Synthesis of Hydrido–Iridium(III) Complexes from a Trifluoromethanesulphonato Intermediate

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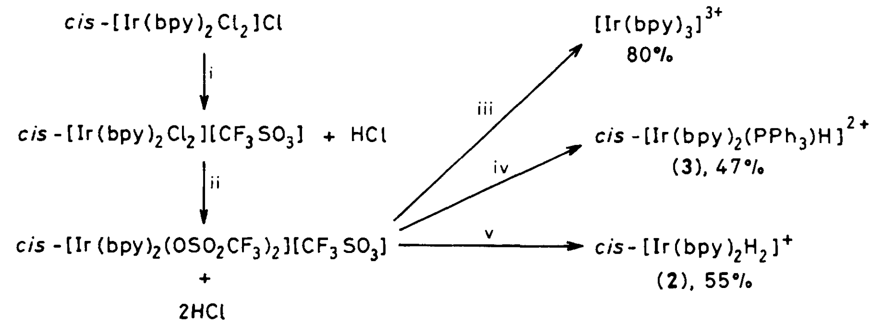
The versatile new precursor to bis-2,2′-bipyridine complexes of Ir^{III}, *cis*-$[Ir^{III}(bpy)_2(OSO_2CF_3)_2][CF_3SO_3]$ (bpy = 2,2′-bipyridine), has been isolated and used for the preparation of the new hydrido complexes of Ir^{III}, *cis*-$[Ir(bpy)_2(PPh_3)H][PF_6]_2$ and *cis*-$[Ir(bpy)_2H_2][PF_6]$, and for an improved, high-yield synthesis of $[Ir(bpy)_3][PF_6]_3$.

Iridium(III) complexes of 2,2′-bipyridine (bpy) are difficult to prepare and purify[1] compared to the isoelectronic and isostructural analogues of Ru^{II} and Os^{II}. The underlying synthetic chemistry of the $Ir(bpy)_2^{3+}$ unit is largely unexplored owing to, among other factors, its kinetically sluggish substitution rates. This is an unfortunate situation since bis-2,2′-bipyridine complexes of Ir^{III} have provided a basis for chemical systems with interesting electrochemical,[2,3] photochemical,[4] photophysical,[5] and catalytic properties.[6]

One of our recent interests has been in developing synthetic routes to Werner-type complexes which have hydrido or alkyl ligands in the co-ordination sphere,[7,8] with the ultimate goal being to discover new electrochemically and photochemically induced chemistry involving these ligands. Useful synthetic intermediates in this type of chemistry are trifluoromethanesulphonato complexes which have proved to be especially labile precursors for the substitutionally inert second and third row transition metals.[9]

Following this lead, we find that *cis*-$[Ir^{III}(bpy)_2(OSO_2CF_3)_2][CF_3SO_3]$ (**1**) can be made easily and is a valuable



Scheme 1. *Reagents and conditions:* i, CF_3SO_3H in CH_2Cl_2, 25 °C; ii, CF_3SO_3H in $C_6H_4Cl_2$-*o*, heat; iii, bpy in $(CH_2OH)_2$, heat, 5 h; iv, PPh_3 in $(CH_2OH)_2$, heat, 1 h; v, KBH_4 in $EtOH–H_2O$, heat, 30 min.

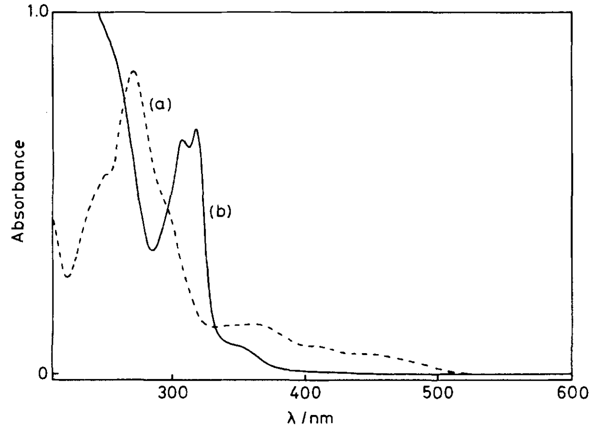


Figure 1. Electronic spectra of (a) *cis*-$[Ir(bpy)_2H_2][PF_6]$ (**2**) and (b) *cis*-$[Ir(bpy)_2(PPh_3)H][PF_6]_2$ (**3**) recorded in CH_3CN solution.

precursor to new and unusual hydrido complexes of Ir^{III}. As an intermediate it also provides a convenient precursor for a high-yield preparation of $[Ir(bpy)_3]^{3+}$.

cis-$[Ir(bpy)_2(OSO_2CF_3)_2][CF_3SO_3]$
(**1**)

