Influence of the Length of the Quaternisation Group on the Cyclometallation of $[M(2,4'\text{-R-bipy})Cl_3]$ ($M = Pt^{II}$ or Pd^{II}; 2,4'-R-bipy = 1'-alkyl-2,4'-bipyridinium)

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Solid-state thermolysis of the 1'-alkyl-2,4'-bipyridinium complexes $[M(2,4'\text{-R-bipy})Cl_3]$ ($M = Pd^{II}$ or Pt^{II}; R = H, Me, Bu, C_6H_{13}, C_8H_{17} or $C_{10}H_{21}$) gave the cyclometallated complexes $[M(2,4'\text{-R-bipy} - H)Cl_2]$ in quantitative yield. For M = Pd there is no clear variation of the cyclometallation temperature with the length of the alkyl chain, whereas the temperature of cycloplatination decreases steadily as the length of the alkyl chain increases. The extent of cyclometallation in aqueous solution depends on the solubility of the complex and decreases as the hydrophobicity of the chain increases.

Compounds which form metallacycles contain an electron-pair donor (commonly nitrogen or phosphorus) and a carbon σ or π donor to form a chelate. For direct cycloplatination or cyclopalladation, there is initial co-ordination of the metal to the donor atom, followed by ring closure with the aliphatic or aromatic carbon atom and loss of H^+.[1] The majority of the ring-closure steps that have been studied have utilised the more accessible $[Pd(HL)_2Cl_2]$ (HL = neutral ligand) complexes as there is a limited number of examples of the simplest precursor, $[Pd(HL)Cl_3]^-$. The presence of two ligands on the metal complicates mechanistic studies as there are various possibilities for the intermediate(s), *e.g.* $[\{Pd(HL)Cl(\mu\text{-}Cl)\}_2]$ or [Pd(HL)-L(Cl)], leading to the final product $[\{PdL(\mu\text{-}Cl)\}_2]$.[2,3]

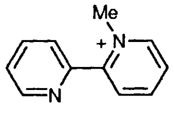
We have shown[4-8] that blocking one of the nitrogen atoms in 2,2'- or 2,4'-bipy* with an alkyl group does not prevent the resulting cations **I** and **II** from behaving as bidentate ligands since the chelating mode is achieved *via* N, $C^{3'}$ co-ordination to form the cyclometallated complexes. The precursor *N*-donor complex $[M(mbipy)X_3]$ ($M = Pt^{II}$ or Pd^{II}, mbipy = 2,2'-mbipy or 2,4'-mbipy) is isolable and cyclometallates in water.

The positive charge on the ligand determines the metal:anion ratio and leads to the following differences with respect to other cyclometallated systems: (*i*) the monodentate complexes $[M(mbipy)X_3]$ are neutral and easily prepared, whereas $[M(HL)X_3]^-$ ions are rare; the reaction of the ligand HL with $[MX_4]^{2-}$ gives $[M(HL)_2X_2]$ which may react further to give a cyclometallated complex; (*ii*) the cyclometallated complex $[M(mbipy - H)X_2]$ is a monomer, with the ligand being a zwitterion; generally, cyclometallated complexes of Pt^{II} and Pd^{II} are dinuclear with halide or acetate bridges (*e.g.* compounds **1** and **2** in Scheme 1 [7,9]); (*iii*) for a given ligand, cycloplatinated are less common than cyclopalladated compounds; cycloplatination of *N*-alkylated bipyridyl is readily achieved.[4,7]

The complexes $[M(2,4'\text{-mbipy})X_3]$ ($M = Pd^{II}$ or Pt^{II}) have been shown to cyclometallate in the solid state upon thermolysis.[11] In this paper we examine the influence of the length of the alkyl chain of $2,4'\text{-R-bipy}^+$ on the cyclometallation in solution and in the solid state.

Experimental

Infrared spectra (4000–200 cm^{-1}) were recorded as Nujol mulls on a Perkin Elmer 983 spectrophotometer; proton nuclear magnetic resonance spectra in $CDCl_3$ at 200.13 MHz on a Bruker 200 spectrometer at 25 °C. The chemical shifts were measured relative to $CDCl_3$ at δ 7.25. The elemental analyses were carried out by the Microanalytical Laboratory, Department of Chemistry of the National University of Singapore. The solid-state syntheses were performed in a Gallenkamp muffle furnace. Thermogravimetric analyses were carried out on a Stanton Redcroft TG1000 thermal analyser. Heating rates were 20 °C min^{-1} on samples of *ca.* 5 mg in dry air (25 cm^3 min^{-1}). The platinum and palladium salts were obtained from Johnson Matthey, 2,4'-bipy and the alkyl iodides from Aldrich.



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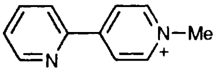

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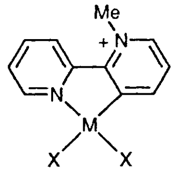

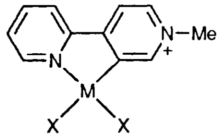

The salt [2,4'-mbipy]I was prepared by the method described previously.[7] The use of an excess of MeI (2 mol) reduces the reaction time to 2 h and the product crystallises from the hot solution in greater than 90% yield. There is no evidence for the formation of the dimethylated species. The complexes $[M(2,4'\text{-mbipy})Cl_3]$, $[M(2,4'\text{-mbipy} - H)Cl_2]$ (M = Pd or Pt)[7] and $[Pt(2,4'\text{-Hbipy})Cl_3]$ **3**[10] were prepared according to literature methods.

