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N-Methyl-2,2′-Bipyridylium Complexes: Synthesis and Cyclometallation of $M(bpyMe)X_3$ (M = Pt, Pd; X = Cl, Br)

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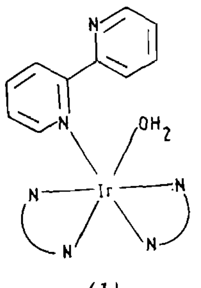
The N-methyl-2,2′-bipyridylium ion, $[bpyMe]^+$, reacts with K_2MX_4 (M = Pd, Pt; X = Cl, Br) to give a monodentate bipyridyl complex $M(bpyMe)X_3$. In the case of platinum, these compounds react further to give the cyclometallated complexes $Pt(bpyMe\text{-}H)X_2$.

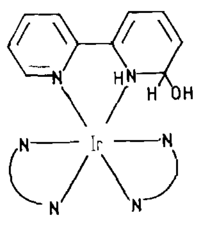
Introduction

The ligand 2,2′-bipyridyl (bpy), which (due to the possibility of rotation about the 2,2′-bond) can be considered to be intermediate in flexibility between 1,2-diaminoethane and 1,10-phenanthroline always displays bidentate behaviour, except when it acts as a bridging ligand (although the existence of such bridged complexes has not been proved conclusively [1–3]). However, species containing a monodentate bpy have been postulated [4, 5] as intermediates in the aquation of $[Fe(bpy)_3]^{3+}$ and such a species is observed in the reaction of bpy with $[Al(Me_2SO)_6]^{3+}$ [6].

The only potential example [7] of a complex with a monodentate bipyridyl ligand, viz. $Ir(bpy)_3Cl_3 \cdot 4H_2O$, has been the subject of a controversial debate [8–13]. This species was originally formulated by Watts *et al.* [8] as the bisequis** complex $[Ir(bpy)_2H_2O(bpy)]Cl_3 \cdot 3H_2O$ (*1*) which contains one monodentate and two bidentate bipyridyl groups. However, this was disputed by Gillard *et al.* [9] who, on the basis of the ^1H NMR spectrum, formulated the complex as the 'covalent hydrate' $[Ir(bpy)_2(bpy\text{-}H_2O)]^{3+}$ (*2*). A recent X-ray structure determination [14] has shown that the complex (*3*) in fact contains all three dipyridyl ligands chelated to the metal, with one ligand coordinated *via* the nitrogen on one ring and the C(3) of the other (cyclometallated) ring.



(*1*)



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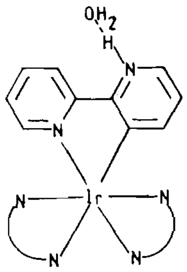

(*3*)

We have recently reported [15] the preparation of complexes of the N-methylbipyridylium cation $[bpyMe]^+$. The existence of these complexes, which are of the type $M^{II}(bpyMe)X_3$ (M = Co, Ni, Cu, Zn; X = Cl, I, NO_3), shows that 2,2′-bipyridyl is sterically capable of behaving as a monodentate ligand in complexes of C_{3v} symmetry. We describe here the preparation of square planar complexes of the $[bpyMe]^+$ ion, together with a novel cyclometallation of the platinum(II) compounds.

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**A prefix meaning two and a half.

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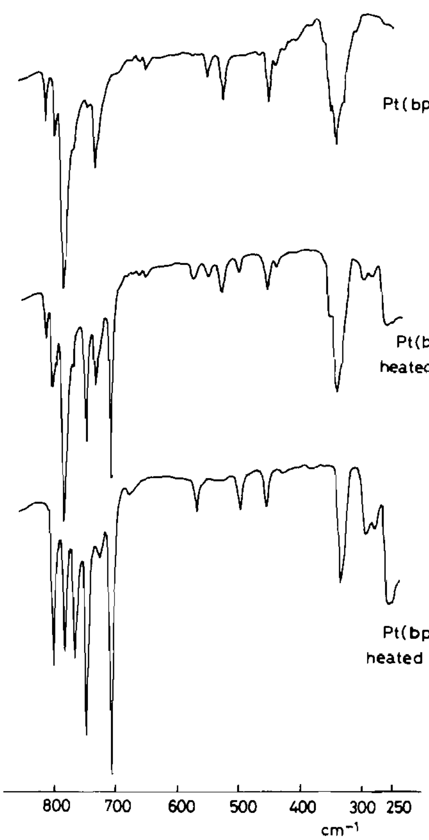
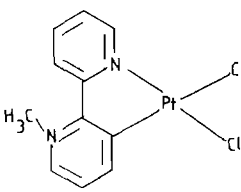


Fig. 1. Changes in the infra-red spectrum of Pt(bpyMe)Cl$_3$ on heating.

