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MONO- AND DI-CYCLOPLATINATED DERIVATIVES OF BENZALAZINES

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Summary

The reaction of $(p\text{-RC}_6\text{H}_4\text{CH=N})_2$ ($\text{R} = \text{NO}_2$, Cl, H, NMe_2) with $\text{PtCl}_4{}^{2-}$ has been studied. Cyclometallation only occurs when R = Cl, giving mixtures of the mono- and di-metallated compounds, $[\text{PtCl}(p\text{-ClC}_6\text{H}_3\text{CH=N–N=CH}(p\text{-ClC}_6\text{H}_4))]_2$ and $[\text{PtCl}(p\text{-ClC}_6\text{H}_3\text{CH=N})]_n$, that react with phosphines, $\text{PR}'_3 = \text{PPh}_3$, PEt_3, $\frac{1}{2}$dppe, to yield $[\text{PtCl}(p\text{-ClC}_6\text{H}_3\text{CH=N–N=CH}(p\text{-ClC}_6\text{H}_4))(\text{PR}'_3)_2]$ and $[\text{PtCl}(p\text{-ClC}_6\text{H}_3\text{CH=N})(\text{PR}'_3)_2]_2$, respectively. (For the structures of these products see the Scheme.) The ionic compound $\{[\text{Pt}(p\text{-ClC}_6\text{H}_3\text{CH=N})(\text{dppe})]_2\}(\text{ClO}_4)_2$ is formed from $[\text{PtCl}(p\text{-ClC}_6\text{H}_3\text{CH=N})]_n$ and dppe in the presence of NaClO_4. The results obtained can be explained in terms of electrophilic attack of the metal on the aromatic rings. Structures for the new compounds are assigned on the basis of IR and NMR (^{1}H, ^{13}C, ^{31}P) spectra.

Introduction

Cyclometallation reactions, specially of N-donor ligands, have attracted much attention in the past few years [1] but the cyclometallation of these ligands by platinum has been little studied in contrast to those of P-donor ligands [2].

Azobenzene and *N,N*-dimethylbenzylamines react readily with palladium(II) chloride to give complexes having carbon-to-metal σ bonds, but with platinum(II) chloride the reactions require longer times and the yields are poorer [3,4]. Moreover, with imines, only the palladium(II)-cyclometallated compounds are formed [5], and with platinum(II) only the σ(N)-coordinated complexes can be obtained (6). Some other cycloplatinated complexes have been obtained from organolithium [7] and organomercury [8] reagents, but the reactions do not involve the activation of the C–H bond of the organic ligands.

To the best of our knowledge, no binuclear cyclometallated compound of N-donor ligands with platinum has been reported. Recently, we have described the obtention of binuclear cyclopalladated [9] and binuclear mixed metal (Pd, Pt) cyclometallated compounds of benzalazines [10]. In continuation of our studies on cyclometallation of benzalazines, we report here the preparation of the mono- and

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di-cyclometallated platinum complexes $[\overline{\mathrm{PtCl}(p\text{-}\mathrm{ClC_6H_3CH{=}N}}\mathrm{-N{=}CH}(p\text{-}\mathrm{ClC_6H_4}))]_2$ and $[\overline{\mathrm{PtCl}(p\text{-}\mathrm{ClC_6H_3CH{=}N}})]_n$ *.

Results and discussion

The reaction of $\mathrm{PtCl_4^{2-}}$ (1 mmol) with the azines $(p\text{-}\mathrm{RC_6H_4CH{=}N})_2$ (2 mmol) ($\mathrm{R = NO_2}$, Cl, H, $\mathrm{NMe_2}$) was carried out in anhydrous acetic acid under reflux for 24 h. In the case of $(p\text{-}\mathrm{ClC_6H_4CH{=}N})_2$ a very insoluble red precipitate (A) was formed, and on treatment with an excess of $\mathrm{PEt_3}$ this gave the dimetallated complex $[\mathrm{PtCl}(p\text{-}\mathrm{ClC_6H_3CH{=}N})(\mathrm{PEt_3})_2]_2$ (IIa) and $[\mathrm{PtCl_2(PEt_3)_2}]$ together with a small amount of the monometallated complex $[\mathrm{PtCl}(p\text{-}\mathrm{ClC_6H_3CH{=}N{-}N{=}CH}(p\text{-}\mathrm{ClC_6H_4}))(\mathrm{PEt_3})_2]$ (Ia). These were separated by column chromatography on silica gel. Compound (Ia) was obtained by reaction of $\mathrm{PEt_3}$ with the orange precipitate (**B**) formed on adding water to the acetic acid solution.

