Preparation, Spectroscopic Characterisation, Electrochemical and Photochemical Properties of *cis*-Bis(2,2′-bipyridyl)carbonylruthenium(II) Complexes

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The preparation of a series of *cis*-$[Ru^{II}(L-L)_2(CO)L]^{n+}$ complexes [L–L = 2,2′-bipyridyl (bipy), n = 1, L = H, Cl, or NCS; n = 2, L = H_2O, MeCN, CO, pyridine (py), 4-vinylpyridine (vpy), or 4-methylpyridine (Mepy); L–L = 4,4′-dimethyl-2,2′-bipyridyl (Me_2bipy), n = 1, L = H or Cl; n = 2, L = H_2O or CO] is reported. The C=O stretching frequency, the energy of the d–π^* metal to ligand charge-transfer absorption bands, and the oxidation and reduction potentials of the complexes are found to depend markedly on the σ- and the π-donor abilities of the ligands. In complexes $[Ru(L-L)_2(CO)(H_2O)]^{2+}$ and $[Ru(L-L)_2(CO)Cl]^+$ the water and Cl^- ligands are thermally substitution labile. On u.v. irradiation all complexes except $[Ru(L-L)_2(CO)H]^+$ are efficiently decarbonylated.

In the last decade or so there has been great interest in the chemistry of ruthenium derivatives of 2,2′-bipyridyl.[1] Many of these studies have been concerned with $[Ru(bipy)_3]^{2+}$, mainly because of its unusual photoredox properties and its potential use for the photochemical storage of energy by the photodissociation of water.[2] Indeed much of the interest in this type of compound was stimulated by the report that visible light irradiation of a monolayer sample of a surfactant derivative of $[Ru(bipy)_3]^{2+}$ immersed in water caused evolution of hydrogen.[3a] As later studies[3b–6] indicated that highly purified samples of this surfactant derivative were inactive, a possible explanation for the original observation might be that some catalytically active impurity was present in the original sample. Our initial observation that the preparative method used to prepare one of the starting materials for the surfactant synthesis {*i.e.* $[Ru(bipy)_2Cl_2]$} also yielded substantial quantities of $[Ru(bipy)_2(CO)Cl]^+$ (**1**) suggested that such ruthenium(II) carbonyl derivatives might have interesting catalytic properties.[7] Indeed, shortly afterwards, Cole-Hamilton[8] reported that complex (**1**) catalyses the photochemical water-gas shift reaction, and more recently Tanaka *et al.*[9] have shown that the same complex also catalyses the water-gas shift reaction in the absence of light. A key intermediate appears to be $[Ru(bipy)_2(CO)(H_2O)]^{2+}$ (**2**). In the present paper the isolation and characterisation of this complex is reported and some of its reactions are described.

As the chloride ligand of complex (**1**) is thermally substitution labile and replaceable by other ligands, this compound can be used to synthesise a range of bis(2,2′-bipyridyl)carbonylruthenium(II) complexes.[7,10] The ion $[Ru(bipy)_2(CO)H]^+$ has been prepared by reaction of $[Ru(bipy)_2(CO)Cl]^+$ with $NaBH_4$ in aqueous ethanol solution;[11] $[Ru(bipy)_2(CO)_2]^{2+}$ may be synthesised either by reaction of $[Ru(bipy)(CO)_2Cl_2]$[12] or $[Ru(bipy)(CO)_2(O_3SCF_3)_2]$[13] with bipyridyl or by reaction of $[Ru(bipy)_2Cl_2]$, $AgSbF_6$, and CO.[14] Thus a range of $[Ru^{II}(bipy)_2(CO)L]^{n+}$ derivatives is available in which the electronic properties of the ligand L vary from those of a strong π acceptor (CO) to those of a strong σ donor (H^-). In this paper as well as giving full details of the preparation of the complexes we also report on how their i.r., u.v.–visible, and n.m.r. spectroscopic properties, electrochemical behaviour, and photochemical reactivity depend on this sixth ligand L.

Results and Discussion

Preparation of Complexes.—In a preliminary communication[7] we reported that $[Ru(bipy)_2(CO)Cl]^+$ (**1**), which was characterised by spectroscopic and *X*-ray crystallographic methods, is formed upon reaction of hydrated ruthenium chloride and 2,2′-bipyridyl in dimethylformamide (dmf). It was isolated as its perchlorate or hexafluorophosphate salt in a yield of 30—40%. The principal product is $[Ru(bipy)_2Cl_2]$, giving an overall yield of bis(bipyridyl)ruthenium(II) complexes of greater than 95%. Use of 4,4′-dimethyl-2,2′-bipyridyl (Me_2bipy) rather than bipy yielded the derivatives $[Ru(Me_2bipy)_2Cl_2]$ and $[Ru(Me_2bipy)_2(CO)Cl]^+$. The yield of other ruthenium carbonyl compounds, *e.g.* $[Ru(bipy)_2(CO)_2]^{2+}$, under these conditions is very low. The formation of the chlorocarbonyl complexes is presumably a result of thermal decarbonylation of dmf. Cole-Hamilton and co-workers[8] have also reported the above reaction and noted that the corresponding reaction to yield $[Ru(phen)_2(CO)Cl]^+$ (phen = 1,10-phenanthroline) does not take place when $RuCl_3$ and phen are refluxed in dmf.[8b]

A series of $[Ru(bipy)_2(CO)L]^{n+}$ complexes [L = pyridine (py), 4-methylpyridine (Mepy), 4-vinylpyridine (vpy), poly(4-vinylpyridine) (pvp), or MeCN, n = 2; L = NCS^-, n = 1)] has been prepared by refluxing (**1**) in the presence of excess of ligand L as in equation (1). In order to avoid photodecarbonylation

$$\underset{(\mathbf{1})}{[Ru(bipy)_2(CO)Cl]^+} + L \xrightarrow{H_2O-MeOH} [Ru(bipy)_2(CO)L]^{n+} + Cl^- \qquad (1)$$

these reactions were carried out in the dark. The yields for thermal displacement of chloride were high and the reactions proceed in all cases with retention of the *cis* configuration.

