

## REACTIONS OF DIMETHYL- AND DIPHENYL-MERCURY WITH DIHALOBIS(ISOCYANIDE)PALLADIUM(II) COMPLEXES

B. CROCIANI, M. NICOLINI\*

*Centro di Chimica Tecnolgia Composti Metallorganici Elementi Transizione, C.N.R., Venezia (Italy) and Istituto di Chimica Generale dell'Universita, Padova (Italy)*

and R.L. RICHARDS

*School of Molecular Sciences, University of Sussex, Brighton BN9 1QJ (Great Britain)*

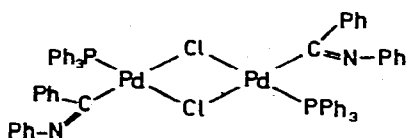
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### Summary

The reaction of *cis*-[PdCl<sub>2</sub>(CNR)<sub>2</sub>] (R = Ph, *p*-MeC<sub>6</sub>H<sub>4</sub>, *p*-MeOC<sub>6</sub>H<sub>4</sub>) and *trans*-[PdI<sub>2</sub>(CNPh)<sub>2</sub>] with HgR'<sub>2</sub> (R' = Me, Ph) followed by addition of PPh<sub>3</sub> (Pd/PPh<sub>3</sub>, 1/2) gives complexes of the type *trans*-[PdX{C(=NR)C(R')=NR}(PPh<sub>3</sub>)<sub>2</sub>] (X = Cl, I) as main products. These bis(imino) compounds may result from double insertion of the coordinated isocyanides into a Pd—R' σ-bond. NaBPh<sub>4</sub> was also found to act like HgPh<sub>2</sub> as a good phenylating agent towards coordinated isocyanide. The reactions of I with methanolic HClO<sub>4</sub> yield cationic compounds: *trans*-[PdX{C(NHR)C(R')=NR}(PPh<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub>; the protonated bis(imino) group may also be formulated as {C(=NR)C(R')NHR} and a fast equilibrium between the two forms probably exists in solution. The factors influencing the reaction with HgR'<sub>2</sub> and spectroscopic data (IR and <sup>1</sup>H NMR) for the complexes are reported and discussed.

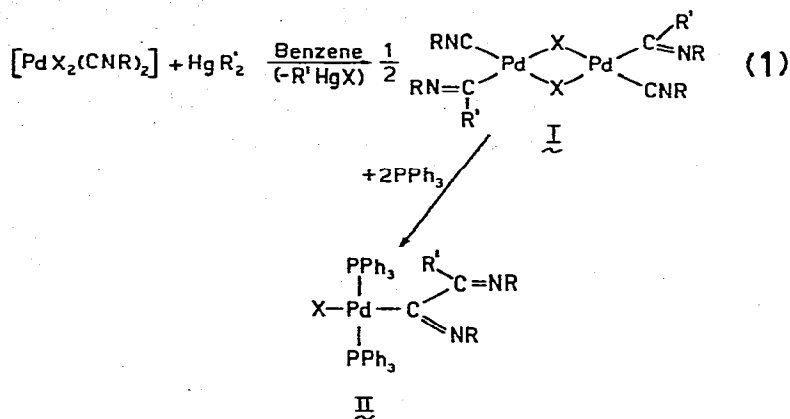
### Results and discussion

In a previous communication we reported the reaction of *cis*-[PdCl<sub>2</sub>(CNPh)<sub>2</sub>](PPh<sub>3</sub>) with a series of aryl derivatives of heavy metals (HgPh<sub>2</sub>, PbPh<sub>4</sub>, PbPh<sub>3</sub>Cl, SnPh<sub>4</sub> and BiPh<sub>3</sub>) [1]. The product of this reaction was a chloro-bridged compound containing an arylimino group σ-bonded to the palladium atom:



\* To whom correspondence should be addressed.

In order to obtain more information about this type of reaction, which is formally an arylation of the coordinated isocyanide, we have now studied the reaction of  $\text{HgR}'_2$  ( $\text{R}' = \text{Me, Ph}$ ) with dihalobis(isocyanide)palladium(II) complexes (eqn. 1). Triphenylphosphine ( $\text{Pd}/\text{PPh}_3 = 1/2$ ) was added when the first



( $\text{X} = \text{Cl}$ ;  $\text{I}$ ;  $\text{R} = \text{Ph, } p\text{-MeC}_6\text{H}_4, p\text{-MeOC}_6\text{H}_4$ ;  $\text{R}' = \text{Me, Ph}$ )

step of reaction 1 was completed.

