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A time-resolved infrared spectroscopic study of [$M(SnR_3)_2(CO)_2$-(α-diimine)] (M = Ru, Os; R = Ph, Me): evidence of charge redistribution in the lowest-excited state

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According to previous electronic absorption, resonance Raman and DFT studies the lowest-energy electronic transition of the Ru^{II} and Os^{II} complexes *trans,cis*-[$M(SnR_3)_2(CO)_2$(α-diimine)] (α-diimine = bpy, *etc.*) has a σ(Sn–M–Sn) $\longrightarrow$ π^*(α-diimine) or sigma-bond-to-ligand charge-transfer (SBLCT) character. Nanosecond time-resolved step-scan IR (s^2-TRIR) spectra of a series of these complexes are reported which indicate that the initial SBLCT excitation is followed by a redistribution of the electron density if this transition has an appreciable charge transfer character. This effect is virtually the same for the Ru and Os compounds, but different for the $SnMe_3$ and $SnPh_3$ complexes. s^2-TRIR spectra of [$Os(SnPh_3)_2(CO)_2(dmb)$] showed the occurrence of an infrared rigidochromic effect in a low-temperature glass.

Introduction

Numerous studies have been concerned with complexes containing a low-valent metal and an α-diimine ligand such as 2,2′-bipyridine (bpy), because of the intriguing properties of their excited states. The complexes [$Ru(bpy)_3$]$^{+2}$ [1–5] and [Re(Cl)-$(CO)_3$(bpy)][6–8] and their derivatives have proved to be good photosensitizers for energy- and electron-transfer particularly because of the long lifetimes and good redox properties of their lowest-excited metal-to-ligand charge-transfer (MLCT) states. MLCT excitation of [$Re(Cl)(CO)_3(bpy)$] causes a decrease of the electron density on the central metal atom and hence of the metal to CO π-back bonding. As a result the carbonyl vibrations shift to higher frequencies on excitation and this is nicely reflected in the time-resolved IR (TRIR) spectra of this complex and related ones.[9–13] Replacement of the chloride in the Re complex by a N- or P-donor ligand changes the energy and the lifetime of this MLCT state without changing its nature. A change of character can, however, be achieved by replacing *e.g.* bpy by dppz (dipyrido[3,2-*a*: 2′,2′-*c*]phenazine). The TRIR spectrum of the complex ion [$Re(PPh_3)(CO)_3(dppz)$]$^+$ shows very small frequency shifts of the CO vibrations on excitation, which is consistent with a ligand-localised relaxed excited state, presumably $^3\pi\pi^*$(dppz).[13] If Cl^- in [$Re(Cl)(CO)_3(bpy)$] is replaced by I^- the excited state obtains a halide(X)-to-ligand charge-transfer (XLCT) character[14] and the same holds for the complexes [$Ru(X)(Me)(CO)_2$(α-diimine)] (α-diimine = bpy; R′-DAB: *N*,*N*′-di-R′-1,4-diaza-1,3-butadiene).[15–17] The nanosecond time-resolved IR (TRIR) spectrum of [Ru(Cl)(Me)-$(CO)_2$(iPr-DAB)] exhibits a shift of the two ν(CO) vibrations on going from the ground state to the relaxed excited state of *ca.* +50 cm^{-1}, which is consistent with the MLCT character of this state.[17] The resonance Raman (rR) spectra show that the corresponding transition to the Franck–Condon states of [$Ru(I)(Me)(CO)_2$(iPr-DAB)] has virtually pure XLCT character and does not influence the electron density at the central metal atom.[15] However, the two ν(CO) vibrations of this complex shift on going from the ground state to the relaxed excited state by +25.5 and +39.5 cm^{-1}, respectively, which indicates that upon relaxation the excited state obtains mixed MLCT–XLCT character.[17] Hence by combining the results from resonance Raman and TRIR spectra valuable information can be obtained about charge redistribution processes in the excited state.