As was the case with the cycloplatinated compounds of N-alkyl-N-nitrosoanilines (11), we could not purify these intermediate solids (A) and (B). In view of the nature of the products obtained in the reaction with $\mathrm{PEt_3}$ we suggest that (A) is a mixture of $[\overline{\mathrm{PtCl}(p\text{-}\mathrm{ClC_6H_3CH{=}N}})]_n$ (II), $[\overline{\mathrm{PtCl}(p\text{-}\mathrm{ClC_6H_3CH{=}N}}\mathrm{-N{=}CH}(p\text{-}\mathrm{ClC_6H_4}))]_2$ (I), and the non-metallated compound, and that (**B**) is I in a more or less pure state..

In an attempt to produce compounds I and II separately we used the appropriate stoichiometric amount of reactants (1/1 or 2/1; mmol $\mathrm{PtCl_4^{2-}}$/mmol $(p\text{-}\mathrm{ClC_6H_4CH{=}N})_2$), but the only result was a fall in the yields of the metallated compounds, a mixture of the mono- and di-metallated compounds again being obtained.

In the case of $\mathrm{R = NO_2}$ a yellow precipitate was obtained, which upon further treatment with $\mathrm{PEt_3}$ gave $[\mathrm{PtCl_2(PEt_3)_2}]$ and the free azine; this suggests that the yellow precipitate was not a C-metallated compound. The benzalazines (R = H, $\mathrm{NMe_2}$) did not give the desired metallated complexes, decomposition of the ligands occurring instead. In methanol, a solvent in which the cycloplatination of some N-ligands has been observed [11], the benzalazines were recovered unchanged after 24 h shaking.

Comparison of these results with those obtained with $\mathrm{PdCl_2}$ [9] clearly shows that platinum(II) has a poorer metallating capacity than palladium(II) since decomposition of the azine (R = H) takes place before metallation.

For the cyclopalladation reaction of N-donor ligands such as azobenzene [12], *N,N*-dimethylbenzylamines [4] or azines [9] it has been suggested that an electrophilic substitution takes place after the coordination of the ligand to the metal. No comparative studies of the platination have been carried out but an electrophilic substitution has been suggested for the reaction of $\mathrm{PtCl_4^{2-}}$ with *N,N*-dimethylbenzylamines [4] on the basis solely of analogy with the results obtained for palladium(II). The behaviour shown of the benzalazines studied is consistent with an electrophilic mechanism.

When the azine with R = Cl was treated with $\mathrm{PtCl_4^{2-}}$ in refluxing acetic acid for 5–6 h, no C-metallated compound was formed, but after 24 h the mono- and