Although no detailed mechanistic studies have been carried out it is probable that $[Ru(bipy)_2(CO)(H_2O)]^{2+}$ is an intermediate in the above reactions and also in the water-gas shift reaction catalysed by $[Ru(bipy)_2(CO)Cl]^+$.[9] The aquo-complex was initially isolated in an attempt to prepare the monodentate bipyridine complex $[Ru(bipy)_2(bipy\text{-}N)(CO)]^{2+}$ by thermal displacement of chloride from (**1**) by bipy. Instead it was found that the carbonyl complex $[Ru(bipy)_2(CO)(H_2O)]^{2+}$ (**2**) was formed along with unreacted (**1**). The proportion of (**2**) in the product mixture was found to depend on the concentration of bipy used, suggesting that its formation

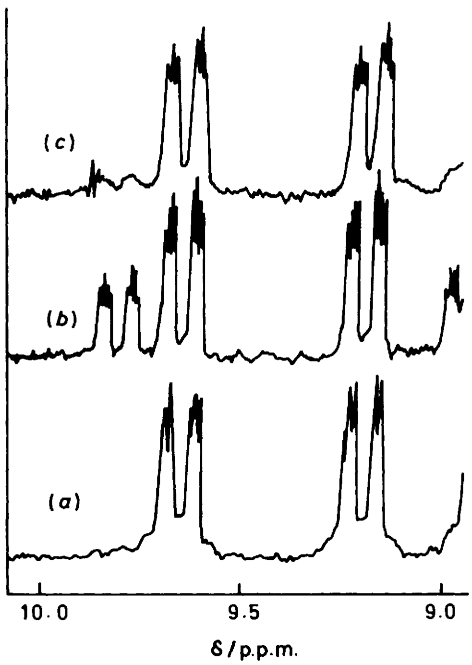

Figure 1. 80-MHz ^1H N.m.r. spectra of $[Ru(bipy)_2(CO)(H_2O)][PF_6]_2$ in perdeuterioacetone: (*a*) immediately after preparation of the solution; (*b*) after standing for 3 h; (*c*) after addition of a small amount of D_2O to (*b*)

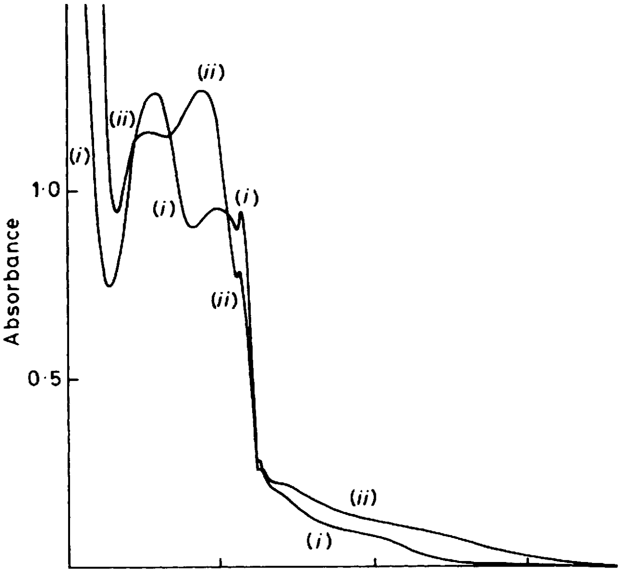

Figure 2. U.v.–visible spectra of $[Ru(bipy)_2(CO)(H_2O)][PF_6]_2$ (2.1×10^{-5} mol dm^{-3}) in (*i*) pH 6.5 buffer–methanol (4:1, v/v) and (*ii*) pH 12 buffer–methanol (4:1, v/v)

might be base catalysed. Use of sodium hydroxide rather than bipy led to complete conversion of complex (**1**) into (**2**). The latter is highly reactive and it was found, for example, that its dissolution in acetonitrile or acetone resulted in rapid conversion into $[Ru(bipy)_2(CO)(MeCN)]^{2+}$ and $[Ru(bipy)_2(CO)(Me_2CO)]^{2+}$ respectively. Due to its instability the acetone complex was not isolated. Evidence for its formation was obtained from i.r. spectroscopy [the band for (**2**) initially at 1 998 cm^{-1} in acetone solution being replaced upon standing by one at 1 983 cm^{-1}] and ^1H n.m.r. evidence (see Figure 1). Thus a fresh sample of complex (**2**) dissolved in dry acetone exhibits two low-field doublets centred at 9.67 and 9.22 p.p.m. [see Figure 1(*a*)]. On standing the signals due to (**2**) decrease and a new doublet appears, centred at 9.85 p.p.m. Another new doublet is centred at about 8.97 p.p.m. but is partly obscured by other bipy resonances [see Figure 1(*b*)]. On addition of a small amount of D_2O complex (**2**) is reformed [see Figure 1(*c*)]. If a molecular sieve is added to the n.m.r. sample as in Figure 1(*b*) the displaced water is removed and after standing overnight almost complete conversion into the acetone complex occurred. These data support the view that the aquocarbonyl complex (**2**) could be an intermediate in the formation of other $[Ru(bipy)_2(CO)L]^+$ compounds from (**1**) in aqueous solution.

Addition of NaOH to an aqueous solution of $[Ru(bipy)_2(CO)(H_2O)]^{2+}$ results in a change in the u.v.–visible spectrum (Figure 2) which is reversible under addition of acid. This is consistent with the existence of an equilibrium of the type (2)

$$\underset{(\mathbf{2})}{[Ru(bipy)_2(CO)(H_2O)]^{2+}} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} [Ru(bipy)_2(CO)(OH)]^+ \quad (2)$$

and from a study of the pH dependence of the spectral change the pK_a for complex (**2**) was determined to be 8.95 ± 0.2.