Preparations.—[2,4'-R-bipy]I (R = Bu, C_6H_{13}, C_8H_{17} *or* $C_{10}H_{21}$). The solvent and reaction times for the quaternisation depend on the alkyl group, as summarised in Table 1. In a typical synthesis, 2,4'-bipy (6.4 mmol) and the alkyl iodide (8.1 mmol) were used. When R = Bu the compound crystallises as bright yellow needles on cooling the reaction mixture. For R = C_6H_{13} or C_8H_{17}, diethyl ether was added to the reaction mixture to crystallise the product. For R = $C_{10}H_{21}$, diethyl ether was added to the reaction mixture pre-cooled in ice. The salts were isolated and washed several times with diethyl ether and stored in a desiccator.

The salt $[2,4'\text{-R-bipy}]NO_3$ was prepared by adding $AgNO_3$

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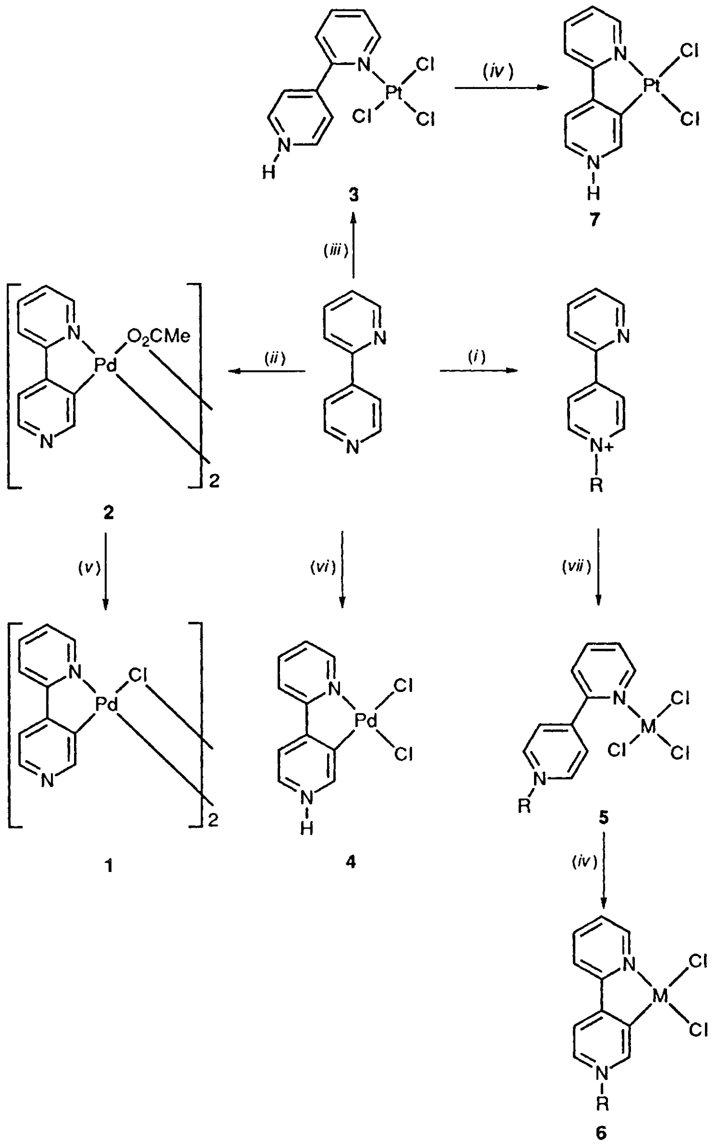
* Abbreviations used in this paper: 2,2'-bipy = 2,2'-bipyridine; 2,4'-bipy = 2,4'-bipyridine; 2,2'-mbipy = 1-methyl-2,2'-bipyridinium; 2,4'-mbipy = 1-methyl-2,4'-bipyridinium; 2,4'-R-bipy = 1'-alkyl-2,4'-bipyridinium; 2,2'-mbipy – H = 1-methyl-2,2'-bipyridin-3-ylium; 2,4'-R-bipy – H = 1'-alkyl-2,4'-bipyridin-3'-ylium.



Scheme 1 Reactions of 2,4'-bipy and quaternised 2,4'-bipy with platinum(II) and palladium(II) salts. R = Me, Bu, C_6H_{13}, C_8H_{17} or $C_{10}H_{21}$; M = Pd^{II} or Pt^{II}. (*i*) (*a*) RI, (*b*) $AgNO_3$; (*ii*) $[Pd(O_2CMe)_2]$,[7,9] $MeCO_2H$; (*iii*) $[PtCl_4]^{2-}$, HCl;[10] (*iv*) heat; (*v*) HCl;[7,9] (*vi*) $[PdCl_4]^{2-}$, HCl;[10] (*vii*) $[MCl_4]^{2-}$

Table 1 Preparation of [2,4'-R-bipy]I

R	Solvent[a]	Temperature of reaction	Reaction time	Melting point (°C)	Yield (%)
Me[b]	Ethanol	Reflux	6 h	190–192	70
Bu	Butan-1-ol	Reflux	4 h	130–140	95
C_6H_{13}	Nitrobenzene	Ambient	18 h	127–132	70
	Ethanol	Reflux	4 h		35
C_8H_{17}	Nitrobenzene	Ambient	2 d	74–76	70
$C_{10}H_{21}$	Iododecane	70 °C	7 min	42	45

[a] Compound crystallised from solution using diethyl ether, except R = Me. [b] Ref. 7, also see text.

in water to an equivalent amount of the iodide salt in acetone. The precipitate of silver iodide was removed by centrifugation. Any excess of silver ions remaining in the solution was removed with lithium chloride to prevent the formation of $Ag_2[MCl_4]$.

