

TRIR studies of ruthenium-tin complexes

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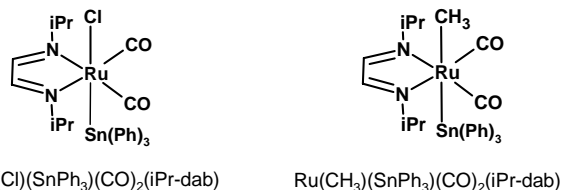
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Introduction

Ruthenium complexes constitute an important group of catalysts and photochemical reagents. They exhibit a rich photochemistry and have been widely studied by steady state methods, ns time-resolved methods and more recently by ultrafast electronic absorption methods (TRVIS). However TRVIS is not suitable for the study of reaction dynamics since this technique is not structurally sensitive enough to elucidate the often complicated photochemical reactions. TRIR is emerging as a promising technique for photochemical reactions in the ps time domain and previously we have studied the dissociative photochemistry of $[\text{Ru}(\text{X})_2(\text{CO})_2(\text{bpy})]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) complexes by TRIR¹). Ruthenium-tin clusters comprises an interesting group of complexes since the photoreactions proceed via homolytic bond splitting of the Ru-CH₃ bond or the Ru-SnPh₃ bond²⁻⁵) rather than CO dissociation.

The reaction is highly selective and produces 95% methyl radical and only 5% triphenyltin radicals. Presently TRIR is the only method to characterise the excited state and the short-lived intermediates.



Scheme 1

Stufkens and co-workers first identified the reactive sigma bond to ligand charge transfer (SBLCT) excited state in the CH₃-Ru-Sn cluster and identified a wavelength dependent mechanism of photoinduced bond-homolysis. Through CIDEP EPR studies they concluded that irradiation into the long wavelength absorption bands leads to slow bond homolysis from a relaxed triplet excited state. On the other hand, from higher excited states, the reaction was postulated to proceed ultrafast prior equilibration. The time-resolution of the EPR experiments is not fast enough to directly detect the excited product, relying rather on the spin configuration of the formed radical pair. Herein we present a TRIR study of the complexes $[\text{Ru}(\text{Cl})(\text{SnPh}_3)(\text{CO})_2(\text{iPr-dab})]$ and $[\text{Ru}(\text{CH}_3)(\text{SnPh}_3)(\text{CO})_2(\text{iPr-dab})]$, scheme 1 (iPr-dab = N,N'-diisopropyl-1,4-diazabutadiene).

Results

Excitation of $[\text{Ru}(\text{Cl})(\text{SnPh}_3)(\text{CO})_2(\text{iPr-dab})]$ in CH₂Cl₂ produces two negative bands at 2032 and 1973 cm⁻¹ due to the depletion of the ground state within the experiment time resolution of 2 ps (Figure 1). In addition two rather broad positive bands are found at 2051 and 2003 cm⁻¹ due to a transient species formed. There is a small shift to higher energy and a narrowing of the transient bands occurring with a time constant of 27 ps after excitation. The shift to higher energy is 20 and 30 cm⁻¹. There is no significant decay during the duration of the experiment of 1000 ps.

The transient spectra of $[\text{Ru}(\text{CH}_3)(\text{SnPh}_3)(\text{CO})_2(\text{iPr-dab})]$ show entirely different dynamics. Upon excitation into the lowest energy absorption band (Figure 2), two bleach IR bands due to the depletion of the ground state at 2002 and 1944 cm⁻¹ at 2 ps two positive bands at 2012 and 1955 cm⁻¹ are formed these bands narrows and grows during the following 12 ps due to dissipation of excess vibrational energy. The IR bands represent an excited state where the carbonyls experience less π -back bonding. The excited state decays with a lifetime of 797 \pm 21 ps. With a similar time constant, 821 \pm 30 ps, two bands due to a new species grow in. The product bands absorb at 1984 and 1919 cm⁻¹, reaching maximum intensity at 3000 ps and remains constant for the following 1000 ps. There is no bleach recovery until the end of the time interval investigated. The higher energy bands are more pronounced in the more polar solvent CH₃CN and the conversion is somewhat faster, 608 \pm 27 ps for the product rise and 658 \pm 32 ps for the transient decay.

