Journal of Organometallic Chemistry, 438 (1992) 253–263
Elsevier Sequoia S.A., Lausanne
JOM 22820

Organometallic nucleophiles. Mechanism of halide displacement at saturated carbon by 2-pyridyl and 4-pyridyl complexes $[M(dmtc)(C_5H_4N\text{-}C^n)(L)]$ ($M = Pd, Pt$; dmtc = dimethyldithiocarbamate; $n = 2,4$; L = tertiary phosphine)

L. Canovese, P. Uguagliati
Dipartimento di Chimica, Università di Venezia (Italy)

F. Di Bianca
Dipartimento di Chimica Inorganica, Università di Palermo (Italy)

and B. Crociani
Dipartimento di Scienze e Tecnologie Chimiche, II Università di Roma, Via O. Raimondo, 00173 Roma (Italy)

(Received March 3, 1992)

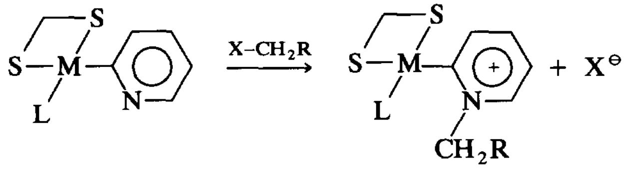
Abstract

A mechanistic study is reported of nucleophilic halide substitution by pyridyl complexes $[M(dmtc)(C_5H_4N\text{-}C^2)(L)]$ (M = Pd or Pt; L = PMe_3, PEt_3 or PPh_3) and $[Pd(dmtc)(C_5H_4N\text{-}C^4)(L)]$ (L = PMe_3 or PPh_3) on organic halides XCH_2R (X = Cl or Br; R = $CH{=}CH_2$, COMe, Ph, or CN) in various solvents, yielding the pyridylium derivatives $[M(dmtc)\{(1\text{-}CH_2R)C_5H_4N\text{-}C^2\}(L)]^+$ and $[Pd(dmtc)\{(1\text{-}CH_2R)C_5H_4N\text{-}C^4\}(L)]^+$, respectively. The kinetics obey a second-order rate law: rate = $k_2[XCH_2R][Complex]$. A similar rate law is observed for the analogous reactions involving 4-dimethylaminopyridine (4-dmapy) as the nucleophile. The effects of solvent and leaving group, and the largely negative activation entropies, are in line with S_N2 substitution at saturated carbon. The nucleophilic power (k_2) generally increases with increasing basicity (pK_a) of the pyridine nitrogen. Both these parameters depend on the position and nature of the substituent in the pyridine ring, in the order 2-M(dmtc)(L) > 4-NMe_2 > 4-Pd(dmtc)(L). The electron-release of the metal-containing groups appears to be essentially inductive.

Introduction

2-Metallated pyridines are of current interest for their enhanced basic and nucleophilic properties [1–3]. In the complexes *trans*-$[PdBr(C_5H_4N\text{-}C^2)(PEt_3)_2]$

Correspondence to: Professor B. Crociani.



(1)

M	L	X	R
Pt	PPh_3 (**1**)	Br	$CH{=}CH_2$
Pt	PPh_3 (**1**)	Cl	COMe, CN, Ph
Pt	PMe_3 (**2**)	Cl	CN
Pt	PEt_3 (**3**)	Cl	CN
Pd	PMe_3 (**4**)	Cl	CN

Scheme 1.

[1b] and [Pt(dmtc)(C_5H_4N-C^2)(PPh_3)] [4] the 2-pyridyl group is much more basic than pyridine itself, as shown by the pK_a values of 8.04, 9.60, and 4.47, respectively (in water-dioxane at an ionic strength of 0.1 mol dm^{-3}). On the other hand, the high nucleophilicity is exemplified by the ability of the 2-pyridyl nitrogen in some platinum(II) derivatives to displace even chloride ions from chlorinated solvents [3c,5]. Therefore, 2-pyridyl complexes appear to be promising substrates for studying (i) their possible catalytic role as strong nucleophiles in a wealth of organic reactions and (ii) their application in organic syntheses involving pyridinium intermediates [6]. In a preliminary study [4] we have shown that in nucleophilic substitutions at saturated carbon the 2-pyridyl ligand of [Pt(dmtc)(C_5H_4N-C^2)(PPh_3)] is *ca.* 30 times more effective than 4-dimethylaminopyridine (4-dmapy), which is widely used as a "hypernucleophilic" catalyst [7].