Another series of complexes that shows only minor changes in electron density at the central metal atom on going to the lowest excited state, are the metal–metal bonded compounds [$M(SnR_3)_2(CO)_2$(α-diimine)] (M = Ru, Os; R = Me, Ph).[18–25] DFT calculations on the model complex [$Ru(SnH_3)_2(CO)_2$-(H-DAB)] show that the lowest-energy electronic transition has a σ(Sn–M–Sn) $\longrightarrow$ π^*(α-diimine) or sigma-bond-to-ligand charge-transfer (SBLCT) character with only small contributions of the central metal atom and the carbonyls to the frontier orbitals.[18] This is confirmed by the absence of resonance enhancement for ν_s(CO) in the Raman spectra of the [$M(SnR_3)_2(CO)_2$(α-diimine)] complexes.[19,24] Because of the SBLCT character of their excited states these complexes have some unusual properties. They undergo photo-induced M–Sn bond homolysis at room temperature since the SBLCT transition involves removal of electron density from the σ(Sn–M–Sn) bonding orbital. However, because of the dissociation barrier in the SBLCT state this photoreaction does not occur anymore at low temperature and under these circumstances the complexes have very long emission lifetimes compared to related compounds having a lowest MLCT state. For instance, [$Ru(Cl)(Me)(CO)_2$(iPr-DAB)] emits at 650 nm in a 2-MeTHF glass at 90 K from its MLCT state with a lifetime of 0.3 μs,[16] whereas [$Ru(SnPh_3)_2(CO)_2$(iPr-DAB)] emits from its SBLCT

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Table 1 ν(CO) vibrational frequencies and force constants in the ground (GS) and lowest-excited (ES) states of $[M(SnR_3)_2(CO)_2(\alpha\text{-diimine})]$

Compound		ν_{sym}/cm^{-1}	$\nu_{antisym}/cm^{-1}$	$\Delta\nu_{ES-GS}/cm^{-1}$	$k_{CO}/N\ m^{-1}$	$k_{CO,CO}/N\ m^{-1}$
1 $[Ru(SnMe_3)_2(CO)_2(dmb)]$	GS	1983	1922	+13, +12	1540	48
	ES	1996	1934		1560	49
2 $[Ru(SnPh_3)_2(CO)_2(dmb)]$	GS	1995	1936	+9, +9	1561	47
	ES	2004	1945		1575	47
3 $[Os(SnPh_3)_2(CO)_2(dmb)]$	GS	1984	1921	+5, +6	1540	50
	ES	1989	1927		1549	49
4 $[Ru(SnMe_3)_2(CO)_2(iPr\text{-}DAB)]$	GS	1985	1929	+7, −2	1547	45
	ES	1992	1927		1551	52
5 $[Ru(SnPh_3)_2(CO)_2(iPr\text{-}DAB)]$[a]	GS	2006	1955	0, −10	1579	36
	ES	2006	1945		1571	45
6 $[Os(SnPh_3)_2(CO)_2(iPr\text{-}DAB)]$	GS	1997	1939	−3, −4	1565	46
	ES	1994	1935		1559	47
7 $[Ru(SnPh_3)_2(CO)_2(pAn\text{-}DAB)]$	GS	2011	1959	+7, −6	1592	42
	ES	2018	1953		1593	52

[a] This study and ref. 19.

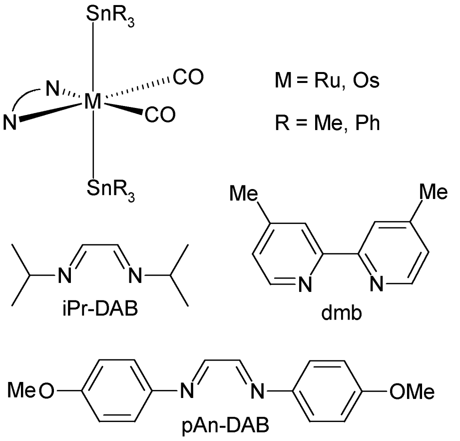

Fig. 1 Schematic structures of the complexes and the α-diimine ligands used.

