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# Nucleophilic attack by 2-pyridylpalladium(II) and platinum(II) complexes on the organic chlorides $ClCH_2R$ ($R = COMe, CN, Ph, Cl$)

Bruno Crociani *, Francesca Di Bianca, Alberta Fontana
*Dipartimento di Chimica Inorganica, University of Palermo, Palermo (Italy)*

Roberta Bertani
*Centro Chimica Tecnologia Composti Metallorganici Elementi Transizione, C.N.R., University of Padova, Padova (Italy)*

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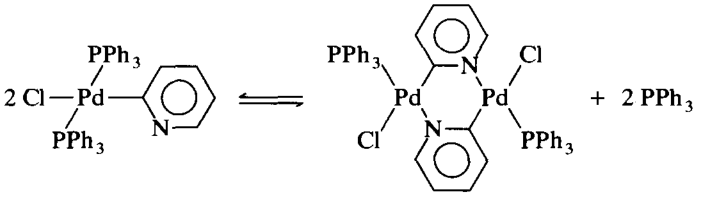
## Abstract

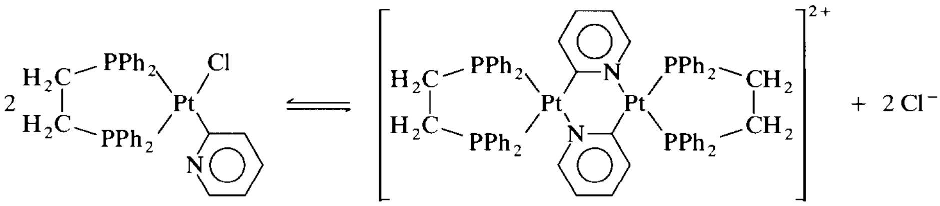
The 2-pyridyl complexes *trans*-$[MCl(C_5H_4N\text{-}C^2)(PPh_3)_2]$ (M = Pd, **1a**; M = Pt, **1b**), $[MCl(C_5H_4N\text{-}C^2)(dppe)]$ (M = Pd, **2a**; M = Pt, **2b**) and $[M(dmtc)(C_5H_4N\text{-}C^2)(PPh_3)]$ (M = Pd, **3a**; M = Pt, **3b**) react with the chlorides $ClCH_2R$ (R = COMe, CN, Ph) to give cationic products containing the 2-pyridylium ligands $(1\text{-}CH_2R)C_5H_4N\text{-}C^2$. The rate of nucleophilic displacement of the chloride ion from $ClCH_2R$ depends on the central metal (Pt > Pd), on the coordination geometry (**1** < **2** ~ **3**) and on the substituent R (COMe > CN > Ph for the reactions with **3b**). Like **1b** and **2b**, complex **3b** also reacts with dichloromethane to give $[Pt(dmtc)\{(1\text{-}CH_2Cl)C_5H_4N\text{-}C^2\}(PPh_3)]^+$. The reaction of the binuclear compound $[\{PdCl(\mu\text{-}C_5H_4N\text{-}C^2,N)(PPh_3)\}_2]$ with chloroacetone in the presence of chloride ion yields the zwitterionic derivative *cis*-$[PdCl_2\{(1\text{-}CH_2COMe)C_5H_4N\text{-}C^2\}(PPh_3)]$. The cationic products have been isolated and characterized as perchlorate salts.

## Introduction

The 2-pyridyl ligand in the complexes *trans*-$[MX(C_5H_4N\text{-}C^2)(L)_2]$, $[MX(C_5H_4N\text{-}C^2)(dppe)]$ (M = Pd, Pt; X = Cl, Br; L = tertiary phosphines; dppe = 1,2-bis(diphenylphosphino)ethane), and $[C_5H_5Rh(Me)(CO)(C_5H_4N\text{-}C^2)]$ can be readily *N*-methylated by use of $Me_2SO_4$ or MeI [1,2]. The enhanced nucleophilicity of the 2-pyridyl nitrogen is also demonstrated by the establishment of equilibria (reactions 1 and 2), which involve displacement of $PPh_3$ and $Cl^-$ ligands, respectively, and formation of binuclear species with C,N-bridging 2-pyridyl groups [3,4]:

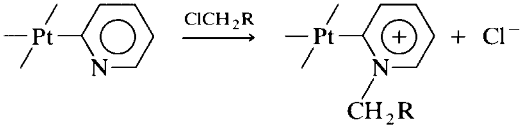


(1)



(2)

Furthermore, it has recently been observed that the complexes *trans*-[PtCl($C_5H_4N$-$C^2$)($PPh_3$)$_2$] and [PtCl($C_5H_4N$-$C^2$)(dppe)] react slowly in chlorinated solvents, such as dichloromethane and 1,2-dichloroethane, with nucleophilic substitution of $Cl^-$ ions, as shown in eq. 3 [4]:



(3)

(R = Cl, $CH_2Cl$)

These findings prompted us to carry out a comparative study of the nucleophilic properties of structurally related 2-pyridylpalladium(II) and platinum(II) complexes of the type *trans*-[MCl($C_5H_4N$-$C^2$)($PPh_3$)$_2$] (**1**), [MCl($C_5H_4N$-$C^2$)(dppe)] (**2**) and [M(dmtc)($C_5H_4N$-$C^2$)($PPh_3$)] (**3**) (M = Pd, Pt; dmtc = dimethyldithiocarbamate) in reactions with a series of chloro-derivatives $ClCH_2R$ (R = COMe, CN, Ph, Cl).