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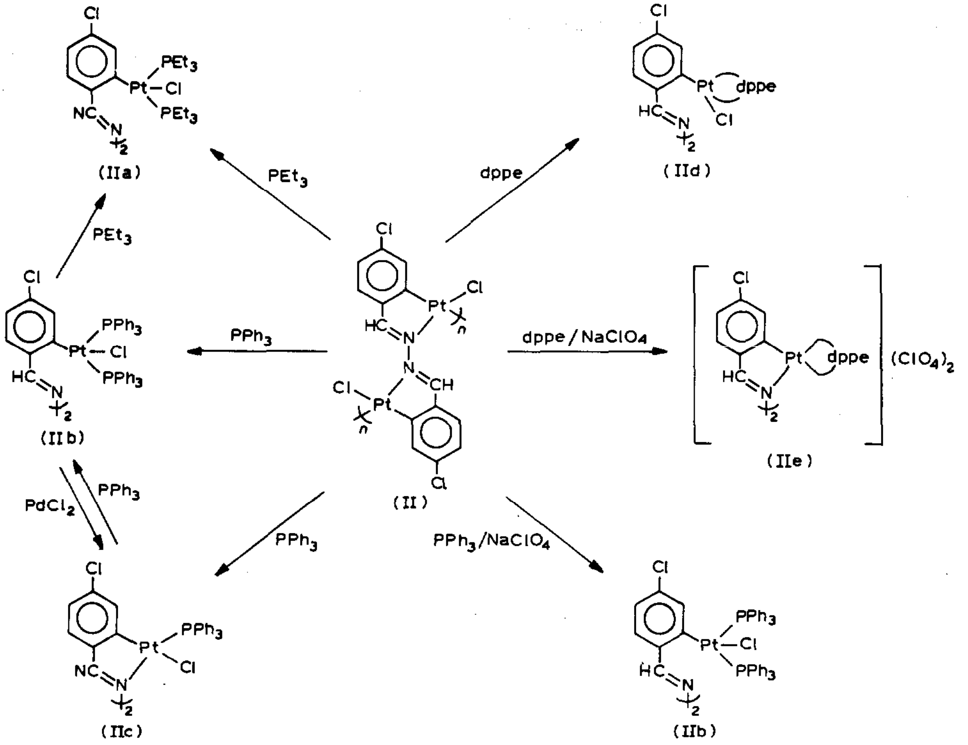
* The designation *p*-Cl in the complexes indicates that the Cl is *para* to the nitrogen-containing ligand, which itself is *ortho* to platinum, as shown in Scheme 1.



SCHEME 1

di-metallated compounds I and II were obtained. For $R = NO_2$, although the formation of the initial non-metallated complex occurred, the electrophilic attack of coordinated platinum(II) on the aromatic rings, which would be deactivated by the strongly electron-withdrawing NO_2 groups, does not take place. The lower metallating capacity of platinum(II) results in decomposition of the more electron-rich azines ($R = H, NMe_2$) before metallation.

The reactivity of compound II with phosphines is summarized in Scheme 1; similar results were obtained with the monoplatinated complex I. Treatment of I or II with an excess of PR'_3 (PEt_3 or PPh_3) in refluxing chloroform yielded $[PtCl(p\text{-}ClC_6H_3CH{=}N{-}N{=}CH(p\text{-}ClC_6H_4))(PR'_3)_2]$ (Ia, Ib) or $[PtCl(p\text{-}ClC_6H_3CH{=}N)(PR'_3)_2]_2$ (IIa, IIb). The cyclometallated compounds, $[PtCl(p\text{-}ClC_6H_3CH{=}N{-}N{=}CH(p\text{-}ClC_6H_4))(PPh_3)]_2$ (Ic) and $[PtCl(p\text{-}ClC_6H_3CH{=}N)(PPh_3)]_2$ (IIc) were obtained directly by action of a small amount of PPh_3 on compounds I or II. These compounds, Ic and IIc, were also obtained by the reaction of $PdCl_2$ with $[PtCl(p\text{-}ClC_6H_3CH{=}N{-}N{=}CH(p\text{-}ClC_6H_4))(PPh_3)_2]$ (Ib) or $[PtCl(p\text{-}ClC_6H_3CH{=}N)(PPh_3)_2]_2$ (IIb), the $PdCl_2$ trapping the phosphine released from Ib and IIb to give $[PdCl_2(PPh_3)_2]$.

Dppe reacts with the cyclometallated polymer II in refluxing acetone to give either the neutral compound $[PtCl(p\text{-}ClC_6H_3CH{=}N)(dppe)]_2$ (IId) or, when a relatively large anion such as perchlorate is present, the ionic compound $\{[Pt(p\text{-}ClC_6H_3CH{=}N)(dppe)]_2\}(ClO_4)_2$ (IIe). On the other hand, with PPh_3, II yields only the neutral compound IIb, even in the presence of $NaClO_4$.

