

Coordination properties of imino(2-pyridyl)methylpalladium(II) compounds. Preparation and thermal rearrangement of binuclear adducts with palladium(II) and platinum(II) chlorides

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Abstract

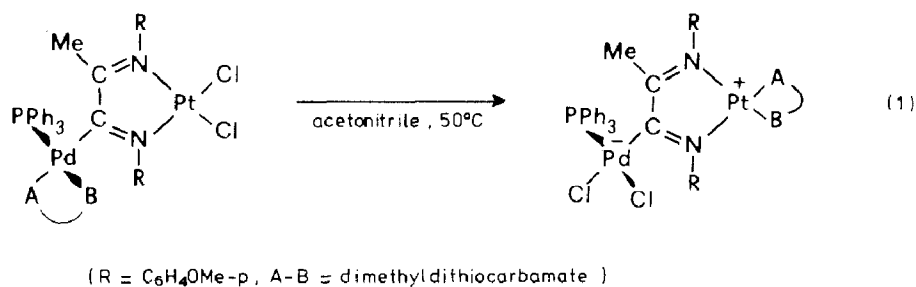
The imino(2-pyridyl)methylpalladium(II) compound py-2-C(R')=NR ($\text{R} = \text{C}_6\text{H}_4\text{OMe-}p$, $\text{R}' = \text{trans-PdCl(PPh}_3)_2$) reacts with $[\text{PdCl}_2(\text{CH}_2=\text{CHPh})]_2$, $[\text{PdCl}_2(\text{N}\equiv\text{CMe})_2]$, and $\text{K}[\text{PtCl}_3(\text{CH}_2=\text{CH}_2)]$ to give binuclear complexes $[\text{MCl}_2\{\text{py-2-C(R')=NR}\}]$ ($\text{M} = \text{Pd, Pt}$), in which the α -diimino group acts as a chelating bidentate ligand. In hot 1,2-dichloroethane, these complexes undergo a PPh_3 and chloride ligand exchange at rates which depend markedly on the metal M ($\text{Pd} \gg \text{Pt}$), to yield the new derivatives $[\text{MCl(PPh}_3)\{\text{py-2-C(cis-PdCl}_2(\text{PPh}_3))=\text{NR}\}]$. The ligand exchange is followed by a much slower decomposition to $[\text{MCl}_2(\text{PPh}_3)_2]$. Labile intermediates of the same type, $[\text{MCl(PPh}_3)\{\text{RN}=\text{C(cis-PdCl}_2(\text{PPh}_3))\text{C(R'')=NR}\}]$, are formed also in the thermal decomposition of $[\text{MCl}_2\{\text{RN}=\text{C(R')-C(R'')=NR}\}]$ ($\text{R} = \text{C}_6\text{H}_4\text{OMe-}p$; $\text{R}' = \text{trans-PdCl(PPh}_3)_2$; $\text{R}'' = \text{H, Me}$). The reactions of the dimethyldithiocarbamate derivative $\text{py-2-C(Pd(dmtc)(PPh}_3))=\text{NR}$ ($\text{R} = \text{C}_6\text{H}_4\text{OMe-}p$) with $\text{K}[\text{PtCl}_3(\text{CH}_2=\text{CH}_2)]$ and $[\text{PdCl}_2(\text{N}\equiv\text{CMe})_2]$ yield the different products $[\text{PtCl}_2\{\text{py-2-C(Pd(dmtc)(PPh}_3))=\text{NR}\}]$ and $[\text{Pd(dmtc)}\{\text{py-2-C(cis-PdCl}_2(\text{PPh}_3))=\text{NR}\}]$, respectively.

Introduction

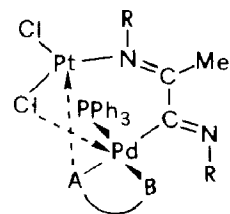
In recent years the coordination chemistry of 1,2-bis(imino)ethanes $\text{RN}=\text{CHCH}=\text{NR}$ has been extensively studied because of the versatile bonding properties of the flexible $\text{N}=\text{CHCH}=\text{N}$ α -diimino unit [1]. The reactions of these compounds with $[\text{PdCl}_2(\text{N}\equiv\text{CPh})_2]$, $\text{K}[\text{PtCl}_3(\text{CH}_2=\text{CH}_2)]$ and $[\{\text{MCl}_2(\text{L})\}_2]$ ($\text{M} = \text{Pd, Pt}$; $\text{L} = \text{olefin, tertiary phosphine or arsine}$) yield a variety of complexes in which the α -diimines

may act as either σ - N -monodentate, σ, σ - N, N' -bridging bidentate, or σ, σ - N, N' -chelating bidentate ligands [2–6].

Similar reactions with the corresponding derivatives $\text{RN}=\text{C}(\text{R}')\text{C}(\text{R}'')=\text{NR}'''$ ($\text{R} = \text{R}''' = \text{C}_6\text{H}_4\text{OMe-}p$, $\text{R}'' = \text{Me}$, $\text{R}' = \textit{trans}$ - $\text{PdCl}(\text{PPh}_3)_2$ or $\text{Pd}(\text{A-B})(\text{PPh}_3)$ ($\text{A-B} =$ bidentate anionic ligand); $\text{R} = \text{C}_6\text{H}_4\text{OMe-}p$, $\text{R}'' = \text{R}''' = \text{Me}$, $\text{R}' = \textit{trans}$ - $\text{PtCl}(\text{PPh}_3)_2$) generally give σ, σ - N, N' -chelate adducts of the type $[\text{MCl}_2\{\text{RN}=\text{C}(\text{R}')\text{C}(\text{R}'')=\text{NR}'''\}]$ ($\text{M} = \text{Pd, Pt}$) [7–9]. In some cases, however, these binuclear complexes undergo an exchange of ancillary ligands between the different metal centers, as shown in eq. 1.