## Results and discussion

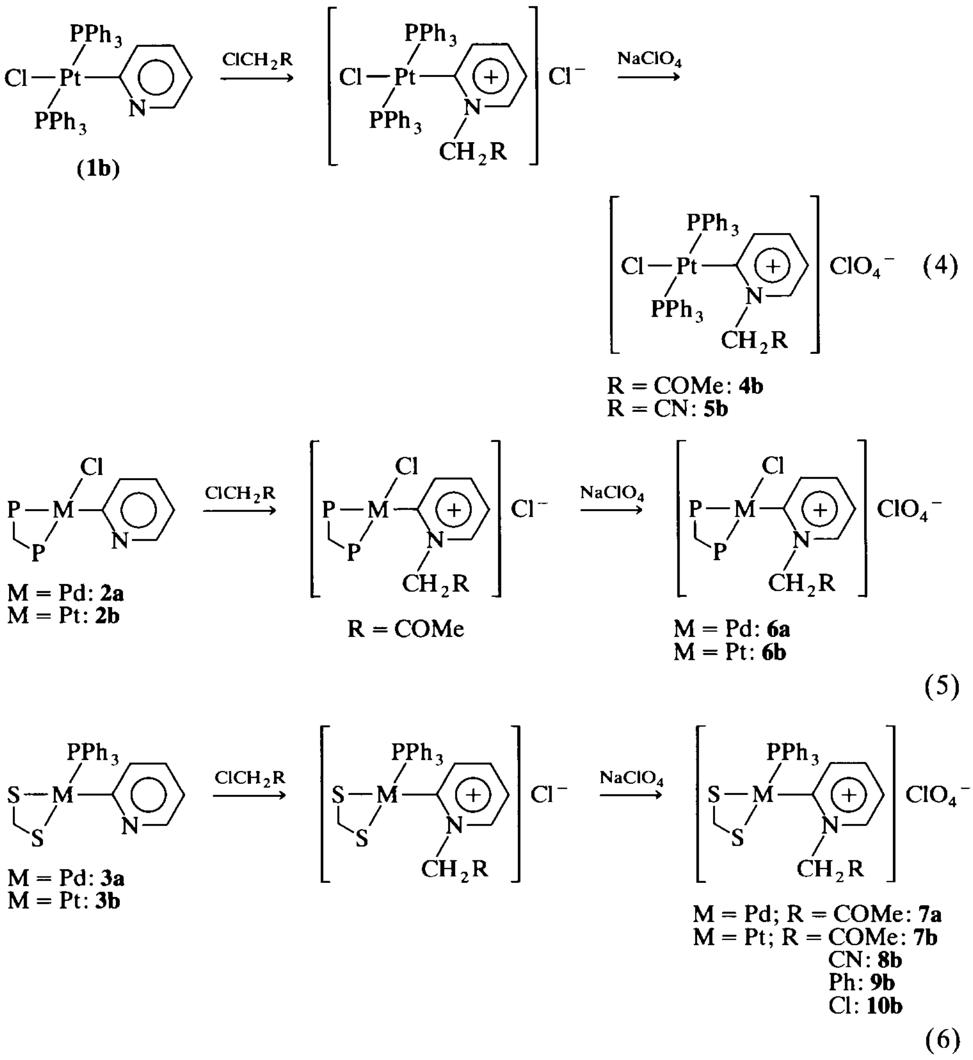
### *Nucleophilic substitution of chloride ions from $ClCH_2R$*

Complexes **1**–**3**, containing a terminal 2-pyridyl ligand, react with $ClCH_2R$ to yield cationic 1-$CH_2R$-2-pyridylium products through displacement of chloride ions by the 2-pyridyl nitrogen (Scheme 1).

The reactions were generally carried out in acetone at ambient temperature with a large excess of $ClCH_2R$. The final cationic products were isolated and characterized as perchlorate salts.

Reaction 4 occurs smoothly for the platinum(II) complex **1b**, whereas the palladium(II) analog **1a** gives predominantly the binuclear compound [{PdCl($\mu$-$C_5H_4N$-$C^2$,*N*)($PPh_3$)}$_2$] (see eq. 1 and Experimental). The first step in reactions 4–6 can be observed by monitoring the increase in the electric conductivity of the acetone solutions. Under pseudo-first-order conditions, the specific conductivity values $\chi_t$ at various times fit well the mono-exponential law $\chi_t = \chi_\infty + (\chi_0 - \chi_\infty)\exp(-tk_{obs})$, from which the pseudo-first-order rate constants $k_{obs}$ can be evaluated (Table 1).