These results indicate, by analogy with those for the dicyclopalladated compounds [13], that the Pt–Cl bond *trans* to N is cleaved first, and when a bidentate phosphine is used the second phosphorus atom replaces the other Cl ligand to give ionic species, which can be isolated only if a bulky anion such as ClO_4^- is present.

As far as phosphine exchange reactions of organometallic square-planar complexes are concerned, it is known that the more basic and less bulky phosphines can usually replace less basic and bulkier phosphines, but for platinum compounds this substitution is very difficult to achieve. The ready formation of IIa from IIb suggests that an intramolecular nucleophilic attack of the nitrogen atom on platinum is involved [14].

Characterization of compounds

The new compounds are yellow (orange in the case of IIc and Ic) air stable solids. Triethylphosphine compounds decompose to give $[PtCl_2(PEt_3)_2]$ and the starting azines if their solution in chloroform are kept for long periods.

Analytical data and decomposition temperatures are given in Table 1. Their diamagnetic behaviour indicates a square-planar arrangement of the ligands surrounding the platinum atoms. The low values of the molar conductivity in anhydrous acetone (10^{-4} mol dm^{-3} solutions) at 20°C correspond to non electrolytes for the neutral compounds (1–4 Ω^{-1} cm^2 mol^{-1}) and to a 1/2 electrolyte for the ionic compound (195 Ω^{-1} cm^2 mol^{-1}).

The IR spectra show the typical bands of the coordinated phosphines [15] and benzalazines [16]. The ν_{asym}(C=N) frequencies are given in Table 1. The ν_{asym}(C=N) bands for compounds IIc and IIe, which contain Pt–N bonds (1600 and 1590 cm^{-1}), appear at frequencies lower than in free azine (1630 cm^{-1}), in agreement with the expected decrease in bond order upon coordination of the nitrogen. For compounds

TABLE 1

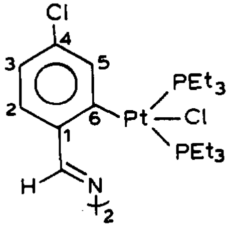
ANALYTICAL DATA, MELTING POINTS, IR AND $^{31}P\{^1H\}$ NMR DATA

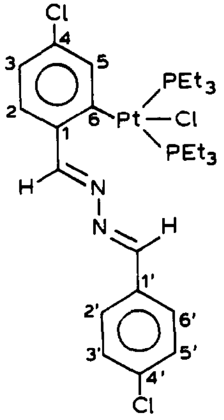
Compound	Analysis (Found (calcd.)(%))			M.p. (°C)	IR (cm^{-1})	δ(P) [b]	J(P–Pt)
	C	H	N		ν_{asym}(C=N)	(ppm)	(Hz)
IIa	37.7 (37.75)	5.6 (5.67)	2.4 (2.31)	241–242	1620	13.6	2651
IIb	57.9 (57.85)	3.8 (3.81)	1.7 (1.56)	(300–302) [a]	1610	22.8	2969
IIc	47.5 (47.63)	3.0 (3.04)	2.2 (2.22)	(188–190) [a]	1600	21.8	4478
IId	51.8 (51.71)	3.8 (3.68)	2.1 (1.83)	(212–214) [a]	1615	–	–
IIe	47.7 (47.72)	3.5 (3.40)	2.0 (1.68)	(170–172) [a]	1590	39.1 46.0	3884 1948
Ia	42.2(42.03)	5.2(5.25)	3.8(3.77)	154–155	1610 1630	13.7	2649
Ib	57.8(58.23)	3.4(3.81)	2.6(2.72)	(232–234) [a]	1610 1630	22.1	3047
Ic	49.5(49.98)	3.0(3.14)	3.0(3.64)	(218–220) [a]	1600 1630	20.6	4378

[a] With decomposition. [b] Relative to H_3PO_4, in $CDCl_3$.

