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Solid-state cyclometallation of the 1-methyl-2,4′-bipyridinium complexes of palladium^{II} and platinum^{II}

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Abstract

The complexes $[M(2,4'\text{-bpyMe})X_3] \cdot nH_2O$ (M = Pd, Pt; X = Cl, Br; 2,4′-bpyMe = 1-methyl-2,4′-bipyridinium, n = 0, 1, 2) cyclometallate with elimination of HX to give $[M(2,4'\text{bpyMe-H})X_2]$ in the solid state on heating or upon microwave irradiation. Thermal analysis (TGA, DTA, DSC) in conjunction with infrared spectroscopy indicates that these complexes cyclometallate in the temperature range 160–260°C. The ease of cyclometallation is Pd > Pt and Cl > Br.

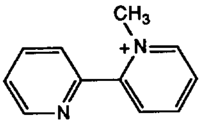
The time of cyclometallation with microwave irradiation depends on the mode of irradiation.

Key words: Platinum (II); Palladium (II); Bypiridine; Cyclometallation; Solid-state; Microwave heating

1. Introduction

The cyclometallation of an organic ligand depends on the nature of the ligand, the metallating agent, the solvent, the presence of a base and the temperature of the reaction [1]. It is generally assumed that the initial stage in direct cyclometallation is the coordination of the donor atom of the ligand to the metal, followed by metallation on the aliphatic or aromatic atom to form a chelate. Although the structure of the intermediate before ring closure is uncertain, it would naturally depend on the ligand (HL) and the metallating agent [2]. There are a very few examples [3] of the isolation of the simplest derivative, $[M(HL)X_3]^-$ (M = Pd, Pt; X = anion) which cyclometallates with the evolution of HX. Due to the complexity of orthometallation, very little direct comparison has been made between cycloplatination and cyclopalladation.

We have been studying [4–9] the chemistry of the bipyridine cations 1-methyl-2,2′-bipyridinium (**1**) and 1′-methyl-2,4′-bipyridinium (**2**)



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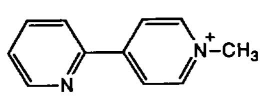

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which react with $[MX_4]^{2-}$ (M = Pd, Pt) to form the zwitterions $[M(L)X_3]$ (**3** and **4**; X = Cl, Br) [4,6]. The following abbreviations are used: 2,2′-bpyMe = 1-methyl-2,2′-bipyridinium, 2,4′-bpyMe = 1′-methyl-2,4′-bipyridinium. TGA = thermogravimetric analysis; DTA = differential thermal analysis; DCS = differential scanning calorimetry.

We have previously shown [4,6,8] that both $[M(2,2'\text{-bpyMe})X_3]$ and $[M(2,4'\text{-bpyMe})X_3]$ (M = Pt, Pd; X = halide), when heated in water, form the cyclometallated complexes, $[M(L\text{-}H)X_2]$ (**5** and **6**) in quantitative yield with the evolution of HX. Due to the zwitterionic

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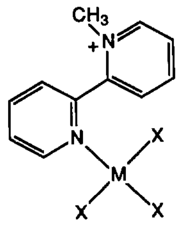

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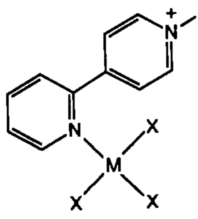

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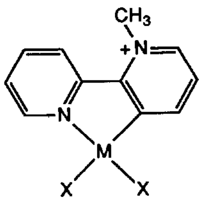

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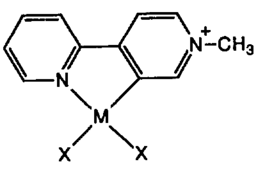

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TABLE 1. Reaction Times for the Cyclometallation of $[M(L)X_3]$

M	Ligand	X	Colour of $[M(L)X_3]$	Time [a] (h)	Colour of $[M(L-H)X_2]$
Pt	2,2′-bpyMe	Cl	yellow	36	orange
Pd	2,2′-bpyMe	Cl	orange brown	11	fawn yellow
Pd	2,2′-bpyMe	Br	orange red	20	orange
Pt	2,4′-bpyMe	Cl	yellow	6	orange
Pd	2,4′-bpyMe	Cl	orange	2 min	bright yellow
Pd	2,4′-bpyMe	Br	red	2	brown yellow

[a] In water under reflux. These are maximum times for a moderate amount of water. The reaction time can be reduced by using a larger amount of water, since this increases the quantity of complex in solution.

character of the metallated ligand, the complexes **5** and **6** are monomers rather than the usual halo-bridged dimers common for other orthometallated complexes.