$[M(2,4'\text{-R-bipy})Cl_3]$ **5** (M = Pt^{II} *or* Pd^{II}). The conditions required for the preparation of $[M(2,4'\text{-R-bipy})Cl_3]$ depend on the length of the alkyl chain, as summarised in Table 4. The complexes were prepared by methods similar to those used to synthesise $[M(2,4'\text{-mbipy})Cl_3]$.[7] Typical quantities were 0.45 mmol of the ligand and 0.44 mmol of $M_2[MCl_4]$ in 15–20 cm^3 of the solvent.

For R = C_6H_{13}, C_8H_{17} or $C_{10}H_{21}$, a solution of the metal salt in acetone–water was added dropwise to the solution of $[2,4'\text{-R-bipy}]NO_3$ in acetone. The solution appears deep red (Pt^{II}) or orange-brown (Pd^{II}). If there was formation of a buff-pink (Pt^{II}) or fawn (Pd^{II}) precipitate during the addition (formation of $[2,4'\text{-R-bipy}]_2[MCl_4]$), acetone was added to redissolve the solid. The complex gradually separates out. The platinum complexes with longer alkyl chains separate as orange oils. They were separated from the mother-liquor and trituration with acetone or acetone–diethyl ether furnished the complexes as crystalline solids.

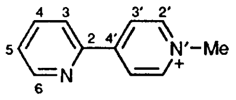
$[\mathrm{M}(2,4'\text{-R-bipy}-\mathrm{H})\mathrm{Cl}_2]$ **6** (M = $\mathrm{Pt^{II}}$ *or* $\mathrm{Pd^{II}}$). *Solid-state synthesis*. The complexes $[\mathrm{M}(2,4'\text{-R-bipy})\mathrm{Cl}_3]$ (100–300 mg) were placed in a muffle furnace, pre-equilibrated at the required temperature (Table 7), for 30 min and then cooled to room temperature in a desiccator. The change in colour is a good indication of cyclometallation (orange-brown to creamy yellow for Pd; bright yellow to orange-red for Pt) as is the weight loss which corresponds to 1 mol of HCl. The extent of the reaction was confirmed by infrared spectroscopy.

Solution synthesis. The complexes $[\mathrm{M}(2,4'\text{-R-bipy})\mathrm{Cl}_3]$ prepared *in situ* were heated either in water (short alkyl chains) or in water–acetone (longer alkyl chains), as in ref. 7. The solids were filtered off, washed with water and dried in a vacuum.

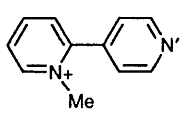
Results and Discussion

Ligands.—The [2,4'-R-bipy]I salts (R = Me, Bu, $\mathrm{C_6H_{13}}$, $\mathrm{C_8H_{17}}$ or $\mathrm{C_{10}H_{21}}$) were prepared by treating 2,4'-bipy with the corresponding alkyl iodide. The reaction conditions, melting points and microanalytical results are summarised in Tables 1 and 2. All the compounds crystallise as yellow needles. An increase in the length of the alkyl chain results in a decrease in the melting point of [2,4'-R-bipy]I [see Fig. 1(*a*)].

Monoquaternisation of 2,4'-bipy can lead to the formation of two isomers (*viz*. N'R **IIa** and NR **IIb**). We have previously



IIa



IIb

shown[7] that methylation of 2,4'-bipy produces only one isomer (*i.e.* **IIa**) and dimethylation does not occur even in the presence of an excess of iodomethane in ethanol. This is consistent with other studies[12] which demonstrate that azaheterocycles preferentially undergo quaternisation at the least-hindered nitrogen atom.

The ^{1}H NMR spectra of the [2,4'-R-bipy]I salts are summarised in Table 3. The spectra are practically identical for R larger than Me, consisting of two doublets for the 4' ring and four multiplets for the 2 ring. Quaternisation results in deshielding of the aromatic protons.[13] The protons 2' and 3' are considerably more deshielded than those in the other ring, indicating that the site of alkylation is the N'.

$[\mathrm{M}(2,4'\text{-R-bipy})\mathrm{Cl}_3]$.—The $[\mathrm{M}(2,4'\text{-R-bipy})\mathrm{Cl}_3]$ complexes **5** (M = Pt or Pd; R = alkyl) were prepared by the reaction of $[2,4'\text{-R-bipy}]\mathrm{NO}_3$ with $\mathrm{K_2[MCl_4]}$ in acetone–water. For R = $\mathrm{C_6H_{13}}$, $\mathrm{C_8H_{17}}$ or $\mathrm{C_{10}H_{21}}$, the metal salt in water was added to the ligand in a large volume of acetone to prevent precipitation of the salt $[2,4'\text{-R-bipy}]_2[\mathrm{MCl_4}]$. For the ligands with the longer alkyl chains, the platinum complexes separate as an orange oily mass which was triturated with neat acetone or acetone–diethyl ether to obtain the complexes in crystalline form. Table 4 summarises the reaction conditions. The complexes crystallise as bright yellow powders (platinum) or orange-brown needles (palladium). Table 5 summarises the microanalytical results.

