*Journal of Organometallic Chemistry*, 269 (1984) 295–304
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# PREPARATION AND REACTIONS OF 1-METHYLPYRID-6-ONE-2-YL COMPOUNDS OF PALLADIUM(II) AND PLATINUM(II)

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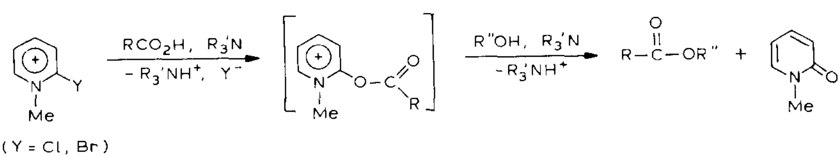
(Received January 31st, 1984)

## Summary

The compounds *trans*-[MCl{(1-Me)$C_5H_3$(6-O)N-$C^2$}$(L)_2$] (M = Pd, Pt; L = $PPh_3$, $PMe_2Ph$), can be prepared from the reaction of the corresponding 1-methyl-6-chloro-2-pyridylium cationic complexes, *trans*-[MCl{(1-Me)$C_5H_3$(6-Cl)N-$C^2$}$(L)_2$]$ClO_4$, with a mixture of acetic acid, ethanol, and triethylamine in the molar ratio M/$MeCO_2H$/EtOH/$NEt_3$ of 1/3/3/4. The rate is slow compared to that of the 1-methyl-2-chloropyridinium cation under similar conditions, and is markedly affected by the steric and electronic effects of the *trans*-MCl$(L)_2$ unit. The novel 1-methylpyrid-6-one-2-yl derivatives have been characterized by conventional spectroscopic techniques and by reactions involving either protonation and methylation of the carbonyl group or migratory insertion of isocyanides into the Pd–$C^2$ bond.

## Introduction

The 1-methyl-2-halopyridinium salts are effective substrates for the activation of carboxylic acids, and are conveniently employed in the synthesis of organic compounds, such as carboxylic esters, amides and thiol esters, under mild conditions (i.e. in the absence of strong acids or bases) [1]. The activation mechanism is thought to involve the rapid formation of a 1-methyl-2-acyloxypyridinium intermediate by nucleophilic attack of a carboxylate ion, followed by reaction with a protic nucleophile in the presence of tertiary amine as proton acceptor, as shown in eq. 1 for the preparation of carboxylic esters:

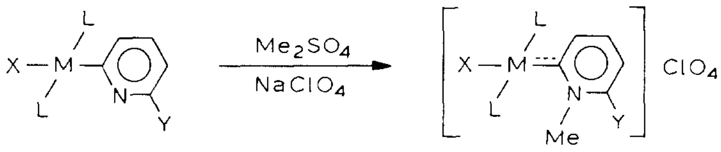



(1)

In the course of the reaction the pyridinium cation is converted into 1-methyl-2-pyridone.

In a previous paper we reported the facile *N*-methylation of 2-pyridylpalladium(II) and -platinum(II) complexes (Y = H) [2]:



(2)

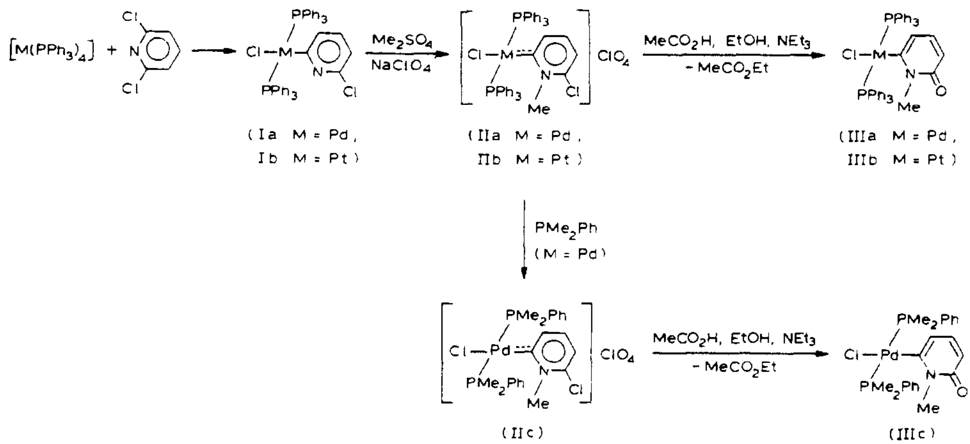
( X = Cl, Br, M = Pd, Pt, L = tertiary phosphine )