The reaction time for cyclometallation in water (Table 1) depends on the metal, the ligand and the halide. Thus, the ease of cyclometallation is Pd > Pt, $(2,4'\text{-bpyMe})^+ > (2,2'\text{-bpyMe})^+$, $Cl^- > Br^-$ [4,6,8]. The shorter reaction times for the Pd^{II} complexes reflect

TABLE 2. Summary of the Thermal Analysis Results

Complex	Thermogravimetric analysis [a]						DTA [b]	DSC [c]
	ΔT [d] (°C)	T_{max} [e] (°C)	Residue	Loss in weight (%)		Species lost	T_{max} [e] (°C)	T_{max} [e] (°C)
				Found	Calc.			
$[Pd(2,4'\text{-bpyMe})Cl_3]\cdot 2H_2O$	40–160	110	$[Pd(2,4'\text{-bpyMe})Cl_3]$	8.3	8.6	$2H_2O$	110 (−)	broad (−)
	160–170	160	$[Pd(2,4'\text{-bpyMe-H})Cl_2]$	8.4	8.6	HCl	167 (−)	162 (−)
	360–395	385		16.7	16.9	2Cl + ligand		
	395–420	404	Pd/PdO	40.5	40.5			
$[Pt(2,4'\text{-bpyMe})Cl_3]\cdot H_2O$	50–145	112	$[Pt(2,4'\text{-bpyMe})Cl_3]$	3.8	3.7	H_2O	115 (−)	125 (−)
	160–260	210	$[Pt(2,4'\text{-bpyMe-H})Cl_2]$	7.2	7.4	HCl	216 (−)	220 (−)
	340–410	385		14.1	14.5	2Cl + ligand	384 (−)	
	420–460	444	Pt	35.3	34.9			
$[Pd(2,4'\text{-bpyMe})Br_3]$	200–250	232	$[Pd(2,4'\text{-bpyMe-H})Br_2]$	14.9	15.5	HBr	236 (−)	233 (−)
	360–430	405		29.8	30.9	2Br + ligand		
	440–600	544	Pd/PdO	34.1	33.0			
$[Pd(2,4'\text{-bpyMe-H})Cl_2]$	360–410	397	Pd/PdO	71.0	69.7	2Cl + ligand		
$[Pt(2,4'\text{-bpyMe-H})Cl_2]$	360–420	385		16.0	16.3	2Cl + ligand		
	430–480	442	Pt	39.5	39.0			
$[Pd(2,4'\text{-bpyMe-H})Br_2]$	375–430	411		41.9 [f]	36.7 [g]	2Br + ligand		
	445–565	478						
		540	Pd/PdO	34.8 [f]	39.0 [g]			

[a] The palladium complexes decompose to mainly Pd metal which rapidly oxidises to PdO, which in turn decomposes to the metal at 820°–840° (T_{max} = 840°). The weight losses are calculated relative to the metal.

[b] DTA, differential thermal analysis, (−) = endotherm.

[c] DSC, differential scanning calorimetry, (−) = endotherm.

[d] Temperature range of the decomposition.

[e] Peak temperature.

[f] Total found = 76.7% g. Total calculated for 2Br + ligand = 75.7%.

the general higher reactivity of Pd^{II} compared to Pt^{II}. The complexes of (2,2′bpyMe)$^+$ undergo cyclometallation less readily probably due to the obstruction to ring closure caused by the N-methyl group.

Recently, there has been considerable interest in the application of microwave irradiation to chemical synthesis [10]. Most of the reports have concentrated on reactions in solution, but there have been a few solid-state studies [10,11].

We present here our results on the cyclometallation of [M(2,4′-BpyMe)X$_3$] in the solid state, using both thermal and microwave activation.