The complexes with a short alkyl chain (R = Me or Bu) are practically insoluble in all solvents. As the length of R is increased the solubility in organic solvents increases. However, the solubility is insufficient for NMR spectroscopy except in dimethyl sulfoxide, where the spectra and conductance measurements indicate solvolysis of the ligand.[14]

The infrared spectra of the complexes are, as would be expected, practically identical and they are essentially the same as that of $[\mathrm{Pt}(2,4'\text{-mbipy})\mathrm{Cl}_3]$ which has been illustrated previously[7] (see also Fig. 2). The salient features are (*a*) a strong band at 1640 cm^{-1} (ring-stretching mode of a *N*-alkylated pyridine ring), (*b*) a medium-intensity band at 1595–1600 cm^{-1} indicative of complex formation *via* the pyridine nitrogen atom[15] and (*c*) the M–Cl stretching bands in the region 340–320 cm^{-1}, consistent with a C_{2v} trichloro complex.[16] The complex $[\mathrm{Pt}(2,4'\text{-mbipy})\mathrm{Cl}_3]$ has been characterised by a crystal structure determination.[7]

Table 2 Elemental analyses* (%) of [2,4'-R-bipy]I

R	C	H	N
Me	44.2 (44.3)	3.7 (3.7)	9.4 (9.4)
Bu	49.1 (49.4)	5.0 (5.0)	8.2 (8.2)
$\mathrm{C_6H_{13}}$	52.3 (52.2)	5.8 (5.8)	7.6 (7.6)
$\mathrm{C_8H_{17}}$	54.5 (54.6)	6.3 (6.4)	7.1 (7.1)
$\mathrm{C_{10}H_{21}}$	56.4 (56.6)	6.9 (6.9)	6.6 (6.6)

* Calculated values in parentheses.

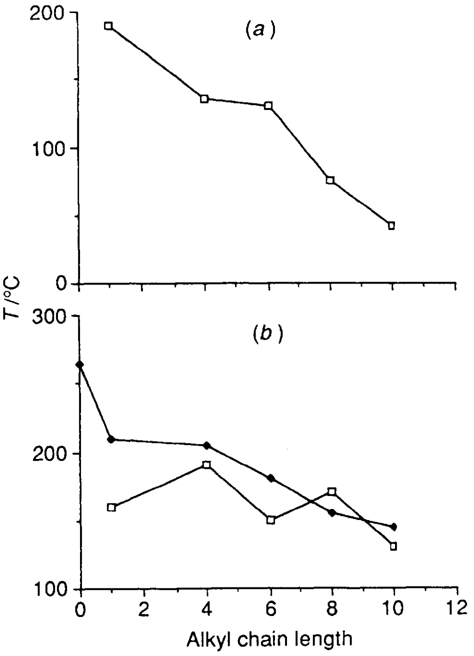


Fig. 1 (*a*) Melting point of [2,4'-R-bipy]I as a function of the length of the alkyl chain R. (*b*) Cyclometallation temperature of the complexes $[\mathrm{M}(2,4'\text{-R-bipy})\mathrm{Cl}_3]$ as a function of the length of the alkyl chain R (M = Pd, □; Pt, ◆)

$[\mathrm{M}(2,4'\text{-R-bipy}-\mathrm{H})\mathrm{Cl}_2]$.—*In solution*. The complexes $[\mathrm{M}(2,4'\text{-R-bipy})\mathrm{Cl}_3]$ (R = alkyl group) were heated in water under reflux. When R = Me or Bu this affords the cyclometallated complexes $[\mathrm{M}(2,4'\text{-R-bipy} - \mathrm{H})\mathrm{Cl}_2]$ **6**. The palladium(II) complexes are fawn-yellow while the platinum(II) complexes are orange-red. The reaction times for cyclopalladation of the methyl and butyl compounds are similar ($\approx$10 min), whereas cycloplatination of the butyl compound takes somewhat longer than for the methyl compound (10 as compared to 6 h).

The palladium complexes where R = $\mathrm{C_6H_{13}}$, $\mathrm{C_8H_{17}}$ or $\mathrm{C_{10}H_{21}}$ cyclometallate completely only in dilute solution. By contrast, cycloplatination of the complexes with these ligands is incomplete (*ca.* 30% conversion) after prolonged heating in water (15–24 h) even in dilute solution. Complete conversion could not be achieved for the platinum complexes with the longer alkyl chains.