Since reaction 2 could be extended to 6-chloro-2-pyridyl derivatives (Y = Cl) in good yields, we have studied the activity of the resulting 2-metallated-6-chloropyridinium cations in reactions of type 1 in order: (i) to investigate the influence of the steric and electronic properties of the *trans*-$MX(L)_2$ unit on the reaction course, and (ii) to prepare complexes containing the new 1-methylpyrid-6-one-2-yl group σ-bonded to the central metal.

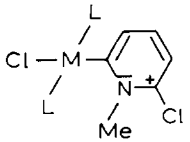
## Results and discussion

The reactions studied are shown in Scheme 1.

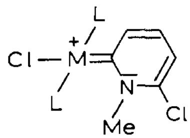
SCHEME 1



Oxidative addition of 2,6-dichloropyridine to $[M(PPh_3)_4]$ yields the 6-chloro-2-pyridyl complexes Ia and Ib, which can be conveniently methylated by an excess of $Me_2SO_4$ to give the 1-methyl-6-chloro-2-pyridylium cationic compounds IIa and IIb. The $PMe_2Ph$ derivative IIc is obtained by ligand substitution from the $PPh_3$ analogue IIa. All the complexes of type II react with a mixture of acetic acid, ethanol and triethylamine (molar ratio II/$MeCO_2H$/EtOH/$NEt_3$ = 1/3/3/4) to give the corresponding 1-methylpyrid-6-one-2-yl products III, with different rates (and yields) depending on the nature of the central metal M and the phosphine ligand (see Experimental). This reaction closely parallels that of 1-methyl-2-halopyridinium cations shown in eq. 1, even though the latter is considerably faster under similar conditions. The lower reactivity of the substrates II results essentially from unfavourable steric and electronic properties of the σ-bonded *trans*-$MCl(L)_2$ group. The equivalence of the two phosphorous nuclei in II, as shown by the $^{31}P$ NMR data in Table 2, and the occurrence of two separate P-Me triplets (1/1 integration ratio) in the $^1H$ NMR spectrum of IIc (Table 2) indicate a molecular structure in which the planar (1-Me)$C_5H_3$(6-Cl)N-$C^2$ ligand is orientated perpendicularly to the coordination plane, with hindered rotation about the metal–carbon bond. In this geometry, the formation of a labile 1-methyl-6-acetato-2-pyridylium intermediate by nucleophilic attack of the acetate ion at the $C^6$ carbon atom of the pyridine ring is markedly hampered by the *trans* phosphine ligands. On the other hand, the electrophilic character of the $C^6$ carbon atom (illustrated by the limiting formula **A**) is also reduced by *d* electron back-donation from the central metal M (represented by the carbene-like limiting structure **B**):



(**A**)



(**B**)

Significant contribution by limiting structures of type **B** to the electronic configuration of 1-protonated and 1-methylated 2-pyridyl-palladium(II) and -platinum(II) derivatives has already been recognized [2].

These steric and electronic factors also account for the observed reactivity sequence in complexes II: IIc > IIa > IIb. The reaction rate decreases (i) when, for M = Pd, the $PMe_2Ph$ phosphine (cone angle 125° [3a]) is replaced by the bulkier $PPh_3$ ligand (cone angle 145° [3b]), as a consequence of the increased steric crowding around the reaction site, and (ii) when, for L = $PPh_3$, the central metal is changed from Pd to Pt, the latter effect probably being due to an increased contribution of the canonical form **B**.