state at 633 nm with a lifetime of 260 μs.[19] The increase in lifetime is due to the fact that the latter complex is much less distorted in its SBLCT state with respect to the ground state than $[Ru(Cl)(Me)(CO)_2(iPr\text{-}DAB)]$ in its MLCT state. This is evident from the much smaller energy difference between the lowest-energy absorption and emission in the case of $[Ru(SnPh_3)_2(CO)_2(iPr\text{-}DAB)]$ ($\Delta E = 5275\ cm^{-1}$)[19] compared to $[Ru(Cl)(Me)(CO)_2(iPr\text{-}DAB)]$ ($\Delta E = 9655\ cm^{-1}$).[16]

In order to investigate the bonding properties in their SBLCT state and the possible occurrence of charge redistribution after SBLCT excitation just as in the case of $[Ru(I)(Me)(CO)_2(iPr\text{-}DAB)]$[15], we have undertaken a nanosecond step-scan time-resolved IR spectroscopic (s^2-TRIR) study of the complexes $[M(SnR_3)_2(CO)_2(\alpha\text{-diimine})]$ (M = Ru, Os; R = Me, Ph). In this study the central metal atom, the R group, the α-diimine and the medium were varied. The results of this study are interpreted with the help of DFT MO calculations on the model complexes $[Ru(SnH_3)_2(CO)_2(iPr\text{-}DAB)]$ and $[Ru(SnH_3)_2(CO)_2(bpy)]$. Fig. 1 shows the schematic structures of the complexes and the α-diimine ligands used and the numbering of the complexes is presented in Table 1.

Experimental

Materials and preparations

The compounds $[M(SnR_3)_2(CO)_2(\alpha\text{-diimine})]$ [M = Ru or Os; R = Me or Ph; α-diimine = 4,4′-dimethyl-2,2′-bipyridine (dmb), *N*,*N*′-diisopropyl-1,4-diaza-1,3-butadiene (iPr-DAB), or *N*,*N*′-di-(*p*-methoxyphenyl)-1,4-diaza-1,3-butadiene (pAn-DAB)] were prepared according to published procedures.[19,24]

Time-resolved spectroscopy

Time-resolved infrared measurements were performed on 0.5–1 mmol frozen BuCN–PrCN (5 : 4 v/v) solutions of the complexes at 77 K using a step-scan FTIR interferometer. In the case of $[Os(SnPh_3)_2(CO)_2(dmb)]$ spectra were also recorded at 298 K. A detailed description of the Nottingham time-resolved step-scan FTIR (s^2-TRIR) apparatus is given elsewhere.[26] Briefly, the apparatus consists of a commercially available step-scan FTIR spectrometer (Nicolet Magna 860) equipped with a 100 MHz 12-bit digitizer and a 50 MHz MCT detector interfaced to a Nd–YAG laser (Spectra Physics GCR 12). Synchronization of the Nd–YAG laser with data collection was achieved by means of a pulse generator (Stanford DG535). The signal passes a Low-Noise Preamplifier (Stanford Research System, Model SR560) which was set up at 1 MHz for these experiments. Experiments at 77 K were performed in a home-built two-window cryogenic IR cell, with CaF_2 windows and Teflon spacers regulating the pathlength.[27]

Molecular orbital calculations

The ground state electronic structures were calculated by density functional theory (DFT) methods using the ADF2000.2[28,29] program package and Gaussian 98.[30] A time dependent DFT technique was used for the excited state calculations.

Within Gaussian 98, Dunning's polarized valence double ζ basis sets[31] were used for C, N, O and H atoms and the quasirelativistic effective core pseudopotentials and corresponding optimized set of basis functions[32] for Ru, Os and Sn.[33] In these calculations, the hybrid Becke's three parameter functional with the Lee, Yang and Parr correlation functional (B3LYP)[34] were used. Within the ADF program, Slater type orbital (STO) basis sets of triple ζ quality with 3d polarization functions for C and additional p functions for metals were employed. The inner shells were represented by a frozen core approximation, *viz.* 1s for C, N, O, 1s–3d for Ru, 1s–4d for Os and 1s–4p for Sn were kept frozen. The following density functionals were used within ADF: a local density approximation (LDA) with VWN parametrization of electron gas data or a functional including Becke's gradient correction[35] to the local exchange expression in conjunction with Perdew's gradient correction[36] to the LDA expression (BP). The scalar relativistic (SR) zero order regular approximation (ZORA) was used within this study.