An intramolecular mechanism was proposed, involving a transition state with a σ - N -monodentate α -diimino group [8]:



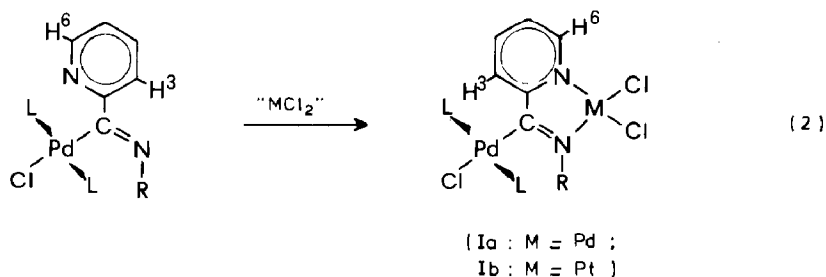
The coordination behaviour of pyridine-2-carbaldimines, $\text{py-2-CH}=\text{NR}$, towards palladium(II) and platinum(II) substrates has been less investigated. Such interesting ligands, containing different N-donor atoms, appear to be exclusively σ, σ - N, N' -chelate in the four- and five-coordinate complexes $[\text{MClX}(\text{py-2-CH}=\text{NR})]$ ($\text{X} = \text{Cl, Me}$) [10–12] and $[\text{PtClX}(\eta^2\text{-olefin})(\text{py-2-CH}=\text{NR})]$ ($\text{X} = \text{Cl, Me}$) [10,12], and in the cationic complexes $[\text{M}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{py-2-CH}=\text{NR})]^+$ ($\text{M} = \text{Pd, Pt}$) [13].

The availability of the analogues $\text{py-2-C}(\text{R}')=\text{NR}$ ($\text{R} = \text{C}_6\text{H}_4\text{OMe-}p$; $\text{R}' = \textit{trans}$ - $\text{PdCl}(\text{PPh}_3)_2$, $\text{Pd}(\text{dmtc})(\text{PPh}_3)$, ($\text{dmtc} =$ dimethyldithiocarbamate)) [14], prompted us to compare their reactions with various substrates containing the MCl_2 grouping ($\text{M} = \text{Pd, Pt}$) with those of the α -diimines, $\text{RN}=\text{C}(\text{R}')\text{C}(\text{R}'')=\text{NR}$ ($\text{R} = \text{C}_6\text{H}_4\text{OMe-}p$; $\text{R}'' = \text{H, Me}$; $\text{R}' = \textit{trans}$ - $\text{PdCl}(\text{PPh}_3)_2$, $\text{Pd}(\text{dmtc})(\text{PPh}_3)$) [7].

Results and discussion

Preparation and characterization of the binuclear complexes I

The imino-(2-pyridyl)methyl derivative, $\text{py-2-C}(\text{R}')=\text{NR}$ ($\text{R}' = \textit{trans}$ - $\text{PdCl}(\text{PPh}_3)_2$), reacts with chloro-palladium(II) and platinum(II) complexes containing weakly coordinated olefins or nitriles according to eq. 2.



(L = PPh₃ , R = C₆H₄OMe-*p*)

("MCl₂" : $\frac{1}{2}$ [PdCl₂(CH₂=CHPh)]₂, [PdCl₂(N≡CMe)₂], K[PtCl₃(CH₂=CH₂)])

The formulation of the binuclear adducts I is based on molecular weight measurements, elemental analyses, IR spectra (Table 1), ¹H and ³¹P NMR spectra (Table 2).

Complex Ib is a monomer in 1,2-dichloroethane (see Experimental). The IR spectra of I exhibit two ν (M–Cl) bands in the range 353–335 cm⁻¹, in accord with a *cis* square-planar geometry around the metal M, and a ν (Pd–Cl) band of the *trans*-PdCl(PPh₃)₂ unit at slightly higher frequencies (4–14 cm⁻¹) than in the uncoordinated starting compound (296 cm⁻¹) [14]. Like the pyridine-2-carbaldimines in the complexes [MCl₂(py-2-CH=NR)] [10,11], the imino(2-pyridyl)methyl moiety of I is σ, σ -*N, N'*-chelated to the metal M, as indicated by the deshielding of the pyridyl H⁶ proton resonance and by the low-frequency shift of the imino C=N stretching vibration (at 1572 cm⁻¹ in the free ligand [14]) upon coordination. This is further supported by the observation of ¹⁹⁵Pt satellites with a value of ³J(Pt–H) of 40.5 Hz for the δ (H⁶) signal of Ia (cf. the ¹⁹⁵Pt–H⁶ coupling constants of ca. 37 Hz reported for [PtCl₂(py-2-CH=NR)] [10,11]). The conformational change of the α -diimino group upon chelation brings the H³ proton close to the *d*⁸ palladium center of the *trans*-PdCl(PPh₃)₂ group (above its coordination plane), thus causing a remarkable downfield shift for the δ (H³) resonance [15]. In contrast, the *ortho*-AA' protons of the C₆H₄OMe-*p* N-substituent in I are shielded by ca. 0.5 ppm relative to the corresponding protons of [MCl₂(py-2-CH=NR)] (M = Pd, Pt; R = C₆H₄OMe-*p*) [11], owing to the predominant shielding effect of the phenyl ring current of the mutually *trans*-PPh₃ ligands in the PdCl(PPh₃)₂ imino-carbon substituent.

Thermal rearrangement of I

The binuclear complexes I are stable for several days in halogenated solvents at room temperature. However, when their solutions in 1,2-dichloroethane are kept at 80 °C, there is an exchange of PPh₃ and Cl⁻ ligands between the Pd and M metal centers, as shown in Scheme 1.