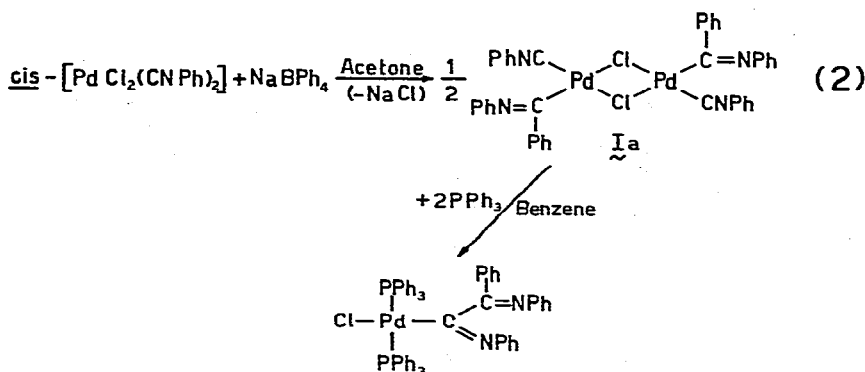
The reaction with  $\text{HgPh}_2$  is very fast and gives partial decomposition of the products (formation of metallic palladium) even at  $0^\circ\text{C}$ . For this reason and the troublesome separation of  $\text{PhHgCl}$  (see experimental) the yields of II are not high ( $\sim 50\%$ ). The reaction with  $\text{HgMe}_2$  is much slower and occurs with little decomposition. After the separation of  $\text{MeHgCl}$  the yields of II vary in the range 70-80% in repeated experiments.

The intermediates I are not very soluble in benzene, but they redissolve promptly on treatment with  $\text{PPh}_3$ , giving a yellow-orange solution. They are rather unstable and difficult to purify. However the proposed formulation is consistent with the IR spectra  $4000\text{-}250\text{ cm}^{-1}$  of the crude products I in the solid, characterized by a strong band at ca.  $2200\text{ cm}^{-1}$  ( $\nu(\text{C}\equiv\text{N})$  of coordinated isocyanide), a strong and broad band at  $1600\text{-}1550\text{ cm}^{-1}$  ( $\nu(\text{C}=\text{N})$  of the immino group) and, for  $\text{X} = \text{Cl}$ , a medium intensity band in the range  $340\text{-}310\text{ cm}^{-1}$  ( $\nu(\text{Pd}-\text{Cl})$ ). For  $\text{R} = p\text{-MeOC}_6\text{H}_4$ ,  $\text{R}' = \text{Me}$  and  $\text{X} = \text{Cl}$ , it was possible to get a product I satisfactorily pure, the IR spectrum of which exhibits the bands of bridging chlorides at  $316, 280$  and/or  $260\text{ cm}^{-1}$ , but its  $^1\text{H NMR}$  spectrum in  $\text{CDCl}_3$  shows an extensive decomposition of the complex in this solvent.

In order to ascertain the nature of the intermediates and the course of reaction 1 we have investigated the reaction with the milder phenylating agent  $\text{NaBPh}_4$  (eqn. 2).

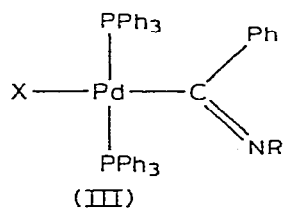
Under these conditions the compound Ia precipitated during its formation and could be easily purified from the contaminating  $\text{NaCl}$ . Its IR spectrum is characterized by the  $\nu(\text{C}\equiv\text{N})$  band of coordinated phenylisocyanide at  $2185\text{ cm}^{-1}$  and by  $\nu(\text{C}=\text{N})$  of the phenylimino group at  $1555\text{ cm}^{-1}$ . The  $\text{Pd}-\text{Cl}_{\text{bridging}}$  stretching frequencies occur at  $319$  and  $245\text{ cm}^{-1}$ .

This complex also reacts smoothly with  $\text{PPh}_3$  to give a product of type II ( $\text{X} = \text{Cl}$ ;  $\text{R} = \text{Ph}$ ;  $\text{R}' = \text{Ph}$ ).



The first step of reactions 1 and 2 is probably the formation of a very reactive complex  $[\text{PdX}(\text{R}')(\text{CNR})_2]$  containing a  $\text{Pd}-\text{R}'$   $\sigma$ -bond [2], which promptly rearranges to I. A complex like this, *trans*- $[\text{PdI}(\text{Me})(\text{CNBu}-t)_2]$ , was obtained from the oxidative addition of MeI to  $\text{Pd}(\text{CNBu}-t)_2$ , was obtained from the oxidative addition of MeI to  $\text{Pd}(\text{CNBu}-t)_2$  in *n*-hexane at  $0^\circ\text{C}$  [3]. This was rather stable in the solid but an insertion into the  $\text{Pd}-\text{Me}$  bond took place in toluene solution. The final addition of  $\text{PPh}_3$  yields the complexes II by splitting the halogen bridges and promoting the insertion of the coordinated isocyanide of I [4].

When  $\text{R}' = \text{Ph}$  but not when  $\text{R}' = \text{Me}$ , reaction 1 gives also mono-inserted products III.



These were identified by comparison of their IR and  $^1\text{H}$  NMR spectra with those of authentic samples prepared in another way [1]. These compounds are clearly formed from I by isocyanide displacement [5].

This difference in reactivity is probably related to the different steric requirements of the phenylimino and methylimino groups. Steric hindrance was found to play an important role in the single and multiple insertion of isocyanide into palladium to carbon  $\sigma$ -bonds [6].

