Characterization of Metal-to-ligand Charge-transfer and Intraligand Transitions of *fac*-$[Re(CO)_3L(X)]$ Complexes [L = Di-imine; X = Halide or $Mn(CO)_5$] and Explanation of the Photochemistry of $[Re(CO)_3L\{Mn(CO)_5\}]$ using the Resonance Raman Effect

By **Roelof W. Balk, Derk J. Stufkens,*** and **Ad Oskam**, Anorganisch Chemisch Laboratorium, University of Amsterdam, J. H. van't Hoff Instituut, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

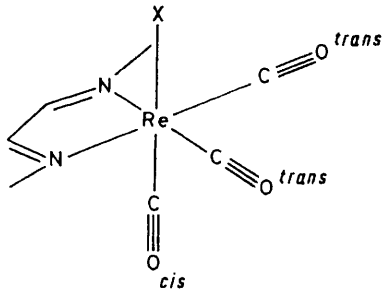
The resonance Raman (r.R.) spectra of a series of $[Re(CO)_3L(X)]$ complexes [L = aryl or alkyl *NN'*-disubstituted-ethane-1,2-di-imine or 2-(*N*-monosubstituted-iminomethyl)pyridine; X = Cl or Br], obtained by excitation within the lowest-energy absorption band are reported. The influence of the ligand L and of the halogen atom X is discussed. The excitation profiles of $[Re(CO)_3(p\text{-}MeC_6H_4N{=}CHCH{=}NC_6H_4Me\text{-}p)Cl]$ are compared with those of the free ligand, *NN'*-di(*p*-tolyl)ethane-1,2-di-imine. These spectra revealed that upon excitation within both metal-to-ligand charge-transfer and intraligand transitions also resonance enhancement occurs of a carbonyl stretching mode. The low-temperature r.R. spectra of $[Re(CO)_3(NC_5H_4CH{=}NC_6H_4Me\text{-}p)\{Mn(CO)_5\}]$ are reported and used for the characterization of the electronic absorption spectrum and for the explanation of the photochemistry of this complex.

In recent articles[1-7] we reported the resonance Raman (r.R.) spectra of a series of $[M(CO)_{4-x}L(L')_x]$ complexes (M = Cr, Mo, or W; L = di-imine; L' = phosphine or isocyanide; $x = 0$ or 1), obtained by excitation within their lowest-energy metal-to-ligand charge-transfer (m.l.c.t.) transitions. Special attention was paid to the r.R. effect of $\nu(CO^{cis})$ and $\nu(C{\equiv}N)$, the stretching modes of the carbonyl and isocyanide ligands *cis* with respect to the di-imine ligand L. This effect was explained by an interaction between virtual molecular orbitals having predominantly L π^* and CN–R π^* or CO π^* character, respectively.

In this article we extend these studies to a series of *fac*-$[Re(CO)_3L(X)]$ complexes. When X = Cl or Br, the metal has a d^6 configuration, and a direct relationship with the results of the Group 6B analogues is therefore expected. When X = $Mn(CO)_5$, the rhenium metal is formally zerovalent, having a d^7 configuration. This has a pronounced influence on the properties of the complexes, as shown by several authors.[8-11] Some controversy exists about the assignment of the electronic absorption spectra[10,11] and in order to elucidate the character of the electronic transitions, we studied the r.R. effect for one representative complex.

This article consists of three parts. First, we report the properties of the lowest-energy m.l.c.t. transitions for a series of rhenium d^6 complexes, as derived from the r.R. results, in comparison with those of the zerovalent Group 6B complexes reported earlier. In the second part we present the excitation profiles of a representative complex, and finally, we report the r.R. spectra of a binuclear rhenium–manganese complex upon excitation within the visible region of the spectrum. In this latter complex, the di-imine ligand is σ,σ bonded to the rhenium metal atom *via* the nitrogen lone pairs, while the $Mn(CO)_5$ moiety occupies a position *cis* with respect to the di-imine ligand, resulting in the formation of a single Re–Mn σ bond.

The structure of a representative complex is shown below.



X = Cl, Br, or $Mn(CO)_5$

EXPERIMENTAL

The complexes were prepared following standard procedures.[11-13]

Electronic absorption and i.r. spectra were measured on Cary 14 and Perkin-Elmer model 283 spectrophotometers respectively.

Resonance Raman spectra were recorded on a Jobin–Yvon HG 2S Ramanor, using an SP model 171 Ar^+ ion laser and CR models 490 and 590 tunable dye lasers with rhodamine 6G, sodium fluorescein, and $PhCH{=}CHC_6H_4SO_3H\text{-}3$ in ethylene glycol as dyes and cyclo-octatetraene as photosensitizer, in combination with an Anaspec 300-S tunable monochromator with a bandpass of *ca.* 0.4 nm. Light detection was by standard photo-counting techniques, employing a RCA C31034 or a Hamamatsu R 943 photomultiplier tube.