The hydride complexes $[Ru(bipy)_2(CO)H]^+$ and $[Ru(Me_2bipy)_2(CO)H]^+$ were prepared by reaction of the chlorocarbonyl complexes with $NaBH_4$ as described elsewhere[11] [*e.g.*, equation (3)]. The dicarbonyl complexes $[Ru(bipy)_2(CO)_2]^{2+}$ and $[Ru(Me_2bipy)_2(CO)_2]^{2+}$ were obtained by a different route namely by reaction of *cis*-$[Ru(bipy)(CO)_2Cl_2]$ with excess of bipy, *e.g.* as in equations (4) and (5).[12] The $[Ru(bipy)(CO)_2Cl_2]$ used in step (5) was the yellow form which had a satisfactory elemental analysis and was fully spectroscopically characterised.[12] Use of methanol as a solvent in reaction (4b) gave a red-purple compound having properties similar to the complex previously described by Wilkinson and co-workers[15] and also identified as $[Ru(bipy)(CO)_2Cl_2]$. In our hands no satisfactory elemental analysis of this compound could be obtained and its identity is at present uncertain.

$$[Ru(bipy)_2(CO)Cl]^+ \xrightarrow[H_2O-EtOH]{BH_4^-} [Ru(bipy)_2(CO)H]^+ \quad (3)$$

$$RuCl_3{\cdot}xH_2O \xrightarrow[EtOH]{(a)\ CO} [\{Ru(CO)_2Cl_2\}_n] \xrightarrow[EtOH-H_2O]{(b)\ bipy} [Ru(bipy)(CO)_2Cl_2] \quad (4)$$

$$[Ru(bipy)(CO)_2Cl_2] + bipy \xrightarrow[Heat]{MeOH-H_2O} [Ru(bipy)_2(CO)_2]^{2+} \quad (5)$$

Infrared Spectroscopy.—All $[Ru(bipy)_2(CO)L]^{n+}$ complexes exhibit a strong sharp band in the region 1 930—2 020 cm^{-1} (see Table 1) due to the CO stretching vibration. The dicarbonyl complex has two bands, at 2 035 and at 2 084 cm^{-1}, in agreement with its *cis* geometry. The observed variation of $\nu(CO)$ for $[Ru(bipy)_2(CO)L]^{n+}$ can be explained by the influence of the ligand L. The value of the $\nu(CO)$ is generally taken as a measure of the amount of back donation from the metal to CO, the band shifting to lower energy as the back donation increases. The extent of this back donation is determined by the bonding properties of the ligand L. Thus for complexes with back-bonding ligands L such as MeCN the CO stretching vibration occurs at higher energy, whereas for complexes where L is an electron donor, *e.g.* H^-, $\nu(CO)$ is found at lower energy. Similar behaviour has been observed for the NO^+ stretching vibration in $Ru(bipy)_2$ complexes of NO^+, which is isoelectronic with CO.[16]

Table 1. Some spectroscopic data for $[Ru(bipy)_2(CO)L]^{n+}$ complexes

Compound	$\nu(CO)^a/cm^{-1}$	Electronic spectral data^b
$[Ru(bipy)_2(CO)H]PF_6$	1 930	448 (3.49), 353 (3.70), 275 (4.48)^c
$[Ru(bipy)_2(CO)Cl]PF_6$	1 970	415 (sh) (3.34), 353 (sh) (3.66), 313 (4.20), 282 (4.42), 262 (4.36)
$[Ru(bipy)_2(CO)(NCS)]PF_6$	1 982	380 (sh) (3.14), 340 (sh) (3.28), 313 (3.95), 290 (4.09), 249 (4.12)
$[Ru(bipy)_2(CO)(py)][ClO_4]_2$	1 980	380 (sh) (3.42), 310 (4.37), 300 (4.36), 255 (4.45)^c
$[Ru(bipy)_2(CO)(H_2O)][PF_6]_2$	1 995	390 (sh) (3.23), 340 (sh) (3.98), 313 (4.65), 296 (4.66), 256 (4.77)
$[Ru(bipy)_2(CO)(vpy)][PF_6]_2$	1 995^d	388 (sh) (3.23), 312 (4.65), 302 (4.66), 256 (4.77)
$[Ru(bipy)_2(CO)(Mepy)][PF_6]_2$	2 000	405 (sh) (3.17), 353 (sh) (3.43), 313 (4.36), 305 (4.36), 298 (4.35), 262 (4.53)
$[Ru(bipy)_2(CO)(MeCN)][ClO_4]_2$	2 015	370 (sh) (3.76), 313 (4.80), 303 (4.75), 255 (4.85)
$[Ru(bipy)_2(CO)_2][PF_6]_2$	2 035, 2 084	316 (sh) (4.48), 310 (sh) (4.52), 303 (4.54), 249 (4.56)
$[Ru(Me_2bipy)_2(CO)Cl]PF_6$	1 980	420 (sh) (3.11), 348 (sh) (3.39), 312 (3.96), 290 (sh) (4.14), 272 (4.21), 256 (sh) (4.14)
$[Ru(Me_2bipy)_2(CO)H]PF_6$	1 900	445 (3.52), 352 (3.79), 272 (4.46)^c
$[Ru(Me_2bipy)_2(CO)_2][PF_6]_2$	2 044, 2 098	316 (sh) (4.48), 310 (sh) (4.52), 303 (4.54), 249 (4.56)
$[Ru(Me_2bipy)_2(CO)(H_2O)][PF_6]_2$	1 988	390 (sh) (3.15), 338 (sh) (3.81), 310 (4.27), 300 (4.30), 256 (4.56)

^{a} I.r. spectra recorded in KBr. ^{b} Recorded in ethanol; λ/nm with log ε in parentheses. ^{c} Solvent MeCN. ^{d} Recorded in Nujol.