In the present paper we shall report a detailed mechanistic investigation of halide displacement from XCH_2R ($X = Cl$ or Br; $R = CH{=}CH_2$, COMe, Ph, or CN) by 2-pyridyl and 4-pyridyl palladium(II) and platinum(II) complexes.

Results and discussion

The 2-pyridyl complexes **1**–**4** react with organic halides according to eq. 1 of Scheme 1.

The 2-pyridylium products of reaction 1 involving complex **1** and $ClCH_2R$ ($R = COMe$, CN, or Ph) have been isolated and characterized as perchlorate salts, as described in a recent paper [8]. The analytical and relevant spectral data for some new derivatives are reported in the Experimental section.

The kinetics of reaction 1 were monitored by either conductometric or UV-Vis spectrophotometric techniques in various solvents and at different temperatures. A more than 10-fold excess of XCH_2R was generally used to ensure pseudo-first order conditions. The pseudo-first-order rate constants appeared to obey the simple second-order rate law, eq. (2).

$$k_{obs} = k_2[XCH_2R] \qquad (2)$$

TABLE 1

pK_a values of the 2-pyridyl complexes [M(dmtc)(C_5H_4N-C^2)(L)] and second-order rate constants for reaction 1

Complex	M	L	pK_a [a]	XCH_2R	Solvent	10^4k_2 [b] (mol^{-1} dm^3 s^{-1})
1	Pt	PPh_3	9.60	$BrCH_2CH{=}CH_2$	MeCN	1777 ± 8 [c]
1				$ClCH_2COMe$		160.0 ± 0.7
1				$ClCH_2CN$		52.7 ± 0.3
1				$ClCH_2Ph$		33.0 ± 0.4
1				$ClCH_2CN$	Me_2CO	45.3 ± 0.2
1				$ClCH_2CN$	1,4-Dioxane	15.1 ± 0.1
2	Pt	PMe_3	9.30	$ClCH_2CN$	MeCN	35.2 ± 0.3
3	Pt	PEt_3	9.50	$ClCH_2CN$	MeCN	34.8 ± 0.5 [d]
4	Pd	PMe_3	9.08	$ClCH_2CN$	MeCN	14.5 ± 0.2

[a] Measured by potentiometric titration with $HClO_4$ in water/dioxane 1/1 vol/vol at 25°C and ionic strength ($LiClO_4$) 0.1 mol dm^{-3}. [b] At 25°C. [c] 1780 ± 6 as measured conductimetrically under second-order conditions (molar ratio 1 : $BrCH_2CH{=}CH_2$ 1 : 3). [d] 35.1 ± 0.2 as measured conductimetrically under pseudo-first order conditions with excess of metal complex over $ClCH_2CN$.

with no statistically significant contribution from a first-order path (Table 1, Fig. 1).

For the reaction of **1** with $BrCH_2CH{=}CH_2$ in MeCN, the k_2 value obtained under second-order conditions (molar ratio **1**: $BrCH_2CH{=}CH_2$ 1 : 3, Fig. 2) was virtually identical to that observed under pseudo-first-order conditions. Consistently, for the reaction of **3** with $ClCH_2CN$ in MeCN, practically coincident k_2 values were measured under pseudo-first-order conditions that were realized

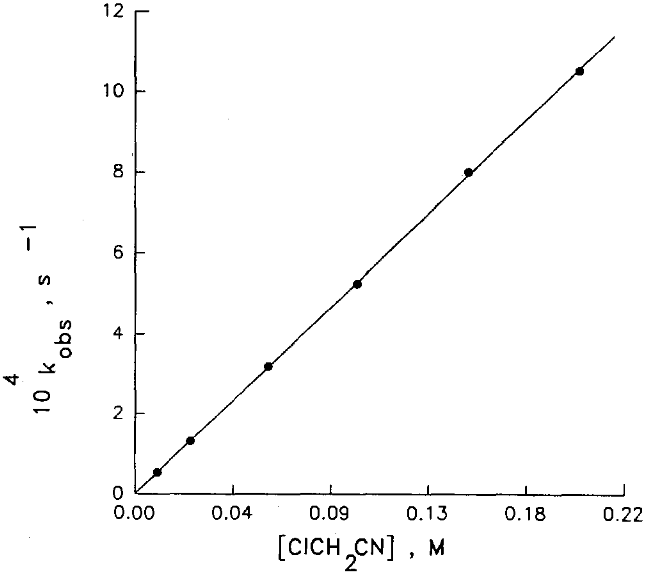


Fig. 1. Plot of k_{obs} *vs.* [$ClCH_2CN$] for the reaction of **1** with $ClCH_2CN$ in acetonitrile at 25°C.