In the case of  $\text{R} = p\text{-MeC}_6\text{H}_4$  and  $\text{R}' = \text{Ph}$ , the complexes II and III could not be separated by fractional precipitation. The  $^1\text{H}$  NMR spectrum of the mixture showed a ratio II/III of ca. 2/1 which became 5/1 when reaction 1 was carried out in the presence of free isocyanide (molar ratio  $\text{cis-}[\text{PdCl}_2(\text{CN-}p\text{-MeC}_6\text{H}_4)_2]/\text{CN-}p\text{-MeC}_6\text{H}_4 \approx 1$ ). The complexes II and III were characterized by elemental analysis (Table 1), IR spectra (Table 2) and  $^1\text{H}$  NMR spectra (Table 3). Molecular weight measurements show that they are monomeric in 1,2-dichloroethane solutions (see Experimental).

Compounds II are closely related to the products obtained by double insertion of cyclohexylisocyanide into the  $\text{Pd}-\text{Me}$   $\sigma$ -bond of the complexes

TABLE I  
ANALYTICAL AND PHYSICAL DATA

Compound <sup>a</sup>	Colour	M.p. <sup>b</sup> (°C)	Analysis Found (calcd.) (%)				$\Lambda_M$ ( $\Omega^{-1} \text{ cm}^2$ $\text{mole}^{-1}$ )
			C	H	N	X	
[PdCl {C(=N-p-MeOC <sub>6</sub> H <sub>4</sub> )C(Ph)=N-p-MeOC <sub>6</sub> H <sub>4</sub> } (PPh <sub>3</sub> ) <sub>2</sub> ] (IIb)	deep yellow	160 (dec.)	68.8 (68.98)	4.9 (4.89)	2.7 (2.77)	3.5 (3.51)	
[PdCl {C(=N-p-MeOC <sub>6</sub> H <sub>4</sub> )C(Me)=N-p-MeOC <sub>6</sub> H <sub>4</sub> } (PPh <sub>3</sub> ) <sub>2</sub> ] (IIc)	yellow	175-180 (dec.)	67.3 (67.16)	5.1 (5.00)	2.9 (2.96)	3.8 (3.74)	
[PdCl {C(Ph)=N-p-MeOC <sub>6</sub> H <sub>4</sub> } (PPh <sub>3</sub> ) <sub>2</sub> ] (IIIa)	pale-yellow	165-170 (dec.)	68.0 (68.50)	4.9 (4.87)	1.6 (1.59)	4.2 (4.04)	
[PdCl {C(=N-p-MeOC <sub>6</sub> H <sub>4</sub> )C(Me)=N-p-MeOC <sub>6</sub> H <sub>4</sub> } (PPh <sub>3</sub> ) <sub>2</sub> ] (IIId)	yellow	170-175 (dec.)	68.8 (69.51)	5.1 (5.17)	3.0 (3.06)	4.0 (3.87)	
[PdCl {C(Ph)=N-p-MeOC <sub>6</sub> H <sub>4</sub> } (PPh <sub>3</sub> ) <sub>2</sub> ] (IIIb)	pale-yellow	170 (dec.)	69.0 (69.77)	4.8 (4.91)	1.6 (1.62)	4.2 (4.12)	
[PdCl {C(=NPh)C(Ph)=NPh} (PPh <sub>3</sub> ) <sub>2</sub> ] (IIId)	yellow	165-170 (dec.)	70.3 (70.82)	4.6 (4.78)	2.9 (2.95)	3.9 (3.73)	
[PdCl {C(Ph)=NPh} (CNPh) <sub>2</sub> ] (IIa)	pale-yellow	153 (dec.)	56.0 (56.49)	3.6 (3.56)	6.5 (6.59)	8.0 (8.34)	
[PdCl {C(Me)=N-p-MeOC <sub>6</sub> H <sub>4</sub> } (CN-p-MeOC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> ] (Ib)	greenish-yellow	183 (dec.)	47.9 (48.24)	4.1 (4.04)	6.6 (6.62)	8.5 (8.37)	
[PdCl {C(=NPh)C(Me)=NPh} (PPh <sub>3</sub> ) <sub>2</sub> ] (IIe)	yellow	173 (dec.)	68.5 (69.00)	4.9 (4.88)	3.2 (3.20)	4.1 (3.99)	
[PdCl {C(=NPh)C(Me)=NPh} (PPh <sub>3</sub> ) <sub>2</sub> ] (IIIc)	deep-yellow	170-175 (dec.)	62.0 (62.55)	4.5 (4.46)	2.8 (2.86)	13.0 (12.95)	
[PdCl {C(NH-p-MeOC <sub>6</sub> H <sub>4</sub> )C(Ph)=N-p-MeOC <sub>6</sub> H <sub>4</sub> } (PPh <sub>3</sub> ) <sub>2</sub> ]ClO <sub>4</sub> (IVb)	red	170 (dec.)	62.7 (62.74)	4.6 (4.54)	2.5 (2.52)	6.4 (6.39)	
[PdCl {C(NH-p-MeOC <sub>6</sub> H <sub>4</sub> )C(Me)=N-p-MeOC <sub>6</sub> H <sub>4</sub> } (PPh <sub>3</sub> ) <sub>2</sub> ]ClO <sub>4</sub> (IVc)	orange	175 (dec.)	60.8 (60.73)	4.7 (4.61)	2.7 (2.67)	6.8 (6.76)	
[PdCl {C(NH-p-MeOC <sub>6</sub> H <sub>4</sub> )C(Me)=N-p-MeOC <sub>6</sub> H <sub>4</sub> } (PPh <sub>3</sub> ) <sub>2</sub> ]ClO <sub>4</sub> (IVd)	orange-yellow	160 (dec.)	62.5 (62.64)	4.7 (4.76)	2.7 (2.76)	7.0 (6.98)	
[PdCl {C(NHPh)C(Ph)=NPh} (PPh <sub>3</sub> ) <sub>2</sub> ]ClO <sub>4</sub> (IVe)	yellow-brown	120-125 (dec.)	63.9 (64.04)	4.4 (4.42)	2.6 (2.67)	6.8 (6.75)	
[PdCl {C(NHPh)C(Me)=NPh} (PPh <sub>3</sub> ) <sub>2</sub> ]ClO <sub>4</sub> (IVe)	yellow-brown	160 (dec.)	61.5 (61.99)	4.5 (4.49)	2.8 (2.84)	7.2 (7.18)	
[PdCl {C(NHPh)C(Me)=NPh} (PPh <sub>3</sub> ) <sub>2</sub> ]ClO <sub>4</sub> (IVf)	orange-yellow	160 (dec.)	56.3 (56.73)	4.2 (4.11)	2.6 (2.59)	3.3 (3.28)	
						Cl	
						I	
						12.1 (11.75)	