Infrared spectroscopy was used to follow the extent of the reaction. The disappearance of the band at 1640 cm^{-1}, which is present in the spectrum of $[\mathrm{M}(2,4'\text{-R-bipy})\mathrm{Cl}_3]$ but not in that of the cyclometallated complex, indicates the extent of the reaction (see Fig. 2). The metal content obtained from

Table 3 Proton NMR spectral data[a] for [2,4'-R-bipy]I

R	H^3	H^4	H^5	H^6	$H^{2'}$	$H^{3'}$	NCH_2
—	≈7.80[b]	≈7.80[b]	7.31	8.74	8.72	7.89	—
Me	8.18	7.96	7.50	8.79	9.28	8.75	4.71[c]
Bu	8.18	7.93	7.48	≈8.78	9.41	8.76	4.93
C_6H_{13}	8.21	7.94	7.48	≈8.78	9.40	8.78	4.93
C_8H_{17}	8.21	7.93	7.47	≈8.78	9.39	8.77	4.93
$C_{10}H_{21}$	8.21	7.93	7.47	≈8.78	9.39	8.77	4.93

[a] In $CDCl_3$ solution. [b] Overlapping resonances. [c] NCH_3.

Table 4 Preparation of $[M(2,4'\text{-R-bipy})Cl_3]$

R	M*	Solvent	Reaction time, *t*/h (temperature)	Yield (%)	Remarks
Me	Pd	Water	1 (ambient)	80	Ref. 7
	Pt	Water	2 (60 °C)	80	Ref. 7
Bu	Pd	Water	2 (ambient)	75	
	Pt	Water	24 (ambient) 1 (60 °C)	70	
C_6H_{13}	Pd	Acetone–water	5 (ambient)	80	
	Pt	Acetone–water	24 (ambient)	80	Oily mass, triturated with acetone
C_8H_{17}	Pd	Acetone	15 (ambient)	65	
	Pt	Acetone–water	24 (ambient)	65	Initially brown droplets formed (discarded)
$C_{10}H_{21}$	Pd	Acetone–water	36 (ambient)	50	
	Pt	Acetone–water	2 (60 °C) 15 (ambient)	45	Yellow-orange oil, triturated alternatively with acetone and ether

* Metal used as $K_2[MCl_4]$ in water and as $Li_2[MCl_4]$ in water–acetone.

Table 5 Elemental analyses[a] (%) of $[M(2,4'\text{-R-bipy})Cl_3]$

M	R	C	H	N
Pd[b]	Me	31.4 (31.5)	3.5 (3.6)	6.5 (6.7)
Pt[b]		26.1 (26.0)	2.7 (3.0)	5.6 (5.5)
Pd	Bu	39.3 (39.5)	3.9 (4.0)	6.5 (6.6)
Pt		32.5 (32.7)	3.3 (3.3)	5.4 (5.4)
Pd[c]	C_6H_{13}	41.2 (41.5)	4.8 (4.8)	5.8 (6.1)
Pt[d]		35.0 (35.4)	4.1 (3.9)	5.0 (5.2)
Pd	C_8H_{17}	44.4 (44.8)	5.1 (5.2)	5.7 (5.8)
Pt		37.5 (37.9)	4.2 (4.4)	4.9 (4.9)
Pd	$C_{10}H_{21}$	46.7 (47.1)	5.6 (5.7)	5.4 (5.5)
Pt		39.7 (40.1)	4.8 (4.9)	4.7 (4.7)

[a] Calculated values in parentheses. [b] Two molecules of water of crystallisation. [c] 0.5 molecules of water of crystallisation; Cl 23.1 (23.0) %. [d] Cl 19.4 (19.6) %.

$$2[Pd(2,2'\text{-mbipy})Cl_3] \xrightarrow[\text{heat}]{\text{water}} trans\text{-}[Pd(2,2'\text{-mbipy})_2Cl_2]^{2+}$$

$$+ [PdCl_4]^{2-} \xrightarrow{\text{heat}} [Pd(2,2'\text{-mbipy}-H)Cl_2] + HCl$$

Scheme 2

thermogravimetric analysis also provides a useful indication of the extent of cyclometallation. The complexes $[M(2,4'\text{-R-bipy})Cl_3]$ and $[M(2,4'\text{-R-bipy} - H)Cl_2]$ have similar solubilities and cannot be separated by recrystallisation.

We have previously shown[6,17] that cyclometallation of $[Pd(2,2'\text{-mbipy})Cl_3]$ is not a direct reaction as it might appear. Instead it is a cyclic process involving a rearrangement to the bis compound, *trans*-$[Pd(2,2'\text{-mbipy})_2Cl_2]^{2+}$ (Scheme 2), which cyclometallates with elimination of one $[2,2'\text{-mbipy}]^+$ ligand which reforms the bis complex from $[PdCl_4]^{2-}$. It is likely that cyclopalladation of the $[2,4'\text{-R-bipy}]^+$ complexes follows a similar path. In that case a long hydrophobic chain on the ligand will reduce the solubility of the complexes in water which in turn will slow the rate of conversion into the cyclometallated product.

In the solid state. The complexes $[M(2,4'\text{-R-bipy})Cl_3]$ ($M = Pd^{II}$, R = alkyl group; $M = Pt^{II}$, R = H or alkyl group), when heated as solids, undergo cyclometallation with the loss of 1 mol of HCl to yield $[M(2,4'\text{-R-bipy}-H)Cl_2]$ quantitatively. This was observed with all the ligands studied and applies to the platinum as well as the palladium compounds.

