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Hydrolysis of α-Diimino Groups σ-Bonded to Palladium(II)

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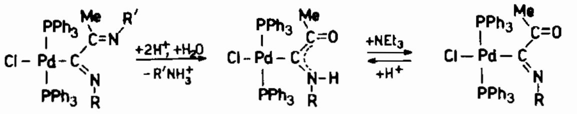
In previous papers we have described the facile protonation reaction [1] and the coordination properties [2] of α-diimino groups σ-bonded to palladium(II).

In this note we report the hydrolysis reaction of this organic moiety upon treatment with an excess of a strong mineral acid and water:



I II III

Ia, R = R' = p-C_6H_4OMe
Ib, R = R' = C_6H_{11}
Ic, R = C_6H_{11}; R' = p-C_6H_4OMe
IIa, IIIa, R = p-C_6H_4OMe
IIb, IIIb, R = C_6H_{11}

The reaction occurs at room temperature in CH_2Cl_2 solution on addition of either gaseous HCl and a few drops of water or a concentrated aqueous solution of $HClO_4$. Under these conditions the α-diimino group of complex **I** is at first quickly protonated [1] and then slowly attacked by water to yield the cationic acetyl–imino derivatives **II**.

The hydrolysis occurs on the imino group not bonded to the central metal as clearly indicated by the reaction of complex **Ic** having different substituents on the nitrogen atoms. In this case, complex **IIb** and p-methoxyphenylammonium cation are formed, the latter product originating from hydrolysis of the imino group not directly involved in the bond to palladium. It is to be noted that the same product **IIb** can also be prepared from the reaction of **Ib**, where both R and R' are cyclohexyl groups.

The σ-bonded imino group is not hydrolysed (nor is the palladium–carbon bond cleaved) during the course of the reaction, probably because of steric hindrance of the bulky triphenylphosphine ligands and reduced electrophilic character of the carbon atom (and correspondingly increased stabilisation of the Pd–C bond) by partial d→π* back-donation.

The organic moiety of **II** may be considered as a coordinated (acetyl)(amino)carbene ligand, this view being supported by the reversible deprotonation reaction to the neutral acetyl–imino derivatives **III**. The protonation of σ-bonded imino groups is a well-recognised method of preparing carbene complexes [3–7].

All products have been characterised by elemental analysis, conductivity measurements, IR and ^1H n.m.r. spectra.

The cationic derivatives **II** are better isolated as perchlorate salts. They behave as uni–univalent electrolytes in methanol solution (Λ_M = 100 ohm^{-1} cm^2 mol^{-1} for both complexes at 10^{-3} *M* concentration).

The most relevant features of IR spectra are reported in Table I.

The C–O and C–N stretching frequencies of the acetyl–imino groups in **III** are little affected by protonation. On the contrary, the ν(Pd–Cl) bands are considerably shifted from 248–255 cm^{-1} in **III** to 322–328 cm^{-1} in **II**, because of a markedly reduced *trans*-influence of the protonated acetyl–imino ligand [1].

The number of bands in the IR spectrum of complex **IIa** indicates the presence of two isomers both in the solid state and in $CHCl_3$ solution, presumably resulting from different conformations of the unsa-

TABLE I. Characteristic IR Bands (cm^{-1})^a.

Complex	ν(N–H)	ν(C=O)	ν(C=N)	ν(Pd–Cl)
IIa	3240w (3230sh) 3190m (3180m) 3130m (3120m)	1690s (1688s) 1672m (1675sh)	1550m (1550m) 1540sh (1540sh)	328m 320sh
IIb	3190ms (3175ms)	1695s (1693s)	1575m,br (1582ms)	322m
IIIa		1678s (1674s)	1555ms,br (1553ms,br)	255m
IIIb		1683s (1679s)	1581ms,br (1583ms,br)	248m

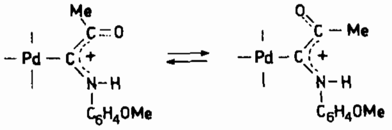
^{a}Figures in parentheses refer to $CHCl_3$ solution.

turated ligand. According to the formula of eqn. 1, a delocalised π-electron system would confer a partial double bond character also to the C–C bond between the acetyl and imino groups.

However, the ^{1}H n.m.r. spectra of complex **IIa** at room temperature and at –60 °C show no evidence for isomers, the only effect observed at low temperature being a broadening of the methyl signals of the –OMe and –CO–Me groups.

The position and pattern of the phenyl protons resonances for the p-MeOC$_6$H$_4$ N-substituent indicate a *cis* arrangement of this group and the palladium atom relative to the C–N bond by comparison with the spectra of the α-diimino derivatives **Ia** and **Ic** and their ZnCl$_2$ adducts [8].

On this basis, it seems likely that the isomers observed in the IR spectra arise from restricted rotation around the C–C bond:



The inability of the ^{1}H n.m.r. spectra to distinguish between the two species may be due either to accidental degeneracy of the methyl signals or, more likely, to a relatively fast rate of interconversion (even at –60 °C) in the n.m.r. time scale.

A similar behaviour was found also for the alkoxalyl complex, *trans*-[PtCl(COCO$_2$Me)(PPh$_3$)$_2$], for which two conformers were detected in the IR spectrum in CHCl$_3$ solution, while only one methyl signal was reported in its ^{1}H n.m.r. spectrum [9].