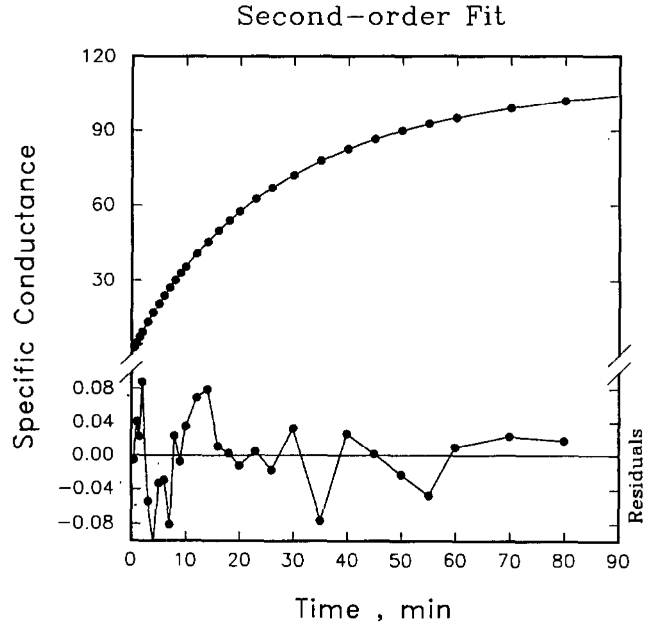
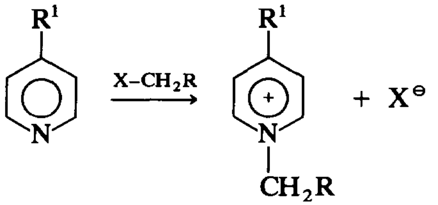


Fig. 2. Non-linear fit of χ_t *vs.* time data to the Onsager-corrected second-order law (see Experimental section) for the reaction of **1** with $BrCH_2CH=CH_2$ in acetonitrile at 25°C (specific conductance in $\mu S\ cm^{-1}$).

either with an excess of $ClCH_2CN$ over the complex or *vice versa*. In any case, the reactions were driven completely to the right. The rates of reaction 1 are also unaffected by the presence of either the free base L or halide X^-, suggesting that the process consists of a nucleophilic substitution at the saturated carbon by the 2-pyridyl nitrogen of **1**–**4**.

In agreement with this mechanistic picture are the activation enthalpies and the largely negative activation entropies observed for the reactions of **1** with $ClCH_2CN$ ($\Delta H^{\#}$ 43.3 ± 1 kJ mol^{-1}, $\Delta S^{\#}$ -142 ± 3 J K^{-1} mol^{-1}), with $BrCH_2CH=CH_2$ ($\Delta H^{\#}$ 29.7 ± 2 kJ mol^{-1}, $\Delta S^{\#}$ -160 ± 3 J K^{-1} mol^{-1}), and of **2** with $ClCH_2CN$ ($\Delta H^{\#}$ 48.2 ± 1 kJ mol^{-1}, $\Delta S^{\#}$ -129 ± 2 J K^{-1} mol^{-1}) in MeCN. These values are in line with those reported for classical S_N2 reactions at saturated carbon, involving pyridine nucleophiles, in which substantial charge-separation occurs in the transition state with attendant solvent organization. Whereas the activation enthalpy reflects essentially the strength of the carbon–halogen bond, the $\Delta S^{\#}$ values are mainly determined by reorganization of solvent around the leaving halide, concomitant with the buildup of negative charge in the course of the displacement [9]. Consistently, the activation process is favoured by increased polarity of the solvent, other things being equal, as can be seen from the solvent reactivity order: 1,4-dioxane < acetone < acetonitrile.

As for the effect of the substituent R, the observed reactivity trend COMe > CN > Ph results from a balance of steric and electronic factors, the latter being related to the different abilities of the unsaturated groups to stabilize the incipient positive charge in the transition state [9b].