<sup>a</sup> For the more exact formulation of protonated complexes see text. <sup>b</sup> All melting points are uncorrected. <sup>c</sup> Methanolic solutions  $10^{-3} M$  at 25°C.

TABLE 2  
CHARACTERISTIC IR BANDS ( $\text{cm}^{-1}$ )

Compound	$\nu(\text{N-H})$	$\nu(\text{C=N})$	$\nu(\text{Pd-Cl})$	Other bands
IIb		1620(sh), 1540m	278m	
IIc		1616(sh), 1555m	265m	
IIIa		1568ms	290m	
IIId		1620ms, 1550ms	279m	
IIIb		1570ms	289m	
IIa		1610ms, 1550ms	281m	
Ia		1555ms(br)	320m, 245m	2185vs [ $\nu(\text{C}\equiv\text{N})$ ]
Ib		1575s(br)	316m, 280m, 260(sh)	2185vs [ $\nu(\text{C}\equiv\text{N})$ ]
Ile		1617ms, 1550ms	270m	
IIf		1618ms, 1564ms	n.r.	
IVb	3220w, 3200(sh)	1530mw	319m	1090vs(br) [ $\nu(\text{Cl-O})$ ]; 624vs [ $\delta(\text{Cl-O})$ ]
IVc	3240(sh), 3190ms, 3130mw	1605(sh), 1544mw	322(sh), 313m	1110vs, 1075vs [ $\nu(\text{Cl-O})$ ]; 620vs [ $\delta(\text{Cl-O})$ ]
IVd	3230(sh), 3190m, 3125mw	1615m, 1540mw	320m	1115vs, 1068vs [ $\nu(\text{Cl-O})$ ]; 626vs [ $\delta(\text{Cl-O})$ ]
IVa	3220(sh), 3195m, 3135mw	1609m, 1545m	320m	1100vs(br) [ $\nu(\text{Cl-O})$ ]; 626vs [ $\delta(\text{Cl-O})$ ]
IVe	3175mw, 3120m	1604mw, 1545m	320(sh), 310m	1100vs(br) [ $\nu(\text{Cl-O})$ ]; 626vs [ $\delta(\text{Cl-O})$ ]
IVf	3220(sh), 3190w, 3140w	1615mw, 1550mw	n.r.	1110vs, 1065vs [ $\nu(\text{Cl-O})$ ]; 626vs [ $\delta(\text{Cl-O})$ ]