Proton N.M.R. Spectroscopy.—The compounds $[Ru(bipy)_2(CO)L]^{n+}$ show a complex series of resonances in the 7.5—10.0 p.p.m. region, indicative of a *cis*-$Ru^{II}(bipy)_2$ species in which all 16 bipy protons are in different environments. (By contrast the ^1H n.m.r. spectrum of bipy protons of a *trans* complex would be very much simpler.[10,17]) In the *cis* geometry the 6′ protons are found at lower field than the other bipy protons, and as their position depends markedly on the nature of the ligand L this can conveniently be used to monitor reactions of the complexes (*e.g.* as in Figure 1).

Electronic Spectra.—The u.v.–visible data for $[Ru(bipy)_2(CO)L]^{n+}$ are given in Table 1. Below 300 nm the spectra are dominated by strong bands which may be assigned to bipy-localised $\pi \longrightarrow \pi^*$ transitions as is the case for other $Ru(bipy)_2$ complexes. Unlike most other $Ru(bipy)_2$ compounds no well resolved $d_\pi \longrightarrow \pi^*$ bands are observed in the visible part of the spectrum, with the exception of that for $[Ru(bipy)_2(CO)H]^+$. It is however probable that the poorly resolved weak absorptions between 350 and 450 nm are due to such $d_\pi \longrightarrow \pi^*$ transitions. This substantial shift to higher energy may be explained by stabilisation of the d_π levels, caused by a strong back donation from the metal to the carbonyl ligand. It is expected that if the ligand L has back-bonding ability a further shift to higher energy is obtained and this is indeed found for $[Ru(bipy)_2(CO)_2]^{2+}$. For this compound the metal-to-ligand charge-transfer (m.l.c.t.) bands are completely hidden by the much stronger $\pi \longrightarrow \pi^*$ bipy-based transitions. By contrast, where L is a strong electron donor, *e.g.* H^-, a shift to short wavelengths is not observed and well resolved $d_\pi \longrightarrow \pi^*$ bands are found.[11] In addition to the above features an intense (log ε > 4) sharp band is observed at about 313 nm for all carbonyl complexes reported with the exception of the hydride complex. The position of this band is not sensitive to the nature of the sixth ligand L and it is therefore unlikely that this band is associated with a transition involving this sixth ligand or indeed with a transition involving the metal *d* electrons. While it is possible that this absorption is due to an intraligand $\pi \longrightarrow \pi^*$ transition of the co-ordinated CO, there exists a striking similarity between the spectra of such ruthenium(II) carbonyl complexes and those of $Ru^{III}(bipy)_2$.[18,19] It might therefore be argued that the electron-withdrawing capability of CO causes a reduction in electron density at the bipy ligands comparable with that experienced in ruthenium(III) complexes, and we suggest that the band at 313 nm is the lower-energy component of the bipy-based $\pi \longrightarrow \pi^*$ transition. As predicted by this, photolabilisation of CO and replacement by a poorer π-acceptor ligand results in increased intensity of the high-energy component of the $\pi \longrightarrow \pi^*$ band and the band at 313 nm is no longer observed (see Figure 3). It may also be noted from Figure 2 that formation of $[Ru(bipy)_2(CO)(OH)]^+$ from (**2**) causes not

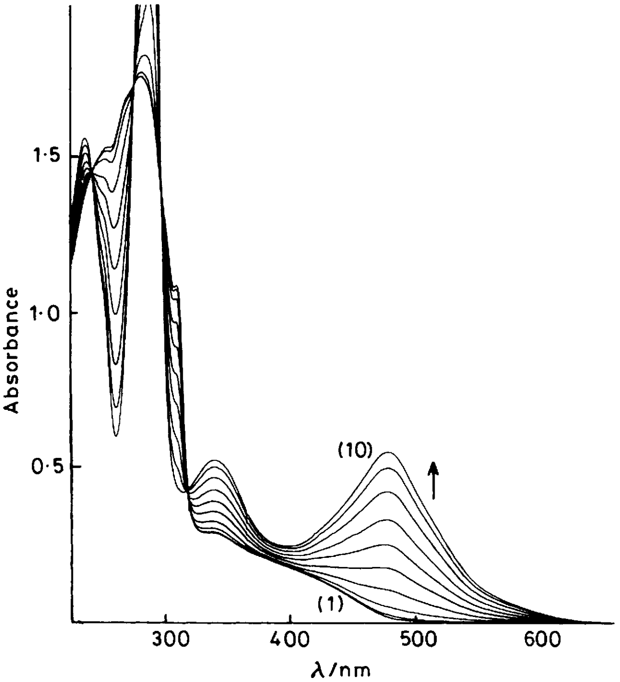

Figure 3. Photosolvation of $[Ru(bipy)_2(CO)Cl]PF_6$ in acetonitrile monitored by u.v.–visible spectroscopy. Total irradiation time: (1) 0, (2) 45 s, (3) 2.5 min, (4) 7.5 min, (5) 15 min, (6) 25 min, (7) 40 min, (8) 65 min, (9) 100 min, and (10) 157 min

Table 2. Photochemical reactions of $[Ru(bipy)_2(CO)L]^{n+}$ complexes in co-ordinating solvents[a]

Complex	Solvent	Product[b]
$[Ru(bipy)_2(CO)Cl]^+$	MeOH	$[Ru(bipy)_2(H_2O)Cl]^+$
	MeCN	$[Ru(bipy)_2(MeCN)Cl]^+$
	Pyridine	$[Ru(bipy)_2(py)Cl]^+$
$[Ru(bipy)_2(CO)(Mepy)]^{2+}$	MeOH	$[Ru(bipy)_2(H_2O)(Mepy)]^{2+}$
	Pyridine	$[Ru(bipy)_2(py)(Mepy)]^{2+}$
$[Ru(bipy)_2(CO)(pvp)]^{2+}$	MeOH	$[Ru(bipy)_2(H_2O)(pvp)]^{2+}$
	Pyridine	$[Ru(bipy)_2(py)(pvp)]^{2+}$
$[Ru(bipy)_2(CO)(MeCN)]^{2+}$	MeCN	$[Ru(bipy)_2(MeCN)_2]^{2+}$
$[Ru(bipy)_2(CO)H]^+$	MeOH	*c*
$[Ru(bipy)_2(CO)_2]^{2+}$	MeOH	$[Ru(bipy)_2(CO)(H_2O)]^{2+}$ and $[Ru(bipy)_2(H_2O)_2]^{2+}$

[a] Solutions {*ca.* 1×10^{-4} mol dm^{-3} in $[Ru(bipy)_2(CO)L]^{n+}$} irradiated with u.v. and visible radiation from a 250-W xenon-arc lamp and the reaction course followed spectrophotometrically. [b] By comparison with independently prepared samples. [c] See text.