The r.R. spectra were recorded with a spinning cell from 0.5×10^{-3}—5×10^{-3} mol dm^{-3} solutions of the complexes and from 2×10^{-3}—30×10^{-3} mol dm^{-3} solutions of the ligands in chloroform and benzene. For the excitation profiles, the spectra were measured in $CHCl_3$, while the 1 210 cm^{-1} band of this solvent was used as internal standard. Spectra of dispersions of complexes in $K[NO_3]$ or KBr pellets were measured using a similar device to that described by Clark and Turtle.[14] For these experiments a molar ratio of *ca.* 1 : 1 000 of complex to $K[NO_3]$ or KBr was used.

Raman intensities were measured with a Hewlett–Packard model 10 calculator using a 9864 A digitizer and corrected for the sensitivity of the spectrophotometer.

The rhenium(I) complexes were stable in the laser beam, while the binuclear rhenium–manganese complex could only be measured at low temperatures.

RESULTS AND DISCUSSION

Resonance Raman Spectra of $[Re(CO)_3L(X)]$ *Complexes* (X = Cl *or* Br).—We studied the r.R. spectra upon excitation within the lowest-energy absorption band of the complexes, its position varying from 400 to 520 nm in benzene solution. The complexes all exhibit strong luminescence at room temperature in solution upon excitation within the m.l.c.t. bands, in agreement with the results of Wrighton and co-workers[12,15] for $[Re(CO)_3L(X)]$ complexes with L = 1,10-phenanthroline and 2,2′-bipyridine. Fortunately, however, this luminescence occurs in the red region of the spectra (*ca.* 650 nm) and the Raman spectra were not obscured by these emissions even when the spectra were excited with λ *ca.* 600 nm (see *e.g.* Figure 6).

Resonance enhancement was observed for several ligand modes and for one CO stretching mode. In the low-frequency region very weak r.R. effects were found for some metal–carbon stretching and δ(M–C–O) modes, whereas the symmetrical metal–nitrogen stretching vibration, which is expected at *ca.* 250 cm^{-1} according to earlier results for Group 6B complexes, could not be detected. In the case of the chloro-complexes a prominent band appeared at *ca.* 290 cm^{-1}, which was absent in the spectra of the corresponding bromo-complexes. We assign this band to the rhenium–chloride stretching vibration, in agreement with values reported in the literature for closely related complexes.[16,17]

The enhancement of intensity of ligand modes confirms the m.l.c.t. character of the absorption band. The resonance enhancements were much smaller than for the $[M(CO)_{4-x}L(PR_3)_x]$ complexes (M = Cr, Mo, or W; $x = 0$ or 1) in solutions with the same optical density. This is probably due to the smaller ε values for the m.l.c.t. band of the rhenium complexes (for the tungsten complexes ε varies from 8 000 to 16 000 dm^3 mol^{-1} cm^{-1}). The r.R. intensity profile follows the slope of the absorption band and is not substantially red-shifted with respect to this band.[18,19] The r.R. spectra are dominated by skeletal ligand stretching modes, which are all polarized to some extent ($\rho < \frac{3}{4}$). This observation and the fact that excitation takes place within allowed transitions, means that the Raman emission is most likely Franck–Condon scattering.[20-23] This is supported by the above mentioned strong dependence of the r.R. effect on the ε value going from Group 6B to 7B complexes.[23]

In the i.r. spectra of the rhenium complexes, three strong ν(CO) modes were observed, which confirms the facial structure of the complexes. The r.R. spectra however, showed only one ν(CO) mode at *ca.* 2 020 cm^{-1}. Wuyts and van der Keelen[24] investigated the i.r. spectra of the closely related *fac*-$[Mn(CO)_3L_2(X)]$ complexes (L = PR_3, AsR_3, or SbR_3; X = Cl or Br), while Brisdon *et al.*[16] investigated the i.r. spectra of the isoelectronic $[M(CO)_3L(X)]^-$ complexes (M = Cr, Mo, or W; L = 1,10-phenanthroline or 2,2′-bipyridine; X = Cl, Br, or I). Although there is some controversy concerning the correct assignment of the three ν(CO) bands,[13] in both of these articles the highest-frequency band is assigned to ν_{sym}(CO) of the carbonyls *cis* with respect to the halogen atom.

During our studies of the r.R. effect induced by the m.l.c.t. transitions of the analogous $[M(CO)_{4-x}L(PR_3)_x]$ complexes, resonance enhancement of Raman intensity could only be detected for one carbonyl stretching mode. This vibration has been assigned by several authors to the symmetrical stretching mode of the carbonyls *cis* to the di-imine ligand (A_1^2) in the case of the $[M(CO)_4L]$ complexes.[6,25,26] The corresponding resonance-enhanced mode of the $[M(CO)_3L(PR_3)]$ complexes has also been assigned to the *cis* carbonyl stretching mode.[2,3,6] Since a similar r.R. effect is expected for the corresponding $[Re(CO)_3L(X)]$ complexes upon excitation within the m.l.c.t. band, the resonance-enhanced band in the CO stretching region must also be attributed to a stretching mode of the carbonyl ligand *cis* with respect to L and *trans* with respect to the halogen X.