TABLE 3

 $^1\text{H}$  NMR SPECTRA <sup>a</sup>

Compounds	Signals	Assignment	
IIb	3.75s [3]	OMe	
	3.84s [3]	OMe	
	6.1-5.7m [2]	$-\text{C}_6\text{H}_4-$	
	6.45-6.1m [2]	$-\text{C}_6\text{H}_4-$	
	7.05-6.45m [9]	$\text{Ph} + -\text{C}_6\text{H}_4-$	
	8.3-7.05m [30]	$\text{PPh}_3$	
IVb	3.79s [3]	OMe	
	3.85s [3]	OMe	
	6.1-5.8m [2]	$-\text{C}_6\text{H}_4-$	
	7.0-6.3m [6]	$-\text{C}_6\text{H}_4- + \text{Ph}$	
	8.0-7.0m [33]	$\text{PPh}_3 + \text{Ph}$	
	8.4-8.1m [2]	$-\text{C}_6\text{H}_4-$	
IIc	11.4 s	$\text{N}-\text{H}^b$	
	1.29s [3]	$\text{C}-\text{Me}$	
	3.83s [3]	OMe	
	3.88s [3]	OMe	
	6.2-6.0m [2]	$-\text{C}_6\text{H}_4-$	
	6.9-6.6m [4]	$-\text{C}_6\text{H}_4-$	
IVc	8.0-7.0m [32]	$\text{PPh}_3 + -\text{C}_6\text{H}_4-$	
	1.51s [3]	$\text{C}-\text{Me}$	
	3.87s [6]	OMe	
	6.5-6.2m [2]	$-\text{C}_6\text{H}_4-$	
	7.0-6.7m [4]	$-\text{C}_6\text{H}_4-$	
	7.9-7.1m [30]	$\text{PPh}_3$	
IIIa	8.6-8.3m [2]	$-\text{C}_6\text{H}_4-$	
	11.1s	$\text{N}-\text{H}^b$	
	3.88s [3]	OMe	
	8.6-6.5m [39]	$\text{PPh}_3 + \text{Ph} + -\text{C}_6\text{H}_4-$	
	IIIb + IIg <sup>c</sup>	2.21s	$\text{C}_6\text{H}_4-\text{Me}$
		2.34s	$\text{C}_6\text{H}_4-\text{Me}$
2.40s		$\text{C}_6\text{H}_4-\text{Me}$	
6.0-5.8m		$-\text{C}_6\text{H}_4-$	
6.3-6.0m		$-\text{C}_6\text{H}_4-$	
8.0-6.5m		$\text{PPh}_3 + \text{C}_6\text{H}_4- + \text{Ph}$	
IIIb	2.40s [3]	$\text{C}_6\text{H}_4-\text{Me}$	
	8.1-6.5m [39]	$\text{PPh}_3 + -\text{C}_6\text{H}_4- + \text{Ph}$	
IIId	1.30s [3]	$\text{C}-\text{Me}$	
	2.33s [3]	$\text{C}_6\text{H}_4-\text{Me}$	
	2.41s [3]	$\text{C}_6\text{H}_4-\text{Me}$	
	6.2-5.9m [2]	$-\text{C}_6\text{H}_4-$	
	8.2-6.7m [36]	$\text{PPh}_3 + -\text{C}_6\text{H}_4-$	
IVd	1.53s [3]	$\text{C}-\text{Me}$	
	2.34s [3]	$\text{C}_6\text{H}_4-\text{Me}$	
	2.40s [3]	$\text{C}_6\text{H}_4-\text{Me}$	
	6.3-6.1m [2]	$-\text{C}_6\text{H}_4-$	
	8.0-6.9m [34]	$\text{PPh}_3 + -\text{C}_6\text{H}_4-$	
	8.5-8.2m [2]	$-\text{C}_6\text{H}_4-$	
IIe	11.35s	$\text{N}-\text{H}^b$	
	1.36s [3]	$\text{C}-\text{Me}$	
	6.3-6.9m [ $\sim$ 2]	$\text{N}-\text{Ph}$	
IVe	8.2-6.9m [ $\sim$ 38]	$\text{PPh}_3 + \text{N}-\text{Ph}$	
	1.58s [3]	$\text{C}-\text{Me}$	
	6.4-6.0m [2]	$\text{N}-\text{Ph}$	
	7.8-6.8m [36]	$\text{PPh}_3 + \text{N}-\text{Ph}$	
IIIf	8.6-8.3m [2]	$\text{N}-\text{Ph}$	
	1.25s [3]	$\text{C}-\text{Me}$	
	6.3-5.9m [2]	$\text{N}-\text{Ph}$	
	8.0-6.8m [38]	$\text{PPh}_3 + \text{N}-\text{Ph}$	

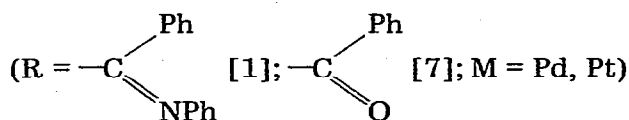
TABLE 3 (continued)

Compounds	Signals	Assignments
IVf	1.52s [3] 6.6-6.3m [2] 8.0-7.0m [36] 8.6-8.4m [2] 11.3s	C—Me N—Ph PPh <sub>3</sub> + N—Ph N—Ph N—H <sup>b</sup>

<sup>a</sup> In ppm from TMS or CH<sub>2</sub>Cl<sub>2</sub> as internal standard; integration values are given in square brackets, s = singlet, m = multiplet. <sup>b</sup> Spectrum recorded at -60°C. <sup>c</sup> The overall spectrum refers to the mixture IIg/IIb 5/1 (IIg = [PdCl{C(=N-*p*-MeC<sub>6</sub>H<sub>4</sub>)C(Ph)=N-*p*-MeC<sub>6</sub>H<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>}; see text).

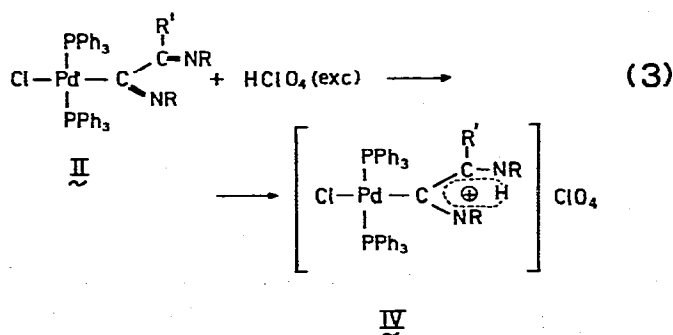
*trans*-[PdI(Me)L<sub>2</sub>] (L = tertiary phosphine) [6]. Their IR spectra show two  $\nu(\text{C}=\text{N})$  bands of the bis(imino) group in the ranges 1620-1610 and 1564-1540 cm<sup>-1</sup> respectively. The Pd—Cl stretching vibration was found at rather low frequency (281-265 cm<sup>-1</sup>), thus indicating a configuration with the chlorine *trans* to the palladium-to-carbon  $\sigma$ -bond.