2. Results

[Pd(2,4′-bpyMe)Cl$_3$]·2H$_2$O cyclometallates in the solid-state on heating in an oven at 140°C for about 1 h. At the same temperature [Pt(2,4′-bpyMe)Cl$_3$]·H$_2$O only loses the water of crystallisation and heating to 200°C for 1 h is required to effect cyclometallation. [Pd(2,4′-bpyMe)Br$_3$] is less reactive still and shows no reaction at 200°C.

IR spectroscopy is an excellent technique for monitoring these reactions as characteristic changes occur in the aromatic and metal–halogen stretching regions of the spectrum. These changes have been described previously together with figures of the relevant spectra [4,6]. The major changes on cyclometallation are: the disappearance of the band at 1640 cm^{-1} (ring stretching mode); the disappearance of the bands at 855 and 785 cm^{-1} (C–H out of plane deformation modes); and modification of the M–Cl stretching modes at 340–320 cm^{-1} and the appearance of a new M–Cl band at *ca.* 270–250 cm^{-1} (M–Cl bond *trans* to the newly formed M–C bond).

The thermal decomposition of [M(2,4′-bpyMe)X$_3$]·nH$_2$O (M = Pd, Pt; X = Cl, Br; n = 0, 1, 2) **4** was investigated by thermogravimetric analysis, differential thermal analysis and differential scanning calorimetry and the results are summarised in Table 2.

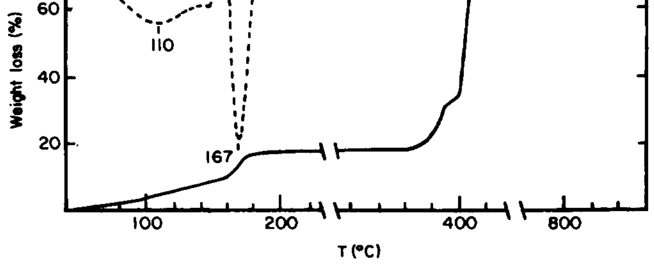


Fig. 1. Thermogravimetric and differential thermal analysis (inset, endotherms are negative) curves for [Pd(2,4′-bpyMe)Cl$_3$]·2H$_2$O.

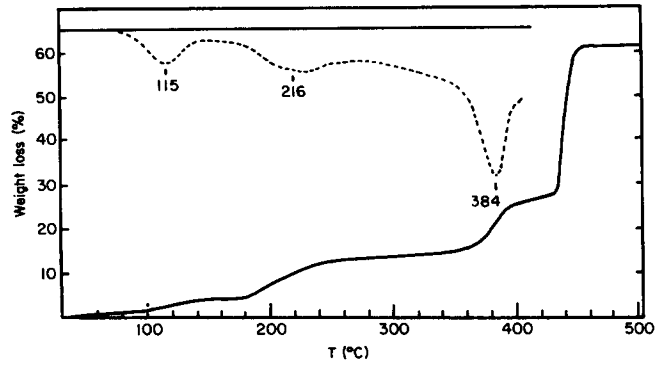


Fig. 2. Thermogravimetric and differential thermal analysis (inset, endotherms are negative) curves for [Pt(2,4′-bpyMe)Cl$_3$]·H$_2$O.

The first weight loss for [Pd(2,4′-bpyMe)Cl$_3$]·2H$_2$O (Fig. 1) is a broad step from ambient temperature to 160°C which corresponds to the loss of water of crystallisation. This is followed closely by the loss of one mole of HCl with concomitant cyclometallation to give [Pd(2,4′-bpyMe–H)Cl$_2$]. Further heating shows two close-spaced weight loss steps (360–420°C) in which chlorine and the ligand (2,4′-bpyMe–H) are lost to leave palladium metal. The metal rapidly oxidises under these conditions and redecomposition to the metal does not occur until *ca.* 820°C.

Differential thermal analysis shows endotherms at 110° and 167°C which correspond to the peak temperatures in the TGA at 110° and 163°C respectively. Differential scanning calorimetry shows a broad endotherm corresponding to the dehydration and a sharp endotherm corresponding to the cyclometallation step.