Reaction (i) is slow and can be readily monitored by ³¹P NMR spectroscopy. The ligand exchange takes ca. 8 h for completion for M = Pd, and ca. 4 days for M = Pt. In both cases, it is followed by an even slower decomposition (iii) of the zwitterionic compound IIa and IIb to form a small amount of *trans*-[PdCl₂(PPh₃)₂] (δ (³¹P) 23.3 ppm in CDCl₃) and *cis*-[PtCl₂(PPh₃)₂] (δ (³¹P) 14.3 ppm, ¹J(Pt–P) 3678 Hz in

(Continued on p. 416)

Table 1
Analytical data and characteristic IR bands

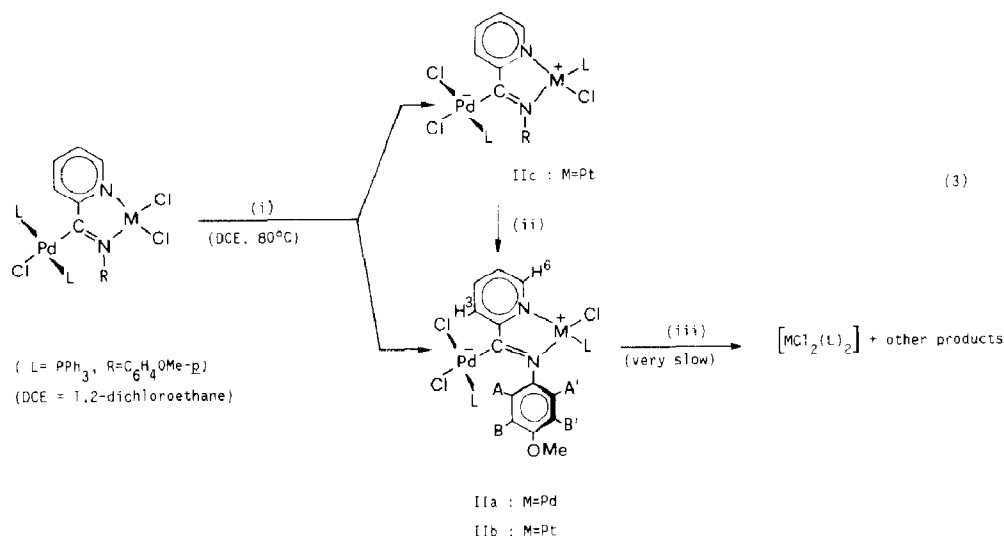
Compound (R = C ₆ H ₄ OMe- <i>p</i> ; L = PPh ₃)	Analyses (Found (calcd) (%))				IR (cm ⁻¹)			
	C	H	N	Cl	ν(C=N)	ν(M-Cl) ^a	ν(Pd-Cl) ^b	Other bands
[PdCl ₂ {py-2-C(PdClL ₂)=NR}] (Ia)	55.5 (55.78)	3.9 (3.92)	2.6 (2.66)	10.2 (10.08)	1510sh ^c	353ms 336m	300m	
[PtCl ₂ {py-2-C(PdClL ₂)=NR}] (Ib)	51.3 (51.46)	3.6 (3.61)	2.4 (2.45)	9.4 (9.30)	1505sh ^c	350m 335ms	310m	
[PdClL{py-2-C(PdCl ₂ L)=NR}] (IIa)	54.9 (55.78)	3.8 (3.92)	2.5 (2.66)	10.5 (10.08)	1510sh ^c	353m	305m 273m	
[PtClL{py-2-C(PdCl ₂ L)=NR}] (IIb)	51.4 (51.46)	3.6 (3.61)	2.4 (2.45)	9.4 (9.30)	1505sh ^c	348m	300m 277m	
[PtClL(py-2-CH=NR)ClO ₄ ^d	46.2 (46.28)	3.3 (3.38)	3.5 (3.48)	8.6 (8.81)	1615sh	349m,br		1095vs[ν(Cl-O)] 623s[δ(Cl-O)] 1547ms[ν(C=N)] ^e
[PtCl ₂ {py-2-C(Pd(dmte)L)=NR}] (VIIIb)	42.1 (42.27)	3.3 (3.34)	4.2 (4.35)	7.4 (7.34)	1505sh ^c	342ms 330sh		368m[ν(Pd-S)] 1560s,br[ν(C=N)] ^e
[Pd(dmte){py-2-C(PdCl ₂ L)=NR}] (IXa)	46.3 (46.54)	3.7 (3.68)	4.7 (4.79)	8.1 (8.08)	1510sh ^c		300m 274ms	382m[ν(Pd-S)]

^a Vibrations involving the metal center (M = Pd, Pt) σ, σ-*N, N'*-chelated to the α-diimino group. ^b Vibrations of the *trans*-PdCl(PPh₃)₂ and *cis*-PdCl₂(PPh₃) units. ^c Tentative assignment: the ν(C=N) band is partially masked by the intense absorption of the C₆H₄OMe-*p* substituent at ca. 1500 cm⁻¹. ^d Mixture of isomers IIIc and IIIb. ^e Vibration of the dmte ligand.

Table 2
Selected ^1H and ^{31}P NMR Data ^a

Compound (R = C ₆ H ₄ OMe- <i>p</i> ; L = PPh ₃)	Solvent	2-Pyridyl protons ^b		<i>p</i> -Methoxyphenyl protons ^c		Dmte protons		^{31}P resonances
		H ³	H ⁶	AA'	BB'	O-CH ₃	N-CH ₃	
py-2-C(PdCl ₂)=NR ^d	CD ₂ Cl ₂	mk ^e	8.45m	mk ^e	6.85m	3.89s		20.8s
[PdCl ₂ {py-2-C(PdCl ₂)=NR}] (Ia)	CD ₂ Cl ₂	8.57m	8.79m	6.88m	6.58m	3.87s		20.2s
[PtCl ₂ {py-2-C(PdCl ₂)=NR}] (Ib)	CD ₂ Cl ₂	8.40m	9.26m	6.88m	6.60m	3.89s		20.3s
[PdCl ₂ {py-2-C(PdCl ₂)=NR}] (IIa)	CD ₂ Cl ₂	9.57m	8.93m	8.06m(A) ^f ; 6.48m(B) ^f ;		3.69s	5.64m(A'B') ^f	27.1s; 26.5s
[PtCl ₂ {py-2-C(PdCl ₂)=NR}] (IIb)	CD ₂ Cl ₂	9.55m	9.20m	8.03m(A) ^f ; 6.45m(B) ^f ;		3.68s	5.63m(A'B') ^f	25.9t ⁴ J(Pt-P) 12.2 6.5t
[PtCl(py-2-CH=NR)]ClO ₄ ^g (IIIb)	CD ₂ Cl ₂	8.38m	9.45m	6.77m	6.25m	3.65s		¹ J(Pt-P) 3899 5.6t ¹ J(Pt-P) 3766
py-2-C(Pd(dmtc)L)=NR ^d	CD ₂ Cl ₂	mk ^e	8.60m	mk ^e	6.85m	3.85s		29.4s
[PtCl ₂ {py-2-C(Pd(dmtc)L)=NR}] (VIIIb)	CD ₂ Cl ₂	8.83m	9.56m	mk ^h	mk ^h	3.86s		28.3s
[Pd(dmtc){py-2-C(PdCl ₂ L)=NR}] (IXa)	CDCl ₃	9.48m	7.98m	mk ^e	6.87m	3.90s	3.08s; 3.05s	27.5s

