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Time-Resolved Absorption, Infrared, and Resonance Raman Spectra of the Complexes [Ru(X)(R)(CO)$_2$(α-Diimine)] (X = Halide; R = Alkyl): Influence of X on the Charge Transfer Character of the Lowest Excited State

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Abstract: Nanosecond time-resolved absorption (TA), resonance Raman (TR^3), and infrared (TRIR) spectra are reported for several complexes [Ru(X)(R)(CO)$_2$(α-diimine)] (X = Cl, Br, I; R = Me, Et; α-diimine = *N,N'*-diisopropyl-1,4-diaza-1,3-butadiene (iPr-DAB), pyridine-2-carbaldehyde-*N*-isopropylimine (iPr-PyCa), 2,2'-bipyridine (bpy)). This is the first instance in which the TA, TR^3, and TRIR techniques have been used to probe excited states in the same series of complexes. The TA spectra of the iodide complexes show a transient absorption between 550 and 700 nm, which does not depend on the solvent but shifts to lower energy in the order iPr-DAB > bpy > iPr-PyCa. This band is assigned to an intraligand transition. For the corresponding chloride and bromide complexes this band occurs at higher energy, most probably because of a change of character of the lowest excited state from XLCT to MLCT. The TRIR spectra show an increase in ν(CO) (and k(CO)) on promotion to the excited state; however, the shifts $\Delta\nu$(CO) show a decrease in the order Cl$^-$ > Br$^-$ > I$^-$. The TR^3 spectra of the excited complexes [Ru(X)(R)(CO)$_2$(iPr-DAB)] show ν_s(CN) of the iPr-DAB ligand 50−80 cm^{-1} lower in frequency than for the complexes in their ground state. This frequency shift decreases in the order Cl$^-$ > Br$^-$ > I$^-$, indicating a decrease of CT character of the lowest excited state in this order. However, going from X = Br to I, the effect on $\Delta\nu$(CO) is much larger than the decrease of $\Delta\nu_s$(CN). This different effect on the CO- and CN-stretching frequencies is assigned to a gradual change in character of the lowest excited state from MLCT to XLCT when Cl$^-$ is replaced by Br$^-$ and I$^-$. This result confirms a similar conclusion derived from previous resonance Raman and emission experiments on these complexes.

Introduction

Polypyridyl complexes such as [Ru(bpy)$_3$]$^{2+}$ and [Re(L)(CO)$_3$(bpy)]$^{0/+}$ (L = halide, N-donor) have been extensively studied because of their potential application in photochemically driven molecular devices.[1−11] These complexes possess long-lived ^{3}MLCT states. Especially time-resolved resonance Raman (TR^3) spectroscopy has proven to be very useful in characterizing these states with respect to, *e.g.*, charge localization in mixed-ligand complexes.[12−21] In some cases this technique has been used to probe intermediates in intramolecular electron or energy transfer processes following MLCT excitation.[22−24] Time-resolved IR (TRIR) spectroscopy has been successfully applied to study the MLCT states of complexes containing ligands such as CO or CN$^-$, which obtain high oscillator strengths for their stretching vibrations upon coordination.[25−32] Thus, TRIR spectroscopy has been used to study the lowest ^{3}MLCT state of [Re(Cl)(CO)$_3$(4,4'-bpy)$_2$],[25,26] to probe the

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(1) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Zelewski, A. v. *Coord. Chem. Rev.* **1988**, *84*, 85.

(2) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159.

(3) Kalyanasundaram, K.; Grätzel, M.; Pelizetti, E. *Coord. Chem. Rev.* **1986**, *69*, 57.

(4) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193.

(5) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163.

(6) Fox, M. A., Chanon, M., Eds. In *Photo-induced electron transfer;* Elsevier: New York, 1988.

(7) Balzani, V.; Sabbatini, N.; Scandola, F. *Coord. Chem. Rev.* **1987**, *86*, 319.

(8) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis Horwood: Chichester, England, 1989.

(9) Krausz, E. R.; Ferguson, J. *Prog. Inorg. Chem.* **1989**, *37*, 293.

(10) Juris, A.; Campagna, S.; Bidd, I.; Lehn, J.-M.; Ziessel, R. *Inorg. Chem.* **1988**, *27*, 4007.

(11) Stufkens, D. J. *Comments Inorg. Chem.* **1992**, *13*, 359.

(12) Bradley, P. G.; Kress, N.; Hornberger, B. A.; Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 7441.

(13) Smothers, W. K.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 1067.

(14) McClanahan, S.; Hayes, T.; Kincaid, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 4486.

(15) Danzer, G. D.; Kincaid, J. R. *J. Phys. Chem.* **1990**, *94*, 3976.

(16) Danzer, G. D.; Golus, J. A.; Kincaid, J. R. *J. Am. Chem. Soc.* **1993**, *115*, 8643.

(17) Treffert-Ziemelis, S. M.; Golus, J. A.; Strommen, D. P.; Kincaid, J. R. *Inorg. Chem.* **1993**, *32*, 3890.

(18) Turro, C.; Bosman, S. H.; Leroi, G. E.; Barton, J. K.; Turro, N. J. *Inorg. Chem.* **1994**, *33*, 1344.

(19) Bell, S. E. J.; Al-Obaidi, A. H. R.; Hegarty, M.; Hester, R. E.; McGarvey, J. J. *J. Phys. Chem.* **1993**, *97*, 11599.

(20) Al-Obaidi, A. H. R.; Gordon, K. C.; McGarvey, J. J.; Bell, S. E. J.; Grinshaw, J. *J. Phys. Chem.* **1993**, *97*, 10942.

(21) Perng, J.; Zink, J. I. *Inorg. Chem.* **1990**, *29*, 1158.