For comparison, the $k_{obs}$ value for the corresponding reaction of 4-dimethylaminopyridine (4-DMAP) with chloroacetone is also included in Table 1. These kinetic data were all obtained under the same experimental conditions and can be used to gain useful information about the relative nucleophilicity of the 2-pyridyl complexes, since a recent kinetic investigation on the analogous reactions of **3b** with chloroacetonitrile or 3-bromopropene in acetonitrile has shown that an $S_N2$



(1b)

R = COMe: 4b
R = CN: 5b

(4)

M = Pd: 2a
M = Pt: 2b

R = COMe

M = Pd: 6a
M = Pt: 6b

(5)

M = Pd: 3a
M = Pt: 3b

M = Pd; R = COMe: 7a
M = Pt; R = COMe: 7b
CN: 8b
Ph: 9b
Cl: 10b

(6)

(P–P = 1,2-bis(diphenylphosphino)ethane;
S–S = dimethyldithiocarbamate)

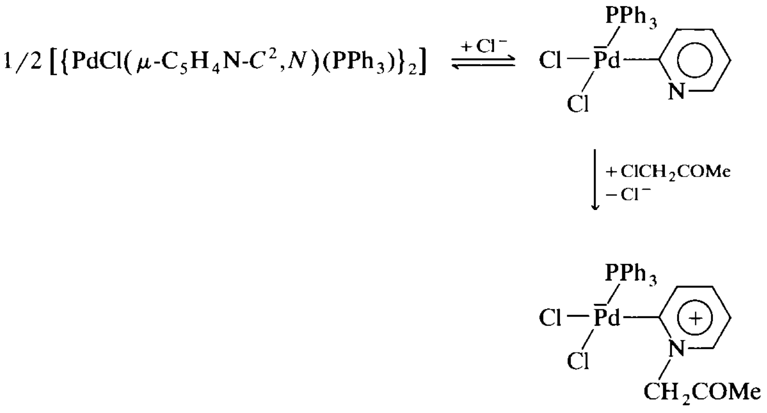
Scheme 1.

mechanism operates, without any appreciable contribution from an $S_N1$ solvolytic step [5]. As can be seen, the rates of nucleophilic substitution depend on the central metal (M = Pd < Pt, for the structurally related complexes **2** and **3**), on the geometry of the complex (M = Pd, **2a** ≈ **3a**; M = Pt, **1b** < **2b** ≈ **3b**), and on the substituent R of the chloro-derivative (R = COMe > CN > Ph ≫ Cl, for the reactions with **3b**). The influence of the electronic and steric properties of R is currently being examined in a detailed mechanistic study , but we note here that the fall in reactivity of the *trans* complex **1b** relative to the *cis* compounds **2b** and **3b** can be attributed to the bulk of the *trans* $PPh_3$–Pt–$PPh_3$ unit, which leads to increasing steric crowding around the reacting 2-pyridyl nitrogen.

As previously observed for the reactions of chloroacetone or 3-bromopropene with 4-DMAP and **3b** [5], the nucleophilic substitution of chloride ions in the reaction of 4-DMAP with $ClCH_2COMe$ is slower than the corresponding reactions of the platinum(II) complexes **2b** and **3b** (~ 30 times slower) and of the palladium(II) complexes **2a** and **3a** (~ 13 times slower). This is a further evidence for the greater nucleophilic power of the 2-pyridyl nitrogen in **2** and **3**, in spite of the large steric requirements of the metal-containing substituents MCl(dppe) and $M(dmtc)(PPh_3)$ $\sigma$-bonded to the $C^2$ pyridyl carbon.

When $CH_2Cl_2$ is used as the electrophile, the reactions are more conveniently carried out in neat dichloromethane, as previously reported for **1b** and **2b** [4]. Only for the platinum(II) complex **3b**, however, does a clean reaction take place, as shown by the changes in the $CD_2Cl_2$ $^{31}P$ NMR spectra with time (Fig. 1). The time required for completion (~ 24 h at 30°C) indicates that in this case also, the *cis* complex **3b** is more reactive than the *trans* derivative **1b**. For the latter compound, the reaction with $CH_2Cl_2$ was found to go to completion in approx. 48 h under comparable conditions [4]. The 2-pyridylpalladium(II) complexes **1a**–**3a** are rather unstable in $CH_2Cl_2$ solution; with time, complex **1a** rearranges to the binuclear species $[\{PdCl(\mu\text{-}C_5H_4N\text{-}C^2,N)(PPh_3)\}_2]$ in accord with equilibrium 1, whereas **2a** and **3a** slowly decompose to give a mixture of various products (as shown by $^{31}P$ NMR spectroscopy), the nature of which has not been further investigated.