Table 3. Electrochemical data (V) for some $[Ru(bipy)_2(CO)L]^{n+}$ complexes[a]

Compound	$Ru^{2+/3+}$	Ligand-based reductions
$[Ru(bipy)_2(CO)Cl]PF_6$	1.50 (80)	−1.34 (80), −1.56 (75)
$[Ru(bipy)_2(CO)H]PF_6$	1.03[b]	−1.55 (60), −1.75 (80)
$[Ru(bipy)_2(CO)(NCS)]PF_6$	1.47[b]	−1.25 (90), −1.46 (80)
$[Ru(bipy)_2(CO)(vpy)][PF_6]_2$	—	−1.20 (60), −1.39 (60)
$[Ru(bipy)_2(CO)(py)][ClO_4]_2$	—	−1.19 (80), −1.37 (85)
$[Ru(bipy)_2(CO)(MeCN)][ClO_4]_2$	—	−1.18 (70), −1.38 (60)
$[Ru(bipy)_3]^{2+}$[c]	1.35	−1.33, −1.52

[a] All redox potentials were measured in CH_3CN, 0.1 mol dm^{-3} NEt_4ClO_4, scan rate 200 mV s^{-1}, *vs.* s.c.e. using a platinum working electrode; values in parentheses are peak-to-peak separations. [b] Irreversible oxidation. [c] Ref. 23.

only the shifting of the m.l.c.t. bands to lower energy but also a reduction in the intensity of the band of 313 nm and an enhancement of that at about 280 nm. Similarly the absence of the band at 313 nm for the hydrido-complex can be explained by the higher electron density on the ruthenium atom.

Photochemistry.—U.v. irradiation of $[Ru(bipy)_2(CO)L]^{n+}$ causes CO dissociation and, in a co-ordinating solvent, the corresponding $[Ru(bipy)_2(solvent)L]^{n+}$ complex is formed [equation (6), L = Cl, Mepy, pvp, or MeCN] (Table 2). In

$$[Ru(bipy)_2(CO)L]^{n+} \xrightarrow[\text{solvent}]{h\nu} [Ru(bipy)_2(solvent)L]^{n+} \qquad (6)$$

each case the u.v.–visible spectra show clear isosbestic points, indicating that secondary products are unimportant. For example, Figure 3 shows the photolysis of $[Ru(bipy)_2(CO)Cl]^+$ in acetonitrile. Quantum yields for this photodecarbonylation reaction were found to be 0.09 for irradiation at 313 nm and 0.03 at 365 nm, revealing that the reaction at shorter wavelength is substantially more efficient. Similar behaviour has been reported previously for other d^6-carbonyl complexes and is consistent with more than one excited (probably *d–d*) state being the reactive species.[20–22]

Unlike the other $[Ru(bipy)_2(CO)L]^{n+}$ the complex $[Ru(bipy)_2(CO)H]^+$ does not photolyse efficiently on irradiation at 365 nm or longer wavelengths ($\varphi < 0.001$). When methanol solutions are subjected to prolonged irradiation with short-wavelength u.v. light a species showing an absorption maximum at *ca.* 400 nm is formed. The nature of this species is at present unknown. The relatively low photoreactivity of this hydride complex is consistent with it having an m.l.c.t. excited state at lower energy than the reactive (probably triplet *d–d*) excited states.

Electrochemistry.—The redox properties of some of the compounds were investigated by cyclic voltametry in acetonitrile using 0.1 mol dm^{-3} NEt_4ClO_4 as the electrolyte. The data obtained are listed in Table 3.

The only compound for which a reversible $Ru^{2+/3+}$ redox couple is observed [at +1.50 V *vs.* saturated calomel electrode (s.c.e.)] is (**1**). The $Ru^{2+/3+}$ redox couple is irreversible for the H^- and NCS^- complexes while for $[Ru(bipy)_2(CO)L]^{2+}$ no oxidation is observed for potentials up to +2.0 V *vs.* s.c.e. The absence of a $Ru^{2+/3+}$ oxidation for the dications points to a stabilisation of Ru^{II} in these compounds compared to $[Ru(bipy)_3]^{2+}$,[21,23] a probable consequence of the back-bonding ability of CO. Introduction of a ligand L with a negative charge, *e.g.* H^-, Cl^-, or NCS^-, reduces the redox potential. This reflects the change in charge of the complexes and the donor properties of these ligands. The decomposition of the hydrido and NCS^- complexes upon oxidation is, most likely, caused by subsequent oxidation of the H^- or NCS^- ligand followed by its loss and the resultant formation of the $[Ru(bipy)_2(CO)(solvent)]^{2+}$ complex.

Reduction potentials are observed for all compounds between −0.80 and −1.80 V *vs.* s.c.e. It is known that in the reduction of bipy complexes of Ru^{II} the extra electron is located on the bipy ligands rather than on the metal centre.[21,24] The potentials of these reductions may be regarded as a measure of the π-back-bonding properties of the ligands.

Conclusions

It may be seen that $[Ru(bipy)_2(CO)Cl]^+$ is a useful starting material for the preparation of a range of $[Ru(bipy)_2(CO)L]^{n+}$ complexes. These complexes are obtained in yields higher than 75% by thermal displacement of the chloride ligand and no evidence for decarbonylation is observed. U.v. photolysis of $[Ru(bipy)_2(CO)Cl]^+$ leads to loss of CO but not of Cl^-, a clear example of an antithermal photochemical reaction. Efficient photodecarbonylation is also found for the other carbonyl complexes with the notable exception of the hydrido-complex.

