Excited-state Properties and Reactivity of $[ReCl(CO)_3(2,2'\text{-bipy})]$ (2,2′-bipy = 2,2′-bipyridyl) studied by Time-resolved Infrared Spectroscopy

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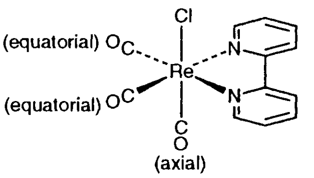
Fast time-resolved infrared spectroscopy shows that the ν(CO) bands of the important CO_2-reducing complex, $[ReCl(CO)_3(2,2'\text{-bipy})]$ **1** (2,2′-bipy = 2,2′-bipyridyl), shift up in frequency in the metal to ligand charge-transfer excited state and that the anion $\mathbf{1}^-$, generated by reaction of the excited state with triethylamine, shows a lowering in frequency of the ν(CO) bands significantly different from those of related but non-reducing complexes.

Since the demonstration[1] of the ability of $[ReCl(CO)_3(2,2'\text{-bipy})]$ **1** (2,2′-bipy = 2,2′-bipyridyl) to act as a catalyst in the photoreduction of CO_2, there has been much interest in this and related complexes.[2] This has reinforced interest in the excited-state properties of **1**. There is a low-lying metal to ligand charge-transfer (m.l.c.t.) state, with considerable triplet character,[3] and with a relatively long lifetime (25 ns in MeCN[2d] and 50 ns in CH_2Cl_2[2e]). The time resolved resonance-Raman spectrum[4] of this excited state shows vibrational features assigned to the 2,2′-bipyridyl anion ($2,2'\text{-bipy}^-$), and hence the state is best described as $[Re^{II}Cl(CO)_3(2,2'\text{-bipy}^-)]$; no ν(CO) resonance-enhanced bands were observed. Although the IR spectrum of the ground state shows three ν(CO) bands (the a′, a″ and a′ modes expected for a molecule with C_S vibrational symmetry), the resonance-Raman spectrum[5] shows enhancement of only the highest frequency ν(CO) mode. The excited state is quenched by triethanolamine or triethylamine, with a rate constant[2b,c,e] of $\approx 5 \times 10^7$ dm^3 mol^{-1} s^{-1}, to produce, presumably, $[ReCl(CO)_3(2,2'\text{-bipy})]^-$ $\mathbf{1}^-$, although the ion was not positively identified. This anion, which is probably the important substitution-sensitive intermediate in the CO_2 reduction cycle, can also be generated [and the ν(CO) IR bands observed, and hence the anion positively identified] by either



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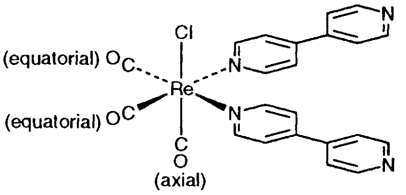

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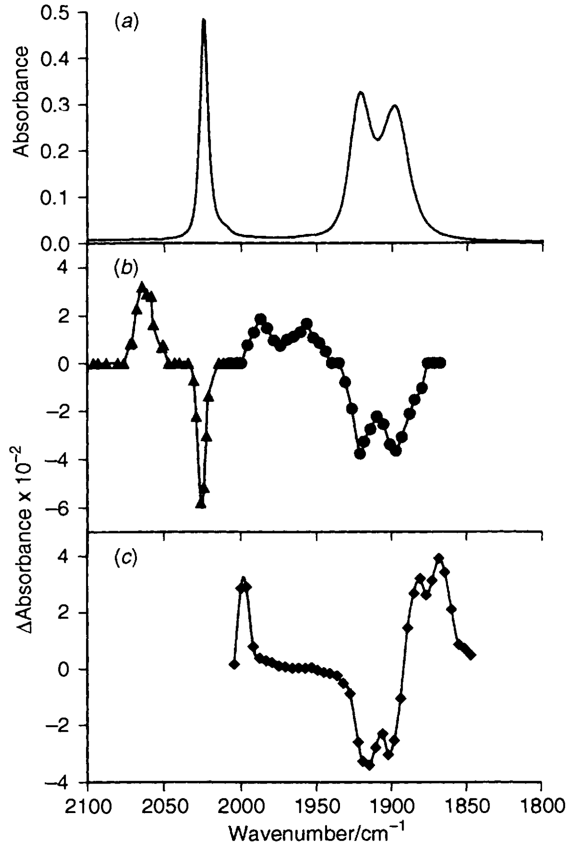