The complex $[\{PdCl(\mu\text{-}C_5H_4N\text{-}C^2,N)(PPh_3)\}_2]$, in which the 2-pyridyl nitrogens are coordinated to the palladium centres, shows no tendency to react with chloroacetone even under forcing conditions (large excess of $ClCH_2COMe$ and prolonged refluxing in 1,2-dichloroethane). However, in the presence of $Cl^-$ ions a slow reaction occurs, presumably through reversible formation of a mononuclear intermediate with a terminal 2-pyridyl ligand:



(7)

**(11a)**

*Characterization of reaction products*

The products of reaction 4–7 were characterized by elemental analysis, molar conductivity measurements, IR spectroscopy (Table 2), and $^1H$ and $^{31}P$ NMR spectroscopy (Table 3). All the cationic derivatives behave as uni-univalent electrolytes in acetone [6], whereas complex **11a** has a negligible molar conductivity, in agreement with its zwitterionic nature. The *cis* geometry of **11a** is suggested by the

Table 1

Pseudo-first-order rate constants (±5%) for reactions 4–6 [a]

| Compound | $ClCH_2R$ | $10^2 \times k_{obs}$ ($min^{-1}$) |
|---|---|---|
| **1b** | R = COMe | 0.36 |
| **2a** | COMe | 2.38 |
| **2b** | COMe | 5.32 |
| **3a** | COMe | 2.33 |
| **3b** | COMe | 5.87 |
| **3b** | CN | 1.47 |
| **3b** | Ph | 0.44 |
| **3b** | Cl | – [b] |
| 4-DMAP | COMe | 0.18 |

[a] From changes of specific conductivity with time for the reactions of the 2-pyridyl complexes **1**–**3** or 4-DMAP at initial concentrations of $10^{-3}$ *M*, with $ClCH_2R$ at initial concentration of $5 \times 10^{-2}$ *M*, in acetone at 25°C. [b] Too slow to measure.

appearance of two ν(Pd–Cl) bands, at 306 and 290 $cm^{-1}$, in the IR spectrum. In the starting complexes **3** and their derivatives **7a**–**10b**, the dmtc group is characterized by a strong ν(C⩦N) absorption in the range 1540–1570 $cm^{-1}$, the position of which (at wave numbers higher than 1485 $cm^{-1}$) points to a bidentate chelation of the dimethyldithiocarbamate ligand [7]. In the products **4b**, **6**, **7** and **11a**, the ν(C=O) band of the $(1\text{-}CH_2COMe)C_5H_4N\text{-}C^2$ moiety falls in the narrow range 1738–1743 $cm^{-1}$, very close to the ν(C=O) value of 1736 $cm^{-1}$ observed for the pyridinium compound $[(1\text{-}CH_2COMe)(4\text{-}NMe_2)C_5H_4N]ClO_4$, isolated from the reaction of 4-DMAP with chloroacetone (see Experimental). This suggests that the carbonyl group of the $(1\text{-}CH_2COMe)C_5H_4N\text{-}C^2$ ligand is not involved in coordination with the central metal.

In the $^1H$ NMR spectra, the methyl protons of the dmtc group in complexes **3** and **7**–**10b** give rise to two distinct singlets in the range 3.31–3.20 ppm, indicating a rigid coordination geometry in solution, with a chelating dimethyldithiocarbamate ligand. For the $(1\text{-}CH_2R)C_5H_4N\text{-}C^2$ groups, the $NCH_2$ resonance appears as a singlet, in the complexes with a *trans* geometry (**4b** and **5b**), or as an AB system, in the complexes, with a *cis* geometry **6**–**10b** and **11a**. This difference can be rationalized in terms of a rigid structure in solution (without any fast exchange of ligand coordination site on the NMR time scale), in which the pyridyl plane is perpendicular to the mean coordination plane, and with hindered rotation around the M–$C^2$ bond. Thus, in the *trans* complexes there is a plane of symmetry perpendicular to the mean coordination plane and passing through the Pt, Cl and pyridyl ring atoms, which results in equivalence of the methylene protons as well as that of the *trans* phosphorus atoms in the $^{31}P$ NMR spectra. A configuration of this type was revealed in the solid state for *trans*-$[MCl\{(1\text{-}R')C_5H_4N\text{-}C^2\}(PMe_2Ph)_2]ClO_4$ (M = Pd, Pt; R' = H, $CH_2Cl$) by X-ray structural analyses [8,9]. On the other hand, in the *cis* complexes the absence of such a plane (and of any other element of symmetry) induces chirality on the metal centre, with concomitant diastereotopic behaviour of the methylene protons. As shown by models, the lack of free rotation around the M–$C^2$ bond is mainly due to steric interaction between the $(1\text{-}CH_2R)C_5H_4\text{-}C^2$ group and the *cis* phosphorus ligand.

