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Synthesis, Characterisation, Electrochemical Properties, Photochemical Properties, and Reactivity of Bis(2,2′-bipyridyl)hydridoruthenium Complexes

John M. Kelly
Chemistry Department, Trinity College, University of Dublin, Dublin 2, Ireland
Johannes G. Vos *
School of Chemical Sciences, National Institute for Higher Education, Dublin 9, Ireland

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Complexes $[Ru(bipy)_2H(L)]X$ (bipy = 2,2′-bipyridyl; L = CO or PPh_3, X = PF_6; L = $AsPh_3$, X = ClO_4) and $[Ru(Me_2bipy)H(CO)]PF_6$ (Me_2bipy = 4,4′-dimethyl-2,2′-bipyridyl) have been synthesised by the reaction of the corresponding $[Ru(bipy)_2Cl(L)]^+$ complex or $[Ru(Me_2bipy)Cl(CO)]^+$ respectively with sodium tetrahydroborate in aqueous ethanol. In dilute acid $[Ru(bipy)_2H(CO)]^+$ yields $[Ru(bipy)_2(OH_2)(CO)]^{2+}$ and hydrogen gas. $[Ru(bipy)_2H(CO)]^+$ is relatively photostable compared with $[Ru(bipy)_2H(PPh_3)]^+$. The phosphine and arsine complexes show, in general, an increased reactivity compared to the carbonyl complexes.

Recent interest in 2,2′-bipyridyl (bipy) complexes of ruthenium has been intense, principally because of the useful properties of $[Ru(bipy)_3]^{2+}$ as a 'sensitiser' for the photodissociation of water by visible light.[1] Most of these systems are based on the photo-induced transfer of an electron to an acceptor (such as 1,1′-dimethyl-4,4′-bipyridinium dichloride, which can subsequently react over a catalyst to give hydrogen, while the $[Ru(bipy)_3]^{3+}$ formed may yield oxygen in the presence of a suitable catalyst. Alternative schemes based on the photoreduction of $[Ru(bipy)_3]^{2+}$ have also been proposed. A quite different approach based on metal–hydride complexes has been discussed, although, to the best of our knowledge no successful systems have been demonstrated. However, bis(2,2′-bipyridyl)hydridoruthenium complexes have been suggested as intermediates in the photo-induced water–gas shift reaction promoted by $[Ru(bipy)_2Cl(CO)]^+$ [2,3] and it is possible that they may even have been involved as impurities in the monolayer assemblies of surfactant $[Ru(bipy)_3]^{2+}$-type derivatives which were initially reported to cause the photodissociation of water.[4] In an earlier preliminary communication we described the preparation of $[Ru(bipy)_2H(CO)]^+$ and its reaction with acid to give $[Ru(bipy)_2(OH_2)(CO)]^{2+}$.[5] In this paper we give further details about $[Ru(bipy)_2H(CO)]^+$ and report on the preparation of the analogous phosphine and arsine complexes $[Ru(bipy)_2H(L)]^+$ (L = PPh_3 or $AsPh_3$). Very recently Meyer and co-workers[6] have described some related ruthenium and osmium hydride complexes.

Results

The complexes $[Ru(bipy)_2H(L)]^+$ (L = CO, PPh_3, or $AsPh_3$) were prepared by reaction of the corresponding $[Ru(bipy)_2Cl(L)]^+$ with sodium tetrahydroborate in aqueous ethanol solution [equation (1)]. The compound $[Ru(Me_2bipy)_2H(CO)]^+$ (Me_2bipy = 4,4′-dimethyl-2,2′-bipyridyl) was prepared by the same route from $[Ru(Me_2bipy)_2Cl(CO)]^+$. The carbonyl–hydride complexes and $[Ru(bipy)_2H(PPh_3)]^+$ were precipitated as their hexafluorophosphate salts by addition of NH_4PF_6. In the case of the $AsPh_3$ derivative, treatment with NH_4PF_6 led to decomposition of the complex, probably because of reaction of the hydride with the weakly acidic NH_4^+ ion; this complex was isolated using $NaClO_4$.† It was also noted that yields of the arsine and phosphine complexes were higher when a large excess of $NaBH_4$ was used, presumably because these reaction mixtures are more alkaline. Both carbonyl complexes were purified by column chromatography on neutral alumina using acetone as eluant. However the phosphine and arsine derivatives could not be purified in this way as they decomposed when similarly treated.