The close resemblance between the i.r. and r.R. spectra of a rhenium and a tungsten complex is shown in Figure 1. The bands at 2 019 cm^{-1} in the spectrum of $[Re(CO)_3(NC_5H_4CH{=}NPr^i)(Cl)]$ and at *ca.* 1 930 cm^{-1} in the spectrum of $[W(CO)_3(NC_5H_4CH{=}NPr^i)\{P(OMe)_3\}]$ belong to $\nu(CO^{cis})$. The 1 400—1 650 cm^{-1} region of the r.R. spectra of Figure 2 contains the most strongly enhanced ligand modes, which are ν(CN) at 1 614 cm^{-1}, ν(pyI) at 1 589 cm^{-1}, ν(pyII) at 1 556 cm^{-1}, and ν(pyIII) † at 1 467 cm^{-1} for $[Re(CO)_3(NC_5H_4CH{=}NPr^i)Cl]$ [2,6] (py = pyridine). For the corresponding RN=CHCH=NR complexes, strong enhancement of ν_{sym}(CN) is observed in this region.

A remarkable feature of the r.R. spectra of the $[Re(CO)_3(NC_5H_4CH{=}NR)X]$ complexes is the rather strong enhancement of intensity of ν(pyI) (at *ca.* 1 590 cm^{-1}), which band was found to be very weak in the r.R. spectra of some $[M(CO)_4(NC_5H_4CH{=}NR)]$ complexes (M = Cr, Mo, or W) upon excitation within the (lowest-energy) m.l.c.t. transition.[6]

Going from the tungsten to the rhenium complex, the intensities of both $\nu(CO^{cis})$ and ν(CN) increase with respect to those of ν(pyII) and ν(pyIII) (Figure 1). Enhancement of intensity of $\nu(CO^{cis})$ upon excitation within the m.l.c.t. transition has been explained with an excited-state interaction between molecular orbitals mainly localized at the di-imine ligand and at the *cis* carbonyl groups, respectively.[6] The intensity of $\nu(CO^{cis})$ with respect to the ligand modes appeared to increase among others with the charge-transfer character of the m.l.c.t. transition, for which the solvatochromism (solvent

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† Nomenclature from L. G. Ward, T. L. Meek, and G. E. Cheney, *Inorg. Chim. Acta.*, 1970, **4**, 43.