Complex (**1**) was synthesised by preparing *cis*-$[Ir(bpy)_2Cl_2]Cl$[10] which was converted into the trifluoromethanesulphonate salt in CH_2Cl_2 solution, purified by column chromatography on neutral alumina with acetonitrile, and subsequently heated at reflux in 1,2-dichlorobenzene with a 20 times molar excess of anhydrous CF_3SO_3H (see Scheme 1). The pale yellow complex (**1**) was obtained in virtually quantitative yield (95%) and can be purified by recrystallization from $CH_3CN–Et_2O$; however, material obtained directly from the preparation can be used for synthetic purposes with satisfactory results after washing copiously with Et_2O.†

As shown in Scheme 1, (**1**) reacts with 20 times molar excess of bpy in ethylene glycol to form $[Ir(bpy)_3]^{3+}$ which is isolated as the PF_6^- salt.[11] This preparation is a considerable improvement over the previously published melt procedure which gives only a moderate yield of the tris-complex, an unusual cyclometallated bpy–Ir species,[12] and a host of unidentified by-products.[13]

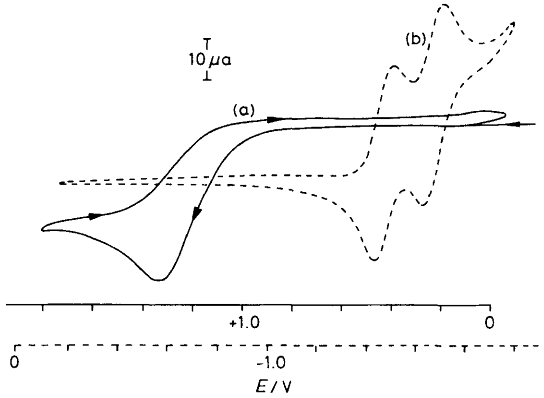


Figure 2. Cyclic voltammogram of the hydrido complex *cis*-$[Ir(bpy)_2H_2][PF_6]$ (**2**) [(a) is an oxidative scan; (b) is a reductive scan] which was taken in CH_3CN solution with 0.1 M Bu_4NPF_6 as supporting electrolyte at a Pt bead working electrode using a scan rate of 200 mV/s; potentials are *vs.* the saturated sodium chloride calomel electrode.

Two unusual Werner-type hydrido complexes, *cis*-$[Ir(bpy)_2H_2]^+$ (**2**) and *cis*-$[Ir(bpy)_2(PPh_3)H]^{2+}$ (**3**) were prepared as their PF_6^- salts from (**1**) by a fairly straightforward procedure. The dihydride was obtained by borohydride reduction in $EtOH–H_2O$ and the monohydride by heating (**1**) with PPh_3 in ethylene glycol at reflux (see Scheme 1).‡ Both complexes were purified by column chromatography using procedures developed earlier for Ru–bpy complexes.[14]

Complexes (**2**) and (**3**) possess interesting spectral and electrochemical properties. As shown in Figure 1 the hydrido complexes absorb light in the visible or near u.v. *via* optical transitions which are metal to ligand charge-transfer (M.L.C.T.) in nature. The existence of such excited states raises the possibility of M.L.C.T.-induced redox chemistry involving the hydride group; in fact both complexes are photochemically unstable in aerated CH_3CN solution.

Figure 2 shows the cyclic voltammogram for (**2**) in which there are two unusual and distinctive features. The first is the reversible character of the two bpy localized reduction processes (at −1.47 and −1.68 V; in CH_3CN at a Pt working electrode *vs.* the standard calomel electrode) which stands in contrast to the irreversible behaviour observed in other bis-bpy complexes of Ir^{III}.[2] The second feature is that the peak

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† A satisfactory elemental analysis was obtained; the ^1H n.m.r. spectrum in CH_3CN shows four doublets and four triplets (in the first order) which extend from δ 9.22—7.41 *vs.* $SiMe_4$ as an internal standard.

‡ Both salts gave satisfactory elemental analyses and were assigned the *cis*-bpy configuration from their ^1H n.m.r. (CD_3CN solution) spectra; (**2**) has four doublets and four triplets (in the first order) in the aromatic region and an Ir–H resonance at δ −17.90 while (**3**) has no apparent magnetic symmetry in the aromatic region and a doublet in the Ir–H region at δ −17.80 and −17.88.

current for the oxidation indicates that more than one electron is involved in the net redox process; this implies a different redox mechanism for (**2**) than for the one-electron oxidations of the isoelectronic monohydrides, *cis*-[M(bpy)$_2$(CO)H]$^+$[7] (M = Ru, Os) and *fac*-[Re(bpy)(CO)$_3$H].[8] The electrochemical and associated photochemical aspects of these new hydrido complexes will be discussed elsewhere.

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