TABLE 2

PROTON AND $^{13}C\{^1H\}$ NMR DATA [a] OF COMPOUNDS Ia AND IIa


(IIa)


(Ia)

Compound	^1H				^{13}C			
	Azomethine	Aromatic	CH_2	CH_3	Azomethine	Aromatic	CH_2	CH_3
Ia		7.57d(H^5) [c]				150.1(C^6)		
						136.8(C^1) [f], (C^5) [f]		
	9.58(11.0) [b]	6.97d(H^3) [d]			168.5	135.6(C^4)		
						127.5(C^2)		
		7.84d(H^2) [d]	1.64m	1.07q		123.0(C^3)	7.7t	13.7q
						137.2($C^{1'}$)		
	8.61s	7.41d($H^{3'}H^{5'}$) [d]			159.2	133.0($C^{4'}$)		
						129.4($C^{6'}$, $C^{2'}$)		
		7.75d($H^{2'}H^{6'}$) [d]				129.0($C^{3'}$, $C^{5'}$)		
IIa		7.52d(H^5) [e]				147.3(C^6)		
	9.49(11.6) [b]		1.64m	1.06q	166.0	136.8(C^1) [f], (C^5) [f]	7.7t	13.7q
		6.95br. d(H^3) [d]				135.2(C^4)		
						127.2(C^2)		
		7.79d(H^2) [d]				127.9(C^3)		

[a] In $CDCl_3$; chemical shifts in ppm (δ) with respect to internal $SiMe_4$. [b] J(PtH). [c] ^4J(HH) 3.5 Hz. [d] ^3J(HH) 8.5 Hz. [e] ^4J(HH) 2.2 Hz. [f] Tentative assignment.

IIa, IIb, IId, in which there are apparently no Pt–N bonds, the analogous signals appear at ca. 1620 cm^{-1}, suggesting some degree of interaction between Pt and N atoms, as was found in the analogous palladium compound [9]. The bands at 1630 and 1610 cm^{-1} in compounds Ia, Ib can be assigned to the ν_{asym}(C=N) vibrations of the two different imine groups in each compound.

Proton NMR data for compounds Ia and IIa in $CDCl_3$ solution are given in Table 2. The presence of the azomethine signals, one at 9.49 ppm for IIa and two at 9.58 and 8.61 ppm for Ia, support the symmetrical and asymmetrical platinated structures, respectively. In IIa, the two proton signals lie at lower fields than those for the starting, non-metallated azines (8.60 ppm). However, only one azomethine proton signal lies at lower field in Ia; the other signal being in the same position as in the free benzalazine. This downfield shift, stronger than in palladated analogous compound (9.31 ppm) [9], is due to the paramagnetic anisotropy of the metal, indicating that the azomethine proton and platinum atoms are close to one another and that the metallation has occurred in both rings in compound IIa and in only one ring in compound Ia. The azomethine protons near the platinum give rise to a pseudotriplet due to coupling with ^{195}Pt (J(Pt–H) 11 Hz). The unequivocal assignment of the aromatic protons also provides conclusive evidence of the position of platination. The methyl signals of the "PtCl(PEt$_3$)$_2$" group appear as pseudoquintuplets, which is characteristic of a *trans* arrangement of the two phosphines and is due to "virtual coupling".

The ^{13}C NMR spectra of Ia and IIa are summarized in Table 2, and confirm the structures proposed for these compounds. The spectra of the mono- and di-metallated compounds are characterized, respectively, by three and two signals strongly shifted downfield compared with the normal range of values for aromatic carbons. In compound Ia, two of the peaks (159.2, 168.5 ppm) correspond to the two different azomethine carbons, whereas the third (150.1 ppm) must be attributed to the platinated carbon atom in view of the large deshielding experienced by aromatic carbon nuclei as a consequence of the metallation [17]. In compound IIa the two peaks (166.0, 147.3 ppm) correspond to the azomethines and metallated carbons, respectively, in accord with the diplatinated structure proposed.