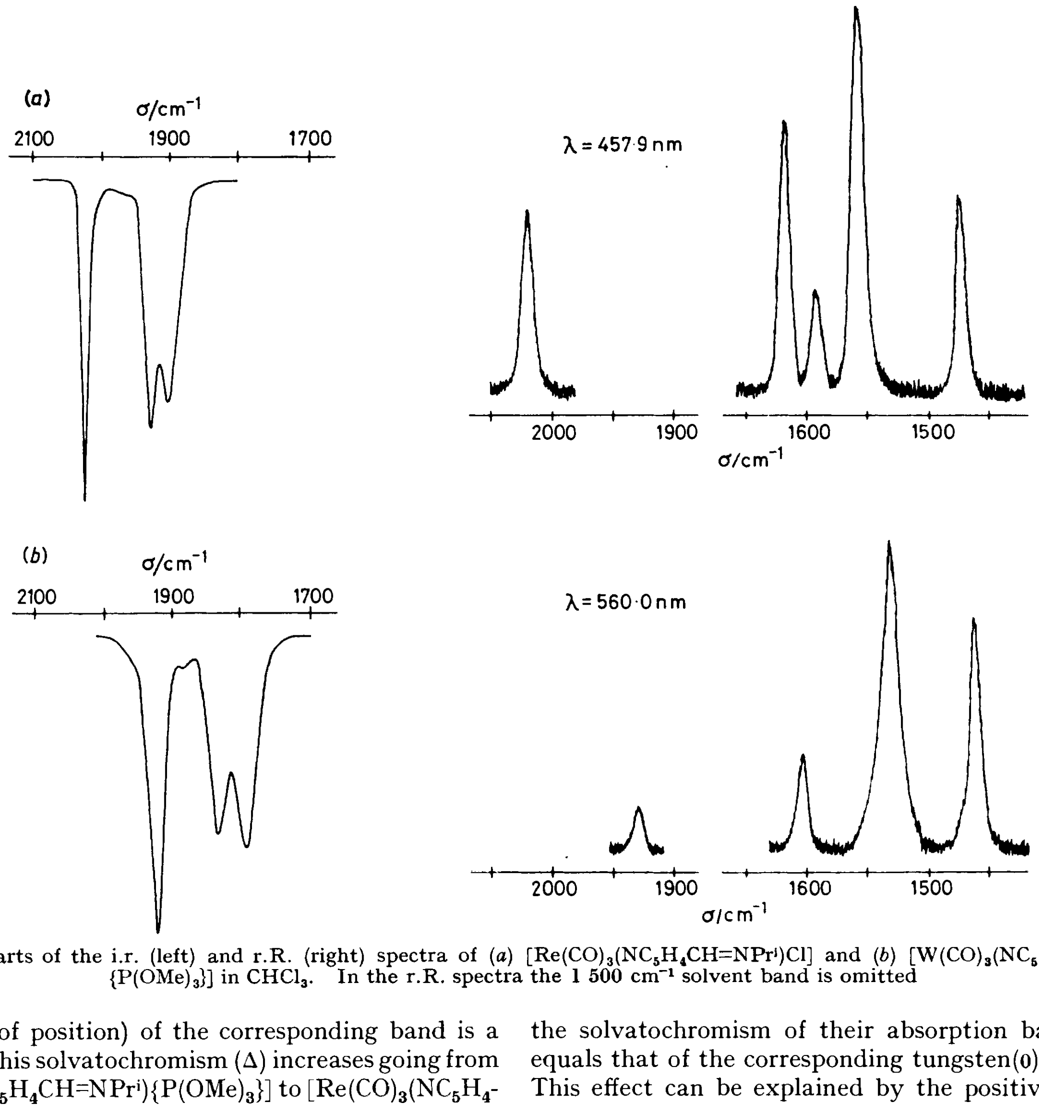

FIGURE 1 Parts of the i.r. (left) and r.R. (right) spectra of (*a*) $[Re(CO)_3(NC_5H_4CH{=}NPr^i)Cl]$ and (*b*) $[W(CO)_3(NC_5H_4CH{=}NPr^i)\{P(OMe)_3\}]$ in $CHCl_3$. In the r.R. spectra the 1 500 cm^{-1} solvent band is omitted

dependence of position) of the corresponding band is a measure. This solvatochromism (Δ) increases going from $[W(CO)_3(NC_5H_4CH{=}NPr^i)\{P(OMe)_3\}]$ to $[Re(CO)_3(NC_5H_4CH{=}NPr^i)Cl]$ and as a result also the intensity of $\nu(CO^{cis})$ increases with respect to *e.g.* ν(pyII) {Δ for $[W(CO)_3(NC_5H_4CH{=}NPr^i)\{P(OMe)_3\}]$ is 1.3×10^3 cm^{-1}}. Furthermore, the intensity of ν(CN) appears to be interrelated with that of ν(CO) because both bands increase in intensity going from the tungsten to the rhenium compound. This effect has been observed before [6] and ascribed to a stronger interaction in the excited state of the carbonyl orbitals with the CN part than with the pyridine part of the di-imine ligand.

Although the solvatochromism of the m.l.c.t. band of the rhenium complexes equals that of the corresponding tungsten and molybdenum tetracarbonyl compounds, the r.R. spectra of the rhenium complexes show a very weak r.R. effect for the symmetrical metal–ligand stretching modes, especially for $\nu_{sym}(M-N)$, compared with the Group 6 metal complexes. This means that the lowest m.l.c.t. excited state of the rhenium complexes has less metal–ligand antibonding character. This will be the case when the m.l.c.t. transitions of the rhenium(I) complexes have more c.t. character. On the other hand, the solvatochromism of their absorption bands nearly equals that of the corresponding tungsten(0) complexes. This effect can be explained by the positive charge of rhenium(I) which causes a decrease of π back bonding from the metal to the di-imine and *trans* carbonyl ligands with respect to tungsten(0). The effect of this positive charge and of the decrease of π back bonding is reflected in a higher energy together with a lower ε value of the m.l.c.t. band and in higher wavenumbers of ν(CN) of the di-imine ligand and of the CO stretching modes of the *trans* carbonyls.[27,28] As a consequence, the component of the dipole moment of the molecule which is directed to the *trans* carbonyls will be smaller for the rhenium(I) complexes. As a result m.l.c.t. transitions of the rhenium(I) complexes with the same charge-transfer character as the corresponding tungsten(0) complexes will show a small solvatochromism for the m.l.c.t. band. On the other hand, when the absorption bands of rhenium(I) and tungsten(0) complexes have the same solvatochromism, the corresponding m.l.c.t. transitions of the rhenium(I) compounds will have more c.t. character.

Going from chloro- to bromo-complexes, neither the absorption spectra nor the r.R. spectra change significantly. For the chloro-complexes enhancement of the

TABLE 1

Ultraviolet–visible spectral results, Raman wavenumbers, and relative intensities for a series of *fac*-[Re(CO)$_3$L(X)] complexes

Complex	Properties of the m.l.c.t. band: σ [a]/ 10^3 cm^{-1}	Δ [b]	Conditions of the Raman spectra (λ/nm)		Raman wavenumbers (cm^{-1}) and relative intensities [c]					
					ν(CO^{cis})	ν$_{sym}$(CN)	ν(Re–X)			
[Re(CO)$_3$(Pr^{i}N=CHCH=NPr^i)Cl]	21.9 (4 100)	1.7	457.9	C_6H_6	2 023 (0.08)	1 547 (1.0)	287 (0.12)			
[Re(CO)$_3$(*p*-MeC$_6$H$_4$N=CHCH=NC$_6$H$_4$Me-*p*)Cl]	19.4 (5 000)	2.2	514.5	C_6H_6	2 026 (0.10)	1 493 (1.0)	291 (0.22)			
[Re(CO)$_3$(Pr^{i}N=CHCH=NPr^i)Br]	21.7 (3 100)	1.7	457.9	C_6H_6	2 022 (0.07)	1 542 (1.0)				
					ν(CO^{cis})	ν(CN)	ν(pyI)	ν(pyII)	ν(pyIII)	$CHCl_3$ 1 210 [d]
[Re(CO)$_3$(NC$_5$H$_4$CH=NPr^i)Cl]	23.4 (3 600)	2.1	457.9	$CHCl_3$	2 019 (0.34)	1 614 (0.63)	1 589 (0.24)	1 556 (1.0)	1 467 [0.51]	
[Re(CO)$_3$(NC$_5$H$_4$CH=NPr^i)Br]	23.1 (3 500)	2.1	457.9	$CHCl_3$	2 020 (0.29) [e] (0.05)	1 614 (0.65) (0.11)	1 588 (0.22) (0.04)	1 556 (1.0) (0.16)	1 471 [0.55] [0.09]	 (1.0)
[Re(CO)$_3$(NC$_5$H$_4$CH=NC$_6$H$_4$Me-*p*)Br]	22.1 (3 500)	2.5	476.5	$CHCl_3$	2 024 (0.22) (0.06)	1 613 (0.27) (0.07)	1 582 (0.22) (0.06)	1 554 (1.0) (0.27)	1 471 [0.40] [0.11]	 (1.0)