Table 2

Analytical and conductivity data. Characteristic IR absorptions

| Compound | Anal. Found (calc.) (%) | | | | Molar conductivity [a] | IR (cm$^{-1}$) [b] | | | |
|---|---|---|---|---|---|---|---|---|---|
| | C | H | N | Cl | | $\nu$(M–Cl) | $\nu$(M–S) | $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ [c] | $\nu$(C=O) [d] |
| [M(dmtc)($C_5H_4N$-$C^2$)($PPh_3$)] | | | | | | | | | |
| M = Pd (**3a**) | 54.8 | 4.4 | 4.9 | | 0.4 | | 366m | 1540s(br) | |
| | (55.07) | (4.44) | (4.94) | | | | | | |
| M = Pt (**3b**) | 47.7 | 3.8 | 4.2 | | 0.8 | | 374m | 1540s(br) | |
| | (47.62) | (3.84) | (4.27) | | | | | | |
| *trans*-[PtCl{(1-$CH_2R$)$C_5H_4N$-$C^2$}$(PPh_3)_2$]$ClO_4$ | | | | | | | | | |
| R = COMe (**4b**) | 53.2 | 3.9 | 1.4 | 7.2 | 127.1 | 304m | | | 1742ms |
| | (53.39) | (3.97) | (1.41) | (7.16) | | | | | |
| R = CN (**5b**) | 53.3 | 3.7 | 2.8 | 7.3 | 127.0 | 310m | | | |
| | (53.09) | (3.73) | (2.88) | (7.29) | | | | | |
| [MCl{(1-$CH_2$COMe)$C_5H_4N$-$C^2$}(dppe)]$ClO_4$ | | | | | | | | | |
| M = Pd (**6a**) | 52.5 | 4.2 | 1.7 | 9.3 | 132.4 | 309m | | | 1738ms |
| | (52.70) | (4.29) | (1.81) | (9.15) | | | | | |
| M = Pt (**6b**) | 47.6 | 3.9 | 1.5 | 8.2 | 131.4 | 308m | | | 1738ms |
| | (47.29) | (3.85) | (1.62) | (8.21) | | | | | |
| [M(dmtc){(1-$CH_2R$)$C_5H_4N$-$C^2$}($PPh_3$)]$ClO_4$ | | | | | | | | | |
| M = Pd, R = COMe (**7a**) | 47.8 | 4.2 | 3.8 | 5.1 | 124.0 | | 372m | 1560s(br) | 1738s |
| | (48.14) | (4.18) | (3.87) | (4.90) | | | | | |
| M = Pt, R = COMe (**7b**) | 43.1 | 3.8 | 3.4 | 4.5 | 130.4 | | 380m | 1570s(br) | 1738s |
| | (42.88) | (3.72) | (3.45) | (4.36) | | | | | |
| M = Pt, R = CN (**8b**) | 41.9 | 3.4 | 5.2 | 4.6 | 139.4 | | 380m | 1560s(br) | |
| | (42.29) | (3.42) | (5.28) | (4.46) | | | | | |
| M = Pt, R = Ph (**9b**) | 46.6 | 3.9 | 3.3 | 4.1 | 140.4 | | 380m | 1550s | |
| | (46.83) | (3.81) | (3.31) | (4.19) | | | | | |
| M = Pt, R = Cl (**10b**) [e] | 38.7 | 3.3 | 3.2 | 12.4 | 133.4 | | 380m | 1560s | |
| | (38.99) | (3.33) | (3.31) | (12.55) | | | | | |
| *cis*-[$PdCl_2${(1-$CH_2$COMe)$C_5H_4N$-$C^2$}($PPh_3$)] ·$H_2O$ (**11a**) | 52.5 | 4.3 | 2.4 | 12.2 | 0.7 | 306m; 290m | | | 1743ms |
| | (52.68) | (4.42) | (2.36) | (11.96) | | | | | |

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[a] In ohm$^{-1}$ cm$^2$ mol$^{-1}$ for $10^{-3}$ *M* solutions in acetone at 25°C. [b] As Nujol mulls. [c] Vibration of the dmtc ligand. [d] Vibration of the 1-$CH_2$COMe substituent. [e] This compound contains 1/2 $CH_2Cl_2$ molecule of crystallization.