The electronic and electrochemical data for the materials obtained are different from those found for $Ru(bipy)_2$ complexes of N-donor ligands, and this can be attributed to the strong back donation from the metal to the carbonyl ligand. The nature of the sixth ligand L is an important factor in determining the extent of this, as is shown by the spectroscopic data.

The complex $[Ru(bipy)_2(CO)(H_2O)]^{2+}$, which has been isolated here for the first time, is probably an intermediate in the thermal reactions of $[Ru(bipy)_2(CO)Cl]^+$. It has previously been proposed[9] that this species is involved in the catalytic cycle suggested for the water-gas shift reaction catalysed by $[Ru(bipy)_2(CO)Cl]^+$.[8,9] It is interesting that for the photochemical water-gas shift reaction catalysed by $[Ru(bipy)_2(CO)Cl]^+$ little hydrogen is produced at pH < 6 while the maximum efficiency is found at pH 9.[8] We have found reversible changes in the u.v.–visible spectrum of $[Ru(bipy)_2(CO)(H_2O)]^{2+}$ in weakly alkaline solution, consistent with deprotonation (pK_a = 8.95) and formation of $[Ru(bipy)_2(CO)(OH)]^+$. This indicates that this hydroxy-species should also be considered in possible reaction mechanisms. Attack of OH^- on the CO ligand which has been proposed in the water-gas shift reaction[8,9] appears to proceed quite slowly at room temperature and is probably responsible for the decarbonylation we observe on prolonged reaction of $[Ru(bipy)_2(CO)(H_2O)]^{2+}$ in weakly alkaline solution.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 599 grating spectrophotometer. Peak positions are accurate to ± 4 cm^{-1} above 2 000 cm^{-1} and ± 2 cm^{-1} below 2 000 cm^{-1}. Samples were prepared as Nujol mulls (on NaCl plates) or KBr discs. Ultraviolet–visible spectra were recorded on a Pye Unicam SP8-200 spectrophotometer using matched 1-cm quartz cells. Absorption coefficients are accurate to 5%. Proton n.m.r. spectra were obtained on a Bruker WP80 Fourier-transform spectrometer. Peak positions (δ values) have an accuracy of 0.01 p.p.m. and the chemical shifts were measured relative to internal $SiMe_4$. Elemental analyses were performed by the Microanalytical Laboratory, University College, Dublin. Cyclic voltammetry was carried out using an E.G and G. Par model 174A polarographic analyser with an E.G. and G. Par 175 Universal Programmer with a platinum electrode as working electrode and a saturated calomel electrode as reference; the supporting electrolyte was 0.1 mol dm^{-3} NEt_4ClO_4 and molecular sieve-dried acetonitrile was used as solvent.

Photolysis experiments were carried out in standard 1-cm quartz cuvettes using either a 150-W high-pressure xenon-arc lamp with appropriate filters or a Thorn MED 250-W medium-pressure mercury lamp and an Applied Photophysics High Radiance Monochromator with 5-nm slit settings. Quantum yields were determined by steady-state irradiation using the line at 313 or 365 nm isolated from the mercury-lamp radiation, with the light intensity being measured by potassium ferrioxalate actinometry before and after each determination.[25,26]

Materials.—The complexes $[Ru(bipy)_2(CO)H]PF_6$ [11] and $[Ru(bipy)_2(CO)(vpy)][PF_6]_2$ [10] were prepared as previously described. Hydrated ruthenium chloride was a loan from Johnson Matthey. The ligand Me_2bipy was synthesised by a literature procedure.[27] All other materials were of reagent grade and were distilled or recrystallised before use.

Procedures for preparation of $[Ru(bipy)_2(CO)L]^{n+}$. In each case the analytical, u.v.–visible, i.r., and ^1H n.m.r. data (Tables 1 and 4) are consistent with the formulae. {For each of the $[Ru(bipy)_2(CO)L]^{n+}$ complexes the signals for at least one of the 6′-protons is clearly separated from those of the other protons. It appears as a broad structured doublet, centred at the given value, due to coupling with the 5′-proton and further coupling with other ring protons, see for example Figure 1.} Fuller details are given by O'Connell.[28]

$[Ru(bipy)_2(CO)Cl]ClO_4$ (**1**). This compound was obtained as a secondary product of the literature synthesis of $[Ru(bipy)_2Cl_2]\cdot 2H_2O$.[3b] In a particular experiment $RuCl_3\cdot xH_2O$ (15.6 g, 0.060 mol) and bipy (18.72 g, 0.12 mol) were heated at reflux in dmf for 8 h. Then acetone (1 dm^3) was added and the $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ crystals obtained were filtered off. Yield: 21 g (68%). Upon addition of an aqueous $NaClO_4$ solution (100 cm^3) to the remaining solution a purple precipitate was formed. Yield: 13.6 g. This crude material was further purified by column chromatography using neutral alumina and acetonitrile–benzene (50:50) as eluant. The solution obtained was concentrated to a volume of about 50 cm^3 and more benzene was added. On standing yellow crystals were formed; these were filtered off, washed with benzene, and dried *in vacuo*. The chromatography of 1 g of crude material gave 800 mg of the pure compound, with an overall yield of 31%. ^1H N.m.r. (CD_3CN): δ 7.0—9.0 (14 H, m, bipy), 9.35 (1 H, m, H$^{6'}$), and 9.57 p.p.m. (1 H, m, H$^{6'}$).

The salt $[Ru(bipy)_2(CO)Cl]PF_6$ was prepared analogously except that NH_4PF_6 was used as precipitant. ^1H N.m.r. $[(CD_3)_2CO]$: δ 7.0—9.0 (14 H, m, bipy), 9.50 (1 H, m, H$^{6'}$), and 9.69 p.p.m. (1 H, m, H$^{6'}$).