(22) Bignozzi, C. A.; Argassi, R.; Garcia, C. G.; Scandola, F.; Schoonover, J. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 8727.

(23) Schoonover, J. R.; Chen, P.; Bates, W. D.; Dyer, R. B.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 793.

(24) McMahon, R. J.; Forcè, R. K.; Patterson, H. H.; Wrighton, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 2670.

0002-7863/95/1517-5579$09.00/0

complete photochemistry of the complexes [$W(CO)_5$(4-Rpy) (R = CN, acetyl)].[27,28] and to elucidate intramolecular energy transfer in [(phen)$(CO)_3$Re(NC)Ru(CN)$(bpy)_2$]$^+$.[29]

In the complexes studied so far, MLCT excitation takes place from metal-d_π orbitals which may be involved in metal-to-ligand π-back-bonding but do not strongly interact with other ligand orbitals. A different situation occurs for the halide complexes [Mn(X)$(CO)_3$(α-diimine)][33,34] and [Ru(X)(R)$(CO)_2$(α-diimine)] (X = halide: R = alkyl: α-diimine = *N,N'*-diisopropyl-1,4-diaza-1,3-butadiene (iPr-DAB), pyridine-2-carbaldehyde-*N*-isopropylimine (iPr-PyCa), 2,2'-bipyridine (bpy)).[35,36] For both types of complexes the electronic transitions to the α-diimine have strongly mixed MLCT/XLCT character due to the interaction of M-d_π and X-p_π orbitals. This interaction gives rise to a bonding and antibonding set of orbitals from which the CT transitions originate. As a result, two absorption bands are observed, the relative intensities of which depend on the metal character of the orbitals involved in the transitions. The halide character of the metal–halide antibonding HOMO will increase going from Cl^- to Br^- and I^- and the character of the lowest-energy transitions will therefore change from MLCT to XLCT in this order. This has been established for the complexes [Mn(X)$(CO)_3$(bpy)] with MO calculations[34] and for several complexes [Ru(X)(R)$(CO)_2$(α-diimine)] with resonance Raman (rR) spectroscopy.[35] RR spectroscopy is a very valuable technique to discriminate between such MLCT and XLCT transitions since only the MLCT and not the XLCT transitions affect the CO bonds indirectly, giving rise to a resonance Raman effect for a symmetrical CO-stretching mode. The change of character of the lowest CT-state going from X = Cl to X = I was also evident from the emission of these [Ru(X)(R)$(CO)_2$(α-diimine)] complexes, which deviated from a normal "energy-gap law" behavior.[36]

The question remains how the observed changes in CT character of the electronic transitions of these [Ru(X)(R)$(CO)_2$(α-diimine)] complexes are preserved in the relaxed ^{3}CT states. The emission spectra merely showed that there is a change of character with X;[36] more detailed information can only be obtained from TR^3 and TRIR spectra. Both techniques were applied to study the complexes [Ru(X)(Me)$(CO)_2$(iPr-DAB)] (X = Cl, Br, I), and the results of this study are reported here, together with the transient-absorption data. The complexes have the general structure shown in Figure 1 and will further be denoted as X/R/α-diimine. This means that, *e.g.*, I/Me/iPr-DAB stands for the complex [Ru(I)(Me)$(CO)_2$(iPr-DAB)].

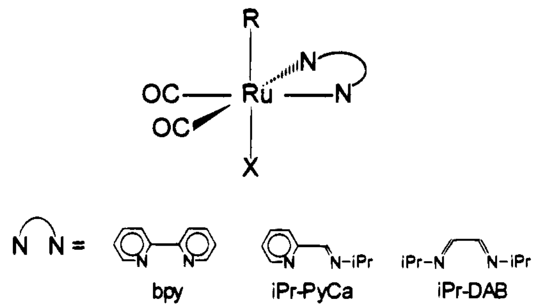

Figure 1. Schematic representation of the complexes [Ru(X)(R)$(CO)_2$(α-diimine)] and the α-diimine ligands 2,2'-bpy, iPr-PyCa and iPr-DAB.

Experimental Section

Materials. Solvents of analytical grade (THF, acetonitrile) or UVASOL quality (toluene, dichloromethane) were dried over sodium wire (THF, toluene) or $CaCl_2$ (CH_2Cl_2, acetonitrile) and freshly distilled under nitrogen. The complexes were prepared according to literature procedures.[35,37] The ^{13}CO-enriched complex [Ru(I)(Me)(^{13}CO)(CO)(iPr-DAB)] was prepared similarly, except that ^{13}CO-enriched [$Ru_3(^{13}CO)_n(CO)_{12-n}$] was used as starting material. The enriched cluster was prepared by irradiating a solution of 0.5 mmol [$Ru_3(CO)_{12}$] in 350 mL of hexane under ^{13}CO atmosphere by a mercury lamp while vigorously stirring the solution until it became colorless (*ca.* 1.5 h). The solution was then stirred for another 24 h in the dark. After releasing ^{13}CO the enriched cluster [$Ru_3(^{13}CO)_n(CO)_{12-n}$] was formed from [$Ru(^{13}CO)(CO)_4$]. This sequence was repeated twice. The mixture of the ^{13}CO-enriched complexes [Ru(I)(Me)$(^{13}CO)_n(CO)_{2-n}$(iPr-DAB)] in CH_2Cl_2 displayed two strong ν(CO) bands at 1983 and 1922 cm^{-1}. In addition, weaker bands were observed at 2013 and 1969 cm^{-1} and at 1936 and 1892 cm^{-1}. The UV–vis spectrum showed the same absorption bands and identical extinction coefficients as the spectrum of the nonenriched complex.[35]

Samples for transient absorption were prepared from optically dilute solutions (*ca.* 10^{-4} M) in freshly distilled solvents, freeze–pump–thaw degassed at least four times, and then sealed under vacuum. Solutions for the TR^3 measurements were prepared in dichloromethane (*ca.* 10^{-3} M). During the experiments the solutions were flushed with argon to exclude oxygen. All solutions for the TRIR experiments were pump–degassed and overpressured at 2 atm with argon.