(3)

R^1	X	R
NMe_2 (4-dmapy)	Br	$CH{=}CH_2$
NMe_2 (4-dmapy)	Cl	COMe, CN, Ph
$Pd(dmtc)(PPh_3)$ (5)	Cl	CN
$Pd(dmtc)(PMe_3)$ (6)	Cl	CN

Scheme 2.

The reaction rates are also affected by both the central metal M and the ancillary ligand L.

$Pt > Pd$ ($L = PMe_3$) and $PPh_3 > PMe_3 \cong PEt_3$ ($M = Pt$)

The higher reactivity of platinum complexes compared to the palladium analogues was already observed under preparative conditions [8]. The influence on L can hardly be rationalized with the present data: the observed reactivity trend bears no relationship to the electron-donor abilities and steric requirements of L, although the rates appear to decrease with decreasing basicity of the 2-pyridyl nitrogen in the complex substrate, as measured by pK_a values. We might infer the operation of different solvation effects either in the starting substrates or in the activated complexes or both.

In order to determine the rate effects of changing the position of substituent on the pyridine ring, we have also studied reaction 3 of XCH_2R with the 4-substituted derivatives 4-dmapy, **5**, and **6** (Scheme 2, Table 2). Some of the 4-pyridylium products were isolated as perchlorate salts (see ref. 8 and Experimental section). Again, reaction 3 obeys the second-order rate law 2. The rates of reaction of 4-dmapy with $ClCH_2R$ change in the order R = COMe > Ph > CN. For the latter

Table 2

pK_a values of 4-pyridyl compounds and second-order rate constants for reaction 3

Compound	R^1	pK_a [a]	XCH_2R	10^4k_2 [b] ($mol^{-1}\ dm^3\ s^{-1}$)
4-dmapy	NMe_2	8.51	$BrCH_2CH{=}CH_2$	56.4 ± 0.8
4-dmapy	NMe_2		$ClCH_2COMe$	9.04 ± 0.6
4-dmapy	NMe_2		$ClCH_2Ph$	2.1 ± 0.3
4-dmapy	NMe_2		$ClCH_2CN$	1.7 ± 0.2
5	$Pd(dmtc)(PPh_3)$	6.50	$ClCH_2CN$	1.05 ± 0.02
6	$Pd(dmtc)(PMe_3)$	6.70	$ClCH_2CN$	0.44 ± 0.02

[a] See footnotes to Table 1. [b] At 25°C in acetonitrile.

two substituents the reactivity order is the reverse of that found for the corresponding reaction with complex **1**, as a consequence of the lower steric requirement of the 4-pyridyl nitrogen nucleophile, which apparently offsets the greater bulkiness of Ph relative to CN.

Replacement of 4-NMe_2 by the 4-Pd(dmtc)(L) substituent brings about a large decrease in basicity (*ca.* two pK_a units), which is attended by only a modest decrease in reactivity towards the $ClCH_2CN$ substrate (from 1.7×10^{-4} to 0.44×10^{-4} mol^{-1} dm^3 s^{-1}). Apparently, the 4-NMe_2 substituent imparts a higher basicity to the pyridine nitrogen, thanks to its greater *mesomeric* electron-releasing ability.

Data in Tables 1 and 2 show that the nucleophilic power of the 2-pyridyl group in complexes **1**–**4** is much larger than that of the so-called "hypernucleophile" 4-dmapy and of the 4-pyridyl complexes **5** and **6**, despite the higher steric crowding around the nucleophilic centre of **1**–**4**. * In particular, when the Pd(dmtc)(PMe_3) group is moved from the 4- to the 2-carbon on the pyridine ring, both the pK_a value and the rate constant k_2 for the reaction with $ClCH_2CN$ increase markedly, suggesting that the electron-donor ability of such a group is mainly *inductive*. This is further supported by an X-ray structural analysis of the 2-pyridyl complex *trans*-[PtCl(C_5H_4N-C^2)(PMe_2Ph)$_2$], which has shown that there is hardly any π back-bonding from the metal to the pyridine ring in the platinum-2-pyridyl bond (Pt-C^2 1.996(8) Å) [5].