Fig. 1 (*a*) Fourier-transform (FT) IR (Nicolet) spectrum in the ν(CO) region of **1** in CH_2Cl_2 ($\approx 5 \times 10^{-4}$ mol dm^{-3}; path length 4 mm); (*b*) TRIR spectrum at ≈ 50 ns after flash from excimer laser of a solution of **1** in CH_2Cl_2 ($\approx 5 \times 10^{-4}$ mol dm^{-3}; path length 4 mm); (*c*) TRIR spectrum at 500 μs after flash from excimer laser of solution of **1** in MeCN ($\approx 5 \times 10^{-4}$ mol dm^{-3}; path length 5 mm) in the presence of triethylamine (≈ 1 mol dm^{-3}). In both (*b*) and (*c*), data points plotted downwards signify loss of ground state of parent, points plotted upwards signify generation of excited state or intermediate. A brief description of the apparatus is given in footnote *, and further details in ref. 11.

Table 1 Infrared vibrational data, in the ν(CO) region (in cm^{-1}), for complexes of type [ReCl(CO)$_3$(LL′)] **A** †

	LL′					
	2,2′-bipy (**1**)			(4,4′-bipy)$_2$ (**2**)		(4-bzpy)$_2$ (**3**)
	(i)	(ii)	(iii)	(iv)	(v)	(vi)
ν(CO) data						
Ground state (**A**)	2024 1921 1899	2023 1917 1899	2019 1914 1893	2027 1926 1891	2026 1922 1895	2027 1923 1895
M.l.c.t. excited state (**A***)	2064 1987 1957			2055 1992 1957		
Anion (**A**$^-$)		1996 1881 1867	1994 1880 1862		2012 1903 1882	2013 1903 1881
Dianion (**A**$^{2-}$)					2002 1890 1868	2001 1886 1865
Shifts and mean shifts in ν(CO)						
A* − **A**	+40 +66 } 55 +58			+28 +66 } 53 +66		
A$^-$ − **A**		−27 −36 } −32 −32	−25 −34 } −30 −31		−14 −19 } −15 −13	−14 −20 } −16 −14
A^{2-} − **A**					−24 −32 } −28 −27	−26 −37 } −31 −30

† Column (i) FTIR (ground state, **A**) and TRIR (excited state, **A***) of **1** in CH$_2$Cl$_2$ solution [see Figs. 1(*a*) and 1(*b*)]; (ii) FTIR (**A**) and TRIR (**A**$^-$) of **1** in MeCN–NEt$_3$ solution [see Fig. 1(*c*)]; (iii) FTIR (**A** and **A**$^-$) of **1** in dmf; the positions of the bands of the anion arise either from photoreduction employing 20% NEt$_3$ or electrochemical reduction with 0.36 mol dm^{-3} NBu$_4$PF$_6$ (see ref. 6); (iv) FTIR (**A**) and TRIR (**A***) of **2** in CH$_2$Cl$_2$ solution (ref. 9); (v) FTIR (**A**, **A**$^-$ and **A**$^{2-}$) of **2** in MeCN–0.1 mol dm^{-3} NBu$_4$ClO$_4$ solution employing electrochemical reduction (see ref. 9); (vi) FTIR (**A**, **A**$^-$ and **A**$^{2-}$) of **3** in MeCN–0.36 mol dm^{-3} NBu$_4$PF$_6$ solution employing electrochemical reduction [see ref. 6(*a*)].

electrochemical reduction[6] of **1** in dimethylformamide (dmf) or by photo-reduction[6b] of **1** in dmf containing NEt$_3$. There are however still many uncertainties in the CO$_2$ reduction mechanism.

Time-resolved infrared (TRIR) spectroscopy is a valuable tool for studying the structure and behaviour of the excited states of co-ordination compounds.[7] Early,[8] and recent more detailed[9] studies, demonstrated that [ReCl(CO)$_3$(4,4′-bipy)$_2$] **2** (4,4′-bipy = 4,4′-bipyridyl), in its long-lived (≈1 μs) m.l.c.t. excited state, shows an upward shift in the frequencies of the three ν(CO) bands (see Table 1); these arise from an increase in the axial and equatorial C–O force constants of ≈80 and ≈86 N m^{-1} respectively. These investigations concentrated on **2**, even though it is not a CO$_2$ reductant,[10] because of the longer lifetime (≈1 μs) of its m.l.c.t. excited state compared with **1** (≈50 ns). We now report TRIR data for the m.l.c.t. excited state of **1**, and for its reaction to give **1**$^-$; and also make comparisons with relevant data. These results are also significant in the interpretation of the ground-state resonance-Raman spectrum of **1**.