^a Spectra recorded at 30 °C; $\delta(^1\text{H})$ values in ppm from TMS as internal standard; $\delta(^{31}\text{P})$ values in ppm from external 85% H₃PO₄, downfield shifts being taken as positive; coupling constants in Hz; s, singlet; t, triplet; m, multiplet; satisfactory integration values have been obtained. ^b The 2-pyridyl protons give rise to second-order spectra, in which each proton appears as a multiplet of characteristic pattern. ^c The *ortho* AA' and *meta* BB' protons of C₆H₄OMe-*p* appear in general as a symmetrical AA'BB' system. ^d Data from ref. 14. ^e Masked by the intense phenyl proton resonances of PPh₃ in the range 7.7–7.1 ppm. ^f ABCD spin system, see text. ^g Spectrum of isomer IIIb of Scheme 2, the imino proton resonates at 9.10 ppm with a ³J(Pt-H) of 94.5 Hz. ^h Masked by the intense phenyl proton resonances of PPh₃ in the range 7.7–6.9 ppm.



Scheme 1

CDCl₃), respectively, together with other unidentified products. The thermal rearrangement of Ia involves the formation of isomer IIa only, whereas the thermal rearrangement of Ib occurs through the geometrical isomers IIb and IIc (see Fig. 1). Both products are initially formed in ca. 1/1 molar ratio, compound IIc being characterized by two $\delta(^{31}\text{P})$ resonances at 27.5 ppm for the Pd-PPh₃ phosphine (with a $^4J(\text{Pt-P})$ of ca. 9 Hz) and at 10.2 ppm for the Pt-PPh₃ phosphine (with a $^1J(\text{Pt-P})$ of 3518 Hz), (spectrum (a)). As the reaction proceeds, compound IIc is converted almost completely into the more stable isomer IIb through the *cis-trans* isomerization step (ii) (spectrum (b)). When the reactions (i) and (ii) are complete, the presence of traces of decomposition products does not prevent the isolation of a pure sample of IIb*.

The far IR spectra of IIa and IIb are characterized by two $\nu(\text{Pd-Cl})$ bands in the range 305–273 cm⁻¹, which are typical of the *cis*-PdCl₂(PPh₃) unit in related binuclear complexes [16], and by one $\nu(\text{M-Cl})$ band at higher frequency (ca. 350 cm⁻¹). The assignment of the coordination geometry at the metal M of IIa and IIb, with the PPh₃ ligand *trans* to the pyridyl nitrogen atom, is essentially based on their ¹H NMR spectra (Table 2). In particular, the pyridyl H⁶ proton has a $^4J(\text{P-H})$ coupling constant of ca. 4 Hz, which agrees well with the corresponding values observed in the following complexes having a tertiary phosphine *trans* to a heterocycle nitrogen [17–19] (see p. 418).

Furthermore, the platinum derivative IIb shows a $^3J(\text{Pt-H}^6)$ coupling of 26.0 Hz, which is considerably smaller than the value of 40.5 Hz for complex Ib, in line with the much higher *trans* influence of PPh₃ relative to a chloride ligand [20].

An interesting feature of the ¹H NMR spectra is the appearance of the C₆H₄OMe-*p* phenyl protons as an ABCD spin system, arising from the fact that the

* The reactions shown in Scheme 1 were studied in 1,2-dichloroethane distilled from KOH, since they appear to be greatly accelerated by traces of HCl present in the commercial solvent.