The calculations were performed in constrained C_{2v} symmetry, with the *z*-axis coincident with the C_2 symmetry axis. The R-DAB ligand and the C atoms of the equatorial CO groups are located in the *yz*-plane, and the SnH_3 axial ligands lie on the *x*-axis.

Table 2 DFT calculated one-electron energies and percentage composition of selected highest occupied and lowest unoccupied molecular orbitals of [Ru(SnH$_3$)$_2$(CO)$_2$(iPr-DAB)] expressed in terms of the composing fragments

	MO	*E*/eV	Prevailing character	Ru	SnH$_3$	CO	R-DAB
Unoccupied							
	15b$_1$	−3.61	π* + iPr-DAB + SnH$_3$	9 (d$_{xz}$); 1 (p$_x$)	24	—	66 (π*)
Occupied							
	14b$_1$	−5.57	SnH$_3$ + π*iPr-DAB + p$_{Ru}$	13 (p$_x$); 1(d$_{xz}$)	51	8	27 (π*)
	10a$_2$	−6.07	d$_{Ru}$	75 (d$_{xy}$)	8	4	12
	13b$_1$	−6.58	d$_{Ru}$	61 (d$_{xz}$); 1 (p$_x$)	17	12	9
	23a$_1$	−6.90	d$_{Ru}$	45 (d$_{z^2}$); 21 (d$_{x^2-y^2}$)	1	26	6

Results and discussion

Ground-state IR spectra

The wavenumbers of the *ν*(CO) bands of complexes **1**–**7** in the ground state (Table 1) are influenced by the α-diimine and SnR$_3$ ligands, by the central metal atom and the medium. The π*-orbital energy of the α-diimine increases in the order pAn-DAB < iPr-DAB < dmb and this has a pronounced effect on the *ν*(CO) frequencies. A decrease in the π-acceptor ability of the α-diimine ligand results in more electron density on the metal being available for π-back donation to the carbonyls. Hence, the *ν*(CO) wavenumbers decrease when the α-diimine is varied from pAn-DAB to iPr-DAB and dmb, as can be seen from a comparison of the ground state (GS) IR data for **7**, **5** and **2** (Table 1). Comparison of the *ν*(CO) band positions of **1** *vs.* **2** and **4** *vs.* **5** shows that replacement of SnMe$_3$ by SnPh$_3$ causes a shift of the CO-stretching vibrations to higher wavenumbers. For example, in the case of [Ru(SnR$_3$)$_2$(CO)$_2$(dmb)] the wavenumbers of the two *ν*(CO) bands of **1** (R = Me) are +12 and +14 cm^{-1} lower than those of **2** (R = Ph). This effect, which is even more pronounced for [Ru(SnR$_3$)$_2$(CO)$_2$(iPr-DAB)] (**4** and **5**), is due to the fact that the SnMe$_3$ ligand donates more negative charge to Ru, by which the d$_\pi$ orbitals are raised in energy with a concomitant increase of π-back bonding to the carbonyls and a lowering of the *ν*(CO) frequencies. This interpretation is in line with the results of the DFT calculations on the model complex [Ru(SnH$_3$)$_2$(CO)$_2$(iPr-DAB)], which show that the π*(CO) orbitals mix with the d orbitals of Ru (Table 2). Changing the central metal atom from Ru to Os (**2** *vs.* **3**, **5** *vs.* **6**) causes a frequency decrease of the *ν*(CO) bands since the higher energy and better overlap with π*(CO) of the d$_\pi$ orbitals of Os causes an increase in metal-to-CO π-back bonding. In order to establish the influence of the medium, the CO frequencies of the photostable complex [Os(SnPh$_3$)$_2$(CO)$_2$(dmb)] were measured both in a BuCN–PrCN (5 : 4 v/v) solution at 298 K and in a glass of the same mixture at 77 K. Only a small shift in the ground state IR *ν*(CO) bands to lower wavenumbers was observed on going from 298 to 77 K.