Spectroscopic Measurements. Electronic absorption spectra were recorded on a Varian Cary 4E UV–vis spectrophotometer. Transient absorption spectra and excited-state lifetimes were obtained using a Nd:YAG laser (Spectra Physics GCR-3, 532 nm, pulse width *ca.* 10 ns) as excitation source or a Quanta Ray dye laser with coumarin 460, pumped by the 355 nm line of the Nd:YAG laser. Perpendicular to the excitation beam a 1450 W high-pressure Xe lamp pulsed with a Müller Elektronik MSPO5 pulser was used as probe light. The sample was protected against continuous irradiation by the probe light by a computer-controlled mechanical shutter. After passing the sample, the probe light was collected into a fibre and transferred to a spectrograph (EG&G Model 1234) equipped with a 150 g/mm grating and a 250 μm slit resulting in a resolution of 6 nm. This spectrograph is coupled to a gated, intensified diode array detector (EG&G Model 1421) which is part of an EG&G OMA III handling system and a 1303 gate pulse amplifier with a 5 ns gate window. The programming of the OMA leads to a time-resolved way of measuring. The difference absorption spectra were obtained by subtraction of probe-light spectra with and without laser excitation. The lifetimes were determined from 20 spectra with a constant incremental delay, by fitting the absorption intensities at fixed wavelengths and varying incremental delays to first-order kinetics.

Time-resolved resonance Raman (TR^3) measurements were carried out using a Q-switched Nd:YAG laser (Quanta-Ray DCR2, pulse width

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[25] Glyn, P.; George, M. W.; Hodges, M.; Turner, J. J. *J. Chem. Soc. Chem. Commun.* **1989**, 1655.

[26] Gamelin, R. D.; George, M. W.; Glyn, P.; Grevels, F.-W.; Johnson, F. P. A.; Klotzbücher, W.; Morrison, S. L.; Russell, G.; Schaffner, K.; Turner, J. J. *Inorg. Chem.* **1994**, *33*, 3246.

[27] Glyn, P.; Johnson, F. P. A.; George, M. W.; Lees, A. J.; Turner, J. J. *Inorg. Chem.* **1991**, *30*, 3543.

[28] Johnson, F. P. A.; George, M. W.; Turner, J. J. *Inorg. Chem.* **1993**, *32*, 4226.

[29] Schoonover, J. R.; Gordon, K. C.; Argazzi, R.; Woodruff, W. H.; Peterson, K. A.; Bignozzi, C. A.; Dyer, R. B.; Meyer, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 10996.

[30] Turner, J. J.; George, M. W.; Johnson, F. P. A.; Westwell, J. R. *Coord. Chem. Rev.* **1993**, *125*, 101.

[31] George, M. W.; Johnson, F. P. A.; Westwell, J. R.; Hodges, P. M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1993**, 2977.

[32] George, M. W.; Poliakoff, M.; Turner, J. J. *Analyst* **1994**, *119*, 551.

[33] Stor, G. J.; Morrison, S. L.; Stufkens, D. J.; Oskam, A. *Organometallics* **1994**, *13*, 2641.

[34] Stor, G. J.; Stufkens, D. J.; Vernooijs, P.; Baerends, E. J.; Fraanje, J.; Goubitz, K. *Inorg. Chem.* **1995**, *34*, 1588.

[35] Nieuwenhuis, H. A.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1994**, *33*, 3212.

[36] Nieuwenhuis, H. A.; Stufkens, D. J.; Vlček, Jr., A. *Inorg. Chem.*, in press.

[37] Kraakman, M. J. A.; Vrieze, K.; Kooijman, H.; Spek, A. L. *Organometallics* **1992**, *11*, 3760.

Table 1. Transient-Absorption Maxima (in nm) and Excited-State Lifetimes (in ns) of X/R/α-Diimine

complex	$\lambda_{\max\,TA}$	τ_{TA}	τ_{em}
Cl/Me/iPr-DAB	420	50	63
Br/Me/iPr-DAB	450, ~530	70	75
I/Me/iPr-DAB	~590	180	177
I/Et/iPr-DAB	~590	70	80
I/Me/iPr-PyCa	~670	(190)[a]	(185)[a]
I/Me/bpy	~640	(390)[a]	(240)[a]

[a] No accurate lifetimes due to photodecomposition during the measurement.

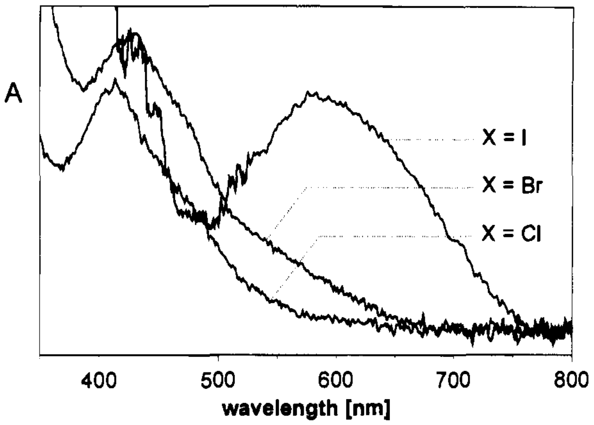

Figure 2. Transient absorption spectra of the complexes X/R/iPr-DAB (X = Cl, Br, I) in their lowest excited state, measured at 20 ns after the 460 nm, 5 ns excitation of a THF solution at ambient temperature.

ca. 9 ns) to populate the excited states of the complexes at an excitation wavelength of 532 nm or by using a Quanta Ray dye laser with coumarin 460, pumped by the 355 nm line of the Nd:YAG laser. As probe light either 460 nm from the dye laser was used or the 416 and 447 nm lines generated by Raman shifting the third harmonic (354.7 nm) of the Nd:YAG laser in hydrogen (first Stokes) or methane (second Stokes), respectively. All measurements were carried out in dichloromethane, degassed by argon bubbling throughout the spectral accumulation. Consistent TA spectra were independently measured in the Amsterdam and Belfast laboratories.