The products of type III are non-conducting and monomeric in 1,2-dichloroethane solution. The presence of the new 1-methylpyrid-6-one-2-yl ligand is fully confirmed by elemental analysis, IR spectra (Table 1) and the $^1H$ NMR spectra (Table 2). The IR spectra in $CH_2Cl_2$ are characterized by a very strong ν(C=O) band at 1635 $cm^{-1}$, with a lower frequency shift of 25 $cm^{-1}$ relative to the same vibration in 1-methyl-2-pyridone [4]. In the $^1H$ NMR spectra, the assignment of the pyridone ring proton resonances is based on the relative coupling constants with the $^{195}Pt$ isotope of the platinum derivative IIIb. These protons give rise to a three-spin system, which in theory should be analyzed as an ABC spectrum. However, because of the chemical shift separation and the small $^4J(H^3–H^5)$ value, a simple first-order analysis is satisfactory for IIIa and IIIb. The observed coupling constants $^3J(H^3–H^4)$

*(Continued on p. 300)*

TABLE 1

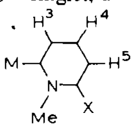
ANALYTICAL, PHYSICAL DATA AND CHARACTERISTIC IR ABSORPTIONS

| Compound | Melting point [a] (°C) | Analyses (%) [b] C | H | N | Cl | Molar conductivity ($ohm^{-1}$ $cm^2$ $mol^{-1}$) [c] | Molecular weight [b] | IR ($cm^{-1}$) ν(C=O) | Heterocycle ring stretching modes [d] | ν(M–Cl) | ν(Cl–O) [e] | δ(Cl–O) [e] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ia | 214 | 63.5 | 4.3 | 1.9 | 9.0 | | | | 1552ms, 1545ms | 293m | | |
| | | (63.22) | (4.27) | (1.80) | (9.10) | | | | 1524s | | | |
| Ib | 217 | 56.8 | 3.9 | 1.7 | 8.2 | | 826 | | 1554ms, 1550ms | 285m | | |
| | | (56.75) | (3.83) | (1.61) | (8 17) | | (867.6) | | 1524s | | | |
| IIa | 241 | 55.9 | 4.0 | 1.6 | 11 8 | 97.9 | | | 1582s, 1533s | 320m | 1095vs | 621s |
| | | (56.46) | (4.06) | (1.57) | (11.90) | | | | | | | |
| IIb | 229 | 50.9 | 3.7 | 1.4 | 11 1 | 96.6 | | | 1587s, 1534s | 314m | 1095vs | 620s |
| | | (51.36) | (3.69) | (1.43) | (10.83) | | | | | | | |
| IIc | 209 | 41.5 | 4 5 | 2.2 | 16.4 | 98.9 | | | 1588s, 1538s | 307m | 1090vs | 624s |
| | | (40.96) | (4.37) | (2.17) | (16.48) | | | | | | | |
| IIIa | 221 | 64.7 | 4.8 | 1.9 | 4.7 | | 820 | 1630sh, 1620vs | 1645m, 1552m | 307m | | |
| | | (65.13) | (4 68) | (1.81) | (4.58) | | (774.5) | [1635vs] [f] | 1486s | | | |
| IIIb | 280 | 58 0 | 4 3 | 1.7 | 4.2 | | 893 | 1625sh, 1619vs | 1640sh, 1555m | 295m | | |
| | | (58.44) | (4.20) | (1.62) | (4.11) | | (863.2) | [1634vs] [f] | 1490s | | | |
| IIIc | 171 | 50.3 | 5.3 | 2.6 | 6 8 | | 535 | 1633vs | 1645sh, 1559m | 301m | | |
| | | (50.21) | (5.36) | (2 66) | (6 74) | | (526.2) | [1635vs] [f] | 1482s | | | |
| IVa | 232 | 57.8 | 4.4 | 1 5 | 8 1 | 104.0 | | | 1600s, 1553m | 317m | 1090vs | 620s |
| | | (58.09) | (4.42) | (1.58) | (7.97) | | | | | | | |
| IVb | 265 | 52.5 | 4.0 | 1.5 | 7.2 | 86 2 | | | 1610s, 1559s | 309m | 1090vs | 623s |
| | | (52.82) | (4.02) | (1.43) | (7.24) | | | | | | | |
| Va | 235 | 57.2 | 4.3 | 1 7 | 8.0 | 119.1 | | | 1600s, 1570ms | 315m | 1095vs | 622s |
| | | (57 65) | (4.26) | (1.60) | (8.10) | | | | | | | |

[a] Uncorrected values. [b] Calculated values in parentheses. [c] For $10^{-3}$ $M$ MeOH solution at 20°C. [d] In the range 1650–1480 $cm^{-1}$ (tentative assignment). [e] Vibrations of the perchlorate anion [f] In $CH_2Cl_2$ solution.