Excited-state IR spectra

The influence of the α-diimine, the co-ligand SnR$_3$, the central metal atom and the medium on the charge redistribution in the SBLCT excited state has been studied by probing the changes in the time-resolved step-scan FTIR (s^2-TRIR) spectra. All studies, except for [Os(SnPh$_3$)$_2$(CO)$_2$(dmb)] (**3**), were performed on the complexes in a frozen BuCN–PrCN solution at 77 K because of their photolability at room temperature. Complex **3** is virtually photostable and for this complex also the influence of the medium (BuCN–PrCN as a solution at room temperature and as a glass at 77 K) was studied. The IR data of the complexes in the ground and lowest-excited state at 77 K are collected in Table 1 and the s^2-TRIR spectra are presented in Fig. 2.

Fig. 2b shows the s^2-TRIR spectrum of [Ru(SnMe$_3$)$_2$(CO)$_2$(dmb)] (**1**) obtained 100 ns after the laser flash. The difference spectrum shows depletion of the two parent *ν*(CO) bands and formation of a transient species with two *ν*(CO) bands at higher frequency. These new bands decay [k_{obs} = 2.8(± 0.5) × 10^4 s^{-1}] at the same rate as the parent is regenerated [k_{obs} = 2.0(± 0.5) × 10^4 s^{-1}]. This rate corresponds to a lifetime of the transient which agrees rather well, taking into account the different concentrations used, with the emission lifetime of the SBLCT state of **1** (60 μs at 77 K).[24] The new CO bands are therefore assigned to this excited state.

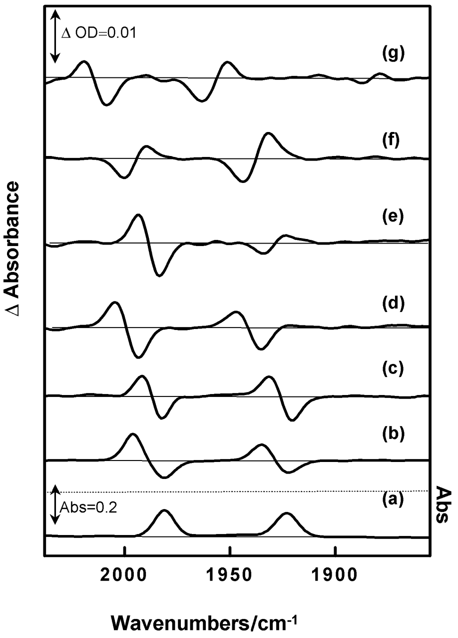

Fig. 2 FTIR spectrum of **1** (a) and s^2-TRIR spectra of complexes **1**–**4** (b–e), **6** (f) and **7** (g) recorded 100 ns after 355 nm excitation at 77 K in BuCN–PrCN (5 : 4 v/v). For the spectrum of **5** see ref. 19.

Influence of the α-diimine. The s^2-TRIR spectral data presented in Table 1 and Fig. 2 show that the frequency shifts of the *ν*(CO) bands on going from the ground to the excited state are rather small and positive for the dmb complexes **1**–**3**, but close to zero or even negative for the R-DAB complexes. For the latter complexes these frequency changes vary from one complex to another. Thus, in the case of [Ru(SnPh$_3$)$_2$(CO)$_2$(pAn-DAB)] (**7**) and [Ru(SnMe$_3$)$_2$(CO)$_2$(iPr-DAB)] (**4**), the two *ν*(CO) vibrations shift in different directions, whereas for [Os(SnPh$_3$)$_2$(CO)$_2$(iPr-DAB)] (**6**) a small downward shift of both bands is observed.