[a] σ ≡ maximum of the m.l.c.t. band in benzene solution; ε (dm^3 mol^{-1} cm^{-1}) is given in parentheses. [b] $\Delta \equiv [\sigma_{CH_3CN} - \sigma_{C_6H_6}]_{max}$. [c] Intensities relative to the strongest ligand band or a solvent mode; the values in the square brackets are not very reliable due to partial overlap with a solvent band. [d] Solvent absorption. [e] Where two relative intensities are given, the first row is with respect to ν(pyII) and the second is with respect to the band of $CHCl_3$ at 1 210 cm^{-1}.

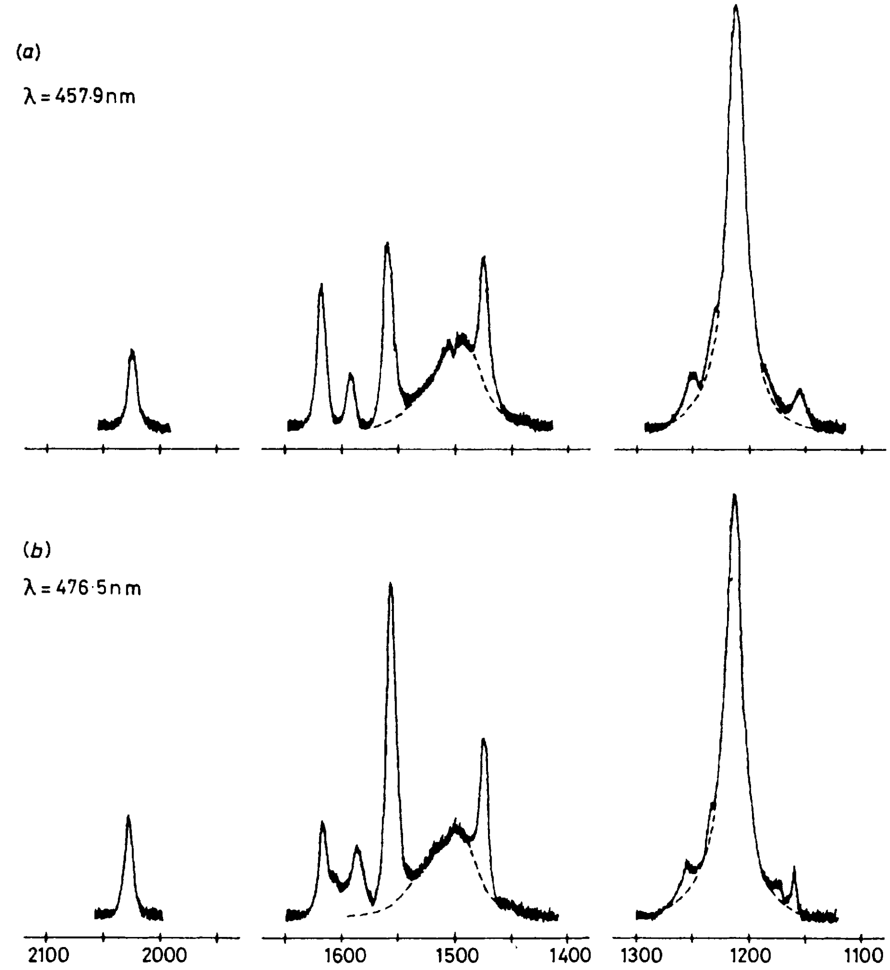

FIGURE 2 Parts of the r.R. spectra of (*a*) [Re(CO)$_3$(NC$_5$H$_4$CH=NPr^i)Br] and (*b*) [Re(CO)$_3$(NC$_5$H$_4$CH=NC$_6$H$_4$Me-*p*)Br] in $CHCl_3$ (1 × 10^{-3} mol dm^{-3}). The solutions have an optical density of 2.6 at these wavelengths (in a 1-cm cell). The dashed curves represent the slope of the 1 210 and 1 500 cm^{-1} solvent bands under those of the complexes

intensity of ν(Re–Cl) is found, which decreases with respect to the intensity of ν_s(CN) going from [Re(CO)$_3$(*p*-MeC$_6$H$_4$N=CHCH=NC$_6$H$_4$Me-*p*)Cl] to [Re(CO)$_3$(Pr^{i}N=CHCH=NPr^i)Cl], but also when [Re(CO)$_3$(*p*-MeC$_6$H$_4$N=CHCH=NC$_6$H$_4$Me-*p*)Cl] is measured in an ionic environment such as K[NO$_3$]. It is therefore not surprising that ν(Re–Br), expected at *ca.* 200 cm^{-1},[16,17] escaped detection in the r.R. spectra of [Re(CO)$_3$(Pr^{i}N=CHCH=NPr^i)Br] in K[NO$_3$].