The results of thermogravimetric analysis (TGA) of $[M(2,4'\text{-R-bipy})Cl_3]$ are summarised in Table 6. The first weight loss (after the loss of any water of crystallisation) corresponds to 1 mol of HCl. Subsequent examination by IR spectroscopy of the residue revealed that the product is the cyclometallated compound $[M(2,4'\text{-R-bipy}-H)Cl_2]$. For R = Me or Bu, the decomposition pattern of the residue matches that of $[M(2,4'\text{-R-bipy}-H)Cl_2]$ prepared in solution. A typical thermogram $\{[Pd(2,4'\text{-R-bipy})Cl_3]\cdot 0.5H_2O$ where $R = C_6H_{13}\}$ is illustrated in Fig. 3. The first two steps correspond to the loss of water and HCl respectively followed by decomposition at high temperature to the metal.

The palladium complexes cyclometallate as solids at a lower temperature than the platinum analogues in the range 130–190 °C, but there is no obvious trend between the cyclometallation temperature and the length of the alkyl chain [see Fig. 1(*b*)]. For the platinum complexes, increasing the length of the alkyl chain reduces the temperature at which cyclometallation occurs.

Examination of the thermal behaviour of the complexes using a hot-stage microscope shows that (except for $R = C_{10}H_{21}$) the compounds do not melt. At the conversion temperature (Table 7) the platinum complexes change from bright yellow $\{[Pt(2,4'\text{-R-bipy})Cl_3]\}$ to red-orange $\{[Pt(2,4'\text{-R-bipy} - H)Cl_2]\}$, whereas the palladium complexes change from orange-brown $\{[Pd(2,4'\text{-R-bipy})Cl_3]\}$ to creamy yellow $\{[Pd(2,4'\text{-R-bipy} - H)Cl_2]\}$. Prior to cyclometallation at 120–140 °C, $[Pt(2,4'\text{-R-bipy})Cl_3]$ ($R = C_{10}H_{21}$) melts at 120 °C to a red oil which only solidifies on cooling.

The $[M(2,4'\text{-R-bipy} - H)Cl_2]$ complexes were prepared on a preparative scale by heating $[M(2,4'\text{-R-bipy})Cl_3]$ as solids for 30 min in a muffle furnace. The latter was set at the temperature (Table 7) at which the rate of elimination of HCl is highest as indicated by differential TGA. Examination of the product using IR spectroscopy revealed that cyclometallation was complete without any decomposition. The temperature of the

Table 6 Thermal decomposition of [M(2,4′-R-bipy)Cl$_3$]

Complex					
M	R	T^a/°C	% Loss	ΔM^b	Species lost (ΔM theoretical)^c
Pt	H	220	9	41	HCl (36.5)
		295	7	32	HCl (36.5)
		404	40	183	Ligand + Cl (191)
Pd	Me	50	9	39	2H$_2$O (36)
		160	7	31	HCl (36.5)
		360	16	67	2Cl (71)
		390	41	172	Ligand (170)
Pt	Me	60	4	19	H$_2$O (18)
		180	9	44	HCl (36.5)
		340	14	69	
		420	36	178	Ligand + 2Cl (241)
Pd	Bu	180	6	25	HCl (36.5)
		300	40	172	Ligand +
		456	21	89	2Cl (284)
Pt	Bu	186	8	39	HCl (36.5)
		279	17	85	2Cl +
		456	37	190	Ligand (284)
Pd	C$_6$H$_{13}$	45	2	11	0.5H$_2$O (9)
		145	7	34	HCl (36.5)
		310	46	213	Ligand +
		419	18	81	2Cl (312)
Pt	C$_6$H$_{13}$	145	6	33	HCl (36.5)
		258	17	92	2Cl +
		409	39	211	Ligand (312)
Pd	C$_8$H$_{17}$	145	6	29	HCl (36.5)
		248	45	217	Ligand +
		438	20	98	2Cl (340)
Pt	C$_8$H$_{17}$	133	6	34	HCl (36.5)
		279	23	131	2Cl +
		447	38	217	Ligand (340)
Pd	C$_{10}$H$_{21}$	107	6	31	HCl (36.5)
		269	51	260	Ligand +
		466	17	87	2Cl (368)
Pt	C$_{10}$H$_{21}$	120	6	36	HCl (36.5)
		204	25	150	2Cl +
		427	37	221	Ligand (368)

[a] Temperature at which weight loss commences. [b] Weight loss, % loss × molecular weight. [c] The steps for the loss of the ligand and the 2Cl are close and often merge with each other.

Table 7 Thermal conversion of [M(2,4′-R-bipy)Cl$_3$] into [M(2,4′-R-bipy − H)Cl$_2$]

		T/°C		
M	R	Conversion^a	Synthesis^b	HCl Loss (TGA)^c
Pd	Me	170	180	160
	Bu	200	195	192
	C$_6$H$_{13}$	150	155	152
	C$_8$H$_{17}$	170	170	169
	C$_{10}$H$_{21}$	130	135	127
Pt	H	260	270	264
	Me	200–210	200	210
	Bu	200–220	220	204
	C$_6$H$_{13}$	180	185	181
	C$_8$H$_{17}$	168	165	157
	C$_{10}$H$_{21}$	120	145	145

[a] Melting point apparatus. [b] Muffle furnace. [c] Peak temperature (differential TGA).