TABLE 2. $^{1}H$ AND $^{31}P$ NMR DATA [a]

| Compound | Heterocycle ring protons | | | $N{-}CH_3$ | $O{-}CH_3$ | Phosphine protons | | $^{31}P$ Resonances |
|---|---|---|---|---|---|---|---|---|
| | $H^3$ | $H^4$ | $H^5$ | | | $P{-}C_6H_5$ | $P{-}CH_3$ | |
| Ia | 6.7–6.5 m | 6.3–6.0 m [b] | | | | 7.8–7.1 m | | 22.2 s |
| Ib | 6.7–6.4 m [c] | 6.3–6.0 m [b] | | | | 7.9–7.2 m | | 23.1 t |
| | $^{3}J(Pt{-}H) = 35.0$ | | | | | | | $^{1}J(Pt{-}P) = 3151$ |
| IIa • | [d] | [d] | 7.2–7.0 m | 3.92 s | | 7.7–7.3 m | | 21.6 s |
| IIb | [d] | [d] | 7.1–6.9 m | 3.91 t | | 7.8–7.2 m | | 18.3 t |
| | | | | $^{4}J(Pt{-}H) = 6.6$ | | | | $^{1}J(Pt{-}P) = 2637$ |
| IIc | 7.9–7.7 m | 7.7–7.5 m | [d] | 3.91 s | | 7.5–7.0 m | 1.85 t | −5.77 s |
| | | | | | | | $J(P{-}H) = 8.0$ [e] | |
| | | | | | | | 1.78 t | |
| | | | | | | | $J(P{-}H) = 7.7$ [e] | |
| IIIa | 5.53 d | 6.43 dd | 5.85 d | 3 08 s | | 7.8–7.2 m | | 21.4 s |
| | $^{3}J(H^3{-}H^4) = 9.0$ | | $^{3}J(H^4{-}H^5) = 7.0$ | | | | | |
| IIIb | 5.48 d [c] | 6.36 dd [c] | 5.95 d | 3.14 t | | 7.8–7.2 m | | 19.7 t |
| | $^{3}J(H^3{-}H^4) = 9.0$ | $^{4}J(Pt{-}H^4) = 12.0$ | $^{3}J(H^4{-}H^5) = 7.2$ | $^{4}J(Pt{-}H) = 5.3$ | | | | $^{1}J(Pt{-}P) = 2917$ |
| | $^{3}J(Pt{-}H^3) = 26.0$ | | | | | | | |
| IIIc | 5.87 d [f] | 6.85 t [f] | 5.87 d [f] | 3.55 s | | 7.7–7.2 m | 1.73 t | −8.03 s |
| | | | | | | | $J(P{-}H) = 7.0$ [e] | |
| | | | | | | | 1.64 t | |
| | | | | | | | $J(P{-}H) = 7.2$ [e] | |
| IVa | | 7.2–6.5 m [b] | | 3.52 s | 3.83 s | 7.7–7.3 m | | 21.8 s |
| IVb | | 7.1–6.3 m [b] | | 3.55 t | 3.88 s | 7.7–7.2 m | | 18.9 t |
| | | | | $^{4}J(Pt{-}H) = 6.4$ | | | | $^{1}J(Pt{-}P) = 2687$ |
| Va | | 7.1–6.5 m [b] | | 3.47 s | 9.81 s,br [g] | 7.8–7.2 m | | 21.6 s |

[a] $^{1}H$ chemical shifts ($\delta$) in ppm from TMS at 30°C in $CD_2Cl_2$; $^{31}P$ chemical shifts ($\delta$) in ppm from external 85% $H_3PO_4$ (downfield shifts taken as positive); coupling constants in Hz; s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet, br = broad; satisfactory integration values have been obtained; heterocycle protons labelling: 

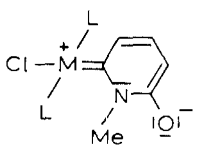
[b] Overlapping multiplets. [c] Signals flanked by $^{195}Pt$ satellites. [d] Masked by the intense phenyl proton resonances. [e] $J(P{-}H) = |^{2}J(P{-}H) + {}^{4}J(P'{-}H)|$. [f] ABX spectrum (line separation 8.0 Hz). [g] $\delta(OH)$ signal observed in the presence of added aqueous $HClO_4$.

and $^3J(H^4-H^5)$ are in a good agreement with those of the corresponding protons in 1-methyl-2-pyridone [5,6]. In complex IIIc a deceptively simple ABX spectrum is observed owing to the occurrence of $\delta(H^3) = \delta(H^5)$.