Going from [Re(CO)$_3$(NC$_5$H$_4$CH=NPr^i)Br] to [Re(CO)$_3$(NC$_5$H$_4$CH=NC$_6$H$_4$Me-*p*)Br] the solvatochromism of the m.l.c.t. band increases, resulting in an increase of r.R. intensities for ν(CO^{cis}) and for the ligand modes with the exception of ν(CN) at 1 618 cm^{-1} (see Figure 2). These spectra were taken with exciting wavelengths having corresponding positions within the m.l.c.t. band (see Table 1) with nearly the same ε value. The decrease of intensity of ν(CN) going from an alkyl substituent to an aryl group at the N atom of the ligand has also been observed for the Group 6B analogues and is most probably due to a decrease of excited-state density at the C=N group of the ligand as a result of conjugation with the aryl group.

The small band appearing as a shoulder at *ca.* 1 600 cm^{-1} of the ν(CN) band in the r.R. spectrum of [Re(CO)$_3$(NC$_5$H$_4$CH=NC$_6$H$_4$Me-*p*)Br] can be assigned to a ν(Ph) of the tolyl group.[29] This vibration is also found at the same frequency in the spectra of [Re(CO)$_3$(*p*-MeC$_6$H$_4$N=CHCH=NC$_6$H$_4$Me-*p*)Cl] in CHCl$_3$ and solid K[NO$_3$] (see below), but could not be detected in the r.R. spectra of the Group 6B analogues, excited within the maxima of their m.l.c.t. bands. The appearance of this band in the r.R. spectra of the rhenium complexes will mainly be caused by pre-resonance with the intraligand (i.l.) transitions appearing in the absorption spectra of [Re(CO)$_3$(*p*-MeC$_6$H$_4$N=CHCH=NC$_6$H$_4$Me-*p*)Cl] at *ca.* 400 nm and of [Re(CO)$_3$(NC$_5$H$_4$CH=NC$_6$H$_4$Me-*p*)Cl] at *ca.* 350 nm.

Excitation Profiles of [Re(CO)$_3$(*p*-MeC$_6$H$_4$N=CHCH=NC$_6$H$_4$Me-*p*)Cl] *and* *p*-MeC$_6$H$_4$N=CHCH=NC$_6$H$_4$Me-*p*.— In order to explain the appearance of ν(Ph) in the r.R. spectra excited within the m.l.c.t. band of the above complex and [Re(CO)$_3$(NC$_5$H$_4$CH=NC$_6$H$_4$Me-*p*)Br] we measured the excitation profiles for one of these complexes together with those of the corresponding free ligand. The complex [Re(CO)$_3$(*p*-MeC$_6$H$_4$N=CHCH=NC$_6$H$_4$Me-*p*)Cl] was chosen because the i.l. transitions of this complex and of the free RN=CHCH=NR ligand are sufficiently low in energy to excite within them, although the free ligand could only be measured in pre-resonance.

Typical r.R. spectra of the free ligand and of the complex are shown in Figures 3 and 4 respectively.

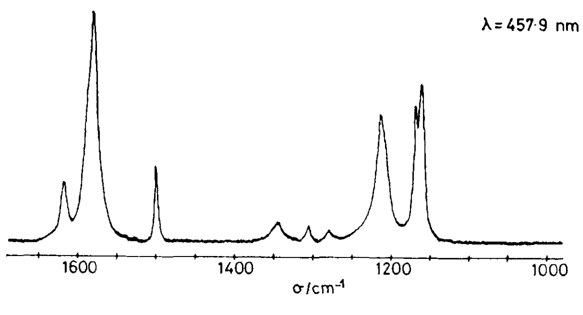

FIGURE 3 High-frequency region of the pre-resonance Raman spectrum of *p*-MeC$_6$H$_4$N=CHCH=NC$_6$H$_4$Me-*p* in CHCl$_3$, excited at 457.9 nm. The 1 210 cm^{-1} band is a solvent band, while the 1 500 cm^{-1} solvent band is omitted. c = 2.7 × 10^{-3} mol dm^{-3}; slit width = 3 cm^{-1}