Fig. 1 illustrates two TRIR experiments with complex **1**. Details of the ν(CO) bands in these experiments are given in Table 1, columns (i) and (ii); other relevant ν(CO) data are also given in Table 1, columns (iii)–(vi). The following conclusions can be drawn.

(*a*) Fig. 1(*b*) shows the ν(CO) IR spectrum of the triplet m.l.c.t. excited state of **1** in CH$_2$Cl$_2$.* All three ν(CO) bands have moved up in frequency from the ground state by an amount similar to that for **2** [*cf.* columns (i) and (iv)]. This upward shift arises from the formal increase in the rhenium oxidation state as an electron is transferred to the 2,2′-bipy ligand. The simplest interpretation is that the energy-factored CO force-field constants, k_{eq} and k_{ax}, each increase by ≈85 ± 10 N m^{-1}. We have recently shown[12] that this implies that the CO bond lengths alter by an amount given by: $\Delta r = (r_2 - r_1) = -0.174\ln(k_2/k_1)$ (with r in Å) = ≈ −0.010 Å. If the ground-state force field of **1** is even only approximately similar to that of **2**, this implies that the normal coordinate which makes the overwhelming contribution to the excited-state distortion coordinate is the totally symmetric high-frequency stretching mode. Hence only the band arising from this coordinate will be enhanced significantly in resonance-Raman spectra involving the m.l.c.t. transition.† There is no need to invoke subtle excited-state interactions.[5]

(*b*) From a comparison of the data in columns (ii) and (iii) it is clear that the species produced on flash photolysis in MeCN–NEt$_3$ solution, and shown in Fig. 1(*c*), is the anion **1**$^-$. With this concentration of NEt$_3$, the triplet m.l.c.t. excited state is too short lived to detect on our apparatus, but there is little doubt that this state is the precursor to the anion. As expected, the spectrum of the anion is long-lived on the time-scale of the TRIR experiment (≈200 ms).

(*c*) The shifts in frequency of the ν(CO) bands of the various complexes are revealing. Note first that the three ground-state

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* Dichloromethane is used as solvent to obtain the TRIR spectrum of the excited state because it is longer lived in this solvent than in MeCN. There is very little difference in the frequencies of the ν(CO) bands in the two solvents. The excimer laser is a Lumonics HyperEx 440 operating at 308 nm, with a pulse width of ≈30 ns and a pulse energy of ≈100 mJ. The spectra below 2000 cm^{-1} were obtained with a continuous-wave CO laser (Edinburgh Instruments PL3) giving ≈100 mW per line and tunable in steps of ≈4 cm^{-1}. The spectrum above 2000 cm^{-1} was obtained with an infrared diode laser (Mütek MDS 1100).

† Note that strictly speaking, the Raman intensity argument applies to the initially excited singlet m.l.c.t. state, rather than the long-lived triplet m.l.c.t. state. However this spin change is very unlikely to affect substantially the excited-state distortion.

frequencies of each of the compounds in Table 1 are very similar; thus in the ground states the ligands have similar effects. For the excited states of **1** and **2**, the shifts from the ground state (**A*** − **A**) are similar, implying that in both cases the change in electron density on the metal is the same. By contrast the shift from neutral to the anion ($\mathbf{A}^-$ − **A**) for **1** is about twice that for [ReCl(CO)$_3$(4,4′-bipy)$_2$] **2** and [ReCl(CO)$_3$(4-bzpy)$_2$] **3** (4-bzpy = 4-benzoylpyridine), and about equal to ($\mathbf{A}^{2-}$ − **A**). The implication is that there is much greater charge 'leakage' to the metal from the bidentate 2,2′-bipy ligand than from the monodentate 4,4′-bipy or 4-bzpy ligand. This is not surprising and, as pointed out by Shu and Wrighton,[6a] explains why $\mathbf{1}^-$ is more substitution-sensitive than $\mathbf{3}^-$; similarly it explains why $\mathbf{2}^-$ will not participate in the reduction cycle. Hence the electron distribution in the excited state is not a good indication of CO$_2$-reduction properties.

In the future we plan to examine the substitution reactions of $\mathbf{1}^-$ and related species using TRIR spectroscopy.

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