The presence of the *trans*-$MCl(L)_2$ group as $C^2$-substituent brings about a marked upfield shift of the pyridone ring and 1-methyl proton resonances. This shielding effect is the result of the phenyl ring currents of the mutually *trans* phosphine ligands [2] (the 1-methylpyrid-6-one-2-yl group lies in a plane perpendicular to the metal-coordination plane, with hindered rotation around the metal–carbon bond, as can be inferred from the $^1H$ and $^{31}P$ NMR data of IIIc) and of increased electron density on the pyridone ring due to *d* electron back-donation from the metal M, as was observed in other complexes containing carbon-bonded heterocyclic ligands [7,8]. The influence of the phenyl ring currents of L is particularly evident in the 1-methyl proton signals (3.08 ppm, IIIa; 3.55, IIIc; 3.59, 1-methyl-2-pyridone [5]), whereas that of increased electron density seems to predominate in the shielding of the $H^5$ ring proton (5.85 ppm, IIIa; 5.87, IIIc; 5.95, IIIb; 6.57, 1-methyl-2-pyridone [5]).

The $^1J(Pt-P)$ coupling constants decrease progressively on going from the 6-chloro-2-pyridyl complex Ib (3151 Hz) to the 1-methylpyrid-6-one-2-yl complex IIIb (2917 Hz) and to the 1-methyl-6-chloro-2-pyridylium derivative IIb (2637 Hz). As proposed for *trans*-$[PtBr(2\text{-py})(L)_2]$ (L = tertiary phosphine; 2-py = 2-pyridyl group) and the corresponding *N*-protonated and -methylated derivatives [2], this effect may be essentially related to a progressively decreasing $\sigma$-donor/$\pi$-acceptor ratio of the $C(sp^2)$-bonded planar ligands, containing delocalized $\pi$ electron systems. In line with this suggestion, the *trans* influence (based on the Pt–Cl stretching frequencies) of the $\sigma$-bonded organic moieties decreases in the same order: $\nu(Pt-Cl)$ 285 $cm^{-1}$, Ib; 295, IIIb; 314, IIb.

In terms of valence bond theory, the above discussed IR and NMR spectral features of III can be interpreted on the basis of a significant contribution of the canonical form **C** to the electronic configuration of these compounds:

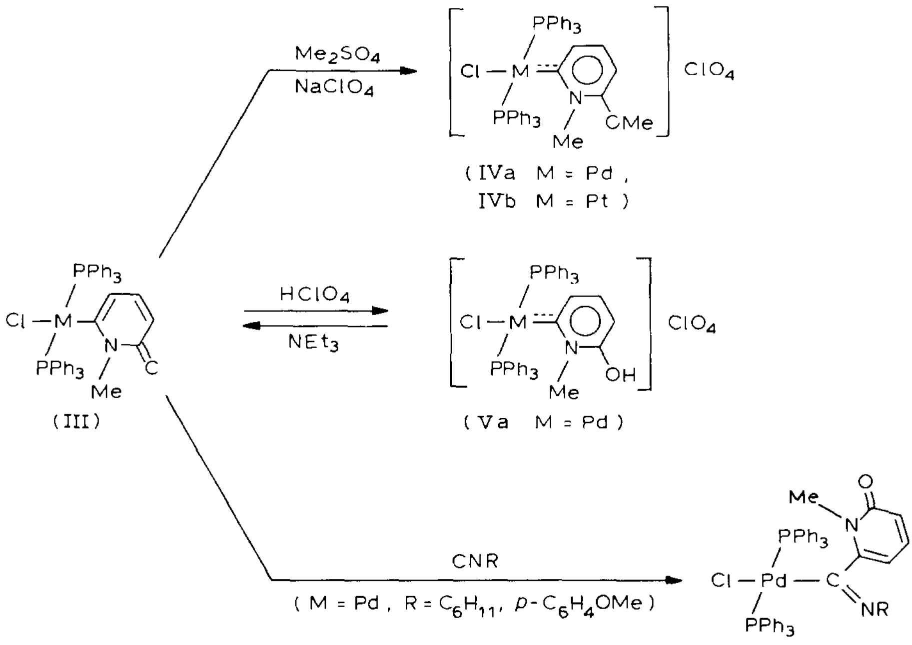


(C)

From a chemical point of view, this is reflected by an increased nucleophilic character of the carbonyl oxygen, which is readily protonated and methylated, as shown in Scheme 2.

The reaction of IIIa with perchloric acid yields the 1-methyl-6-hydroxy-2-pyridylium complex Va, characterized by a $\delta(OH)$ signal at 9.81 ppm (observed only when aqueous $HClO_4$ is added to the $CD_2Cl_2$ solution because of fast exchange of the OH proton with solvent) and by the appearance of a broad $\nu(OH)$ band at ca. 3000 $cm^{-1}$. The acidic nature of the OH proton is also confirmed by the reaction of Va with $NEt_3$, which regenerates the starting compound IIIa. Reaction of IIIa and IIIb with $Me_2SO_4$ gives the 1-methyl-6-methoxy-2-pyridylium complexes IVa and

SCHEME 2




IVb, characterized by $\delta$(OMe) signals at 3.83 and 3.88 ppm, respectively. The products IV and Va, like complexes II, are uni-univalent electrolytes in methanolic solution, the comparatively higher molar conductivity of Va resulting from acidic dissociation of the OH group of this compound. The $\nu$(Pd–Cl) and $\delta(^{31}P)$ values of IVa and Va, and the $\nu$(Pt–Cl), $\delta(^{31}P)$ and $^{1}J$(Pt–P) values of IVb compare well with the corresponding spectral data for IIa and IIb, respectively, in accord with the presence of closely related 1-methyl-2-pyridylium ligands in these cationic complexes.

Complex IIIa reacts with isocyanides (but not with carbon monoxide) with migratory insertion into the Pd–C $\sigma$-bond. Because of some decomposition during the reaction, the products VI cannot be obtained as analytically pure samples. The occurrence of insertion, however, and the formulation of the products are confirmed by IR and $^{1}H$ and $^{31}P$ NMR spectral data (see Experimental).

## Experimental

The complexes $[M(PPh_3)_4]$ and the isocyanides $CNC_6H_{11}$ and $p$-$CNC_6H_4OMe$ were prepared by published methods [9,10]. All other chemicals were reagent grade, and used without further purification. Infrared spectra were recorded with Perkin–Elmer 597 and 580-B instruments, using Nujol mulls and CsI plates in the range 4000–250 cm$^{-1}$. The $^{1}H$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded with a Varian FT 80A spectrometer operating at 79.542 and 32.203 MHz, respectively, at 30°C. The molecular weights were determined in 1,2-dichloroethane at 37°C with a Knauer osmometer. Conductivity measurements were carried out with a Philips PR 9500 bridge at 20°C.

All reactions were carried out at room temperature, unless otherwise stated. When required, an inert atmosphere ($N_2$) was used. The solvents were evaporated to small volume or the dryness under reduced pressure.

*Preparation of trans-[MCl{$C_5H_3$(6-Cl)N-$C^2$}($PPh_3$)$_2$] (I)*

(a) The complex [$Pd(PPh_3)_4$] (11.55 g, 10 mmol), suspended in toluene (ca. 150 ml), was treated with 2,6-dichloropyridine (1.63 g, 11 mmol) under nitrogen. The mixture was stirred at 90°C for 4 h and set aside overnight at room temperature. During this time, some off-white crystals of Ia separated. Concentration to small volume and dilution with diethyl ether gave the crude product Ia, which was dissolved in $CH_2Cl_2$ (ca. 100 ml) and treated with charcoal. After filtration, MeOH (ca. 20 ml) was added to the clear solution, and the more volatile $CH_2Cl_2$ was evaporated off until some precipitate appeared. The precipitation was completed by dropwise addition of $Et_2O$ (Yield, based on the theoretical amount: 7.64 g, 98%).