The time-resolved IR equipment used the 532 or 355 nm line of a pulsed Nd:YAG (Quanta-Ray GCR-12, 7 ns pulse width) as a photolysis source. Almost collinear to the excitation source was a CW IR diode laser (Mütek MDS 1100), which recorded the change in IR absorption. The changes in IR absorption were monitored with a photovoltaic 77 K HgCdTe detector (Laser Monitoring Systems PV 2180) with rise time of *ca.* 50 ns. IR spectra were measured using a "point by point" method in which the IR laser is tuned to a different wavenumber after each excitation. In this way kinetic traces were obtained with positive (new IR absorptions), negative (bleaching of the ground state IR), or no absorptions. After each shot the sample solution was flowed through in order to avoid decomposition of the sample.

Results

Time-Resolved Absorption Spectra. Nanosecond transient absorption (TA) spectra were measured for the complexes as difference spectra. The real spectra of the excited states were obtained by correcting the difference spectra for the ground-state absorptions. The absorption maxima and calculated lifetimes are collected in Table 1. For comparison this table also presents the emission lifetimes, which are very close to the values derived from the TA spectra.

The spectra of the chloride and bromide complexes show a band between 400 and 450 nm (Figure 2, Table 1). For the iodide complexes this wavelength region is not very reliable due to strong absorptions by the ground state. At longer wavelengths the chloride and bromide complexes have a shoulder, which transforms into a separate band at *ca.* 600 nm for the iodide complexes. The position of this band does not depend on R and the solvent, but it shifts to lower energy in the order iPr-DAB > bpy > iPr-PyCa (Figure 3).

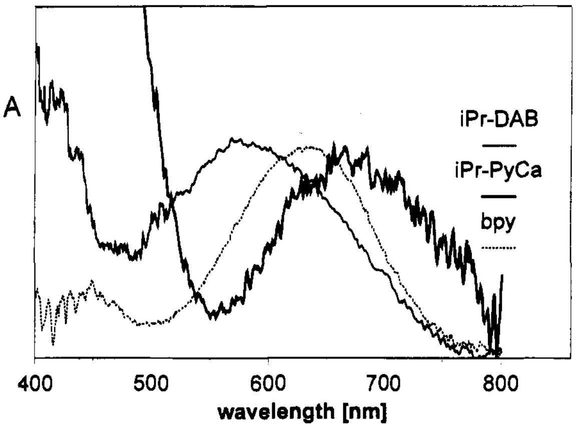

Figure 3. Transient absorption spectra of complexes I/Me/α-diimine (α-diimine = iPr-PyCa, bpy, iPr-DAB) in their lowest excited state, measured at 20 ns after the 460 nm, 5 ns excitation of a THF solution at ambient temperature.

Time-Resolved Resonance Raman Spectra. Nanosecond time-resolved resonance Raman (TR^3) spectra of the three complexes X/Me/iPr-DAB (X = Cl, Br, I) were measured between 1200 and 2100 cm^{-1}. In this frequency region the ground-state resonance Raman spectra showed bands at about 1560 and 2035 cm^{-1}, which have been assigned[35] to ν_s(CN) of the iPr-DAB ligand and to ν_s(CO), respectively.

Single-color TR^3 spectra at increasing laser pulse energies were obtained for solutions of the complexes in CH_2Cl_2, using either a pulsed dye laser (coumarin 460) or the 447 nm line of a Raman shifter. At low pulse energy, the ground-state Raman spectra of the complexes were observed. With increasing laser pulse energy, the TR^3 spectra showed the grow-in of features near 1490 and 1940 cm^{-1} with a concomitant intensity decrease of the 1560 and 2035 cm^{-1} bands. This is illustrated in Figure 4a for the complex Br/Me/iPr-DAB. In Table 2 the observed frequencies at low and high pulse energy are collected. Comparison of the magnitude of the shift in ν_s(CN) between the ground and lowest charge-transfer excited states shows that this shift (=$\Delta\nu_s$(CN)) changes in the order $Cl^- > Br^- > I^-$ (see Figure 4b).

The 1490 cm^{-1} band is assigned to ν_s(CN) of the complex X/Me/iPr-DAB in its lowest charge-transfer state. As a result of the electron transfer to the lowest π^* orbital of the α-diimine, the imine bonds of this ligand will be weakened and the frequency of ν_s(CN) will be lowered with respect to the ground state. Similar shifts to lower frequency have been observed upon MLCT excitation of $[Ru(bpy)_3]^{2+}$,[12] [W(CO)$_4$(α-diimine)],[21] and [Re(Cl)(CO)$_3$(bpy)].[13]

Single-color transient Raman spectra of the complex I/Me/iPr-DAB were compared with those of the ^{13}CO-enriched analogue. The spectra of the ^{13}CO complex exhibited a ν_s(CN) feature at 1490 cm^{-1} as for the ^{12}CO molecule but a new broad feature at 1896 cm^{-1} replaced the 1940 cm^{-1} band in the latter. Both bands are depolarized whereas the corresponding ν_s(CN) Raman band at 1490 cm^{-1} is polarized.