Experimental

1. Kinetics and pK_a measurements

Kinetic runs under second-order conditions were carried out for the reaction of **1** with $BrCH_2CH=CH_2$ in acetonitrile by monitoring changes with time of the specific conductance χ_t of acetonitrile solutions of the reactants (molar ratio $1/BrCH_2CH=CH_2$ 1/3–5 with initial complex concentration of *ca.* 1×10^{-3} mol dm^{-3}). χ_t *vs.* time data were fitted by non-linear regression to the Onsager-corrected second-order law [10,11]

$$\chi_t = \chi_0 + 1000\beta\left(\Lambda_\infty - S\sqrt{\beta}\right)\left(\chi_t \text{ in } \mu S \text{ cm}^{-1}\right)$$

where χ_0 = specific conductance at time = 0; Λ_∞ = molar conductance at infinite dilution of the pyridylium product; $\beta = b(1-E)/(1-qE)$; $q = b/a$; $E = \exp\{(b-a)k_2t\}$; $b = [BrCH_2CH=CH_2]$; a = [**1**]; and with χ_0, Λ_∞, S, and k_2 as the parameters to be refined.

Kinetic runs under pseudo-first order conditions were carried out with a more than tenfold excess of XCH_2R over the metal complex whose concentration was

---

* In line with what was suggested by one of the referees, we have been investigating the possible role of the central metal in assisting the substitution process by coordination of the leaving halide in a concerted, cyclic transition state. If this were the case, nucleophilic substitution should occur with retention of configuration at carbon. Our attempts to study this with commercially available chiral halides, 3-bromocamphor and the methyl ester of 2-chloropropionic acid, were hampered by the extreme slowness of the reaction. Further work is now in progress with other, more reactive chiral substrates.

around 10^{-3} mol dm^{-3}, by fitting χ_t to the mono-exponential rate law

$$\chi_t = \chi_0 + 1000\alpha\left(\Lambda_\infty - S\sqrt{\alpha}\right)$$

where $\alpha = a\{1 - \exp(-k_{obs}t)\}$, and with χ_0, Λ_∞, S and k_{obs} as the parameters to be refined [11]. An analogous treatment was applied to the reactions involving 4-dmapy. Direct specific conductance readings were collected with a digital CDM 83 conductivity meter.

The reaction of **1** with $ClCH_2CN$ in 1,4-dioxane was followed by customary UV-Vis spectrophotometric techniques by fitting A_t *vs.* t absorbance data to the monoexponential law $A_t = A_\infty + (A_0 - A_\infty)\ E$ where $E = \exp(-k_{obs}t)$. The same procedure was adopted for the reaction of **3** with $ClCH_2CN$ in acetonitrile as a check on the reliability and accuracy of the conductivity method. A Perkin–Elmer Lambda 5 spectrophotometer with a thermostatted cell compartment was used.

Activation parameters were determined by fitting $\ln(k_2/T)$ *vs.* $1/T$ at four temperatures in the range 20–40°C, according to a reparametrized Eyring equation to minimize unfavourable parameter correlation effects [12].

The pK_a values of complexes **1–6** and 4-dmapy were evaluated by potentiometric titration with $HClO_4$ in water/dioxane (1:1 vol/vol) at ionic strength of 0.1 mol dm^{-3} ($LiClO_4$) at 25°C, according to literature procedures [13].

All statistical and graphical data analyses were carried out with in-house non-linear regression computer programs written in Turbo Basic ® (Borland International) and implemented on an IBM PS/2 80386 ® personal computing system equipped with an INTEL 80387 ® mathematical coprocessor.

2. *Synthesis and characterization of pyridyl and pyridylium complexes*

The complexes $[M(dmtc)(C_5H_4N\text{-}C^2)(PPh_3)]$ (M = Pd or Pt) and *trans*-$[PdBr(C_5H_4N\text{-}C^4)(PPh_3)_2]$ were prepared by published methods [1b,8]. All chemicals and solvents were reagent grade and were used without further purification. The solvents were evaporated to small volume or to dryness at reduced pressure in a rotary evaporator.

Preparation of $[M(dmtc)(C_5H_4N\text{-}C^2)(L)]$. A suspension of the starting complex $[M(dmtc)(C_5H_4N\text{-}C^2)(PPh_3)]$ (M = Pd or Pt; 1 mmol) in diethyl ether (100 cm^3) was treated with L (PMe_3 or PEt_3, 1.1 mmol) under N_2. After stirring for 12 h the mixture was worked up as follows.