$$cis\text{-}[Ru(bipy)_2Cl(L)]^+ \xrightarrow[H_2O\text{-}EtOH]{NaBH_4} cis\text{-}[Ru(bipy)_2H(L)]^+ \quad (1)$$

Spectroscopic Properties.—^1H N.m.r. spectra of all the complexes show high-field signals (see Table and Experimental section) characteristic of metal hydrides. In the case of the phosphine complex the hydride proton signal is split due to coupling to the ^{31}P of the phosphine. The coupling constant J(P–H) of 32.5 Hz is in the range expected for *cis*-phosphine hydrides.[7] The position of the resonance (see Table) is at higher field in the phosphine and arsine complexes compared to that in the carbonyl compound. The bipyridyl ring protons display the complex pattern of resonances expected for *cis* co-ordination of the unique ligands.[8]

All the hydrido-complexes show an absorption in the i.r. spectrum in the range 1 850—1 950 cm^{-1}. In the arsine and phosphine complexes the medium-intensity broad band in this region may be assigned to a Ru–H stretching vibration.[7] In the carbonyl complexes ν(Ru–H) is presumably masked by the strong absorption at *ca.* 1 930 cm^{-1} which is due to the carbonyl stretching vibration.

Each of the complexes shows two medium intensity (log ε = 3.5—4.0) bands in the near-u.v.–vis. region of the spectrum (see Table). The maximum for the visible band shifts successively to lower energy in the order CO > PPh_3 > $AsPh_3$. $[Ru(bipy)_2Cl(L)]^+$ (L = PPh_3 or $AsPh_3$) also show two bands in this spectral region and these have been assigned to metal–ligand charge-transfer ($d \rightarrow \pi^*$) bands.[9] It is probable that this is also the case here. The fact that the low-energy band occurs at longer wavelength in $[Ru(bipy)_2H(L)]^+$ than in $[Ru(bipy)_2Cl(L)]^+$ may be explained by the stronger σ-donor properties of the hydride ligands.

Cyclic Voltammetry.—The redox chemistry of the hydrido compounds was investigated using cyclic voltammetry. The measurements were conducted in acetonitrile with NEt_4ClO_4 as supporting electrolyte. The data obtained, together with values for some related compounds are listed in the Table. The cyclic voltammograms of $[Ru(bipy)_2H(L)]^+$ reveal an irreversible oxidation, this is most likely a Ru^{II}–Ru^{III} oxidation, followed by

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† Attempts were made to isolate the corresponding PBu^n_3 complex. A good set of spectroscopic data was obtained {^1H n.m.r., δ −12.13 [d, 1 H, J(P–H) = 33.4 Hz]; i.r., ν(Ru–H) at 1 868 cm^{-1}; u.v.–vis., $\lambda_{max.}$ = 359 and 512 nm} but no satisfactory elemental analysis.

Table. Electrochemical and spectroscopic data for bis(2,2′-bipyridyl)hydridoruthenium complexes and some related compounds