A very high *trans* influence of the imino and acyl groups was observed in complexes of the type *trans*-[MCl(R)(PPh<sub>3</sub>)<sub>2</sub>]



On the other hand, a *trans* structure was assigned to the analogous bis(imino) derivatives, [PdI{C(=NC<sub>6</sub>H<sub>11</sub>)C(Me)=NC<sub>6</sub>H<sub>11</sub>}(PMe<sub>2</sub>Ph)<sub>2</sub>] on the basis of <sup>1</sup>H NMR spectra [6].

A characteristic reaction of II is the ready protonation by strong acids, such as HClO<sub>4</sub> in methanol (eqn. 3). Reaction 3 occurs with a rapid change of

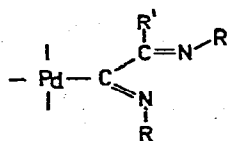


colour from yellow to red/orange-red. It is interesting to note that the bis(imino) group accepts only one proton even with excess of HClO<sub>4</sub>. Complexes IV behave as uni-univalent electrolytes in methanol (Table 1). Their IR spectra show two or three  $\nu(\text{N}-\text{H})$  bands at rather low frequencies (3240-3120 cm<sup>-1</sup>) and two  $\nu(\text{C}=\text{N})$  bands in the range 1620-1530 cm<sup>-1</sup>, the intensity of the latter being considerably lower than that of the corresponding bands of II.

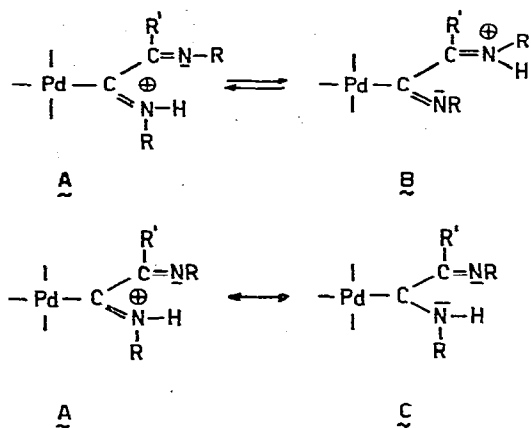
The protonation of the bis(imino) group strongly affects the position of the (Pd—Cl) vibrations, which are shifted by ca. 40 cm<sup>-1</sup> to higher frequencies

(320-310  $\text{cm}^{-1}$ ). This shift appears to be too large to be solely caused by the cationic charge of the complex, and thus the *trans*-influence of the imino-ligand must have been decreased by protonation.

The  $^1\text{H}$  NMR spectra of compounds II, III and IV show the typical signal of the coordination ligands for instance the  $\text{C}_6\text{H}_4\text{X}$  groups ( $\text{X} = \text{Me}, \text{OMe}$ ) appear as  $AA'BB'$  signals in the range 6-7 ppm partly overlapping with the phenyl protons. Because of restricted rotation around the  $\text{C}=\text{N}$  double bonds the imino group may exhibit different configurations. However, only one configuration was observed in solution for II and for IV for which four isomers are possible, and also for the monoimino complexes III, for which only two isomers are possible. The structure of this unique isomer is probably influenced by steric factors as was found for palladium(II) and platinum(II) carbene compounds [8]. Models indicate that for bis(imino) ligands the structure with the least steric hindrance is the following:



The NH signals were not observed in the spectra of IV in  $\text{CDCl}_3$  at room temperature, probably because of a fast exchange of the proton between the two nitrogen atoms of the bis(imino) group:



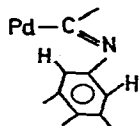
At low temperature ( $-60^\circ\text{C}$ ) only one NH signal was detected in the narrow range 11.1-11.4 ppm indicating that the above equilibrium is almost completely shifted to one side. We suggest form A to be predominant because it can be stabilized by the mesomeric system  $\text{A} \leftrightarrow \text{C}$  in which the limiting structure C contains a carbene type ligand. Furthermore, the interaction between the  $d$  electrons of the metal and the  $\text{C}=\text{N}$  double bond of II in the  $\alpha$ -position is such as to make this nitrogen atom more basic [9].

When  $\text{R}' = \text{Me}$ , the corresponding methyl signals occur at 1.25-1.36 ppm for II and at 1.51-1.58 ppm for IV. Such deshielding effect may be accounted for by a delocalisation of the positive charge over the conjugate double bonds system of the organic moiety. Another consequence of protonation is the appear-



ance of signals at rather low field (8.1-8.6 ppm) due to two protons of a NR group, which were masked by the PPh<sub>3</sub> peaks in the spectra of compounds II. Such signals have a complicated pattern when R = Ph, but when R = *p*-MeC<sub>6</sub>H<sub>4</sub> or *p*-MeOC<sub>6</sub>H<sub>4</sub> they correspond to the symmetrical side of an AA'BB' system. The lower field position compared to the other protons of the NR groups probably arises from an interaction with the central metal as was found for the *ortho* protons of the phenyl groups in the complex [Pd(PPhBu-*t*<sub>2</sub>)<sub>2</sub>] [10].