The interpretation of these differences in shifts requires careful consideration of the nature of the electronic transition as well as the effect of the following charge redistribution on relaxation. The DFT results presented in Tables 2 and 3 show that the π*(CO) orbitals mix with the metal-d orbitals and have a minor contribution to the HOMO and LUMO of the two model complexes. The transition to the Franck–Condon states of ^{1}SBLCT (composed of 88% 14b$_1$ ⟶ 15b$_1$ and 10% 13b$_1$ ⟶ 15b$_1$ for the iPr-DAB complex and 85% 12b$_1$ ⟶ 13b$_1$ and 15% 12b$_1$ ⟶ 14b$_1$ for the bpy one) will therefore hardly

Table 3 DFT calculated one-electron energies and percentage composition of selected highest occupied and lowest unoccupied molecular orbitals of $[Ru(SnH_3)_2(CO)_2(bpy)]$ expressed in terms of composing fragments

	MO	E/eV	Prevailing character	Ru	SnH_3	CO	bpy
Unoccupied							
	$14b_1$	−2.82	π* bpy	2 (d_{xz})	3	—	95 (π*)
	$13b_1$	−3.40	π* bpy	3 (d_{xz}); 1 (p_x)	10	—	86 (π*)
Occupied							
	$12b_1$	−4.95	SnH_3 + π* bpy + p_{Ru}	16 (p_x); 5 (d_{xz})	55	5	19 (π*)
	$8a_2$	−6.11	d_{Ru}	64 (d_{xy})	16	13	7
	$11b_1$	−6.27	d_{Ru}	57 (d_{xz}); 2 (p_x)	21	16	4
	$25a_1$	−6.91	d_{Ru}	48 (d_{z^2}); 9 ($d_{z^2-y^2}$)	11	25	1

Table 4 TD DFT-calculated changes in Mulliken populations (ground state–excited state) on the central atom and individual ligands during the transitions to the lowest ^{1}SBLCT states of the model complexes $[M(SnH_3)_2(CO)_2(L)]$ (M = Ru, Os; L = iPr-DAB, bpy)

	L/fragment	Ru	SnH_3[a]	L	CO[a]
M = Ru	iPr-DAB	0.047	0.134	−0.407	0.046
	bpy	0.128	0.228	−0.649	0.032
M = Os	iPr-DAB	0.065	0.135	−0.429	0.047
	bpy	0.150	0.217	−0.635	0.026

[a] Due to the C_{2v} symmetry the changes on the second SnH_3 or CO group are the same.

influence the electron density at the carbonyls. This is confirmed by the small changes in Mulliken population calculated for the CO orbitals (Table 4) and by the absence of a rR effect for the symmetrical CO-stretching mode in the rR spectra of the complexes under study.[19,24] The SBLCT transition mainly occurs from the SnH_3 ligand orbitals to the α-diimine and more negative charge is transferred from these SnH_3 ligands as well as the p_{Ru} orbital in the case of the $[M(SnH_3)_2(CO)_2(bpy)]$ (M = Ru, Os) model complexes (Table 4). This agrees with the observation that the SBLCT transitions of the dmb complexes **1**–**3** have more charge-transfer character than those of the R-DAB complexes **4**–**7**. For instance, the solvatochromic shift of the absorption band [$\Delta = \nu_{max}(MeCN) - \nu_{max}(toluene)$] decreases on going from $[Ru(SnPh_3)_2(CO)_2(dmb)]$ (**2**) (Δ = 1400 cm^{-1}) to $[Ru(SnPh_3)_2(CO)_2(iPr\text{-}DAB)]$ (**5**) (Δ = 570 cm^{-1}),[24] which implies that the transition of complex **2** has more charge-transfer character than that of its iPr-DAB analogue **5**.