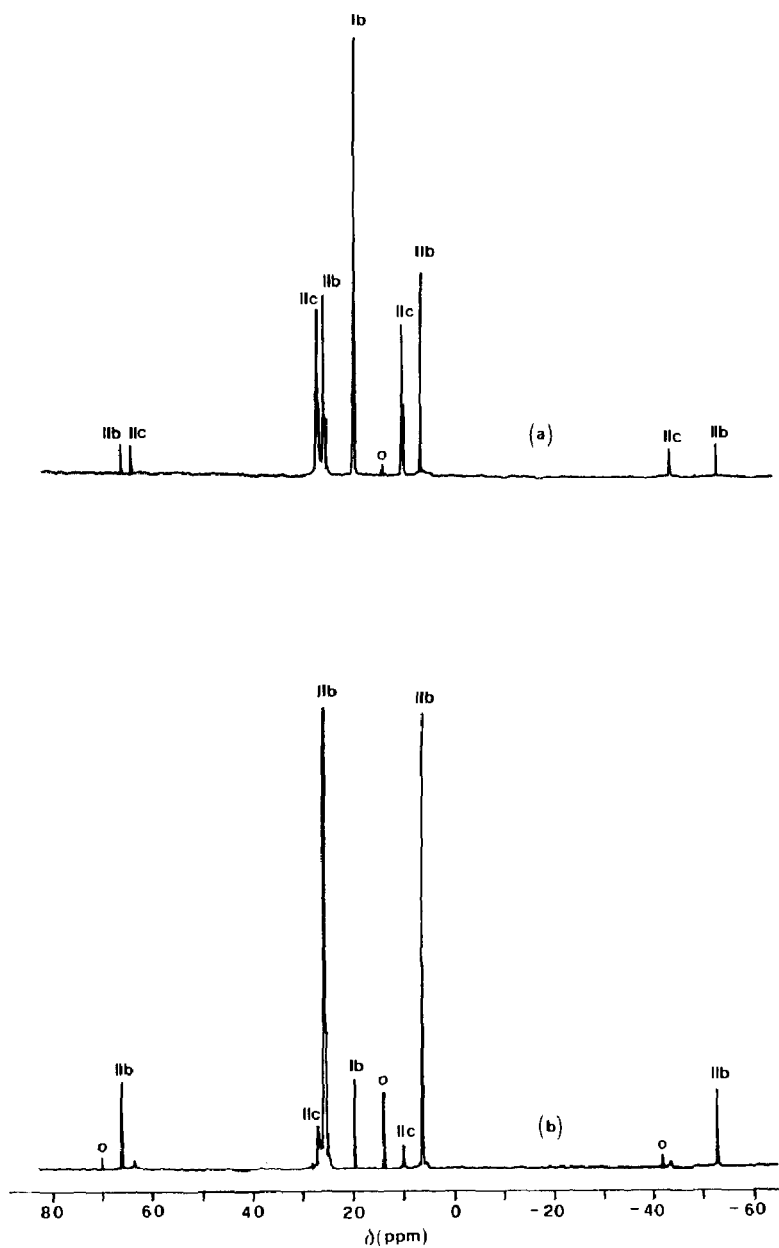
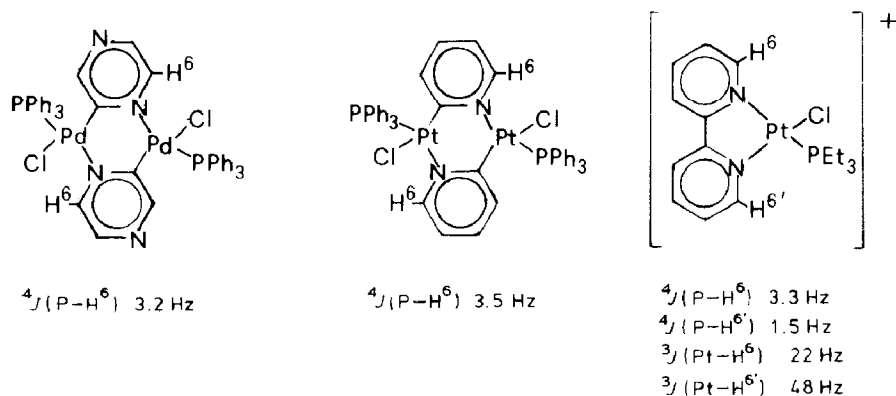


Fig. 1. ^{31}P NMR spectra in CDCl_3 of the reaction mixtures during thermal rearrangement of complex Ib in 1,2-dichloroethane at 80°C : (a) after 8 h; (b) after 4 days (O: $\text{cis-}[\text{PtCl}_2(\text{PPh}_3)_2]$).

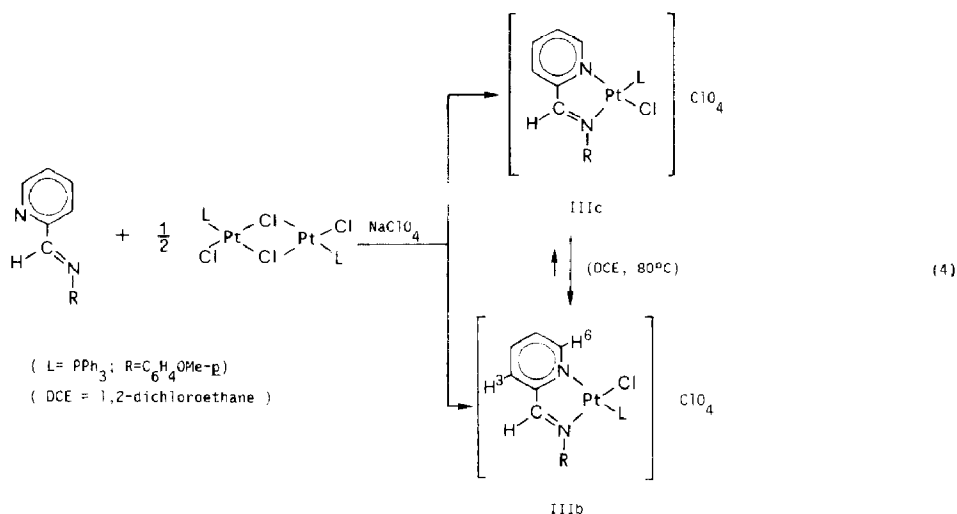
palladium atom of the $\text{cis-PdCl}_2(\text{PPh}_3)$ unit becomes a chiral center in the absence of free rotation around the $\text{Pd-C}_{\text{imino}}$ bond. This is indirectly confirmed by the observation that when the chiral center is absent, as in the related cationic complex IIIb (see Scheme 2), the $\text{C}_6\text{H}_4\text{OMe-}p$ phenyl protons give rise to the usual AA'BB' system (Table 2).



Reaction of *py*-2-CH=NR (*R* = *C*₆*H*₄*OMe-p*) with [*{PtCl*₂(*PPh*₃)₂]₂]

A mixture of geometrical isomers is also formed in the reaction of *py*-2-CH=NR with [*{PtCl*₂(*PPh*₃)₂]₂] (ligand/*Pt* molar ratio 1/1), in the presence of an excess of *NaClO*₄ (eq. 4 of Scheme 2).

The two species are clearly distinguished in the ³¹P NMR spectra ($\delta(^{31}\text{P})$ at 5.6 ppm with a ${}^1J(\text{Pt}-\text{P})$ of 3766 Hz for IIIb; at 10.2 ppm with a ${}^1J(\text{Pt}-\text{P})$ of 3702 for IIIc), whereas a large overlapping of signals occurs in the ¹H NMR spectra. On prolonged heating in 1,2-dichloroethane at 80 °C, however, the isomer IIIc (initially present as ca. 40%) slowly is converted into IIIb until an equilibrium mixture IIIb/IIIc ~ 5/1 is obtained, in which the proton resonances of the predominant species IIIb are easily observed (Table 2). The $\delta(\text{H}^6)$ signal exhibits the same ${}^3J(\text{Pt}-\text{H})$ and ${}^4J(\text{P}-\text{H})$ coupling constants as the corresponding signal of IIb, suggesting that there is a *trans* *N*_{py}-*Pt*-*PPh*₃ geometry also in IIIb, on the basis of the reasoning above. Furthermore, the imino proton resonance at 9.10 ppm is