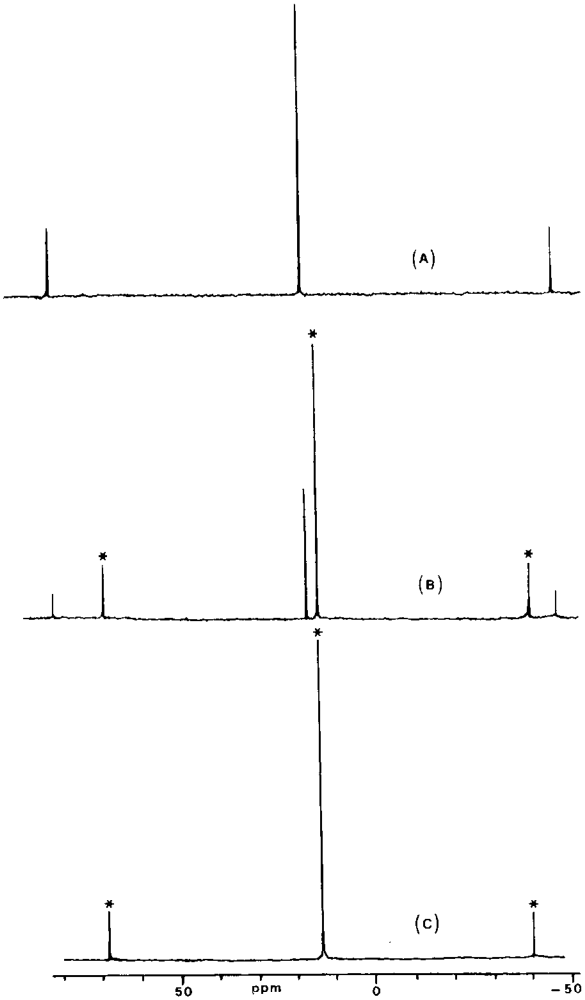

Fig. 1. $^{31}P$ NMR spectra of $[Pt(dmtc)(C_5H_4N\text{-}C^2)(PPh_3)]$ (**3b**) in $CD_2Cl_2$ at 30°C: (A) immediately after dissolution; (B) after 6 h; (C) after 24 h. The signals with an asterisk are from the product $[Pt(dmtc)\{(1\text{-}CD_2Cl)C_5H_4N\text{-}C^2\}(PPh_3)]^+$.

Sterically hindered rotation is also observed for the complexes *trans*-$[PtCl\{(1\text{-}R')C_5H_4N\text{-}C^2\}(PMe_2Ph)_2]ClO_4$ ($R' = Me, CH_2Cl$) in $CD_2Cl_2$ solution [9].

Interestingly, the $N\text{-}CH_2$ signal of compound **11a** becomes a singlet in dimethylsulfoxide (see Table 3). The spectral change on going from $CD_2Cl_2$ to the more coordinating $(CD_3)_2SO$ solvent may arise either from *cis* → *trans* isomerization or from a fast site exchange of the *trans* $PPh_3$ and chloride ligands (promoted by solvent coordination on the central metal), which generates an averaged plane of symmetry. The detection of close $^{31}P$ resonances in both solvents (28.8 ppm in $CD_2Cl_2$ and 28.1 ppm in $(CD_3)_2SO$) favours the latter process.

Table 3

Selected $^1$H and $^{31}$P NMR data[a]