$[Ru(Me_2bipy)_2(CO)Cl]PF_6$. This was prepared by the same procedure as for the PF_6^- salt of (**1**) except that Me_2bipy was used in place of bipy. ^1H N.m.r. $[(CD_3)_2CO]$: δ 2.50 (3 H, s, Me), 2.53 (3 H, s, Me), 2.68 (3 H, s, Me′), 2.72 (3 H, s, Me′), 7.25—8.65 (10 H, m, bipy), 9.25 (1 H, d, H$^{6'}$), and 9.46 p.p.m. (1 H, d, H$^{6'}$).

Table 4. Analytical data (%)*

Compound	C	H	N
$[Ru(bipy)_2(CO)H]PF_6\cdot 0.5(CH_3)_2CO$	43.9	3.3	9.1
	(43.8)	(3.2)	(9.1)
$[Ru(bipy)_2(CO)Cl]ClO_4$	43.6	2.8	10.3
	(43.7)	(2.8)	(9.7)
$[Ru(bipy)_2(CO)(NCS)]PF_6\cdot(CH_3)_2CO$	43.3	2.9	10.0
	(42.7)	(3.1)	(10.0)
$[Ru(bipy)_2(CO)(py)][ClO_4]_2$	42.9	2.8	9.5
	(43.4)	(2.9)	(9.7)
$[Ru(bipy)_2(CO)(H_2O)][PF_6]_2$	32.8	2.7	7.4
	(33.7)	(2.4)	(7.5)
$[Ru(bipy)_2(CO)(vpy)][PF_6]_2$	40.3	3.0	8.4
	(40.2)	(2.8)	(8.4)
$[Ru(bipy)_2(CO)(Mepy)][PF_6]_2$	39.5	2.9	8.4
	(39.3)	(2.8)	(8.5)
$[Ru(bipy)_2(CO)(MeCN)][ClO_4]_2$	39.4	2.7	10.6
	(40.5)	(2.8)	(10.3)
$[Ru(bipy)_2(CO)_2][PF_6]_2$	34.7	2.2	7.3
	(34.7)	(2.1)	(7.4)
$[Ru(Me_2bipy)_2(CO)Cl]PF_6$	44.5	3.3	8.4
	(44.3)	(3.6)	(8.3)
$[Ru(Me_2bipy)_2(CO)H]PF_6$	46.3	3.4	8.4
	(46.7)	(3.9)	(8.7)
$[Ru(Me_2bipy)_2(CO)_2][PF_6]_2\cdot H_2O$	37.5	3.4	6.8
	(37.5)	(3.2)	(6.7)
$[Ru(Me_2bipy)_2(CO)(H_2O)][PF_6]_2\cdot 0.5NH_4PF_6$	33.8	3.4	7.0
	(33.9)	(3.2)	(7.1)
$[Ru(bipy)(CO)_2Cl_2]$	37.4	2.0	7.6
	(37.5)	(2.1)	(7.3)
$[Ru(Me_2bipy)(CO)_2Cl_2]$	41.1	2.8	7.0
	(40.8)	(2.9)	(6.8)

* Calculated values are given in parentheses.

$[Ru(bipy)_2(CO)(NCS)]PF_6\cdot(CH_3)_2CO$. Potassium thiocyanate (102 mg, 1.05 mmol) in water (15 cm^3) was added to $[Ru(bipy)_2(CO)Cl]PF_6$ (224 mg, 0.360 mmol) which had been refluxed in methanol (45 cm^3). To this was added water–methanol (25:75, v/v; 20 cm^3) and the mixture heated at reflux for 7 d. The solution was concentrated by rotoevaporation and then concentrated aqueous NH_4PF_6 was added. The resultant yellow precipitate was filtered off, washed with diethyl ether, recrystallised from acetone–water, and dried *in vacuo*. Yield: 192 mg (83%) of yellow-orange crystals. ^1H N.m.r. $[(CD_3)_2CO]$: δ 7.40—8.91 (14 H, m, bipy), 9.22 (1 H, m, H$^{6'}$), and 9.55 p.p.m. (1 H, m, H$^{6'}$).

$[Ru(bipy)_2(CO)(py)][ClO_4]_2$. The perchlorate salt of (**1**) (300 mg, 0.52 mmol) was heated at reflux in water–methanol (75:25, v/v; 50 cm^3) in the presence of pyridine (2 cm^3) for 8 h. The reaction was carried out in the dark. An orange precipitate was formed after addition of excess of $NaClO_4$. The complex was filtered off, washed with benzene, and dried *in vacuo*. The purity was checked by thin-layer chromatography. Yield: 300 mg (80%). ^1H N.m.r. (CD_3CN): δ 7.3—8.6 (20 H, m, bipy + py) and 9.52 p.p.m. (1 H, m, H$^{6'}$).

$[Ru(bipy)_2(CO)(Mepy)][PF_6]_2$. The perchlorate salt of (**1**) (850 mg, 1.47 mmol) and 4-methylpyridine (430 mg, 4.6 mmol) were refluxed for 22 h in water–methanol (75:25 v/v; 100 cm^3). The product was precipitated as the PF_6^- salt by addition of an concentrated aqueous NH_4PF_6 solution, recrystallised from acetone–ethanol, and dried *in vacuo*. Yield: 1.04 g (90%). The compound was further purified by chromatography on neutral alumina using acetonitrile–benzene (50:50) as eluant. ^1H N.m.r.

(CD_3CN): δ 2.36 (3 H, s, Me), 7.2—8.7 (19 H, m, bipy + py), and 9.48 p.p.m. (1 H, m, $H^{6'}$).