A possible explanation of such a deshielding effect can be given in terms of a structure of the type:



where the *ortho* protons are very close to the palladium atom. In this context it is noteworthy that *ortho*-metallation with formation of a five-membered ring is a well-recognised reaction of many palladium(II) complexes.

### Experimental

The isocyanides were prepared by the methods of Ugi and coworkers [11]. The complexes *cis*-[PdCl<sub>2</sub>(CNR)<sub>2</sub>], *trans*-[PdI<sub>2</sub>(CNPh)<sub>2</sub>] and *cis*-[PdCl<sub>2</sub>(CNR)-(PPh<sub>3</sub>)] were prepared by the standard methods. All other chemicals were reagent grade, and used without further purification.

Infrared spectra were recorded with a Perkin-Elmer 457 grating spectrometer in the range 4000-250 cm<sup>-1</sup> and with a Beckman IR 11 instrument in the range 400-200 cm<sup>-1</sup>. Hexachlorobutadiene mulls and NaCl plates were used in the range 4000-1300 cm<sup>-1</sup>, and Nujol mulls and CsI plates or thin polythene sheets in the range 1700-200 cm<sup>-1</sup>.

The <sup>1</sup>H NMR spectra were recorded with a Varian NV-14 60 MHz instrument using TMS or CH<sub>2</sub>Cl<sub>2</sub> as internal standard.

Molecular weights were measured with a Mechrolab osmometer at 37°C in 1,2-dichloroethane. Conductivity data were obtained on a LKB 8300 B conductivity bridge. Elemental analyses were made by A. Berton and G. Biasioli of the Microanalytical Laboratory, Laboratorio Radioelementi C.N.R., Padova (Italy).

#### *Reaction of cis*[PdCl<sub>2</sub>(CNR)<sub>2</sub>] (R = Ph, *p*-MeC<sub>6</sub>H<sub>4</sub>, *p*-MeOC<sub>6</sub>H<sub>4</sub> with HgPh<sub>2</sub>)

HgPh<sub>2</sub> (0.355 g, 1 mmol) in 20-30 ml of benzene was added dropwise to a stirred suspension of the palladium complex (1 mmol) in 50-70 ml of benzene at 0°C. An immediate reaction took place as shown by sudden change of colour (from yellow to dark-brown) and precipitation of ClHgPh. After 30 min PPh<sub>3</sub> (0.524 g, 2 mmol) was added and allowed to react for another 30 min. The colour became dark-red. The mixture was treated with charcoal and filtered to give a clear deep-red solution. In some cases this solution was further purified by chromatography through a silica gel column using benzene/ethyl ether (1/1 v/v) for elution. The products were finally precipitated by adding ethyl ether

to the concentrated solutions. The small amount of ClHgPh still present was eliminated by sublimation at 70-80°C/10<sup>-2</sup> mmHg and successive reprecipitation from benzene or dichloromethane/ethyl ether. The yields of bis(imino) complexes varied from 50 to 60%.

In this reaction variable amounts of the mono-inserted compounds [PdCl{C(Ph)=NR}(PPh<sub>3</sub>)<sub>2</sub>] were formed. When R = *p*-MeOC<sub>6</sub>H<sub>4</sub>, this product (0.145 g) was precipitated with petr. ether from the resulting solution after filtration to the bis-inserted complex.

When R = *p*-MeC<sub>6</sub>H<sub>4</sub>, the two products could not be separated by fractional precipitation. The reaction in the presence of free *p*-tolylisocyanide (see Results and discussion) was carried out as above.

The molecular weight of [PdCl{C(=N-*p*-MeOC<sub>6</sub>H<sub>4</sub>)C(Ph)=N-*p*-MeOC<sub>6</sub>H<sub>4</sub>}(PPh<sub>3</sub>)<sub>2</sub>] was found to be 1016 (calcd. 1009.8).

*Reaction of cis-[PdCl<sub>2</sub>(CNR)(PPh<sub>3</sub>)] (R = *p*-MeC<sub>6</sub>H<sub>4</sub>, *p*-MeOC<sub>6</sub>H<sub>4</sub>) with HgPh<sub>2</sub>*

HgPh<sub>2</sub> (0.335 g, 1 mmol) dissolved in benzene (20-30 ml) was slowly added to a stirred suspension of the palladium complex (1 mmol) in 50 ml of benzene at 0°C. After 15 min PPh<sub>3</sub> (0.262 g, 1 mmol) was added. The mixture was stirred for 30 min and then concentrated to a small volume (~10 ml) at reduced pressure in order to precipitate most of ClHgPh. After treatment with charcoal and filtration a yellow-orange solution was obtained, from which the products, [PdCl{C(Ph)=NR}(PPh<sub>3</sub>)<sub>2</sub>], were precipitated by adding ethyl ether/petr. ether (1/1 v/v). The remaining ClHgPh was eliminated by sublimation at 70-80°C/10<sup>-2</sup> mmHg and successive reprecipitation from the same solvents. Yields of mono-imino complexes ≈60-70%.