The TR^3 spectra of the corresponding iPr-PyCa complex I/Me/iPr-PyCa showed the four vibrational ground state modes of the α-diimine at low pulse energy. On increasing the pulse energy, the most important effect was the intensity enhancement

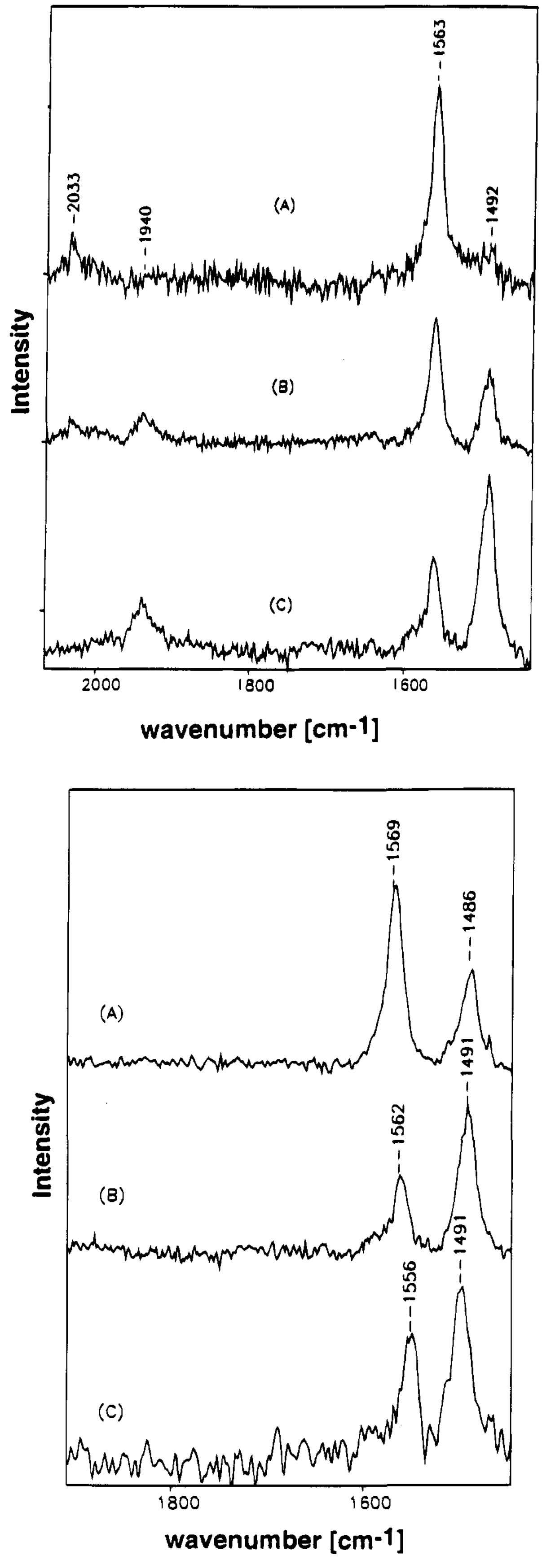

Figure 4. (a, top) Excited-state Raman spectra of Br/Me/iPr-DAB in CH_2Cl_2 as a function of the pulse energy: (A) 2 mJ, (B) 5 mJ, and (C) 5 mJ (tighter beam focus). (b, bottom) Spectra showing the dependence of $\Delta\nu_s(CN)$ on X in CH_2Cl_2 solutions of X/Me/iPr-DAB: (A) X = Cl, (B) X = Br, and (C) X = I.

Table 2. Ground- and Excited-State Raman Bands of X/R/α-Diimine in CH_2Cl_2 between 1400 and 2100 cm^{-1} [a]

	rR bands	
complex	ground state	excited state
Cl/Me/iPr-DAB	1569, 2030	1486, 1940
Br/Me/iPr-DAB	1562, 2033	1491, 1940
I/Me/iPr-DAB	1556, 2032	1491, 1941
I/Et/iPr-DAB	1544	1493, 1935
I/Me/iPr-PyCa	1484, 1532, 1567, 1625	1480, 1534 (vs), 1567, 1625, 1929

[a] λ_{exc} = 460 nm; vibrational frequencies in cm^{-1}; τ in ns.

of a feature at 1533 cm^{-1} and the appearance of a new band at 1928 cm^{-1}. Replacement of the methyl ligand by an ethyl group in I/R/iPr-DAB gave rise to similar single-color Raman characteristics.

In order to prove that the new features indeed belong to the complexes in their lowest excited state, two-color TR^3 spectra of the complexes X/Me/iPr-DAB (X = Cl, I) in CH_2Cl_2 were measured at a range of delay times. These spectra were measured using 532 nm as the pump wavelength and 416 nm as probe laser line. In order to avoid rapid decomposition of the complexes because of the high pulse intensities, a large volume of sample solution was prepared and fresh portions were used for each accumulation.

For both complexes it was found that both bands at *ca.* 1490 and 1940 cm^{-1} decayed at the same rate and thus belong to a single species. Moreover, this decay occurred at *ca.* 200 ns for I/Me/iPr-DAB, and over *ca.* 60 ns for the corresponding chloride complex. These decay rates correspond with the excited-state lifetimes derived from the TA and emission spectra (Table 1). This means that the 1490 and 1940 cm^{-1} bands indeed belong to the complex in its lowest CT state. The three complexes X/Me/iPr-DAB (X = Cl, Br, I) show nearly the same features in their TR^3 spectra, the only difference being the decay rates.