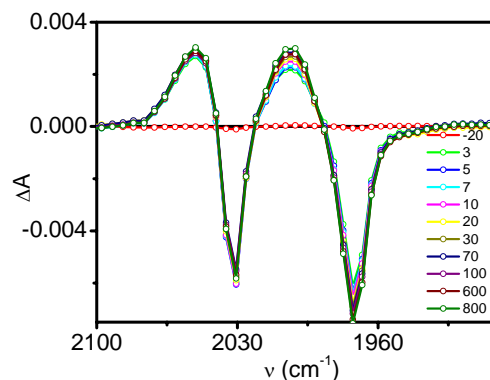


Figure 1. TRIR spectra of $[\text{Ru}(\text{Cl})(\text{SnPh}_3)(\text{CO})_2(\text{iPr-dab})]$ in CH₂Cl₂, after 400 nm excitation. Experimental points separated by 4 to 5 cm⁻¹.

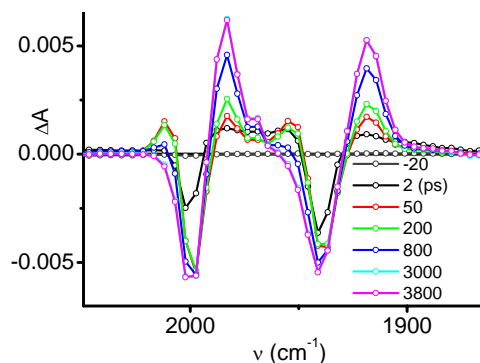


Figure 2. TRIR spectra of $[\text{Ru}(\text{CH}_3)(\text{SnPh}_3)(\text{CO})_2(\text{iPr-dab})]$ in CH₂Cl₂ after 20 nm excitation.

Strikingly when the excitation wavelength is altered to 267 nm the high energy transient species is absent and the product with bands at 1984 and 1919 cm⁻¹ is formed within the instrument rise time of 2 ps (Figure 3). The CO stretching frequencies are

identical with the 520 nm experiment. Furthermore, the product bands have shoulders at approximately 1970 and 1900 cm^{-1} which decay with a time constant of 47 ± 8 ps. The bands due to the main product species are simultaneously increasing with a time constant of 36 ± 5 ps.

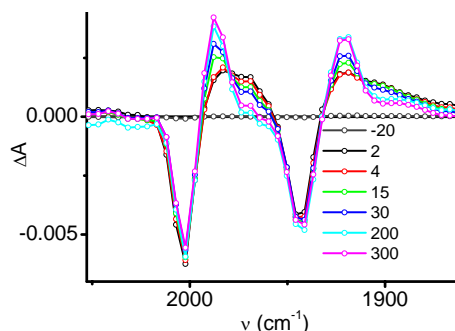


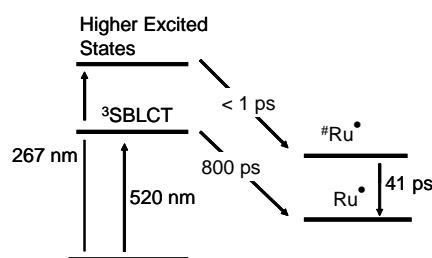
Figure 3. TRIR spectra of $[\text{Ru}(\text{CH}_3)(\text{SnPh}_3)(\text{CO})_2(\text{iPr-dab})]$ obtained with 267 nm excitation in CH_2Cl_2 .