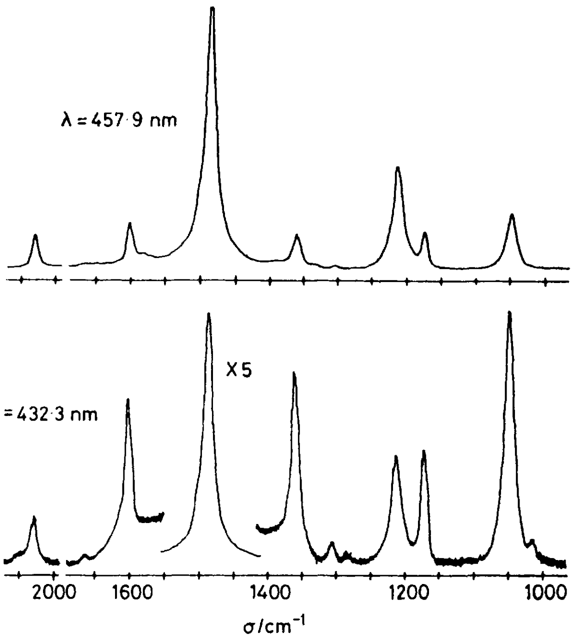

FIGURE 4 High-frequency region of the r.R. spectra of [Re(CO)$_3$(*p*-MeC$_6$H$_4$N=CHCH=NC$_6$H$_4$Me-*p*)Cl] in CHCl$_3$. The 1 210 cm^{-1} band is a solvent band, while the 1 500 cm^{-1} solvent band is obscured by ν_{sym}(C=N) at 1 482 cm^{-1}. c = 5.6 × 10^{-4} mol dm^{-3}

Between 800 and 2 100 cm^{-1} a large number of modes are enhanced in intensity. For *p*-MeC$_6$H$_4$N=CHCH=NC$_6$H$_4$Me-*p* eight modes are observed. The 1 615 cm^{-1} band is the ν(Ph) mode. The ν_{sym}(CN) mode can easily be assigned to the 1 579 cm^{-1} band, because this band shifts *ca.* 100 cm^{-1} to lower frequency upon co-ordination of this ligand. The assignment of the other modes is not certain. All bands are polarized, $\rho \leqslant \frac{1}{3}$, and show sharply increasing excitation profiles towards higher energy (see Figure 5). This points to interaction with a single electronic transition and, since excitation takes place within strongly allowed transitions (ε = 18 000 dm^3 mol^{-1} cm^{-1}) the scattering will most probably be due to an *A* term (Franck–Condon scattering[30]). Figure 5 shows profiles for the 1 615, 1 579, 1 497, and the 1 166 and 1 158 cm^{-1} modes of *p*-MeC$_6$H$_4$N=CHCH=NC$_6$H$_4$Me-*p*. For the last two modes the combined intensity is used. The r.R. spectra show that the excited state is delocalised over the whole ligand since both ring vibrations and ν_{sym}(CN) are enhanced, which agrees with the assignment of the band to a $\pi \rightarrow \pi^*$ transition.[31] The large intensity of ν_{sym}(CN) mainly arises from the fact that the character of the C=N π bond changes from bonding to antibonding during the transition.

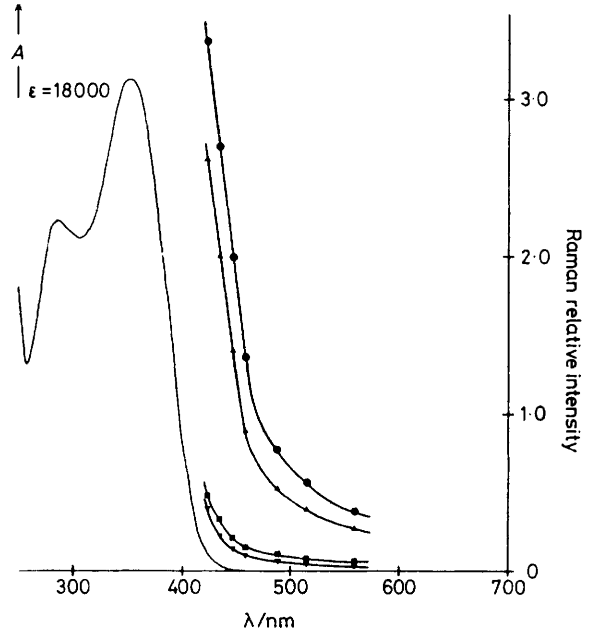

FIGURE 5 Excitation profiles of selected modes of *p*-MeC_6H_4N=CHCH=NC_6H_4Me-*p* in $CHCl_3$ with respect to the 1 210 cm^{-1} solvent band. c = 2.7 × 10^{-3} mol dm^{-3}. 1 579 (●), 1 158, 1 166 (▲), 1 615 (■), 1 497 cm^{-1} (▼). Unmarked curve is absorption spectrum (as in Figure 6)