Table 8 Elemental analyses[a] (%) of [M(2,4′-R-bipy − H)Cl$_2$]

M	R	C	H	N
Pd	Me	37.8 (38.0)	2.9 (2.9)	8.0 (8.1)
Pt		30.0 (30.3)	2.3 (2.3)	6.4 (6.4)
Pd^b	Bu	43.0 (43.2)	4.0 (4.1)	7.0 (7.2)
Pt		35.0 (35.2)	3.3 (3.4)	5.8 (5.9)
Pd^c	C$_6$H$_{13}$	45.6 (46.0)	4.9 (4.8)	6.5 (6.7)
Pt		37.7 (38.0)	4.0 (4.0)	5.4 (5.5)
Pd	C$_8$H$_{17}$	48.2 (48.5)	5.4 (5.4)	6.2 (6.3)
Pt		40.2 (40.5)	4.3 (4.5)	5.2 (5.2)
Pd	C$_{10}$H$_{21}$	50.3 (50.7)	5.9 (6.0)	5.9 (5.9)
Pt		42.4 (42.7)	4.9 (5.0)	4.9 (5.0)

[a] Calculated values in parentheses. [b] Cl 18.3 (18.2)%. [c] Cl 17.2 (17.0)%.

reaction depends on the length of the alkyl group. This technique was successful for all the compounds in the series to give analytically pure cyclometallated compounds (Table 8).

The infrared spectra of the cyclometallated complexes are practically identical and essentially the same as that of [Pt(2,4′-mbipy − H)Cl$_2$] which has been illustrated previously[7] (see also Fig. 2). The salient features are (*a*) the absence of the band at 1640 cm^{-1}, (*b*) a strong band at 1600 cm^{-1}, (*c*) changes in the C–H out-of-plane deformation region (600–900 cm^{-1}) and (*d*) the M–Cl stretching bands at 330 and 260 cm^{-1}, consistent with *cis*-dichloro ligands *trans* to a *C*-donor and an *N*-donor ligand, as confirmed by the crystal structure determination of [Pt(2,4′-mbipy − H)Cl$_2$].[7]

Discussion

As the alkyl group on the 2,4′-bipyridinium ligand is made longer, cyclometallation of the trichloro complexes as solids becomes progressively easier, whereas cyclometallation in water becomes more difficult. Since the cyclometallation temperature is higher than the boiling point of water, the water is not merely providing the thermal medium for the cyclometallation, but

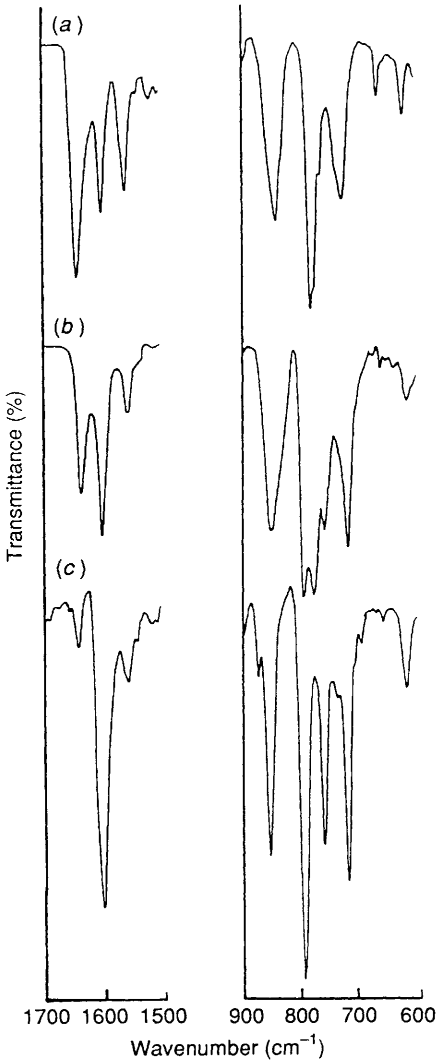


Fig. 2 Diagnostic changes in the IR spectrum on cyclometallation of (*a*) solid [Pt(2,4′-R-bipy)Cl$_3$] (R = C_6H_{13}), (*b*) when heated in water (partially cyclometallated) and (*c*) heated as a solid (completely cyclometallated)

has a role to play as the solvent. It is most likely that the mechanisms of cyclometallation in solution and in the solid state are different.

It is probable that these reactions of the palladium complexes in solution follow the mechanism of the [2,2′-mbipy]$^+$ complex, *i.e.* there is a prior rearrangement of the trichloro complex to the bis complex, *trans*-[Pd(2,4′-R-bipy)$_2$Cl$_2$]$^{2+}$, followed by cyclometallation (Scheme 2). We have results[17] which indicate that the mechanism of cycloplatination is different in that it occurs without any rearrangement. There is no evidence for the formation of *trans*-[Pt(2,4′-R-bipy)$_2$Cl$_2$]$^{2+}$. Perhaps this is related to a higher Pt–N bond strength or the preference of platinum(II) to form *cis* complexes. The platinum(II) complexes where R = H, C_6H_{13}, C_8H_{17} or $C_{10}H_{21}$ could only be cyclometallated by heating [Pt(2,4′-R-bipy)Cl$_3$] as solids. For the longer alkyl chain complexes, this is due in part to a lack of solubility but also to the different mechanism of cyclometallation.

The crystal structures of [Pt(2,4′-mbipy)Cl$_3$][7] and *trans*-[Pd(2,2′-mbipy)$_2$Cl$_2$]$^{2+}$ (ref. 17) indicate that the aromatic rings are perpendicular to the co-ordination plane of the metal such that the proton that is eliminated in the cyclometallation step is situated close to the metal, perhaps partaking in an agostic type of interaction. In the solid-state these complexes have the correct orientation for a thermal reaction.