Discussion

$[\text{Ru}(\text{Cl})(\text{SnPh}_3)(\text{CO})_2(\text{iPr-dab})]$ The TRIR spectra of $[\text{Ru}(\text{Cl})(\text{SnPh}_3)(\text{CO})_2(\text{iPr-dab})]$ in Figure 1 are rather typical of MLCT/XLCT excited states. The relatively small upward shift of 20 and 30 cm^{-1} indicates a lower degree of charge separation in the excited state than in the case of the archetypical $[\text{Re}(\text{Cl})(\text{CO})_3(\text{bpy})]$ where the $\text{A}'(1)1 \nu(\text{CO})$ frequency shift by 39 (CH_2Cl_2) or 40 (MeCN) cm^{-1} upon excitation^{6,7}. This does not necessarily indicate a higher degree of XLCT character of the excited state as compounds featuring the dab ligand show smaller shifts than their corresponding 2,2-bipyridine counterparts. The MLCT/XLCT character is also evident from the strong solvatochromism of the lowest energy absorption band⁸. The complex is photochemically inert and the excited state is long lived. Previous studies has determined the lifetime to 1.1 μs at 293 K in THF⁸.

$[\text{Ru}(\text{CH}_3)(\text{SnPh}_3)(\text{CO})_2(\text{iPr-dab})]$ Upon excitation with a 520 nm laser pulse a transient species formed is consistent with a dicarbonyl with slightly less π back bonding (Figure 2). This indicates that there is some charge transfer to the dab ligand in the excited state. The CO shift is far less than for the chloride complex $[\text{Ru}(\text{Cl})(\text{SnPh}_3)(\text{CO})_2(\text{iPr-dab})]$. This is consistent with calculations showing a strong mixing between the $\text{CH}_3\text{-Ru-Sn}$ σ orbital and the dab π^* orbitals both in the ground state and the excited state giving the latter less CT character. The solvatochromism of this complex is also rather small⁸. The lowest excited state observed at 2 ps after excitation is best described as $\sigma\text{-CH}_3\text{-Ru-Sn}$ to ligand charge transfer. This is a reactive state whose population causes quantitative conversion to a photoproduct. The photoproduct bands are assigned to predominantly the solvated radical $[\text{Ru}(\text{SnPh}_3)(\text{Solv})(\text{CO})_2(\text{iPr-dab})^\cdot]$. This radical has never been observed in solution due to fast dimerisation (in THF) or reaction with the solvent (chlorinated solvents). Its formation could be established by EPR spectroscopy in toluene containing excess PPh_3 ⁹. The bond homolysis is rather slow from the MLCT/SBLCT state and the conversion to the radicals is isosbestic confirming that the quantum yield is close to 1. The reaction of the radical with CH_2Cl_2 produces the chloride complex $[\text{Ru}(\text{CH}_3)(\text{SnPh}_3)(\text{CO})_2(\text{iPr-dab})]$ on a longer timescale. This is not observed in the ps TRIR experiments. The above interpretation is consistent with Stufkens and coworkers prediction that excitation into the lowest occurs from a thermally relaxed $^3\text{SBLCT}$ excited state. The somewhat faster homolysis in the polar solvent is likely to reflect the negative solvatochromism of the compound⁸ the excited state has higher energy and the barrier for the reaction will be lower.

When the compound is excited with UV laser pulses of 270 nm the radicals are formed on a sub picosecond time scale. The radical bands appear already at 2 ps (Figure 3) showing that the product formation must bypass the thermalized³ SBLCT state. Furthermore, the rapidly decaying shoulders at 1970 and 1900 cm^{-1} are typical of vibrationally excited carbonyls (hot excited state). This is a strong evidence of that the product formation arises before thermal relaxation of the excited state. Again this is a verification of the CIDEP EPR studies where the spin polarization pattern suggested that the radical species is formed promptly, *i.e.* before thermal relaxation of the excited state. The photochemistry is summarised in Scheme 2.



Scheme 2

Conclusions

TRIR spectroscopy is a powerful tool for elucidating photochemical reaction mechanisms. This example illustrates that photochemical reactions can occur at vastly different rates from different excited states. 267 nm excitation populates a presumably unbound excited state, which leads to ultrafast bond homolysis. This is fully consistent with Stufkens findings from CIDEP experiments where spin polarization pattern indicated that excitation into the lowest wavelength band yielded bond homolysis from a triplet state, while 267 nm excitation produced a different spin polarization and consequently it was postulated that the homolysis occurred on a timescale comparable with singlet-triplet intersystem crossing.

Acknowledgements

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