The assignment of the other aromatic carbon atoms was based on the values of $\delta(^{13}C)$ in the (p-ClC$_6$H$_4$CH=N)$_2$ entity after allowing for the shifts induced by the *trans*-"PtCl(PEt$_3$)$_2$" [18] substituent on the benzene carbon atoms. However, for some carbon atoms the proposed assignment is ambigous (see Table 2).

The high-field resonances were assigned to the ethyl groups in the phosphorus ligands and in both cases a rather simple pattern emerged. The methylene carbons appear as a pseudoquintuplet as a result of coupling to two equivalent atoms at phosphorus and to platinum. The methyl carbons appear as a pseudotriplet as a result of coupling to platinum. This overall pattern is consistent with the assignment of a *trans* configuration to the complexes. No spin–spin couplings of any aromatic carbon atoms to platinum were observed.

The ^{31}P{^{1}H} NMR spectra of compounds IIa, IIb, IIc, IIe and Ia, Ib, Ic are summarized in Table 1.

The triethylphosphine compounds IIa and Ia exhibit only a single sharp resonance with two satellites due to coupling to platinum-195, indicating a *trans* configuration of the phosphine ligands. The spectra of the triphenylphosphine compounds Ib and IIb, at room temperature consist of a broad central peak ($\omega_{1/2}$ ca. 50 Hz) with broad satellites. When the solutions were cooled the peaks sharpened, and at −50°C were very sharp ($\omega_{1/2}$ ca. 5 Hz), suggesting that these compounds undergo triphenylphosphine exchange in CDCl$_3$ solution. On the other hand, the spectra of Ic and IIc at room temperature consist of sharp signals indicating that there is no such phosphine exchange. As proposed for [PtCl(C$_6$H$_4$–N=N–C$_6$H$_5$)(PPh$_2$Me)$_2$] [14] we suggest a mechanism for the exchange in which internal nucleophilic attack by a nitrogen atom induces loss of a phosphine ligand, and the latter can then enter into intermolecular nucleophilic substitutions. As mentioned above, the ready loss of PPh$_3$ was confirmed by the formation of Ic and IIc from Ib or IIb and PdCl$_2$.

The spectra of IIc and Ic exhibit only a single resonance with ^{195}Pt satellites, clearly showing that for these compounds only one geometrical isomer is present. In addition, bearing in mind that ligands with a small *trans* influence induce large values for ^1J(PtP), we sugest that the phosphorus atoms are *trans* to nitrogen in compounds IIc and Ic.

As expected, the spectrum of IIe shows two phosphorus resonances, each with platinum-195 satellites, which exhibit very different coupling constants (3384, 1948 Hz). These signals are assigned on the basis of relative *trans* influence of phosphorus atoms *trans* to nitrogen and *trans* to carbon, respectively. No coupling between the phosphorus atoms is observed.

Experimental

NMR spectra were obtained on a Varian XL spectrometer (^{1}H, 200 MHz; ^{13}C, 50.31 MHz and ^{31}P, 80.98 MHz). IR spectra were recorded on a Beckman IR-20A as 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 distilled before use. The benzalazines (p-$RC_6H_4CH{=}N)_2$ (R = NO_2, Cl, H, NMe_2) were prepared by published methods [19].

Action of p-chlorobenzalazine on potassium tetrachloroplatinate (II)

A stirred suspension of K_2PtCl_4 (0.41 g, 1 mmol) in anydrous acetic acid (20 cm^3) was treated with p-chlorobenzalazine (0.55 g, 2 mmol) and refluxed for 24 h. The suspension was cooled and the red precipitate (**A**) (0.40 g) filtered off, and washed with water, ethanol and chloroform. Water was added to the remaining acetic acid solution, whereupon an orange solid (**B**) (0.25 g) formed. We were unable to purify and characterize these solids, which were used for the experiments below without further purification.