The loss of the water of crystallisation and of HCl are two separate steps. The infrared spectrum of the solid after heating to 150°C (TGA furnace) showed only dehydration, while the spectrum after heating to 200°C (the colour had changed from golden yellow-orange to bright yellow) indicated that cyclometallation was complete. The TGA curve for this solid was the same as that of authentic [Pd(2,4′-bpyMe-H)Cl$_2$] prepared in solution.

On heating [Pd(2,4′-bpyMe)Cl$_3$]·2H$_2$O on a hot-stage polarising microscope, a colour change is observed at 156–160°C followed by a second change at 185–190°C, at which point the compound is bright yellow. At 400°C the compound had decomposed to a black mass. The TGA curve for [Pd(2,4′-bpyMe-H)Cl$_2$] shows that the two mass loss steps are close together in the range 360–410°C. These are calculated as being due to the loss of the two chlorides and the organic ligand. This is most probably a coincidence and, in

TABLE 3. Microwave irradiation of [M(2,4′-bpyMe)X_3]

Complex	Irradiation Time (min)		Product
	Multi-modal Irradiation (450 W)	Resonance Irradiation (350 W)	
[Pt(2,4′-bpyMe)Cl_3]	60	5	[Pt(2,4′-bpyMe-H)Cl_2]
[Pd(2,4′-bpyMe)Cl_3]	15	1	[Pd(2,4′-bpyMe-H)Cl_2]
[Pd(2,4′-bpyMe)Br_3]	60	5	[Pd(2,4′-bpyMe-H)Br_2]

view of the blackening of the solid, should not be taken to mean that a well-defined species is even formed. Nor is it evident that the chlorides should depart before the combustion of the organic molecule.

The pattern of the TGA curve for [Pt(2,4′-bpyMe)Cl_3]·H_2O (Fig. 2) is similar to that of the palladium analogue in that the loss of water of crystallisation occurs in the same temperature range while cyclometallation (with elimination of one mole HCl) is now at a higher temperature giving two well separated steps. Decomposition of the complex occurs in the range 340–460°C in two steps to leave platinum metal. DTA and DSC give endotherms at the peak temperatures in the TGA.

Stepwise heating to 140°C gives the anhydrous complex and heating to 250°C gives [Pt(2,4′-bpyMe-H)Cl_2] which is orange-brown in colour, suggesting slight decomposition. The thermogram of this solid is identical to that of genuine [Pt(2,4′-bpyMe-H)Cl_2]. Using optical microscopy, the only colour change observed on heating is at 212°C, whence the solid turns from yellow to orange. The compound decomposes at 400°C.

Cyclometallation is more difficult for [Pd(2,4′-bpyMe)Br_3] and occurs in the range 200–250°C, with a colour change from red-brown to yellow-brown (slight decomposition). The DTA and the DSC curves have an endotherm corresponding to the peak temperature of 232°C. Optically, the colour of the solid changes from red to dirty yellow at 240°C. [Pd(2,4′-bpyMe-H)Br_2] decomposes in two steps.

The compounds [M(2,4′-bpyMe)X_3] can also be transformed to the cyclometallated complexes upon irradiation in a microwave oven. However, the rate of reaction depends on the irradiation mode that is used (multimode or resonance). Thus, when the complexes (100 mg samples) were irradiated in a commercial microwave oven (multimode irradiation), there was no reaction unless the samples were placed in a vermiculite bath. The irradiation times for complete reaction are summarised in Table 3.

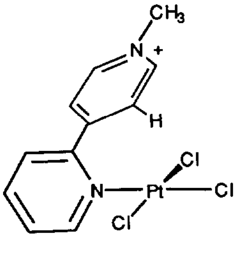
The lack of reaction when the samples are irradiated on their own is related to the small sample size. For this method to be effective compounds with a large dielectric coupling are required and for effective coupling between the solid and the microwaves the sample dimensions need to be greater than one fifth of the wavelength (> *ca.* 3.6 cm). The larger volume of the vermiculite bath results in better absorption of the microwaves leading to a heating effect. In this case a large part of the reaction is purely thermal (due to microwave heating of the vermiculite) since the reaction times are comparable to those obtained in a thermal oven. There may be a small microwave effect as well.

With a single mode resonance cavity, it is possible to concentrate the radiant energy on a small sample and substances with a weak dielectric loss can also be heated efficiently. With this technique, there was a rapid and quantitative cyclometallation of the samples and this is now due to a purely microwave effect. Table 3 gives the reaction times which are now much reduced.