| Compound | 2-Pyridyl protons | | dmtc protons | N-CH$_2$R protons | | $^{31}$P resonances | Solvent |
|---|---|---|---|---|---|---|---|
| | H$^3$ | H$^6$ | N-CH$_3$ | N-CH$_2$- | R = COCH$_3$ | | |
| **3a**[b] | 6.98m | 8.16m | 3.29s, 3.26s | | | 28.4s (br) | CDCl$_3$ |
| **3b**[b] | 7.01m<br>$^3J$(Pt-H) 36.0 | 8.02m | 3.23s, 3.18s | | | 17.0s<br>$^1J$(Pt-P) 4125 | CD$_2$Cl$_2$ |
| **4b** | mk[c] | 7.76m<br>$^4J$(Pt-H) 12.0 | | 5.82s<br>$^4J$(Pt-H) 6.5 | 2.01s | 20.0s<br>$^1J$(Pt-P) 2629 | CD$_2$Cl$_2$ |
| **5b** | mk[c] | 8.27m<br>$^4J$(Pt-H) 13.0 | | 5.61s<br>$^4J$(Pt-H) 5.0 | | 19.2s<br>$^1J$(Pt-P) 2571 | CDCl$_3$ |
| **6a** | mk[c] | mk[c] | | 5.76[d], 5.01[d]<br>$^2J$(H-H) 17.5 | 2.16s | 58.2d, 46.8d<br>$^2J$(P-P) 17.8 | CD$_2$Cl$_2$ |
| **6b** | mk[c] | mk[c] | | 5.95[d], 4.91[d]<br>$^4J$(Pt-H) 5.8,<br>$^2J$(H-H) 17.4 | 2.14s | 39.6[d,e], 39.3[d,f]<br>$^1J$(Pt-P) 2065,<br>$^1J$(Pt-P) 3456<br>$^2J$(P-P) 6.0 | CD$_2$Cl$_2$ |
| **7a** | 7.68m | 8.14m | 3.29s, 3.25s | 5.97[d], 5.69[d]<br>$^2J$(H-H) 17.6 | 2.26s | 29.0s | CD$_2$Cl$_2$ |
| **7b** | 7.63m<br>$^3J$(Pt-H) 42.0 | 8.07m<br>$^4J$(Pt-H) 12.0 | 3.24s, 3.20s | 6.14[d], 5.69[d]<br>$^4J$(Pt-H) 8.4,<br>$^4J$(Pt-H) 3.2<br>$^2J$(H-H) 17.6 | 2.28s | 14.3s<br>$^1J$(Pt-P) 3474 | CD$_2$Cl$_2$ |
| **8b** | 7.80m<br>$^3J$(Pt-H) 40.0 | 8.54m<br>$^4J$(Pt-H) 13.0 | 3.28s, 3.23s | 5.99[d], 5.73[d]<br>$^4J$(Pt-H) 4.6,<br>$^4J$(Pt-H) 3.4<br>$^2J$(H-H) 17.0 | | 13.7s<br>$^1J$(Pt-P) 3426 | CD$_2$Cl$_2$ |
| **9b** | 7.93m<br>$^3J$(Pt-H) 40.0 | 8.02m<br>$^4J$(Pt-H) 12.0 | 3.26s, 3.24s | 6.47[d], 5.00[d]<br>$^4J$(Pt-H) 7.5,<br>$^4J$(Pt-H) 5.7<br>$^2J$(H-H) 14.1 | | 13.6s<br>$^1J$(Pt-P) 3503 | CD$_2$Cl$_2$ |
| **10b** | 7.78m<br>$^3J$(Pt-H) 40.0 | 8.47m<br>$^4J$(Pt-H) 14.0 | 3.27s, 3.22s | 6.49[d], 6.28[d]<br>$^4J$(Pt-H) 5.4,<br>$^4J$(Pt-H) 3.5<br>$^2J$(H-H) 9.8 | | 14.0s<br>$^1J$(Pt-P) 3448 | CD$_2$Cl$_2$ |
| **11a** | mk[c] | 8.08m | | 6.47[d], 5.79[d]<br>$^2J$(H-H) 18.2 | 2.21s | 28.8s | CD$_2$Cl$_2$ |
| | mk[c] | 8.13m | | 6.12s | 2.23s | 28.1s | (CD$_3$)$_2$SO |

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[a] Spectra recorded at 30°C; $\delta(^1H)$ values in ppm from TMS as internal standard; $\delta(^{31}P)$ values in ppm from external 85% $H_3PO_4$, downfield shifts being taken as positive; coupling constants in Hz; s, singlet; d, doublet; m, multiplet; satisfactory integration values have been obtained. [b] Spectra recorded immediately after dissolution. [c] Masked by the intense resonance of phenyl protons. [d] AB system: the chemical shifts have been calculated from the spectral frequencies [10]. [e] *trans* to the C$^2$-bonded heterocyclic ligand. [f] *trans* to the Cl ligand.

## Experimental

The complexes *trans*-$[MCl(C_5H_4N-C^2)(PPh_3)_2]$ (**1**) and $[MCl(C_5H_4N-C^2)(dppe)]$ (**2**) were prepared by published methods [1,3,4]. All chemicals and solvents were reagent grade and were used without further purification. Infrared spectra were recorded with Perkin-Elmer 1430 and 983 instruments, using Nujol mulls and CsI windows in the range 4000–200 $cm^{-1}$. The $^1H$ and $^{31}P-\{^1H\}$ NMR spectra were recorded with a Varian FT 80A spectrometer. The conductivity measurements were carried out with a digital CDM 83 conductivity meter. The solvents were evaporated to small volume or to dryness at reduced pressure in a rotary evaporator.

### *Preparation of $[M(dmtc)(C_5H_4N-C^2)(PPh_3)]$ (3)*

*M = Pd (**3a**).* A solution of sodium dimethyldithiocarbamate dihydrate (0.45 g, 2.5 mmol) in methanol (10 ml) was added to a suspension of $[\{PdCl(\mu-C_5H_4N-C^2,N)(PPh_3)\}_2]$ (0.96 g, 1 mmol) in 80 ml of benzene. After 30 min stirring, the solvents were evaporated to dryness, and the solid residue was extracted with benzene (100 ml) in the presence of activated charcoal. After filtration, the solution was concentrated to small volume and diluted with diethyl ether to precipitate the complex **3a** as pale-yellow microcrystals. The product was purified by reprecipitation from a concentrated $C_6H_6$ solution with $Et_2O$ (0.83 g, 73.2%). This compound must be stored at low temperature (−20°C) because it slowly decomposes at ambient temperature.

*M = Pt (**3b**).* The salt $Na(dmtc) \cdot 2H_2O$ (0.94 g, 5.25 mmol) dissolved in methanol (30 ml) was added to a solution of *trans*-$[PtCl(C_5H_4N-C^2)(PPh_3)_2]$ (**1b**, 2.50 g, 3 mmol) in 100 ml of benzene. The mixture was stirred overnight and worked up as described above for **3a**. Reprecipitation from $C_6H_6/Et_2O$ gave the product as white microcrystals (1.77 g, 90.0%).