The spectroscopic data for complexes **IIb** and **III** indicate that only one of the possible rotational isomers is predominant in chloroform solution.

The N–H signals are not observed in the ^{1}H n.m.r. spectra of complexes **II** at room temperature because of fast exchange of this proton [1]. In the low temperature spectrum of **IIa** the N–H signal appears as a broad band at rather low field (11.7 p.p.m.), confirming the acidic character of this group.

TABLE II. ^{1}H N.m.r. Spectra (CDCl$_3$)^a.

Complex	Signals	Assignment
IIa	1.65 S	$-CO-CH_3$
	3.84 S	$O-CH_3$
	7.1–6.7 M^b	$-C_6H_4-$
	8.1–7.1 M,br	$P-C_6H_5$
	8.6–8.3 M^b	$-C_6H_4-$
	11.7 br	N–H^c
IIb	1.62 S	$-CO-CH_3$
	2.3–0.8 M,br	$-CH_2-$
	4.6 M,br	$N-CH<$
	8.1–7.1 M,br	$P-C_6H_5$
IIIa	1.34 S	$-CO-CH_3$
	3.87 S	$O-CH_3$
	6.9–6.7 M^d	$-C_6H_4-$
	8.1–7.0 M,br	$P-C_6H_5 + -C_6H_4-$
IIIb	1.33 S	$-CO-CH_3$
	2.1–0.9 M,br	$-CH_2-$
	4.4 M,br	$N-CH<$
	8.2–7.0 M,br	$P-C_6H_5$

^{a}δ Values in p.p.m. relative to TMS as internal standard; S = singlet, *M* = multiplet, br = broad, unresolved. ^{b}Symmetrical sides of AA′BB′ pattern. ^{c}Signal observed at –60 °C. ^{d}Side of AA′BB′ pattern, the other being masked by the strong PPh$_3$ resonances.

Experimental

The complexes **Ia** and **Ib** were prepared as previously described starting from *cis*-[PdCl$_2$(CNR)$_2$] with R = p-C$_6$H$_4$OMe and C$_6$H$_{11}$ respectively [1]. The complex **Ic** was prepared with a similar method starting from the mixed derivative *cis*-[PdCl$_2$(CNC$_6$H$_{11}$)(CNp-C$_6$H$_4$OMe)] [8].

Hydrolysis Reactions

The complexes **I** (2mmol) were dissolved in *ca.* 50 ml of CH$_2$Cl$_2$ and treated with an excess of gaseous HCl and a few drops of distilled water. The reaction mixture was stirred overnight, then taken to dryness at reduced pressure. The solid residue was washed several times with water in order to eliminate the soluble ammonium salts, dried *in vacuo* for 3–4 hours, redissolved in a CH$_2$Cl$_2$/MeOH mixture (1/1 in volume) and treated with NaClO$_4$·H$_2$O (0.422 g, 3 mmol). After 30 min the solvents were evaporated at reduced pressure and the product was extracted from the residue with 100 ml of CH$_2$Cl$_2$. After addition of charcoal and filtration, the resulting solution was concentrated to small volume and the product was precipitated by addition of ethyl ether. It was purified by successive reprecipitation from the same solvents.

The hydrolysis reaction was also carried out by treating a CH$_2$Cl$_2$ solution of **I** (1 mmol in 50 ml of solvent) with 1 ml of aqueous HClO$_4$ (70%) and stirring the mixture for one day. The product was recovered as described above, without any further treatment with sodium perchlorate. Yields = 60–70%.

IIa: *Anal.* C$_{46}$H$_{41}$NO$_6$P$_2$Cl$_2$Pd. Calcd.: 58.58, H 4.38, N 1.48, Cl 7.52. Found: C 58.0, H 4.4, N 1.5, Cl 7.7%.

IIb: *Anal.* C$_{45}$H$_{45}$NO$_5$P$_2$Cl$_2$Pd. Calcd.: C 58.80, H 4.93, N 1.52, Cl 7.71. Found: C 59.1, H 4.9, N 1.5, Cl 7.8%.

Deprotonation Reactions

The compounds **II** (1 mmol) were dissolved in *ca.* 50 ml of CH$_2$Cl$_2$ and treated with 4–5 ml of NEt$_3$.

After 10 min the reaction mixture was taken to dryness at reduced pressure. The solid residue was washed several times with water and dried *in vacuo* for 3–4 hours. The crude products were purified by successive reprecipitation from CH_2Cl_2 by addition of ethyl ether (complex **IIIa**) or from benzene by addition of ethyl ether/hexane (complex **IIIb**). Yields = 50–60%.

IIIa: *Anal.* $C_{46}H_{40}NO_2P_2ClPd$. Calcd.: C 65.57, H 4.78, N 1.66, Cl 4.21. Found: C 65.1, H 4.9, N 1.6, Cl 4.3%.

IIIb: *Anal.* $C_{45}H_{44}NOP_2ClPd$. Calcd.: C 66.02, H 5.42, N 1.71, Cl 4.33. Found: C 65.7, H 5.4, N 1.7, Cl 4.5%.

The conductivity and spectroscopic measurements were made as previously described [1].

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