Time-Resolved Infrared Spectra. Time-resolved infrared (TRIR) spectra of the three complexes X/Me/iPr-DAB (X = Cl, Br, I) were obtained by excitation with the 355 or 532 nm line of a Nd:YAG laser. Changes in IR absorption were measured in the CO-stretching region between 1900 and 2150 cm^{-1} and monitored by a diode laser system, which was tuned in steps of 4 cm^{-1}.

The difference spectra of the complexes are shown in Figure 5, and the ground- and excited-state CO-stretching frequencies and force constants are collected in Table 3. Irradiation caused the bleaching of the two CO bands at about 2030 and 1965 cm^{-1} corresponding to the parent, and the appearance of two new bands at higher frequency. Up to now, such a high frequency shift has always been observed with TRIR spectroscopy upon excitation of a metal carbonyl with a lowest MLCT state.[25-28] It reflects the decrease of metal to CO π-backbonding in the MLCT state. In contrast, an XLCT transition will have little effect on the charge density of the metal and as a result only a small influence on ν(CO). The three complexes did not behave identically in this respect. For X = Cl and Br the force constant of the carbonyls increased by about 80 N m^{-1}. For the iodide complex this increase was only *ca.* 55 N m^{-1}, but the effect on the two CO vibrations was clearly different (Table 3). Just as for the TR^3 spectra the lifetimes of the transients agreed with those derived from the emission and TA spectra.

Since the molecules under study possess two equivalent CO groups, the force field involves only two force constants, the principal constant k_{CO} and the interaction constant k_{COCO}.[38] In

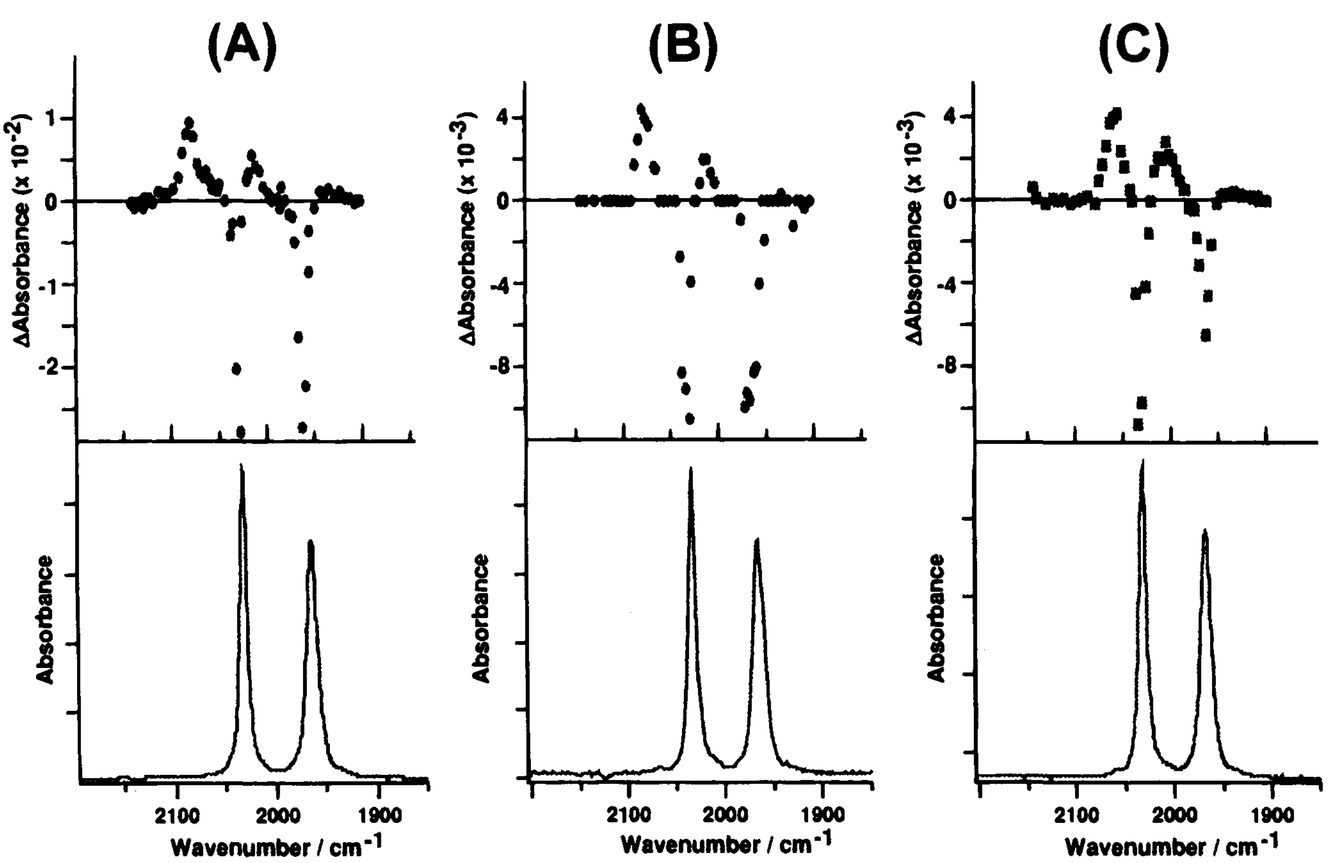

Figure 5. Time-resolved IR spectra of the complexes X/Me/iPr-DAB (X = Cl, Br, I) in their lowest excited state, measured at 60–90 ns after 5 ns excitation of a CH_2Cl_2 solution at ambient temperature; (A) X = Cl (λ_{exc} = 355 nm), (B) X = Br (λ_{exc} = 532 nm), and (C) X = I (λ_{exc} = 532 nm).