$[Ru(bipy)_2(CO)(MeCN)][ClO_4]_2$. The perchlorate salt of (**1**) (300 mg, 0.520 mmol) and acetonitrile (8 cm^3) were heated in methanol (35 cm^3) at reflux for 8 h. After adding an aqueous $NaClO_4$ solution, yellow crystals were obtained on standing. These were filtered off, washed with benzene, and dried *in vacuo*. The purity was checked by t.l.c. Yield: 280 mg (80%). The complex $[Ru(bipy)_2(CO)(MeCN)][PF_6]_2$ was prepared by a similar procedure as above using NH_4PF_6 as precipitant and recrystallising from acetonitrile. ^1H N.m.r. (CD_3CN): δ 3.74 (3 H, s, Me), 7.4—9.0 (14 H, m, bipy), 9.43 (1 H, m, $H^{6'}$), and 9.59 (1 H, m, $H^{6'}$).

$[Ru(bipy)_2(CO)(H_2O)][PF_6]_2$. Sodium hydroxide (1.56 cm^3 of a 1 mol dm^{-3} solution) was added to a refluxing solution of $[Ru(bipy)_2(CO)Cl]PF_6$ (261 mg, 420 mmol) in water–methanol (75:25, v/v; 70 cm^3). This was heated at reflux for 23 h, acidified with HPF_6 (65% aqueous solution), and the product isolated as a yellow powder by addition of concentrated aqueous NH_4PF_6, filtration, and vacuum drying. Yield: 267 mg (85%). ^1H N.m.r. $[(CD_3)_2CO]$: δ 6.50 (2 H, s, H_2O), 7.38—8.93 (14 H, m, bipy), 9.22 (1 H, m, $H^{6'}$), and 9.67 p.p.m. (1 H, m, $H^{6'}$).

$[Ru(Me_2bipy)_2(CO)(H_2O)][PF_6]_2 \cdot 0.5NH_4PF_6$. Sodium hydroxide (1.0 cm^3 of a 1 mol dm^{-3} solution) was added to a refluxing solution of $[Ru(Me_2bipy)_2(CO)Cl]PF_6$ (157 mg, 0.232 mmol) in water–methanol (75:25, v/v; 62 cm^3) and the mixture heated at reflux for 43 h. After cooling, and acidification with 65% aqueous HPF_6, concentrated aqueous NH_4PF_6 was added to yield a yellow precipitate which was collected by suction filtration and vacuum dried. ^1H N.m.r. $[(CD_3)_2CO]$: 2.51 (3 H, s, Me), 2.56 (3 H, s, Me), 2.71 (3 H, s, Me′), 2.75 (3 H, s, Me′), 6.24 (2 H, s, H_2O), 7.23—8.69 (10 H, m, bipy), 8.93 (1 H, d, $H^{6'}$), and 9.35 p.p.m. (1 H, d, $H^{6'}$).

$[Ru(bipy)(CO)_2Cl_2]$. A solution of $[\{Ru(CO)_2Cl_2\}_n]$ was prepared by heating $RuCl_3 \cdot 3H_2O$ (2.79 g) in refluxing ethanol (70 cm^3) for 6 h while carbon monoxide was bubbled through the mixture. This gave a clear blood-red solution which was divided into portions for immediate use. To a portion (30 cm^3) of this solution was added bipy (3.653 g, 23.4 mmol), ethanol (15 cm^3), and water (45 cm^3) and the mixture heated at reflux for 2 h. On cooling, fine yellow needles were deposited. These were collected by suction filtration and vacuum dried. ^1H N.m.r. $[(CD_3)_2CO]$: δ 7.87 (2 H, dd, $H^{5,5'}$), 8.36 (2 H, dd, $H^{4,4'}$), 8.71 (2 H, d, $H^{3,3'}$), and 9.27 p.p.m. (2 H, d, $H^{6,6'}$). U.v.–visible (MeOH): $\lambda_{max.}$ 354 (log ε 3.08), 313 (4.08), 300 (3.99), and 284 nm (3.97).

$[Ru(Me_2bipy)(CO)_2Cl_2]$. To a portion (34 cm^3) of the $[\{Ru(CO)_2Cl_2\}_n]$ solution prepared as above was added Me_2bipy (4.195 g, 22.8 mmol), ethanol (17.5 cm^3), and water (52.5 cm^3), and the mixture heated at reflux for 2 h. On cooling overnight, yellow-white needles separated from solution. ^1H N.m.r. $[(CD_3)_2CO]$: δ 2.64 (6 H, s, Me), 7.66 (2 H, d, $H^{5,5'}$), 8.54 (2 H, s, $H^{3,3'}$), and 9.06 p.p.m. (2 H, d, $H^{6,6'}$). U.v.–visible (MeCN): $\lambda_{max.}$ 338 (log ε 3.17), 310 (4.08), 297 (3.97), 277 (3.97), 248 (sh) (3.94), and 230 nm (4.24).

$[Ru(Me_2bipy)_2(CO)_2][PF_6]_2 \cdot H_2O$. The complex $[Ru(Me_2bipy)(CO)_2Cl_2]$ (151 mg, 0.37 mmol) and Me_2bipy (0.81 mg, 0.44 mmol) were heated at reflux in methanol–water (25:75, v/v; 150 cm^3) for 24 h. Addition of concentrated aqueous NH_4PF_6 to the cooled reaction mixture yielded a yellow precipitate which was collected by suction filtration and dried *in vacuo*. Recrystallisation from ethanol–water gave a yellow microcrystalline solid. ^1H N.m.r $[(CD_3)_2CO]$: δ 2.56 (6 H, s, Me), 2.76 (6 H, s, Me′), 7.49 (2 H, d, H^5), 7.65 (2 H, d, H^6), 7.94 (2 H, d, $H^{5'}$), 8.70 (2 H, s, H^3), 8.76 (2 H, s, $H^{3'}$), and 9.28 p.p.m. (2 H, d, $H^{6'}$).

$[Ru(bipy)_2(CO)_2][PF_6]_2$. The complex $[Ru(bipy)(CO)_2Cl_2]$ (200 mg, 0.52 mmol) and bipy (110 mg, 0.7 mmol) were refluxed in ethanol–water (33:67, v/v; 150 cm^3) for 24 h. Addition of concentrated aqueous NH_4PF_6 yielded white crystals, which were recrystallised from ethanol–water.

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