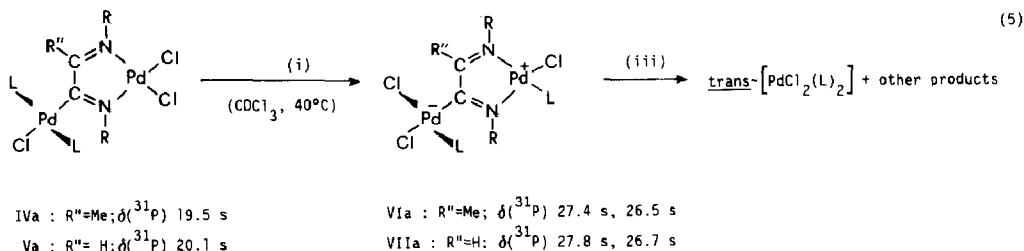
Scheme 2

flanked by two ^{195}Pt satellites with a coupling constant of 94.5 Hz, which is consistent with the imino group being *trans* to a chloride ligand [11,12].

A comparison between the ^3H chemical shift of IIIb (8.38 ppm) and that of IIb (9.55 ppm) reveals the remarkable deshielding effect of the *cis*- $\text{PdCl}_2(\text{PPh}_3)$ imino-carbon substituent, carrying a formal negative charge.

Thermal decomposition of the binuclear complexes IVa and Va

In the light of the present results we decided to reinvestigate the thermal behaviour of the binuclear complexes $[\text{PdCl}_2\{\text{RN}=\text{C}(\text{R}')\text{C}(\text{R}'')=\text{NR}\}]$ ($\text{R} = \text{C}_6\text{H}_4\text{OMe-}p$; $\text{R}' = \text{trans-PdCl}(\text{PPh}_3)_2$; $\text{R}'' = \text{H, Me}$) in chlorinated solvents. The 1,2-bis(imino)propylpalladium(II) adduct IVa can be isolated and characterized [7], since its decomposition to *trans*- $[\text{PdCl}_2(\text{PPh}_3)_2]$ and other unidentified products is sufficiently slow at room temperature [7]. In contrast, the 1,2-bis(imino)ethylpalladium(II) adduct Va proves to be so unstable towards decomposition to *trans*- $[\text{PdCl}_2(\text{PPh}_3)_2]$ that it can only be obtained in situ from the reaction of $\text{RN}=\text{C}(\text{R}')\text{CH}=\text{NR}$ ($\text{R}' = \text{trans-PdCl}(\text{PPh}_3)_2$) [21] with $[\text{PdCl}_2(\text{CH}_2=\text{CHPh})_2]$ (1/0.5 molar ratio). Since both complexes IVa and Va decompose too quickly at 80°C in 1,2-dichloroethane, reaction 5 of Scheme 3 was studied in CDCl_3 at 40°C by ^{31}P NMR spectroscopy.

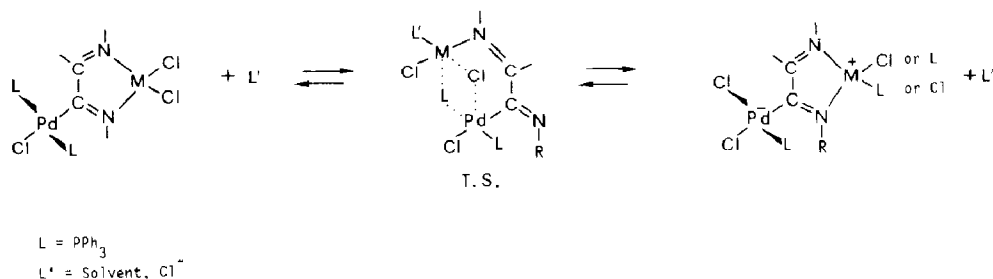


Scheme 3

In both cases, the spectra show the decomposition step (iii) to be preceded by formation of an intermediate (characterized by two 1/1 singlets in the range 27.8–26.5 ppm) which can be reasonably formulated as resulting from the PPh_3 and Cl^- ligand exchange (i) in the light of the close analogy with the ^{31}P NMR spectra of IIa (Table 2). The compounds VIa and VIIa cannot be isolated (as in the case of the zwitterionic complex IIa), because they decompose to *trans*- $[\text{PdCl}_2(\text{PPh}_3)_2]$ and other unidentified products at much faster rates. From the observed spectral changes with time, however, the following reactivity orders for the ligand exchange step (i) of reactions 3 and 5 can be obtained: $\text{Va} > \text{IVa}$; $\text{Va} \gg \text{Ia} \gg \text{Ib}$.

From the results of previous studies on the dissociation of the σ, σ - N, N' -chelate α -diimino ligands in the complexes $[\text{MCl}_2(\text{RN}=\text{CHCH}=\text{NR})]$ and $[\text{MCl}_2(\text{py-2-CH}=\text{NR})]$ ($\text{M} = \text{Pd, Pt}$; $\text{R} = \text{C}_6\text{H}_4\text{OMe-}p$) [11], $[\text{M}(\eta^3\text{-C}_3\text{H}_5)\{\text{RN}=\text{C}(\text{R}'')\text{C}(\text{R}')=\text{NR}\}]^+$ ($\text{M} = \text{Pd, Pt}$; $\text{R} = \text{C}_6\text{H}_4\text{OMe-}p$, $\text{R}'' = \text{H, Me}$) [22], and $[\text{M}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{py-2-CH}=\text{NR})]^+$ ($\text{M} = \text{Pd, Pt}$; $\text{R} = \text{C}_6\text{H}_4\text{OMe-}p$) [13], the ease of the ligand exchange step (i) appears to increase with decreasing stability of the five-membered metallacycle in the binuclear MCl_2 adducts. This observation and the catalytic activity of HCl on reaction 3 can be accommodated within the mechanism of Scheme 4, which involves breaking of the $\text{M}-\text{N}_{\text{imino}}$ bond and formation of a

transition state with a σ,N -monodentate α -diimino moiety, analogous to that proposed for the intramolecular migration of bidentate anionic ligands (eq. 1) [8].