The DFT results indicate that the SBLCT transitions of the bpy model complexes involve only a small population change of the CO orbitals, even smaller than for the iPr-DAB model compounds. These results are fully consistent with the results from the rR spectra, which do not show any rR effect for ν_s(CO) on excitation into the SBLCT transition.[19,24] However, the s^2-TRIR spectra of the dmb complexes **1**–**3** show positive ν(CO) frequency shifts on going from the ground state to the relaxed SBLCT state, whereas these shifts are zero or even negative for the R-DAB complexes **4**–**7** (Table 1). Hence there is a shift of charge on relaxation either in the singlet or triplet excited states or during intersystem crossing just as for $[Ru(I)(Me)(CO)_2(iPr\text{-}DAB)]$[17] (*vide supra*). The magnitude and direction of such a shift is the result of two opposite effects on the electron density at the central metal atom after excitation: electron withdrawal by the SnR_3 ligands and electron donation by the α-diimine radical anion. The former effect is stronger when the SBLCT transition has an appreciable charge-transfer character. This is the case for the dmb complexes and the resulting ν(CO) frequency shifts are positive for these compounds. For the R-DAB complexes the SBLCT transition has less charge-transfer character; the two effects compensate each other or electron donation by the R-DAB radical anion becomes even more important. Charge donation to the metal after occupation of the π* orbital of an α-diimine ligand occurs *e.g.* upon reduction of **5**,[18] where the ν(CO) vibrations shift by −29 and −41 cm^{-1}, respectively. It even occurs upon relaxation in the intra-ligand (ππ*) excited state of $[Re(PPh_3)(CO)_3(dppz)]^+$[13] (*vide supra*). Although the electronic transition of the latter complex-ion has no direct influence on the charge density at Re, the TRIR spectra show ν(CO) frequency shifts of −8 cm^{-1} on going from the ground state to the relaxed excited state.

The force constants and interaction force constants for the ground and excited states (Table 1) were derived from the positions of the stretching vibrations by using Timney's approach.[37] The following assumptions, which have been described in detail,[37] have been applied: (i) there are no changes in symmetry on going from the ground to the excited state and (ii) CO vibrations are distinguished from all the other vibrations in the molecule — the energy-factored force field hence includes only two CO groups, and does not consider any metal-CO or any other vibrations and interactions.

The $k_{CO,CO}$ values of Table 1 are virtually the same for complexes **1**–**3** and **6** in their ground and excited state. However, compounds **4**, **5** and **7**, which contain Ru and R-DAB and are sterically more crowded, show a small increase of $k_{CO,CO}$ (+7, +9, and +10 N m^{-1}, respectively) on excitation. Since the $k_{CO,CO}$ values are sensitive to changes in the angle between the carbonyls, one is tempted to conclude that these small changes in $k_{CO,CO}$ are caused by steric effects within the complexes. However, since the calculated changes in the interaction force constants are almost within the error of the theoretical approach, this conclusion is very tentative. Further information about bond angle changes might in principle be derived from the changes in relative intensities of the two transient IR bands. In principle, the relative intensity of the ν(CO) bands of the excited state should allow estimation of the bond angle between the CO groups. In practice, we have shown[26] that the combination of using low spectral resolution step-scan FTIR data in regions of strong overlap with parent absorptions can lead to anomalous results and we are therefore cautious of further interpretation without performing high resolution s^2-FTIR measurements.

Influence of the metal and the SnR_3 ligand. Replacement of Ru by Os causes the carbonyl vibrations of the complexes in their ground state to shift to lower frequency. For complexes having the same α-diimine and SnR_3 ligand the ν(CO) frequency shifts are in the same direction for the Ru and Os complexes. The $SnMe_3$ complexes **1** and **4** show more positive shifts for their carbonyl frequencies than the analogous $SnPh_3$ compounds **2** and **5**, although their SBLCT transitions have a smaller solvatochromic shift and therefore less charge transfer character.[24] Apparently, the character of the R group of the SnR_3 ligand has also an appreciable influence on the charge redistribution in the Sn–M–Sn moiety after excitation. This is probably due to the fact that both M and R shift some negative charge to Sn on relaxation and that the latter effect is more efficient for R = Ph than for R = Me. As a result, the charge density at the central metal atom and the ν(CO) frequencies are less affected in the case of the $SnPh_3$ complexes.