Table 3. TRIR Data of X/Me/iPr-DAB in CH_2Cl_2[a]

	ground state						excited state							
	ν(CO)													
X	FTIR	TRIR	k^b	k_i^b	τ	$\theta°$	ν(CO) TRIR	k	k_i	τ	$\theta°$	$\Delta\nu^c$	Δk^c	Δr_{CO}
Cl	2031.5	2030[d]	1611	55.2	f	91	2081[d]	1693	55.4	f	84	49.5[d]	82[d]	0.009[d]
	1963	1962[d]					2014[d]					51[d]		
Br	2032	2037[d]	1613	54	120[d]	91	2080[d]	1689[d]	57.8[d]	120[d]	87	48[d]	76[d]	0.009[d]
	1965	1966[d]					2010[d]					45[d]		
		2031[e]					2079[e]	1690[e]	55[e]	f		47[e]	77[e]	0.009[e]
		1967[e]					2012[e]					47[e]		
I	2031.5	2031[d]	1614	52.5	230[d]	93	2058[d]	1671[d]	39.4[d]	245[d]	88	26.5[d]	57[d]	0.006[d]
	1966.5	1967[d]					2010[d]					43.5[d]		
		2033[e]			210[e]		2057[e]	1667[e]	41.8[e]	215[e]		25.5[e]	53[e]	0.006[e]
		1964[e]					2006[e]					39.5[e]		

[a] $\Delta\nu$ in cm^{-1}; k, k_i, and Δk in N m^{-1}; τ in ns; Δr_{CO} in Å. [b] Calculated from FTIR. [c] Calculated from TRIR and FTIR. [d] Excitation wavelength 355 nm. [e] Excitation wavelength 532 nm. [f] Traces too noisy to obtain accurate kinetic fit.

Table 3 the calculated force constants are included. Recently, an empirical relationship relating CO bond length to the energy factored force field (EFFF) force constants, k_{CO}, has been derived.[39] The CO bond length, r_{CO}, is related to k_{CO} by the following relationship

$$r_{CO} = 1.647 - 0.184 \ln k_{CO} \qquad (1)$$

Using this relationship the CO bond length changes in the excited states of transition metal carbonyls have been estimated.[39] We have used this relation to estimate the structural differences of the Cl^-, Br^-, and I^- complexes. The change in bond lengths for the Cl^- and Br^- complexes are approximately the same (0.009 Å), but for the I^- complex this change is considerably smaller (0.006 Å). From the relative intensities of the ν(CO) vibrations the bond angles CO–Ru–CO (θ) in the ground and excited state can be estimated. The bond angles in the ground state are found in the range 91–93°, which is only slightly different from the excited states which fall in the range 88–84°. This means that there is no significant difference in the CO–Ru–CO angles of the ground and excited states. It has to be mentioned here that only in the case of the I^- complex the interaction force constant k_i decreases upon excitation (Table 3).

Discussion

The lowest-energy band in the TA spectra of the iodide complexes does not depend on R and the solvent, but it shifts to lower energy in the order iPr-DAB > bpy > iPr-PyCa

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(38) *Metal Carbonyl Spectra*; Braterman, P. S., Ed.; Academic Press: 1975.

(39) Morrison, S. L.; Turner, J. J. *J. Mol. Struct.* **1994**, *317*, 39.

(Figure 3). The solvent independence excludes the possibility of a MLCT or LMCT transition and points to an intraligand transition of the reduced α-diimine ligand just as for the complexes $[Ru(bpy)_3]^{2+}$ [40] and $[Re(X)(CO)_3(bpy)]$ (X = halide).[41,42]

For the corresponding radicals $[Ru(Me)(L)(CO)_2(\alpha\text{-diimine})]^•$ (L = PrCN, PPh_3), formed by electrochemical reduction of $[Ru(X)(Me)(CO)_2(\alpha\text{-diimine})]$ (X = halide) in the presence of L, the intraligand transition occurs in the same wavelength region. It also shows a similar dependence on the α-diimine (λ_{max} = 500, 640, and 690 nm for α-diimine = iPr-DAB, bpy and iPr-PyCa, respectively, and for L = PrCN).[43] Changing the electron density at the metal by variation of L has a large influence on the energy of this transition of the radicals. Thus, going from L = PrCN to PPh_3 the transition of the radical $[Ru(Me)(L)(CO)_2(iPr\text{-}PyCa)]^•$ shifts from 690 to 590 nm.[43]

Most probably, the same charge effect is responsible for the shift of the intraligand transition of the complexes X/Me/iPr-DAB in their excited state when the iodide is replaced by a chloride or bromide. The transition then shifts to higher energy and is observed as a shoulder of the 400 nm band (see Figure 2). A similar influence of the halide has recently been observed by Rossenaar et al. in the TA spectra of the closely related $[Re(X)(CO)_3(bpy)]$ complexes.[42] Going from X = Cl to Br and I the lowest-energy transition of these complexes in their excited state shifts from 500 to 590 and *ca.* 780 nm. In agreement with the results from the TR^3 and TRIR data to be discussed hereafter, we attribute this influence of X on the intraligand transition to a change of character of the lowest excited state from MLCT to XLCT.

The differences in bond character between the ground state and lowest excited state can be derived from a comparison of the resonance Raman and IR spectra with the TR^3 and TRIR spectra. The ground electronic states of the complexes show a resonance Raman effect for ν_s(CN), and the frequency of this vibration decreases appreciably from top to bottom in Table 2, going from Cl/Me/iPr-DAB to I/Et/iPr-DAB. This frequency decrease is caused by an increase of π-back-bonding as a result of the more electron donating properties of I^- and Et with respect to Cl^- and Me, respectively. Due to the more delocalized character of the ground electronic state of I/Et/iPr-DAB compared to Cl/Me/iPr-DAB, electronic excitation of the former complex will give rise to transfer of less negative charge to iPr-DAB. In fact, this complex merely shows a frequency lowering for ν_s(CN) of 51 cm^{-1} upon CT excitation, whereas the Cl/Me/iPr-DAB complex has its ν_s(CN) frequency lowered by 83 cm^{-1}. The other complexes show a frequency shift in between these two extremes.