(b) A suspension of [$Pt(PPh_3)_4$] (2.49 g, 2 mmol) in toluene (80 ml) containing 2,6-dichloropyridine (0.39 g, 2.6 mmol) was kept at 110°C for 7 h under $N_2$, with stirring. After standing overnight at room temperature, the mixture was worked up as described above for the preparation of Ia, to give the white product Ib (1.49 g, 86%).

*Preparation of trans-[MCl{(1-Me)$C_5H_3$(6-Cl)N-$C^2$}(L)$_2$]$ClO_4$ (II)*

(a) The complexes IIa and IIb were prepared by the following procedure. A solution of I (3 mmol) and $Me_2SO_4$ (3.78 g, 30 mmol) in 80 ml of $CH_2Cl_2$ was refluxed for 4 h and kept overnight at room temperature. Concentration to small volume and dilution with $Et_2O$ gave a white precipitate, which was redissolved in $CH_2Cl_2$ (60 ml). The solution was treated with a solution of $NaClO_4 \cdot H_2O$ (0.84 g, 6 mmol) in 20 ml of MeOH, and stirred for 10 min. The mixture was evaporated to dryness and the solid residue was extracted with $CH_2Cl_2$ (60 ml) and charcoal. After filtration of the extract and concentration, the product was precipitated by dropwise addition of $Et_2O$ (Yield: 95% IIa; 84% IIb).

(b) The complex IIc was prepared as follows: a solution of IIa (1.79 g, 2 mmol) in 100 ml of $CH_2Cl_2$ was treated with $PMe_2Ph$ (0.55 g, 4 mmol) under $N_2$. After stirring for 30 min, the mixture was treated with charcoal and filtered off, and the clear filtrate was concentrated to small volume. Addition of diethyl ether gave the product IIc as a white microcrystalline precipitate. It was purified by reprecipitation from the same solvents (1.15 g, 87%).

*Preparation of trans-[MCl{(1-Me)$C_5H_3$(6-O)N-$C^2$}(L)$_2$] (III)*

The preparation of these compounds was carried out by the following general method. A solution of II (1 mmol) in $CH_2Cl_2$ (50 ml) was treated under $N_2$ with acetic acid, ethanol and triethylamine in a molar ratio II/$MeCO_2H$/EtOH/$NEt_3$ of 1/3/3/4. The mixture was stirred for several hours at either the reflux temperature (ca. 50 °C) or room temperature. The progress of the reaction was monitored isolating both the final product III and the unreacted initial material II by the following procedure. The solvent was evaporated and the oily residue washed with 0.1 *M* aqueous KOH (50 ml). The resulting solid was filtered off, washed two or three times with water, and dried in vacuo. Extraction with warm benzene (ca. 100 ml at 50–60°C) and then with $CH_2Cl_2$ (50 ml) gave a $C_6H_6$ solution of III and a

$CH_2Cl_2$ solution of II, from which the unreacted compound II was recovered as described above for its preparation, whereas the product III was precipitated by adding ethyl ether/n-hexane (1/1 v/v, for IIIa and IIIb) or n-hexane (for IIIc) to the corresponding concentrated solution. Some results are summarized in Table 3. The formation of increasing amounts of ethyl acetate in the course of the reaction was confirmed by GLC analysis. For preparative purposes the reaction was usually carried out at room temperature for 3 d.

*Preparation of trans-[MCl{(1-Me)$C_5H_3$(6-OMe)N-$C^2$}$(PPh_3)_2$]$ClO_4$ (IV)*

The preparation of complexes IVa and IVb by methylation of IIIa and IIIb, respectively, with $Me_2SO_4$ was carried out as for the preparation of complexes IIa and IIb (Yield: 53% IVa; 61% IVb).