(a) $M = Pt$, $L = PMe_3$: the solvent was evaporated to dryness and the residue redissolved in benzene (*ca.* 50 cm^3) in the presence of activated charcoal. After filtration, the solution was concentrated to small volume and diluted with n-pentane to precipitate the white product **2**, which was recrystallized from benzene/n-pentane (0.31 g, 66.0%).

(b) $M = Pt$, $L = PEt_3$: the solvent was evaporated to small volume and precipitation was completed by diluting with n-hexane. The white product **3** was purified by reprecipitation from a concentrated benzene solution with a diethyl ether/n-pentane mixture (1:5 vol/vol) (0.38 g, 74.3%).

(c) $M = Pd$, $L = PMe_3$: the solvent was evaporated to small volume and n-pentane (*ca.* 50 cm^3) was added. The mixture was kept at 0°C overnight to complete the precipitation of **4** as white microcrystals (0.30 g, 78.8%).

Preparation of $[Pd(dmtc)(C_5H_4N\text{-}C^4)(L)]$. (a) $L = PPh_3$: sodium dimethyldithiocarbamate dihydrate (0.27 g, 1.5 mmol) dissolved in 10 cm^3 of methanol

Table 3

Analytical and selected IR data

Compound			C	H	N	ν(M–S)	$\nu(\mathrm{C} \overset{\dots}{-} \mathrm{N})^{a}$
[M(dmtc)(C$_5$H$_4$N–C^2)(L)]							
M = Pt	L = PMe$_3$	(2)	28.2 (28.14)	4.0 (4.08)	5.9 (5.97)	390ms; 365 m	1545 s(br)
M = Pt	L = PEt$_3$	(3)	32.4 (32.87)	4.8 (4.93)	5.4 (5.48)	370 m	1540 s(br)
M = Pd	L = PMe$_3$	(4)	34.4 (34.69)	5.0 (5.03)	7.3 (7.36)	391 m; 366 ms	1535 s(br)
[Pd(dmtc)(C$_5$H$_4$N–C^4)(L)]							
	L = PPh$_3$	(5)	54.7 (55.07)	4.4 (4.44)	4.8 (4.94)	365 m	1520 s(br)
	L = PMe$_3$	(6)	34.5 (34.69)	5.0 (5.03)	7.4 (7.36)	355 m	1520 s(br)
[M(dmtc){(1-CH$_2$CN)C$_5$H$_4$N–C^2}(PMe$_3$)]ClO$_4$							
M = Pt			25.4 (25.64)	3.4 (3.48)	6.8 (6.90)	383 m	1555 s(br)
M = Pd			30.1 (30.01)	4.0 (4.07)	7.9 (8.08)	382 m	1548 s(br)
[Pd(dmtc){(1-CH$_2$CN)C$_5$H$_4$N–C^4}(PMe$_3$)]ClO$_4$			29.5 (30.01)	4.1 (4.07)	8.0 (8.08)	368 m	1540 s(br)
[Pd(dmtc)(C$_5$H$_5$N–C^4)(PMe$_3$)]ClO$_4$ ^{b}			27.3 (27.45)	4.2 (4.19)	5.8 (5.82)	369 m	1550 s(br)

[a] Vibration of the dmtc ligand. [b] The 4-pyridylium ligand is characterized by ν(N–H) bands at 3270 and 3150 cm^{-1}.