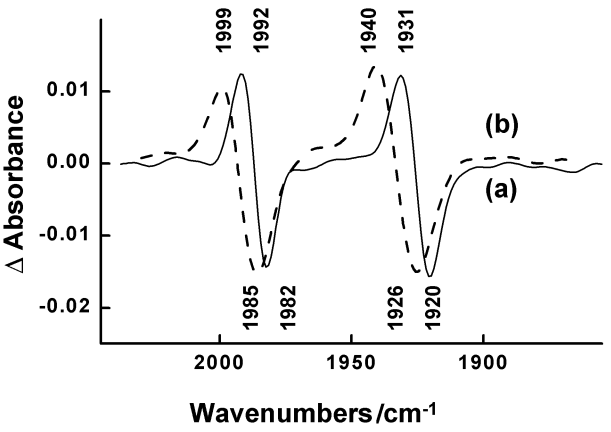

Fig. 3 s^2-TRIR spectra of $[Os(SnPh_3)_2(CO)_2(dmb)]$ (**3**), recorded 100 ns after 355 nm excitation at (a) 77 K, solid line and (b) 298 K, dashed line in a BuCN–PrCN (5 : 4 v/v) mixture.

Influence of the medium. The s^2-TRIR spectra of the complex $[Os(SnPh_3)_2(CO)_2(dmb)]$ (**3**) were measured both at room temperature and at 77 K in a BuCN–PrCN (5 : 4 v/v) glass to study the influence of the medium. It is in fact the only complex for which such a study can be performed since all other complexes under study proved to be too photolabile for s^2-TRIR studies at room temperature. The s^2-TRIR spectrum of $[Os(SnPh_3)_2(CO)_2(dmb)]$ at 77 K has been discussed above.

The s^2-TRIR spectrum of **3** at room temperature (Fig. 3b) shows depletion of the two parent ν(CO) bands and the appearance of a transient with two ν(CO) bands shifted by $+14$ cm^{-1} with respect to those of the parent complex. The frequency shift observed at low temperature (Fig. 3a) is, however, only $+10$ cm^{-1}. This effect, which is called infrared rigidochromism, has been observed before for the complexes $[Re(Cl)(CO)_3(bpy)]$[9,11] and $[Re(Me)(CO)_3(dmb)]$.[38] For the former complex the mean difference in frequency of the CO vibrations between ground and excited state decreases from 58 cm^{-1} in solution at room temperature to 38 cm^{-1} in the low-temperature glass.[9] In the case of **3** a comparable relative decrease of the mean difference is observed. This rigidochromic effect has been rationalised in terms of incomplete charge transfer in the rigid medium since solvent reorientation required to complete the charge transfer after excitation, can not occur in such a medium. Recently, a similar effect was observed for the complex $[Re(Cl)(CO)_3(4,4'\text{-dicarboxy-}2,2'\text{-bipyridine})]$ upon dissolving in DMF and adsorption on a ZrO_2 film.[12] MLCT excitation of this complex causes the high-frequency ν(CO) vibration to shift by $+54$ cm^{-1} in DMF but merely by $+25$ cm^{-1} on the ZrO_2 film. Again this difference was attributed to the absence of solvent reorientation in the case of the ZrO_2 film, and this was supported by the difference in the rise time constants for the shifted bands in solution (4 ps) and on ZrO_2 (1.7 ps).

Conclusions

The s^2-TRIR spectra of the complexes under study, recorded 100 ns after excitation, show ν(CO) frequency shifts on going from the ground state to the relaxed excited state that range from positive in the case of the dmb complexes to zero or negative for the R-DAB complexes. According to the TD-DFT calculations and in agreement with the previously reported resonance Raman spectra, these shifts are not caused by the SBLCT transitions themselves. They result from two opposite processes occurring after excitation: electron withdrawal from the central metal atom by the SnR_3 ligands and electron donation by the α-diimine radical anion. The former effect is stronger for the dmb complexes, in the case of the R-DAB complexes the two effects compensate each other or electron donation by the R-DAB radical anion becomes even more important. It is not clear whether this charge redistribution within the complexes occurs on relaxation in the singlet or triplet SBLCT state or during intersystem crossing between these states. Calculations of the potential energy curves of the SBLCT states are needed to shed more light on this effect.

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