Compound	$E_{\frac{1}{2}}$/V[a]	ν(Ru–H)/cm^{-1}[b]	$\lambda_{max.}$(log ε)/nm[c]	δ(Ru–H)/p.p.m.[d]
$[Ru(bipy)_2H(CO)]PF_6 \cdot 0.5(CH_3)_2CO$	+1.03,[e] −1.56 (80)	1 930[f]	448 (3.49), 353 (3.70)	−11.31
$[Ru(bipy)_2H(PPh_3)]PF_6$	+0.58,[e] −1.60 (100)	1 912	495 (3.86), 343 (3.97)	−12.00
$[Ru(bipy)_2H(AsPh_3)]ClO_4$	+0.57,[e] −1.61 (120)	1 872	510 (3.89), 350 (3.92)	−11.83
$[Ru(bipy)_2Cl(CO)]PF_6$	+1.50, −1.34, −1.56	1 965[f]	415(sh) (3.34), 353(sh) (3.70)[g]	—
$[Ru(bipy)_2Cl(PPh_3)]PF_6$	+0.94, −1.29, −1.47, −1.67	—	545 (3.78), 328 (3.85)[h]	—

[a] Electrolyte: CH_3CN, 0.1 mol dm^{-3} NEt_4ClO_4. Scan rate 200 mV s^{-1}. V *vs.* s.c.e. Values in parentheses are peak-to-peak separations. [b] KBr discs. [c] In CH_3CN. [d] In $(CD_3)_2CO$. [e] Irreversible peak. [f] ν(CO). [g] Ref. 11. [h] Ref. 9.

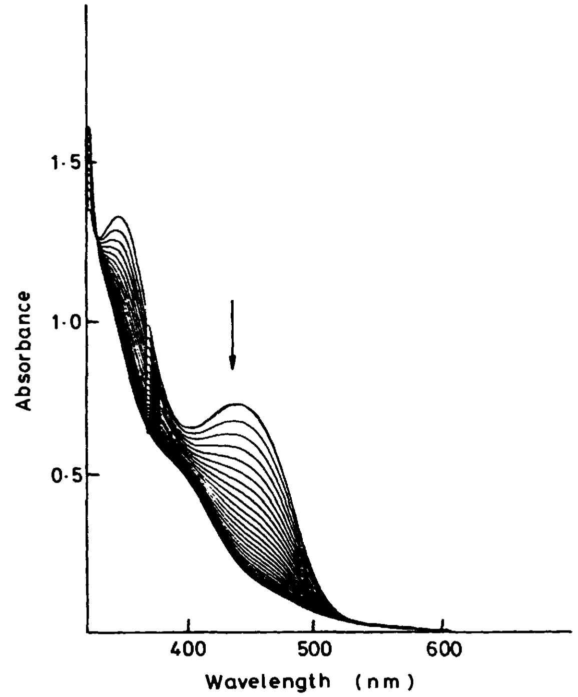

Figure 1. Acid-induced decomposition of $[Ru(bipy)_2H(CO)]^+$ (2.0×10^{-4} mol dm^{-3}) at pH 6.93 in the presence of acetone. Reaction mixture: 1 cm^3 acetone + 2 cm^3 phosphate buffer. Temp. 27 °C. Time between spectra 30 min

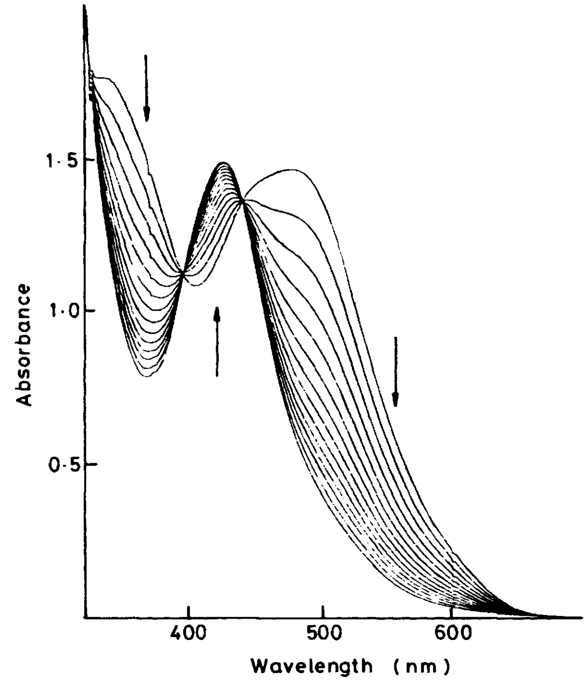

Figure 2. Acid-induced decomposition of $[Ru(bipy)_2H(PPh_3)]^+$ (2.0×10^{-4} mol dm^{-3}) at pH 6.93 in the presence of acetone. For conditions see Figure 1. Time between scans 4 min 46 s