These TR^3 spectra only show that the amount of charge transferred to the ligand is different for the separate complexes under study. They do not, however, provide any evidence for a change of character of the lowest excited state from MLCT to XLCT as derived from the rR[35] and emission[36] spectra.[44] In this respect the TRIR spectra are more revealing.

According to the TRIR spectra the carbonyl stretching vibrations shift to higher frequency upon CT excitation, which implies that the stretching force constant of the carbonyls (*k*, see Table 3) increases. This effect on *k*, Δ*k*, decreases from 82 to 76 N m^{-1} when in Cl/Me/iPr-DAB the Cl^- ligand is replaced by Br^-. At the same time the frequency shift of ν_s(CN), $\Delta\nu_s$(CN), decreases from 83 to 71 cm^{-1}. Thus, both the TRIR and TR^3 spectra reflect the decrease of electron transfer when the ground electronic state becomes more delocalized over metal and α-diimine.

Parallel consideration of the TRIR and TR^3 data helps to enlarge our insight into the electronic character of the ground and excited states of these complexes. Thus, when Br^- is replaced by I^- to give I/Me/iPr-DAB, the effect on $\Delta\nu_s$(CN) is rather small since it merely decreases from 71 to 65 cm^{-1}. At the same time, Δ*k* for the CO-stretching vibrations decreases from 76 to 55 N m^{-1}. In view of the Raman data, this latter effect can only partly be ascribed to a further delocalization of the ground electronic state. It implies that the charge transferred to the ligand originates from an orbital which has less metal and more halide character, since electron transfer from the halide to the α-diimine is not expected to influence strongly the electron density on the carbonyls.

The occurrence of a ν(CO) shift in the TRIR spectra of the iodide complexes suggests that their lowest excited state still possesses some MLCT character, although the ground state rR spectra did not show any ν(CO) enhancement. This discrepancy is not surprising since the rR spectra reflect the differences in bonding properties between the ground state and vibrationally excited singlet CT state, the TRIR and TR^3 spectra those between the ground state and relaxed triplet CT state.

We therefore conclude that, going from the Cl^- to the I^- complexes, two effects influence the characters of the ground- and lowest-excited CT state, *viz.* an increase of mixing between the d_π(Ru) and π^*(iPr-DAB) orbitals and an increase of interaction between the d_π(Ru) and p_π(X) orbitals. According to the time-resolved spectra the latter effect becomes especially important when Br^- is replaced by I^-.

The above data agree with the results from the emission spectra.[36] Replacing Cl^- by Br^- in X/Me/iPr-DAB caused an increase of the emission lifetime at room temperature from 63 to 75 ns. Substitution of Br^- by I^- gave, however, a much larger increase of lifetime to 177 ns. This effect, which was accompanied by a drastic lowering of k_{nr}, could only be explained with a change of CT character of the lowest excited state, since the energy gap law predicted only a very small difference in lifetime for these three complexes. Thus, these time-resolved vibrational data fully confirm our tentative conclusions derived from the emission[36] and absorption and resonance Raman[35] spectra of these complexes.

The ^{13}CO-enrichment studies show that the 1940 cm^{-1} band observed in the TR^3 spectra must be associated with a CO-stretching vibration. Since the band decays with the same lifetime as the excited complex it is apparently attributable to this excited state. However, the reduced diimine ligand-centered transition of the latter would not be expected to cause much resonance enhancement of CO modes. Furthermore, the band is shifted to lower frequencies compared to the ground-state band at 2030 cm^{-1}, though the latter is due to a totally symmetric CO stretch while the 1940 cm^{-1} band is depolarized. A downward frequency shift of a CO mode in the lowest MLCT excited state of a carbonyl complex would be unprecedented.[25-28] The TRIR data presented above show that both CO bands in the ground state of these complexes do indeed shift to higher frequencies upon CT excitation. The possibility that the 1940

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(40) Braterman, P. S.; Harriman, A.; Heath, G. A.; Yellowlees, L. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1801.

(41) Kalyanasundaram, K. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 2401.

(42) Rossenaar, B. D.; Stufkens, D. J.; Vlček, Jr., A. *unpublished results.*

(43) Nieuwenhuis, H. A. Thesis, University of Amsterdam, 1994.

(44) A reviewer has suggested that enhancement of a ν(Ru−I) mode might result if the lowest excited state of the iodide complex is XLCT. Such a resonance enhancement is, however, not expected since excitation takes place into an intraligand transition. Besides, unequivocal assignments are difficult in the low-frequency region, *ca.* 150−250 cm^{-1}, where such modes might be expected.

cm^{-1} band in the TR^3 spectra is a combination of the symmetric 1490 cm^{-1} vibration and an asymmetric ν(Ru−C) mode near 450 cm^{-1} cannot be discounted. The (ground state) IR spectrum of the iodide complex shows several bands in this frequency region and one of these may belong to such a vibration. It may be remarked here that Perng and Zink[21] have reported lower-frequency (and, as in the present case, non-totally symmetric) CO bands in the Raman spectra recorded under pulsed excitation conditions of some W(CO)$_4$(α-diimine) complexes. However, despite the fact that the bands appeared only when the laser flux incident on the sample was increased, they were considered to be due to ground-state molecules.

Conclusions

The above results clearly show that only by combination of TA, TR^3, and TRIR spectral data detailed information can be obtained about the character of the lowest excited state of these X/Me/iPr-DAB complexes.

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