### *Reactions of 2-pyridyl complexes 1, 2 and 3 with $ClCH_2R$ (R = COMe, CN, Ph)*

The starting complex (0.5 mmol), dissolved or suspended in acetone (50 ml), was treated with an excess of $ClCH_2R$ (molar ratio complex/$ClCH_2R$ 1:25). The mixture was stirred for 24 h at ambient temperature to give a clear solution. After addition of $NaClO_4 \cdot H_2O$ (0.14 g, 1 mmol), the solvent was evaporated to dryness and the residue was extracted with $CH_2Cl_2$ (50 ml) in the presence of charcoal. The filtered solution was concentrated to small volume and diluted with $Et_2O$ to precipitate the products as pale-yellow (M = Pd) or white (M = Pt) solids. The yields ranged from 70.0 for **5b** to 94.4 for **6a**, after reprecipitation from $CH_2Cl_2/Et_2O$. Under the same conditions, the complex *trans*-$[PdCl(C_5H_4N-C^2)(PPh_3)_2]$ (**1a**, 0.5 mmol) in the presence of chloroacetonitrile (12.5 mmol) rearranged to $[\{PdCl(\mu-C_5H_4N-C^2,N)(PPh_3)\}_2]$ (0.2 mmol), which separated from the acetone solution and was readily identified from its IR and $^{31}P$ NMR spectra [3].

### *Reaction of 4-dimethylaminopyridine with chloroacetone*

A solution of 4-DMAP (0.25 g, 2 mmol) and $ClCH_2COMe$ (4 ml, 50 mmol) in acetone (100 ml) was set aside for 5 days, then $NaClO_4 \cdot H_2O$ (0.56 g, 4 mmol) was added and the mixture worked up as above to yield the pyridinium salt $[(1-CH_2COMe)(4-NMe_2)C_5H_4N]ClO_4$ as white crystals (0.43 g, 77.1%). Anal. Found:

C, 42.9; H, 5.4; N, 9.9; Cl, 12.7. $C_{10}H_{15}N_2O_5Cl$ calc.: C, 43.09; H, 5.42; N, 10.05; Cl, 12.72%. Molar conductivity: 143.4 $ohm^{-1}$ $cm^2$ $mol^{-1}$ for a $10^{-3}$ *M* acetone solution at 25°C. IR $\nu$(C=O) 1736s $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$): 7.84 (m, 2H); 6.80 (m, 2H) AA'BB' system of pyridine protons; 5.19 (s, 2H, N-$CH_2$-); 3.23 (s, 6H, N($CH_3)_2$); 2.33 (s, 3H, CO$CH_3$) ppm.

*Reaction of [Pt(dmtc)($C_5H_4N$-$C^2$)($PPh_3$)] (3b) with $CH_2Cl_2$*

A solution of complex **3b** (0.33 g, 0.5 mmol) in $CH_2Cl_2$ (50 ml) was kept in a thermostat at 30°C for 2 days. After this time a solution of $NaClO_4 \cdot H_2O$ (0.14 g, 1 mmol), in 5 ml of methanol was added, and the mixture worked up as described for the analogous reactions of **1b** and **2b** [4] to yield [Pt(dmtc){(1-$CH_2Cl$)$C_5H_4N$-$C^2$}($PPh_3$)]$ClO_4 \cdot 1/2$ $CH_2Cl_2$ (**10b**) as a white solid (0.32 g, 75.5%).

*Preparation of* cis-*[$PdCl_2${(1-$CH_2COMe$)$C_5H_4N$-$C^2$}($PPh_3$)] $\cdot H_2O$ (11a)*

Chloroacetone (2 ml, 25 mmol) and tetraphenylphosphonium chloride (0.65 g, 2 mmol) were added to a solution of [{PdCl($\mu$-$C_5H_4N$-$C^2$,*N*)($PPh_3$)}$_2$] (0.96 g, 1 mmol) in 1,2-dichloroethane (~ 100 ml). The mixture was refluxed at 90–93°C for 30 h, during which the progress of the reaction was monitored by IR spectroscopy in the range 1700–1500 $cm^{-1}$ by observing the decrease of the pyridine ring vibration in the starting compound at 1585 $cm^{-1}$ and the concomitant increase of the corresponding vibration in the product at 1618 $cm^{-1}$. After treatment with charcoal and filtration, the resulting solution was evaporated to dryness and the solid was washed with methanol (3 × 20 ml) to dissolve the tetraphenylphosphonium chloride. The crude product **11a**, scarcely soluble in methanol, was purified by two successive precipitations from $CH_2Cl_2/Et_2O$ (0.88 g, 74.2%).

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