p-$RC_6H_3CH{=}NCH_2C_6H_5$)]$_2$ (II). A stirred suspension of $Pd(AcO)_2$ (1.0 g, 4.4 mmol) in anhydrous acetic acid (30 cm^3) was treated with an excess of the imine (8.8 mmol) and refluxed for 1 h. The suspension was cooled and filtered off. The filtrate was concentrated in vacuo and the solid residue obtained after the addition of EtOH was purified by column chromatography over silica gel, with $CHCl_3$ as the eluent, to give II in 30–40% yield.

[Pd(Cl)(p-$ClC_6H_3CH{=}NCH_2C_6H_5$)]$_2$. A stirred suspension in acetic acid (30 cm^3) of $PdCl_2$ (1.1 g, 6 mmol) was treated with an excess of the imine (2.8 g, 12 mmol) and refluxed for 1 h. The suspension was cooled and the precipitate filtered off and washed with water, ethanol and ether. The solid, contained the compound [PdCl(*p*-$ClC_6H_3CH{=}NCH_2C_6H_5$)]$_2$, and was used without further purification in subsequent reactions.

[PdCl(p-$NO_2C_6H_3CH{=}NCH_2C_6H_5$)]$_2$. To a stirred suspension of [Pd(AcO)(*p*-$NO_2C_6H_3CH{=}NCH_2C_6H_5$)]$_2$ (0.57 g, 0.7 mmol) in ethanol, KCl (0.11 g, 1.4 mmol) was added. The mixture was refluxed for 30 min. The resulting yellow precipitate was filtered and washed with water, ethanol and ether to give the expected compound in 70% yield.

[PdX(p-$RC_6H_3CH{=}NCH_2C_6H_5$)$(PEt_3)_2$] (III). A mixture of [PdX(*p*-$RC_6H_3CH{=}NCH_2C_6H_5$)]$_2$ (0.2 mmol), PEt_3 (0.8 mmol) and LiBr (0.07 g, 0.8 mmol) if X = AcO, in acetone (30 cm^3), was refluxed under nitrogen for 30 min and then filtered. The filtrate was concentrated in vacuo. The compounds (III) were precipitated on adding ethanol. Yield 50%.

[PdX(p-$RC_6H_3CH{=}NCH_2C_6H_5$)(PPh_3)] *(IV).* A mixture of [PdX(*p*-$RC_6H_3CH{=}NCH_2C_6H_5$)]$_2$ (0.4 mmol), PPh_3 (0.21 g, 0.8 mmol) and LiBr (0.07 g, 0.8 mmol) if X = AcO, in acetone (30 cm^3) was refluxed for 30 min. The precipitate which formed was filtered off and recrystallized from $CHCl_3$ to give IV in 80% yield.

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