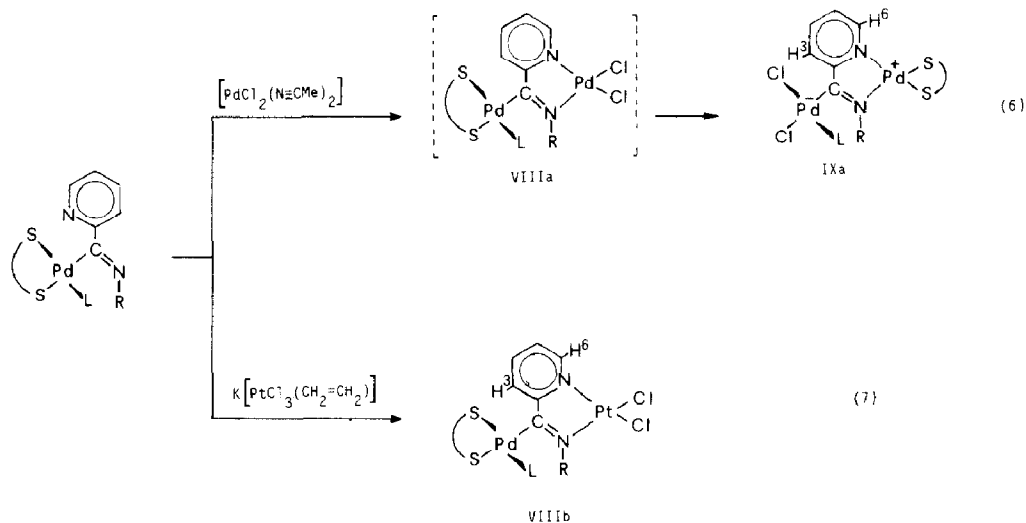


Scheme 4

Reactions of the compound py-2-C(R')=NR (R = C₆H₄OMe-p, R' = Pd(dmtc)(PPh₃))

The greater stability of the PtCl₂ adducts with α -diimines is also responsible for the different products of reactions 6 and 7 of Scheme 5. Reaction 7, with the Zeise's salt, yields the binuclear PtCl₂ adduct VIIIb, analogous to complex Ib of reaction 2. The chelate PtCl₂ group can be easily recognized by the appearance of two ν (Pt-Cl) bands at 342 and 330 cm⁻¹ in the IR spectrum. Moreover, in the ¹H NMR spectrum, the H⁶ pyridyl proton resonance at 9.56 ppm has a ³J(Pt-H) coupling of 40 Hz, very close to the value of 40.5 Hz for δ (H⁶) of Ib.

Reaction 6, with [PdCl₂(N≡CMe)₂], leads almost immediately to the product IXa, probably through a labile intermediate VIIIa. The complex IXa is a non-conducting monomer in 1,2-dichloroethane (see Experimental), and gives IR and ¹H NMR spectra significantly different from those of VIIIb. The presence of the *cis*-PdCl₂(PPh₃) group is indicated by the two ν (Pd-Cl) bands at 300 and 274 cm⁻¹ (cf. the ν (Pd-Cl) values in the range 305–273 cm⁻¹ for IIa and IIb), and by the δ (H³) signal at markedly lowfield (9.48 ppm) (cf. the δ (H³) values at 9.57 and 9.55 ppm for IIa and IIb, respectively).



Scheme 5

The course of each of reactions 6 and 7 parallels that of the corresponding reaction with the α -diimine $\text{RN}=\text{C}(\text{R}')\text{C}(\text{Me})=\text{NR}$ ($\text{R} = \text{C}_6\text{H}_4\text{OMe-}p$, $\text{R}' = \text{Pd}(\text{dmtc})(\text{PPh}_3)$) [7]. Complex VIIIb, however, does not undergo any exchange of dmtc and chloride ligands, even when heated at 50°C in acetonitrile for a long time, in contrast with the behaviour of the PtCl_2 adduct of $\text{R}=\text{C}(\text{R}')\text{C}(\text{Me})=\text{NR}$ under comparable conditions (see eq. 1).

This further indicates that the imino(2-pyridyl)methyl group of $\text{py-2-C}(\text{R}')=\text{NR}$ gives more stable $\sigma, \sigma\text{-}N, N'$ -chelate complexes than the 1,2-bis(imino)propyl moiety of $\text{RN}=\text{C}(\text{R}')\text{C}(\text{Me})=\text{NR}$.

Experimental

The complexes $[\text{PdCl}_2(\text{CH}_2=\text{CHPh})]_2$ [23], $\text{K}[\text{PtCl}_3(\text{CH}_2=\text{CH}_2)] \cdot \text{H}_2\text{O}$ [24], and $[\text{PtCl}_2(\text{PPh}_3)]_2$ [25] were prepared by standard methods. The imino(2-pyridyl)methylpalladium(II) derivatives, $\text{py-2-C}(\text{R}')=\text{NR}$ ($\text{R} = \text{C}_6\text{H}_4\text{OMe-}p$; $\text{R}' = \text{trans-PdCl}(\text{PPh}_3)_2$, $\text{Pd}(\text{dmtc})(\text{PPh}_3)$) were prepared by a published procedure [14]. The 1,2-dichloroethane was distilled from KOH before use. All other chemicals were reagent grade and used without further purification. The solvents were evaporated to small volume or to dryness at reduced pressure in a rotary evaporator. Infrared spectra were recorded with a Perkin-Elmer 983 instrument, using Nujol mulls and CsI windows in the range $4000\text{--}200\text{ cm}^{-1}$. The ^1H and $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra were recorded with a Varian FT80A spectrometer operating at 79.542 and 32.203 MHz respectively, at 30°C . Molecular weights were determined in 1,2-dichloroethane at 37°C with a Knauer osmometer.