The thermograms of the [M(2,2′-bpyMe)Cl_3] complexes also commence with a weight loss step which corresponds roughly to the elimination of one molecule of HCl. This step is immediately followed by further decomposition so that there is no plateau of stability as seen in Figs. 1 and 2. Under isothermal heating at the peak temperature, after a weight loss corresponding to one HCl the solid continues steadily to lose weight. The results are inconclusive and this method is unsatisfactory for the synthesis of cyclometallated 1-methyl-2,2′-bipyridinium complexes.

3. Discussion

Despite numerous reports on cyclopalladation and cycloplatination, the mechanism in solution is not straightforward. The initial complex formed on mixing a ligand with a palladium salt is generally *trans*-[PdL_2X_2] (*e.g.* L = phenylpyridine; X = Cl, OAc), whereas the product of cyclometallation, often carried out in a completely different solvent, is the dimer [Pd(L-H)(μ-X)$]_2$. Thus, 2,4′-bpy reacts with PdX_2 in acetonitile and acetone to yield *trans*-[Pd(2,4′-bpy)$_2X_2$]



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(X = Cl, OAc), presumably with coordination through the least hindered nitrogen atom. The cyclometallation of the acetato complex to [Pd(2,4'-bpy-H)(μ-OAc)]$_2$ [4,12] is carried out in acetic acid.

Indeed, in even the apparently simple system, the cyclometallation of [Pd(2,2'-bpyMe)Cl$_3$] in water to produce [Pd(2,2'-bpyMe-H)Cl$_2$], the trichloro complex dissolves to form *trans*-[Pd(2,2'-bpyMe)$_2$Cl$_2$]$^{2+}$, which is the intermediate in the reaction, as shown by independently heating *trans*-[Pd(2,2'-bpyMe)$_2$Cl$_2$]$^{2+}$ [8].

Presumably in the solid-state the mechanism is more straightforward. [Pt(2,4'-bpyMe)Cl$_3$] crystallises in the monoclinic system [4]. The coordinated pyridine ring is essentially orthogonal to the coordination plane at an angle of 79.1° and the dihedral angle between the aromatic rings is 53°. Hydrogen (10) is close to the platinum and the chloride ligands in the conformation postulated for the transition state in solution. This proximity enables cyclometallation then to take place in a concerted manner.

4. Experimental section

The complexes [M(2,2'-bpyMe)X$_3$], [M(2,4'-bpyMe)X$_3$]·nH$_2$O and [M(2,4'-bpyMe–H)X$_2$] (M = Pd, Pt; X = Cl, Br) were prepared by procedures described previously [4,6].

IR spectra were recorded on a Perkin Elmer 983 spectrometer using CsI plates. Thermogravimetric analysis and differential thermal analysis were carried out on a Stanton Redcroft TG750 thermal analyser. Heating rates were 10–15° per min on samples of *ca.* 5 mg. The TGA runs (platinum boats) were in air and the DTA runs (aluminium boats) were in a nitrogen atmosphere (25 ml min^{-1}). Alumina was the reference in the DTA runs. Differential scanning calorimetry was performing using a DuPont 9909 calorimeter in either air or nitrogen (25 min^{-1}) at 10° per min.

4.1. Solid-state synthesis

Samples of [M(2,4'-bpyMe)Cl$_3$]·nH$_2$O (M = Pd, Pt) (*ca.* 100 mg) were heated in a pre-equilibrated oven until the colour change appeared complete and the IR spectrum indicated complete reaction (about 1 h).

4.2. Microwave techniques

Multimode microwave irradiations were performed at 2450 MHz in a Toshiba ER 7620 oven. The sample (100 mg) in a Pyrex tube was placed in a Pyrex beaker (25 ml) filled with vermiculite and irradiated for the times given in Table 3. For singlemode resonance irradiation, a MES resonance cavity with a MES generator 73-800 [13*] was used. The complex (100 mg) was placed in a Teflon tube at the maximum of electric field at resonance and irradiated for the times given in Table 3.

Acknowledgment

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* Reference number with an asterisk indicates a note in the list of references.