*Preparation of trans-[PdCl{(1-Me)$C_5H_3$(6-OH)N-$C^2$}$(PPh_3)_2$]$ClO_4$ (Va) and its deprotonation to IIIa*

(a) Methanolic $HClO_4$ (5 ml of a 0.22 *M* solution made up by mixing 6 ml of 60–62% aqueous perchloric acid with 250 ml with MeOH) was added to a solution of IIIa (0.39 g, 0.5 mmol) in 40 ml of $CH_2Cl_2$. After 10 min stirring the solution was concentrated to small volume and the product Va was precipitated by adding $Et_2O$. It was purified by reprecipitation from a $CH_2Cl_2/Et_2O$ mixture (0.42 g, 96%).

(b) The complex Va (0.44 g, 0.5 mmol) dissolved in 40 ml of $CH_2Cl_2$ was treated with an excess of $NEt_3$ (0.50 g). After 10 min, the solution was evaporated to dryness and the solid was washed with water, dried in vacuo, and extracted with benzene in the presence of charcoal. After filtration, the clear $C_6H_6$ solution was worked up to give the complex IIIa (0.27 g), as described above for its preparation.

*Reaction of IIIa with CNR (R = p-$C_6H_4$OMe, $C_6H_{11}$)*

A solution of the isocyanide (0.5 mmol) in 5 ml of 1,2-dichloroethane was added dropwise to a stirred solution of IIIa (0.39 g, 0.5 mmol) in 50 ml of 1,2-dichloro-

TABLE 3

PREPARATION OF THE COMPOUNDS IIIa–IIIc

| Starting compound | Reaction temperature | Reaction time | Final product (g, %) | Unreacted material (g) |
|---|---|---|---|---|
| IIa (0.89 g) | RT | 3 d | IIIa (0.32, 41.3) | IIa (0.30) |
| IIa (0.89 g) | ~ 50°C | 6 h | IIIa (0.16, 20.6) | IIa (0.45) |
| IIa (0.89 g) | ~ 50°C | 24 h | IIIa (0.27, 35) | IIa (0.34) |
| IIb (0.98 g) | RT | 3 d | IIIb (0.23, 26.6) | IIb (0.51) |
| IIb (0.98 g) | ~ 50°C | 6 h | IIIb (0.08, 9.3) | IIb (0.75) |
| IIb (0.98 g) | ~ 50°C | 24 h | IIIb (0.18, 20.8) | IIb (0.60) |
| IIc (0.65 g) | RT | 3 d | IIIc (0.45, 85.5) | IIc (trace) |

ethane, under $N_2$. The reaction was monitored by IR spectroscopy, which showed an initial fast coordination of CNR ($\nu$(C$\equiv$N) at 2180 cm$^{-1}$ for R = $p$-$C_6H_4$OMe and at 2200 cm$^{-1}$ for R = $C_6H_{11}$) followed by a slower migration insertion, as indicated by the disappearance of the $\nu$(C$\equiv$N) band and a concomitant increase in intensity of $\nu$(C=N) in the range 1590–1570 cm$^{-1}$. The reaction with $p$-methoxyphenyl isocyanide was complete in ca. 30 min, whereas that with cyclohexyl isocyanide required a much longer time (ca. 24 h). After concentration to small volume, a diethyl ether/n-hexane (1/1 v/v) mixture was added dropwise to precipitate the derivative VI, contaminated by some decomposition products, which were not removed by several reprecipitations and/or recrystallizations from various solvent mixtures. Both complexes VI exhibit the same values for $\nu$(Pd–Cl) (308 cm$^{-1}$), $\delta$(N–Me) (singlet at 3.09 ppm) and $\delta$($^{31}$P) (singlet at 21.4 ppm). The product VI (R = $p$-$C_6H_4$OMe) is further characterized by $\nu$(C=O) and $\nu$(C=N) bands at 1635 and 1572 cm$^{-1}$, respectively, and by a $\delta$(O–Me) singlet at 3.78 ppm, whereas the product VI (R = $C_6H_{11}$) shows $\nu$(C=O) and $\nu$(C=N) bands at 1643 and 1587 cm$^{-1}$, and $\delta$(C–H) and $\delta$($CH_2$) multiplets in the ranges 4.7–4.3 and 1.8–0.8 ppm, respectively.

## Acknowledgments

Financial support from Ministero della Pubblica Istruzione (Research Fund 60%, 1982) is gratefully acknowledged.

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