Table 4

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

Compound	Proton resonances					Phosphorus resonances $\delta(^{31}P)$	Solvent
	H(3) [b]	H(6) [b]	NMe_2 [c]	P–Me	$-CH_2CN$		
$[M(dmtc)(C_5H_4N\text{-}C^2)(L)]$							
M = Pt L = PMe_3 (2)	7.43 m (^3J(Pt–H) = 37.0	8.35 m	3.28 s; 3.27 s	1.47 d ^2J(P–H) = 10.9 ^3J(Pt–H) = 33.0		−25.55 s ^1J(Pt–P) = 3904.6	$CDCl_3$
M = Pt L = PEt_3 (3)	7.45 m ^3J(Pt–H) = 37.7	8.33 m	3.27 s; 3.25 s			8.87 s ^1J(Pt–P) = 3914.2	$CDCl_3$
M = Pd L = PMe_3 (4)	7.37 m	8.38 m	3.29 s	1.26 d ^2J(P–H) = 10.2		−11.51 s	CD_2Cl_2
$[Pd(dmtc)(C_5H_4N\text{-}C^4)(L)]$							
L = PPh_3 (5)	7.07 m [d]	7.66 m [d]	3.29 s; 3.25 s			29.39 s	CD_2Cl_2
L = PMe_3 (6)	7.41 m [d]	7.96 m [d]	3.30 s; 3.28 s	1.28 d ^2J(P–H) = 10.2		−13.05 s	CD_2Cl_2
$[M(dmtc)((1\text{-}CH_2CN)C_5H_4N\text{-}C^2)(PMe_3)]ClO_4$							
M = Pt	8.21 m ^3J(Pt–H) = 42.0	8.76 m ^3J(Pt–H) = 13.0	3.30 s; 3.28 s	1.51 d ^2J(P–H) = 11.2 ^3J(Pt–H) = 40.5	6.18 [e] ^4J(Pt–H) = 3.7 ^2J(H–H) = 17.1 6.12 [e]	−26.62 s ^1J(Pt–P) = 3254.1	CD_2Cl_2
M = Pd	8.24 m	8.83 m ^2J(P–H) = 10.9	3.35 s; 3.32 s ^2J(H–H) = 17.1 6.02 [e]	1.42 d	6.14 [e]	−9.45 s	CD_2Cl_2
$[Pd(dmtc)((1\text{-}CH_2CN)C_5H_4N\text{-}C^4)(PMe_3)]ClO_4$	8.02 m [d]	8.40 m [d] ^2J(P–H) = 10.6	3.32 s; 3.29 s	1.35 d	5.52 s	−15.53 s	CD_2Cl_2
$[Pd(dmtc)(C_5H_5N\text{-}C^4)(PMe_3)]ClO_4$	8.00 m [d]	8.26 m [d] ^2J(P–H) = 10.2	3.32 s; 3.29 s	1.33 d		−13.17 s	$CDCl_2$

[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] Pyridyl protons at position 3 and 6. [c] Dmtc protons. [d] AA′BB′ system. [e] AB system.

was added to a solution of *trans*-[PdBr(C_5H_4N-C^4)($PPh_3)_2$] (0.76 g, 1 mmol) in benzene (100 cm^3). After stirring for 30 min the solvent was evaporated to dryness and the solid residue was extracted with benzene (*ca.* 80 cm^3) in the presence of charcoal. After filtration the solution was concentrated to small volume and then diluted with diethyl ether to precipitate complex **5** as a yellow microcrystalline solid. The product was purified by reprecipitation from a concentrated benzene solution with diethyl ether (0.49 g, 86.4%).

(b) $L = PMe_3$: a suspension of **5** (0.57 g, 1 mmol) in diethyl ether (100 cm^3) was treated with PMe_3 (1.1 mmol) under N_2. The mixture was stirred overnight and the resulting pale yellow product **6** was filtered off and washed with Et_2O (0.27 g, 70.9%).

Preparation of [M(dmtc){(1-CH_2CN)C_5H_4N-C^2}(PMe_3)]ClO_4. The 2-pyridyl complex [M(dmtc)(C_5H_4N-C^2)(PMe_3)] (M = Pd or Pt; 0.5 mmol) was dissolved in acetone (40 cm^3) in the presence of an excess of chloroacetonitrile (10 mmol). The solution was set aside for 3 days. After addition of $NaClO_4 \cdot H_2O$ (1 mmol) the solvent was evaporated to dryness and the residue extracted with dichloromethane (50 cm^3) in the presence of charcoal. The filtered solution was concentrated to small volume and diluted with Et_2O to precipitate the 2-pyridylium products as pale yellow (M = Pd, 78.7%) or white (M = Pt, 88.7%) solids. The platinum derivative has a molar conductivity of 139.0 S cm^2 mol^{-1} in a 10^{-3} mol dm^{-3} acetone solution at 25°C.

Preparation of [Pd(dmtc){(1-CH_2CN)C_5H_4N-C^4}(PMe_3)]ClO_4. The 4-pyridyl complex **6** (0.10 g, 0.26 mmol) was dissolved in neat chloroacetonitrile (2 cm^3). After 36 h a solution of $NaClO_4 \cdot H_2O$ (0.5 mmol) in acetone (5 cm^3) was added. The mixture was stirred for 15 min and the solvents were removed to leave a solid residue which was worked up as described above (reaction of **4** with $ClCH_2CN$) to yield the yellow 4-pyridylium product (0.10 g, 73.9%; $\Lambda_M = 136.0$ S cm^2 mol^{-1} for a 10^{-3} mol dm^{-3} acetone solution at 25°C).