[PtCl(p-ClC$_6$H$_3$CH=N)(PEt$_3$)$_2$]$_2$ (IIa)

A stirred suspension of the red solid (**A**) (0.40 g) in chloroform (25 cm^3) was treated with PEt_3 (0.37 g, 3 mmol) under N_2 and stirring was continued for 2 h. The solid was then filtered off and the solution was concentrated in vacuo and methanol was added. The yellow solid residue was chromatographed on silicagel with $CHCl_3$/MeOH (25/1) as eluent to give IIa (0.15 g).

[PtCl(p-ClC$_6$H$_3$CH=N-N=CH(p-ClC$_6$H$_4$))(PEt$_3$)$_2$] (Ia)

A stirred solution of the orange solid (**B**) (0.25 g) in chloroform (30 cm^3) was treated with PEt_3 (0.60 g, 5 mmol) under N_2, and the stirring was continued for 2 h. The solution was concentrated in vacuo and methanol was added. The yellow solid was recrystallized from $CHCl_3$/EtOH to give Ia (0.25 g).

[PtCl(p-ClC$_6$H$_3$CH=N)(PPh$_3$)$_2$]$_2$ (IIb)

Solid PPh_3 (0.78 g, 3 mmol) was added to a suspension of 0.40 g of the red solid **A** in 25 cm^3 chloroform, and the mixture was refluxed for 2 h. The precipitate was filtered off and recrystallized from CH_2Cl_2/EtOH to give IIb (0.35 g).

[PtCl(p-ClC$_6$H$_3$CH=N-N=CH(p-ClC$_6$H$_4$))(PPh$_3$)$_2$] (Ib)

The orange solid **B** (0.25 g) was dissolved in chloroform (30 cm^3) and PPh_3 (0.39 g, 1.5 mmol) was added. The solution was refluxed for 2 h, then concentrated in vacuo, and methanol was added. The yellow solid obtained was recrystallized from $CHCl_3$/MeOH, to afford Ib (0.30 g).

$[PtCl(p\text{-}ClC_6H_3CH{=}N)(PPh_3)]_2$ (IIc)

(a) A mixture of the red solid A (0.40 g) and PPh_3 (0.20 g) in chloroform (30 cm^3) was refluxed for 1 h. The orange precipitate formed was filtered off and purified by column chromatography on silicagel with $CHCl_3$/MeOH (50/1) as eluent, to give IIc (0.30 g).

(b) Solid $PdCl_2$ (0.08 g, 0.50 mmol) was added to a suspension of IIb (0.44 g, 0.25 mmol) in acetic acid. After 24 h stirring at room temperature the precipitate was collected and recrystallized from acetone, to give IIc (0.22 g, 70% yield).

$[PtCl(p\text{-}ClC_6H_3CH{=}N{-}N{=}CH(p\text{-}ClC_6H_4))(PPh_3)]$ (Ic)

Solid $PdCl_2$ (0.08 g, 0.50 mmol) was added to a suspension of Ib (0.26 g, 0.25 mmol) in acetic acid (25 cm^3). After 24 h stirring at room temperature the solution was evaporated to dryness under reduced pressure. The solid obtained was recrystallized from acetone, to give Ic (0.14 g, 75% yield).

$[PtCl(p\text{-}ClC_6H_3CH{=}N)(dppe)]_2$ (IId)

Solid dppe (0.31 g, 0.8 mmol) was added to a suspension of A (0.40 g) in $CHCl_3$ (25 cm^3) and the mixture was refluxed for 1 h. The solution was filtered and then concentrated in vacuo, and the pale yellow solid residue recrystallized from acetone to give IId (0.37 g).

$\{[Pt(p\text{-}ClC_6H_3CH{=}N)(dppe)]_2\}(ClO_4)_2$ (IIe)

A stirred suspension of A (0.40 g) in Me_2CO (50 cm^3) was treated with dppe (0.40 g, 1 mmol) and $NaClO_4$ (0.24 g, 2 mmol) and the mixture was refluxed for 1 h. After filtration the solution was concentrated in vacuo, and the solid residue recrystallized from $CHCl_2$/MeOH to give IIe (0.40 g).

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