a fast irreversible chemical reaction, possibly loss of H^+. A large shift in the Ru^{II}–Ru^{III} redox potential was observed for the hydride complexes compared to those of the corresponding chloro-complexes. This may be attributed to the increased σ-donor properties of H^- compared to Cl^-, thus stabilising Ru^{III} relative to Ru^{II} in the hydrido-complexes. The first reduction potentials of $[Ru(bipy)_2H(L)]^+$ are also more negative than those of $[Ru(bipy)_2Cl(L)]^+$. It is probable that, as in other ruthenium–bipyridyl complexes[10] the reduction is localised on the bipyridyl ligand and the more negative reduction potential is consistent with increased M → bipy back-bonding in the hydrido-complexes.

Reaction of $[Ru(bipy)_2H(L)]PF_6$ *with Acid.*—The behaviour of the hydride complexes towards acidic solutions was studied by a combination of mass spectrometry, u.v.–vis., and ^1H n.m.r. spectroscopies. Thus hydrogen was detected by mass spectrometry when concentrated aqueous perchloric acid was added to a suspension of $[Ru(bipy)_2H(CO)]PF_6 \cdot 0.5(CH_3)_2CO$ in methanol. Addition of hexafluorophosphoric acid to a $[^2H_6]$acetone solution of $[Ru(Me_2bipy)_2H(CO)]PF_6$ caused immediate disappearance of the hydride proton signal at $\delta = -11.51$ p.p.m.

The reaction of $[Ru(bipy)_2H(L)]^+$ in weakly acidic aqueous organic solution was studied by u.v.–vis. spectroscopy. For example Figure 1 shows the changes in the 300—600 nm region after injection of an acetone solution of $[Ru(bipy)_2H(CO)]^+$ into aqueous pH 6.93 buffer. The decomposition of the hydrido complex is indicated by the disappearance of the band at *ca.* 430 nm, while the band of the product at 380 nm is characteristic of $[Ru(bipy)_2(OH_2)(CO)]^{2+}$.[11] The half-life of the reaction under these conditions is *ca.* 180 min at 27 ± 1 °C. The rate of decomposition of the hydride complex increases as the pH decreases. If an acetonitrile solution of $[Ru(bipy)_2H(CO)]^+$ is added to water with a pH of 5.08 no decomposition is observed over a period of 1 h. These observations suggest that the reaction involved in the aqueous acetone buffer solutions is an acid-catalysed reaction of acetone and $[Ru(bipy)_2H(CO)]^+$, and not simply reaction (2) as previously suggested.[5] Further experiments suggest that acetone is reduced to propan-2-ol.[12] In the absence of acetone reaction (2) is observed in aqueous solutions at lower pH; thus in an aqueous solution at pH 3.0 the decomposition of $[Ru(bipy)_2H(CO)]^+$ proceeded with a half-life of *ca.* 90 min at 30 ± 1 °C.

$$[Ru(bipy)_2H(CO)]^+ + H^+ \longrightarrow [Ru(bipy)_2(OH_2)(CO)]^{2+} + H_2 \quad (2)$$

The remaining hydrido complexes are more sensitive to acid, as indicated in their preparation and isolation (see later). Figure 2 shows the decomposition of $[Ru(bipy)_2H(PPh_3)]^+$ in aqueous acetone at pH 6.93. The half-life under these conditions is *ca.* 20 min at 27 ± 1 °C, and the presumed product is $[Ru(bipy)_2(OH_2)(PPh_3)]^{2+}$. {Under the same conditions $[Ru(bipy)_2H(CO)]^+$ decomposes with a half-life of *ca.* 180 min.}