*Reaction of cis-[PdCl<sub>2</sub>(CNPh)<sub>2</sub>] with NaBPh<sub>4</sub>*

The complex (0.383 g, 1 mmol) suspended in acetone (30 ml) was treated with NaBPh<sub>4</sub> (0.342 g, 1 mmol) at room temperature. Within 30 min a yellow precipitate was obtained. This compound is somewhat soluble in acetone so that the mixture was cooled to -20°C before filtration. The crude product was purified by redissolving in a benzene/dichloromethane mixture (1/1 v/v), concentrating to small volume and precipitating with ethyl ether. The yield of [PdCl{C(Ph)=NPh}(CNPh)<sub>2</sub>] was ca. 50%.

This compound (0.15 g) was treated with PPh<sub>3</sub> (0.270 g, ratio Pd/PPh<sub>3</sub>, 1/2) in benzene (30 ml). After 30 min the mixture was treated with charcoal and filtered, and the resulting yellow-orange solution was concentrated under reduced pressure. The bis(imino) complex, [PdCl{C(=NPh)C(Ph)=NPh}(PPh<sub>3</sub>)<sub>2</sub>], was precipitated by diluting with ethyl ether/petr. ether (1/1 v/v). Yield 75%.

*Reaction of cis-[PdCl<sub>2</sub>(CNR)<sub>2</sub>] (R = Ph, *p*-MeC<sub>6</sub>H<sub>4</sub>, *p*-MeOC<sub>6</sub>H<sub>4</sub>) with HgMe<sub>2</sub>*

The starting complex (1 mmol) was suspended in benzene (70 ml) and treated with HgMe<sub>2</sub> (0.350 g, 1.5 mmol). The mixture was stirred for 7-8 h at room temperature. During this time the colour varied from yellow to greenish-yellow and ClHgMe separated. PPh<sub>3</sub> (0.524 g, 2 mmol) was then added and the colour changed to orange-red. The products were separated from ClHgMe and purified as in the reaction with HgPh<sub>2</sub>. The yields of bis(imino) complexes, [PdCl{C(=NR)C(Me)=NR}(PPh<sub>3</sub>)<sub>2</sub>], varied in the range 70-80%. For R = *p*-

MeOC<sub>6</sub>H<sub>4</sub>, the molecular weight was 960 (calcd. 947.7).

In a further experiment *cis*-[PdCl<sub>2</sub>(CN-*p*-MeOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>] (0.443 g, 1 mmol) was allowed to react with HgMe<sub>2</sub> as above, but no PPh<sub>3</sub> was added at the end of the reaction. The solvent was removed under reduced pressure and the crude product washed several times with ethyl ether. It was separated from ClHgMe by sublimation at 70-80°C/10<sup>-2</sup> mmHg to give a greenish-yellow compound (0.350 g) soluble with decomposition in chlorinated solvents, but sparingly soluble in benzene. A small amount (≈0.100 g) was dissolved in a large volume of benzene, treated with charcoal and filtered. Addition of ethyl ether to the concentrated solution gave the analytically pure complex [PdCl{C(Me)=N-*p*-MeOC<sub>6</sub>H<sub>4</sub>} (CN-*p*-MeOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>].

#### *Reaction of trans-[PdI<sub>2</sub>(CNPh)<sub>2</sub>] with HgMe<sub>2</sub>*

HgMe<sub>2</sub> (0.350 g, 1.5 mmol) was added to a suspension of *trans*-[PdI<sub>2</sub>(CNPh)<sub>2</sub>] in methanol/acetone (2/1 v/v) at room temperature. The mixture was stirred for 3 h and then treated with PPh<sub>3</sub> (0.524 g, 2 mmol). After addition of charcoal and filtration a clear red solution was obtained from which a yellow-orange product precipitated upon concentration. This was filtered off and washed with ethyl ether. The product dissolved almost completely in this solvent, leaving a small amount of [PdI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] and IHgMe on the filter.

The ether solution was diluted with methanol (30 ml). From this mixture the complex [PdI{C(=NPh)C(Me)=NPh}(PPh<sub>3</sub>)<sub>2</sub>] crystallized when ether was slowly removed at reduced pressure. This product was washed with cold methanol and dried under vacuo (yield ≈60%). Molecular weight: 945 (found); 979.1 (calcd.).

The mother liquor was used for the reaction with HClO<sub>4</sub> as described below to give the corresponding protonated complex [PdI{C(NHPh)C(Me)=NPh}-(PPh<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> (0.200 g).

#### *Reaction with HClO<sub>4</sub>*

HClO<sub>4</sub> (2 ml of a methanolic solution 5 × 10<sup>-1</sup> M) were added to a suspension of [PdCl{C(=NR)C(R')=NR}(PPh<sub>3</sub>)<sub>2</sub>] in methanol (≈30 ml). The complex quickly dissolved and the colour changed from yellow to red. Within a few minutes the protonated complex began to precipitate. After 30 min the product was filtered off and the mother liquor was taken to dryness. The solid residue was dissolved in dichloromethane and the resulting solution dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. From this solution the remaining protonated complex was precipitated with ethyl ether (yield 80-90%).

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