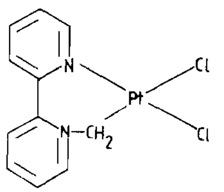
Results and Discussion

When aqueous solutions of K$_2$PdX$_4$ (X = Cl, Br) and [bpyMe]NO$_3$[†] are mixed at room temperature, Pd(bpyMe)X$_3$ separates as an orange powder. The same product is obtained when the reaction is carried out in ethanol using Li$_2$PdX$_4$. Gentle warming (50 °C) is required to prepare the analogous platinum complexes, Pt(bpyMe)X$_3$ (X = Cl, Br), which precipitate as microcrystals. Attempts to prepare the iodo complexes were unsuccessful.

The compounds are air stable, insoluble in all organic solvents, water and dilute hydrochloric acid. They are thermally stable, decomposing at temperatures above 270 °C. The infra-red spectra of the complexes are virtually identical to those of the analogous first-row transition metal complexes. These show the characteristic changes expected for a coordinated pyridine [15] thus indicating that the [bpyMe]$^+$ ion is coordinated to the metal through the pyridyl nitrogen atom.



(4)



(5)

Pt(bpyMe)X$_3$ (X = Cl, Br) was heated (90 °C, 12–15 h) with an equimolar quantity of [bpyMe]NO$_3$ in an attempt to coordinate a second [bpyMe]$^+$ group to the metal. This resulted in the elimination of hydrogen halide and partial conversion of the solid to orange needles which analyse as Pt(bpyMe–H)X$_2$. Complete conversion required 72 h. The solubility properties of these complexes are like those of Pt(bpyMe)X$_3$.

Comparison of the infra-red spectra of Pt(bpyMe–H)X$_2$ with Pt(bpyMe)X$_3$ show changes in both the ring stretching (1650–1500 cm^{-1}) and the out of plane deformation (850–700 cm^{-1}) modes (see Fig. 1). These changes suggest a modification of one of the pyridine rings; this is consistent with the cyclometallation of Pt(bpyMe)X$_3$ at C(3) of the quaternized pyridine ring. The spectra of Pt(bpyMe-H)X$_2$ are different to those of the known compounds Pt(bpy)X$_2$ so that the alternative possibility where MeX is eliminated from Pt(bpyMe)X$_3$ can be discounted.

The strongest bands in the far infra-red spectrum of Pt(bpyMe–H)Cl$_2$ are at 335 and 260 cm^{-1}; these are assigned as the $\nu_{\text{Pt–Cl}}$ modes. The large separation between these bands suggests that the chloride groups are *trans* to two different atoms [16]. It is not possible on this basis to differentiate between a monomeric structure (*4*) and dimeric or oligomeric structures.

It is also conceivable that some metallation occurs at the N-methyl group [17] giving compound (*5*). Although this would be contrary to the empirical rules formulated by Cope [18], it was recently shown [19] that 2-benzylpyridine readily forms six-membered cyclopalladated rings.

All attempts to prepare the analogous palladium(II) complexes by heating a suspension of Pd(bpyMe)X$_3$ (X = Cl, Br) in a variety of solvents (water, petroleum ether, ethanol, 2-methoxyethanol) proved to be unsuccessful, the starting material always being recovered.

As a ligand, [bpyMe]$^+$ can be considered to be similar to 2-phenylpyridine and benzo(h)quinoline which both form cyclometallated complexes readily with platinum(II), palladium(II), rhodium(III) and

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[†] N-methylbipyridylium iodide, bpyMe I, was prepared by heating under reflux equimolar quantities of bpy and iodomethane in 1-butanol for 3 h. The nitrate salt was prepared by metathesis with silver nitrate.

manganese(II) [20]. Pt(bpyMe–H)X_2 is an unusual type of compound in that the ligand itself is acting as a zwitterion as a result of the cyclometallation. Hence, blocking one of the nitrogens of 2,2′-bipyridyl by an alkyl group does not prevent the resulting cation from acting as a chelate.

Further investigations of the $[bpyMe]^+$ ion as a ligand as well as a crystal structure determination of the cyclometallated complex are in progress.

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