Photochemical Stability.—Irradiation with u.v. and/or visible light [xenon lamp ($\lambda > 330$ nm) or medium-pressure mercury lamp (313 or 365 nm)] of an air-saturated acetonitrile solution of $[Ru(bipy)_2H(PPh_3)]^+$ or $[Ru(bipy)_2H(CO)]^+$ gave contrasting results. Photolysis of $[Ru(bipy)_2H(PPh_3)]^+$ gave a product having $\lambda_{max.}$ at 428 nm with pronounced shoulders at *ca.* 456 and 480 nm. Isosbestic points are maintained at 320, 400, and 438 nm to at least 50% completion of the reaction, and there was no evidence for the formation of any intermediate species. The product however would appear to be a mixture of compounds and although no attempt has as yet been made to identify them it would appear that the principal product is probably $[Ru(bipy)_2(MeCN)_2]^{2+}$ ($\lambda_{max.} = 424$ nm). In contrast to this behaviour the reaction of $[Ru(bipy)_2H(CO)]^+$ is very slow and photolysis for moderate periods caused only a slight decrease in the absorption maxima at 353 and 448 nm and an increased absorption between 380 and 440 nm. Assuming that any product would have a substantially different spectrum the quantum yield for decomposition was calculated to be less than 0.001.

Conclusions

The spectroscopic features of the $[Ru(bipy)_2H(L)]^+$ complexes reported show that the hydrido-character of the metal–hydrogen bond depends on the ligand L and is increased in the order CO < PPh_3 < $AsPh_3$. The observed variation of the chemical reactivity with L, *e.g.* the acid-induced decomposition, is of potential interest for the development of hydride complexes with applications in energy-conversion systems and in catalytic processes such as the water–gas shift reaction.

Experimental

U.v.–vis. spectra were recorded on a Unicam SP8-200 or a Shimadzu UV-240 spectrophotometer, i.r. spectra (of samples in KBr discs) on a Perkin-Elmer 599 or 293 spectrophotometer, and ^1H n.m.r. spectra of samples [in $(CD_3)_2CO$ or CD_3CN using $SiMe_4$ as internal standard] on a Bruker WP80 Fourier-transform spectrometer. Cyclic voltammetry was carried out using an E.G and G PAR model 174A polarographic analyser and an E.G and G PAR 175 Universal Programmer with a glassy-carbon electrode as working electrode and a saturated calomel electrode (s.c.e.) as reference; the supporting electrolyte was 0.1 mol dm^{-3} NEt_4ClO_4 and spectroscopic-grade acetonitrile dried over molecular sieves was used as solvent.

$[Ru(bipy)_2H(CO)]PF_6 \cdot 0.5(CH_3)_2CO$ was prepared as previously described.[5] Complexes $[Ru(bipy)_2Cl(L)]X$ (L = PPh_3, X = PF_6; L = $AsPh_3$, X = ClO_4) were prepared by reaction of $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ and L in ethanol–water following the method of Sullivan *et al.*[9] All other reactants were reagent-grade materials and used as received.

cis-$[Ru(bipy)_2H(PPh_3)]PF_6$.—*cis*-$[Ru(bipy)_2Cl(PPh_3)]PF_6$ (250 mg, 0.292 mmol) was dissolved in refluxing ethanol–water (2:1 v/v, 30 cm^3). $NaBH_4$ (300 mg) was added to this solution while still hot and the mixture left to react for a further 20 min. Addition of an aqueous solution of NH_4PF_6 yielded *cis*-$[Ru(bipy)_2H(PPh_3)]PF_6$ (200 mg, 0.243 mmol, 80%) as a dark purple precipitate which was recrystallised from an acetone–toluene mixture (Found: C, 54.8; H, 4.0; N, 6.5. $C_{38}H_{32}F_6N_4P_2Ru$ requires C, 55.5; H, 3.9; N, 6.8%). ^1H N.m.r. $[(CD_3)_2CO]$: δ −12.00 [d, 1 H, J(P–H) = 32.5 Hz], 6.8—7.7 (m, 21 H), 7.7—8.1 (m, 5 H), and 8.3—8.8 (m, 5 H). I.r. (KBr): 3 045w, 1 912m, 1 598w, 1 478m, 1 458m, 1 433m, 1 306w, 1 266w, 1 088m, 1 023w, 1 012w, 998w, 836vs, 753s, 738s, 695s, and 652w cm^{-1}.