Preparation of $[\text{MCl}_2\{\text{py-2-C}(\text{PdCl}(\text{PPh}_3)_2)=\text{NR}\}]$ ($M = \text{Pd}$, Ia; $M = \text{Pt}$, Ib)

(a) The dimer $[\text{PdCl}_2(\text{CH}_2=\text{CHPh})]_2$ (0.14 g, 0.25 mmol) was added to a stirred solution of $\text{py-2-C}(\text{PdCl}(\text{PPh}_3)_2)=\text{NR}$ (0.44 g, 0.5 mmol) in ca. 40 ml of CH_2Cl_2 . The colour of the mixture changed immediately to red-orange. The clear solution was concentrated to small volume and the yellow-orange product Ia was precipitated by dilution with Et_2O . It was purified by reprecipitation from the same solvents (yield 0.47 g, 89.1%, based on the theoretical amount). The binuclear complex Ia was also prepared in 75% yield from the reaction of $\text{py-2-C}(\text{R}')=\text{NR}$ with $[\text{PdCl}_2(\text{N}\equiv\text{CMe})_2]$ (1/1 molar ratio), by following the same procedure.

(b) A solution of $\text{py-2-C}(\text{PdCl}(\text{PPh}_3)_2)=\text{NR}$ (0.44 g, 0.5 mmol) in 50 ml of CH_2Cl_2 was added dropwise to a stirred solution of $\text{K}[\text{PtCl}_3(\text{CH}_2=\text{CH}_2)] \cdot \text{H}_2\text{O}$ (0.19 g, 0.5 mmol) in methanol (6 ml). The colour of the solution changed immediately to red-orange, and KCl began to separate. After 15 min the mixture was taken to dryness, and the solid residue was extracted with CH_2Cl_2 (50 ml) in the presence of charcoal. Filtration of the extract gave a clear solution, which was concentrated and then diluted with Et_2O to precipitate the orange complex Ib. This was purified by reprecipitation from the same solvents (0.49 g, 85.7%). Mol. weight found 1150; calcd. 1143.6.

Thermal rearrangement of complexes I. Preparation of $[\text{MCl}(\text{PPh}_3)\{\text{py-2-C}(\text{PdCl}_2(\text{PPh}_3))=\text{NR}\}]$ ($M = \text{Pd}$, IIa; $M = \text{Pt}$, IIb)

The binuclear complex Ia (0.53 g, 0.5 mmol) or Ib (0.57 g, 0.5 mmol) was dissolved in 1,2-dichloroethane (100 ml) and heated at 80°C . The course of the

thermal rearrangement was monitored by recording the ^{31}P NMR spectra of the reaction mixture at various times: for this purpose, a small portion of the DCE solution (5 ml) was evaporated to dryness and the solid residue was redissolved in CDCl_3 (1 ml). When the reaction was complete, the solvent was evaporated to give the compound IIa (or IIb) contaminated by small amounts of *trans*- $[\text{PdCl}_2(\text{PPh}_3)_2]$ (or *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$) and other unidentified decomposition products.

(a) Complex IIa was purified by fractional precipitation. Diethyl ether (5 ml) was added to a solution of the crude material (0.12 g) in 15 ml of DCE to precipitate the least soluble compound *trans*- $[\text{PdCl}_2(\text{PPh}_3)_2]$. After filtration, the solution was concentrated to ca. 10 ml and diluted with Et_2O (20 ml). After 1 h stirring a flocculent precipitate (0.02 g), consistent of a mixture of decomposition products, was filtered off, and the solution was diluted with a further amount of Et_2O (5 ml), then allowed to stand overnight during which the pure complex IIa separated as a deep-yellow microcrystalline solid (0.07 g).

(b) The crude compound IIb was dissolved in CH_2Cl_2 (ca. 80 ml) and treated with charcoal. After filtration, the solution was concentrated to ca. 10 ml, and the pure product IIb was precipitated as a deep-yellow microcrystalline solid by addition of Et_2O (0.51 g).

Preparation of the complex $[\text{PtCl}(\text{PPh}_3)(\text{py}-2\text{-CH}=\text{NR})]\text{ClO}_4$

A solution of the ligand $\text{py}-2\text{-CH}=\text{NR}$ ($\text{R} = \text{C}_6\text{H}_4\text{OMe}-p$, 0.11 g, 0.5 mmol) and $[\text{PtCl}_2(\text{PPh}_3)_2]$ (0.26 g, 0.25 mmol) in CH_2Cl_2 (10 ml) was treated with an excess of $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (0.14 g, 1 mmol) dissolved in 5 ml of MeOH. After 3 h stirring, the solvents were evaporated to dryness and the solid was extracted with CH_2Cl_2 (30 ml). The solution was treated with charcoal, filtered off, and concentrated to small volume. Dropwise addition of Et_2O precipitated the yellow-brown product, which was further purified by reprecipitation from the same solvent mixture (0.28 g, 69.6%).

Preparation of $[\text{PtCl}_2\{\text{py}-2\text{-C}(\text{Pd}(\text{dmtc})(\text{PPh}_3))=\text{NR}\}]$ (VIIIb)

A solution of $\text{py}-2\text{-C}(\text{Pd}(\text{dmtc})(\text{PPh}_3))=\text{NR}$ (0.35 g, 0.5 mmol) in CH_2Cl_2 (50 ml) was added dropwise to a stirred solution of $\text{K}[\text{PtCl}_3(\text{CH}_2=\text{CH}_2)] \cdot \text{H}_2\text{O}$ (0.19 g, 0.5 mmol) in MeOH (6 ml). The mixture was worked up as described above for the preparation of Ib, to yield the orange product VIIIb (0.37 g, 76.6%).

Preparation of $[\text{Pd}(\text{dmtc})\{\text{py}-2\text{-C}(\text{PdCl}_2(\text{PPh}_3))=\text{NR}\}]$ (IXa)

A solution of $\text{py}-2\text{-C}(\text{Pd}(\text{dmtc})(\text{PPh}_3))=\text{NR}$ (0.35 g, 0.5 mmol) in CH_2Cl_2 (50 ml) was treated with $[\text{PdCl}_2(\text{N}\equiv\text{CMe})_2]$ (0.26 g, 0.5 mmol). After 30 min stirring the mixture was treated with charcoal and filtered. The clear solution was concentrated to small volume and diluted with Et_2O to precipitate the yellow product IXa (0.36 g, 82%). Mol. weight found 860; calcd. 877.4.

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