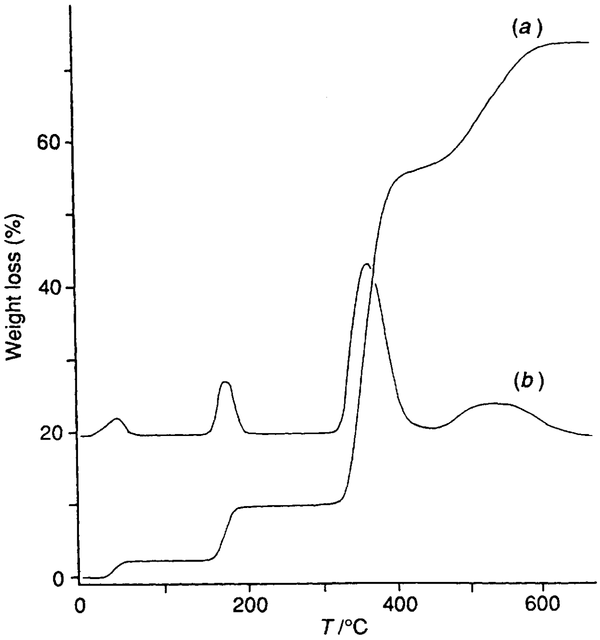


Fig. 3 The TGA (*a*) and differential TGA (*b*) thermograms of [Pd(2,4′-R-bipy)Cl$_3$]·0.5H_2O (R = C_6H_{13}) in air. Heating rate 20 °C min^{-1}

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References

1 O. Omae, *Chem. Rev.*, 1979, **79**, 287; *Coord. Chem. Rev.*, 1979, **28**, 97; E. C. Constable, *Polyhedron*, 1984, **3**, 1037; F. R. Hartley, *Coord. Chem. Rev.*, 1985, **67**, 1; V. V. Dunina, O. A. Zalevskaya and V. M. Potapov, *Russ. Chem. Rev.*, 1988, **57**, 50; G. R. Newkome, W. E. Puckett, V. K. Gupta and G. E. Kiefer, *Chem. Rev.*, 1986, **86**, 451.
2 A. K. Yatsimirskii, *Russ. J. Inorg. Chem.*, 1979, **24**, 1505.
3 N. Barr and S. F. Dyke, *J. Organomet. Chem.*, 1983, **223**, 243.
4 S. Dholakia, R. D. Gillard and F. L. Wimmer, *Inorg. Chim. Acta*, 1983, **69**, 179.
5 F. L. Wimmer and S. Wimmer, *Transition Met. Chem.*, 1985, **10**, 238.
6 F. L. Wimmer and S. Wimmer, *Polyhedron*, 1985, **4**, 1665.
7 P. Castan, F. Dahan, S. Wimmer and F. L. Wimmer, *J. Chem. Soc., Dalton Trans.*, 1990, 2971.
8 P. S. Braterman, J.-I. Song, F. L. Wimmer, S. Wimmer, W. Kaim, A. Klein and R. D. Peacock, *Inorg. Chem.*, 1992, **31**, 5084.
9 E. C. Constable, *J. Chem. Soc., Dalton Trans.*, 1985, 1719.
10 S. Wimmer, manuscript in preparation.
11 P. Castan, B. Labiad, D. Villemin, F. L. Wimmer and S. Wimmer, *J. Organomet. Chem.*, in the press.
12 M. Jastrzebska-Glapa, J. Mlochowski and W. Sliwa, *Pol. J. Chem.*, 1979, **53**, 811; J. Mlochowski and W. Sliwa, *Ann. Soc. Chim. Polonorum*, 1974, **48**, 1469.
13 J. M. Lehn, J. P. Sauvage, J. Simon, R. Ziessel, C. Piccinni-Leopardi, G. Germain, J. P. Declercq and M. Van Meerssche, *Nouv. J. Chim.*, 1983, **7**, 413; I. C. Calder, T. McL. Spotswood and C. I. Tanzer, *Aust. J. Chem.*, 1967, **20**, 1195; R. F. M. White and H. William, in *Physical Methods in Heterocyclic Chemistry*, ed. A. R. Katrinsky, Academic Press, New York, 1971, vol. 4, p. 121.
14 F. L. Wimmer, S. Wimmer, T. G. Appleton and P. Castan, 5th International Conference on the Chemistry of the Platinum Group Metals, St. Andrews, July 1993.
15 F. L. Wimmer, *Inorg. Chim. Acta*, 1987, **130**, 259.
16 D. A. Duddell, P. L. Goggin, R. J. Goodfellow, M. G. Norton and J. G. Smith, *J. Chem. Soc. A*, 1970, 545; P. L. Goggin, R. J. Goodfellow and F. J. S. Reed, *J. Chem. Soc., Dalton Trans.*, 1972, 1298; D. M. Adams and R. E. Christopher, *J. Chem. Soc., Dalton Trans.*, 1973, 2298.
17 F. L. Wimmer, S. Wimmer, R. D. Gillard, M. R. Snow, E. Horn and E. R. T. Tiekink, 5th International Conference on the Chemistry of the Platinum Group Metals, St. Andrews, July 1993.

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