Preparation of [Pd(dmtc)(C_5H_5N-C^4)(PMe_3)]ClO_4. The 4-pyridyl complex **6** (0.25 g, 0.66 mmol) was dissolved in dichloromethane (*ca.* 30 cm^3) and treated with an excess of methanolic $HClO_4$ [3c] (molar ratio **6**/$HClO_4$ 1/3). After stirring for 10 min the *N*-protonated white product was recovered from the resulting solution as previously described for the isolation of 2-pyridylium derivatives [3] (0.29 g, 91.3%; $\Lambda_M = 147.0$ S cm^2 mol^{-1} for a 10^{-3} mol dm^{-3} acetone solution at 25°C).

3. *Analytical and spectral data*

The 2- and 4-pyridyl complexes **2**–**6** and their 2- and 4-pyridylium derivatives were characterized by elemental analysis, IR spectra in the solid (Table 3) and by ^1H and ^{31}P-{^1H} NMR spectra (Table 4).

The ^1H and ^{31}P NMR spectral changes on going from the 2-pyridyl complexes **1**–**4** to the corresponding 2-pyridylium derivatives agree with those observed and discussed in detail in previous papers [3,8]. For the 4-pyridyl compound **6**, a deshielding (0.3–0.6 ppm) of the pyridine protons is observed upon *N*-protonation and *N*-alkylation.

The IR spectra were recorded with Perkin–Elmer 1430 and 983 instruments using Nujol mulls and CsI windows in the range 4000–200 cm^{-1}. The NMR spectra were recorded with a Varian FT 80A spectrometer.

Acknowledgment

Financial support from MURST (Res. Fund 60%) is gratefully acknowledged.

References

1 (a) K. Isobe, E. Kai, Y. Nakamura, K. Nishimoto, T. Miwa, S. Kawaguchi, K. Kinoshita and K. Nakatsu, J. Am. Chem. Soc., 102 (1980) 2475; (b) K. Isobe, Y. Nakamura, T. Miwa and S. Kawaguchi, Bull. Chem. Soc. Jpn., 60 (1987) 149.

2 F.P. Fanizzi, G.J. Sunley, J.A. Wheeler, H. Adams, N.A. Bailey and P.M. Maitlis, Organometallics, 9 (1990) 131.

3 (a) B. Crociani, F. Di Bianca, A. Giovenco and A. Scrivanti, J. Organomet. Chem., 251 (1983) 393; (b) B. Crociani, F. Di Bianca, A. Giovenco and A. Berton, J. Organomet. Chem., 323 (1987) 123; (c) B. Crociani, F. Di Bianca, A. Giovenco, A. Berton and R. Bertani, J. Organomet. Chem., 361 (1989) 255.

4 B. Crociani, F. Di Bianca, P. Uguagliati and L. Canovese, Inorg. Chim. Acta, 176 (1990) 5.

5 B. Crociani, F. Di Bianca, F. Benetollo and G. Bombieri, J. Chem. Res., in press.

6 D.M. Smith, in Comprehensive Organic Chemistry, Vol. 4, Pergamon, Oxford, 1979, p. 3.

7 (a) G. Hofle, W. Steglich and H. Vorbruggen, Angew. Chem., Int. Ed. Engl., 17 (1978) 569; (b) E.F.V. Scriven, Chem. Soc. Rev., 12 (1983) 129.

8 B. Crociani, F. Di Bianca, A. Fontana and R. Bertani, J. Organomet. Chem., 425 (1992) 155.

9 (a) E.M. Arnett and R. Reich, J. Am. Chem. Soc., 102 (1980) 5892; (b) N.S. Isaacs, in Physical Organic Chemistry, Wiley, New York, 1987, Ch. 10.

10 A.A. Frost and R.G. Pearson, in Kinetics and Mechanism, Wiley, New York, 1961, 2nd ed., Ch. 2.

11 B.L. Murr, Jr and V.J. Shiner, Jr, J. Am. Chem. Soc., 84 (1962) 4672.

12 P. Uguagliati, R.A. Michelin, U. Belluco and R. Ros, J. Organomet. Chem., 169 (1979) 115.

13 A. Gustavo Gonzales and F. Pablos, Anal. Chim. Acta, 251 (1991) 321.