cis-$[Ru(bipy)_2H(AsPh_3)]ClO_4$.—*cis*-$[Ru(bipy)_2Cl(AsPh_3)]ClO_4$ (400 mg, 0.468 mmol) was dissolved in refluxing ethanol–water (3:1 v/v, 100 cm^3). $NaBH_4$ (500 mg) was added to this solution when still hot and the mixture allowed to react for 20 min. An aqueous solution of $NaClO_4$ (500 mg) was then added. On standing overnight *cis*-$[Ru(bipy)_2H(AsPh_3)]ClO_4$ (200 mg) 0.244 mmol, 50%) formed as dark purple crystals and was recrystallised from acetone–toluene (Found: C, 55.7; H, 3.8; N, 6.6. $C_{38}H_{32}AsClN_4O_4Ru$ requires C, 55.6; H, 3.9; N, 6.8%). ^1H N.m.r. $[(CD_3)_2CO]$: δ −11.83 (s, 1 H) and 6.7—8.9 (m, 31 H). I.r. (KBr): 3 065w, 3 045w, 1 872m, 1 598w, 1 481m, 1 460m, 1 433m, 1 308w, 1 265w, 1 090s vbr, 1 021w, 1 011w, 998w, 840vs, 743s, 671s, 652w, and 621m cm^{-1}.

cis-$[Ru(Me_2bipy)_2H(CO)]PF_6$.—*cis*-$[Ru(Me_2bipy)_2Cl(CO)]PF_6$ (500 mg, 0.74 mmol) was dissolved in ethanol–water (2:1 v/v, 75 cm^3). $NaBH_4$ (500 mg) was added to this solution when still hot and the mixture was allowed to react for 20 min. Addition of an aqueous solution of NH_4PF_6 (500 mg) precipitated *cis*-$[Ru(Me_2bipy)_2H(CO)]PF_6$ (420 mg, 0.65 mmol, 85%) as light orange crystals. The sample was purified by chromatography on neutral alumina using acetone as eluant and recrystallised from toluene–acetone (Found: C, 46.3; H, 3.9; N, 8.4. $C_{25}H_{25}F_6N_4OPRu$ requires C, 46.6; H, 3.9; N, 8.7%). ^1H N.m.r. $[(CD_3)_2CO]$: δ −11.51 (s, 1 H), 2.49 (s, 6 H), 2.61 (s, 3 H), 2.65 (s, 3 H), 7.2—7.8 (m, 6 H), 8.45—8.7 (m, 4 H), and 9.0—9.15 (q, 2 H). U.v.–vis. (CH_3CN): λ (log ε), 352 (3.79) and 445 (3.52) nm. I.r. (KBr): 3 070vw, 2 920w, 1 900s, 1 615m, 1 480w, 1 440w, 1 415w, 1 300vw, 1 240vw, 1 030w, and 832vs cm^{-1}.

Acid-induced Decomposition of $[Ru(bipy)_2H(CO)]^+$.—A flask containing a suspension of *cis*-$[Ru(bipy)_2H(CO)]PF_6 \cdot 0.5(CH_3)_2CO$ (200 mg, 0.31 mmol) in methanol (25 cm^3) and fitted with a pressure-equalised dropping funnel, containing aqueous 60% perchloric acid, was evacuated. The perchloric acid (*ca.* 2 cm^3) was then added to the mixture. After reaction, a sample of the gas above the mixture was analysed by mass spectrometry (Vacuum Generators Supavac Quadrupole mass spectrometer), a strong peak at $m/e = 2$ indicating the formation of hydrogen.

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