Going to the [Re$(CO)_3$(*p*-MeC_6H_4N=CHCH=NC_6H_4Me-*p*)Cl] complex the situation becomes more complicated. Apart from the i.l. transitions, which peak at 405 nm and have an essentially solvent-independent position, the complex possesses m.l.c.t. transitions. These latter transitions peak at *ca.* 500 nm in chloroform and show a strong solvatochromism (Figure 6). The i.l. transitions of the complex are substantially shifted to lower energy with respect to the free ligand. This shift is largest for the rhenium(I) complex and decreases going to the zero-valent [$M(CO)_4$(*p*-MeC_6H_4N=CHCH=NC_6H_4Me-*p*)] and [$Fe(CO)_3$(*p*-MeC_6H_4N=CHCH=NC_6H_4Me-*p*)] complexes.[32] This effect arises from interaction of π or π* levels of the ligand with filled d_π metal orbitals. Although the *p*-MeC_6H_4N=CHCH=NC_6H_4Me-*p* ligand is forced into a *cisoid* (*syn*) conformation due to σ,σ co-ordination *via* the lone pairs of the N atoms towards the central metal atom, nearly the same ligand modes are observed in the r.R. spectra of [Re$(CO)_3$(*p*-MeC_6H_4N=CHCH=NC_6H_4Me-*p*)Cl] excited at *e.g.* 432.3 nm and of the free ligand excited at 457.9 nm, as can be seen from Figures 3 and 4. This indicates that the vibrations and the i.l. transitions in both the complexed and free ligand have essentially the same character. In the complex, ν(Ph) lies at 1 598 cm^{-1} and ν_{sym}(CN) at 1 482 cm^{-1}. The CN band has a weak shoulder at *ca.* 1 500 cm^{-1} which corresponds with the 1 497 cm^{-1} band of the free ligand. The three bands at 1 358, 1 302, and 1 283 cm^{-1} also correspond for ligand and complex. The two bands at 1 168 and 1 045 cm^{-1} in the r.R. spectra of the complex probably correspond to the doublet at *ca.* 1 162 cm^{-1} in the spectrum of the free ligand. Apart from ligand modes, also $\nu(CO^{cis})$ is enhanced in intensity upon excitation within both the m.l.c.t. and the i.l. transitions. Furthermore, upon excitation within the i.l. transitions a weak band at *ca.* 2 050 cm^{-1} appeared, which probably represents an overtone of the 1 045 cm^{-1} band.

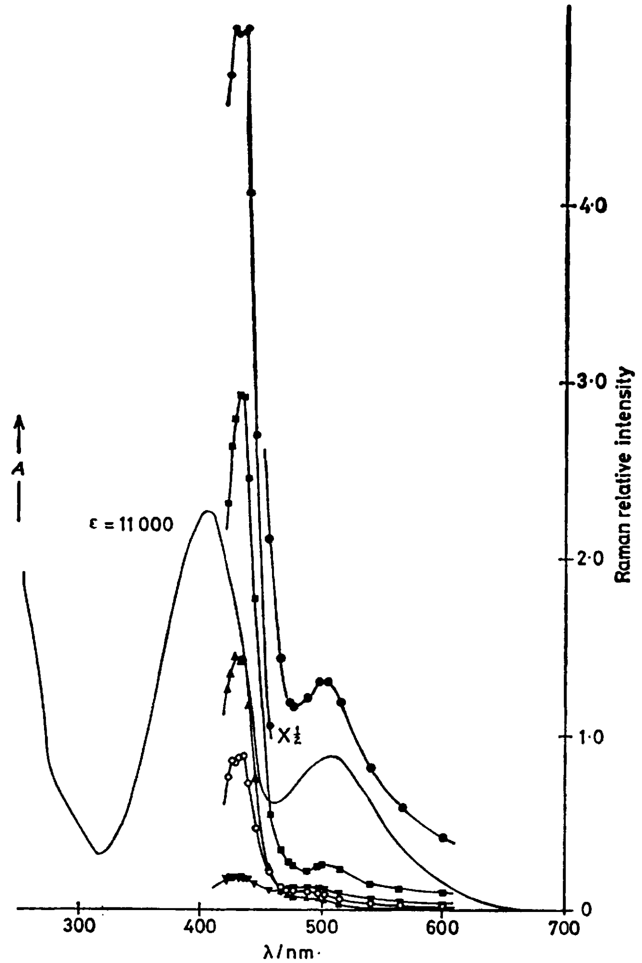

FIGURE 6 Excitation profiles of selected modes of [Re$(CO)_3$(*p*-MeC_6H_4N=CHCH=NC_6H_4Me-*p*)Cl] in $CHCl_3$ with respect to the 1 210 cm^{-1} solvent band. c = 5.6 × 10^{-4} mol dm^{-3}. 1 482 (●), 1 045 (■), 1 358 (▲), 1 598 (○), 2 026 cm^{-1} (▼)

Excitation profiles of some modes of [Re$(CO)_3$(*p*-MeC_6H_4N=CHCH=NC_6H_4Me-*p*)Cl] are shown in Figure 6. We could not excite with laser lines shorter than 422.3 nm, so only the low-energy side of the i.l. (π→π*) band could be studied. The excitation profiles of ν_{sym}(CN) (1 482 cm^{-1}), of the 1 045 cm^{-1} band, and of $\nu(CO^{cis})$ (2 026 cm^{-1}) show two distinct maxima, whereas those of the 1 598 and 1 358 cm^{-1} bands only possess a small shoulder in the region of the m.l.c.t. band. Furthermore, the maxima of the different profiles nearly coincide with each other at *ca.* 500 and 435 nm, respectively, although they slightly shift to lower energy when the frequency of the mode decreases. These shifts may be due to different interference effects for the various modes.[18,33] The shifts are too small to be ascribed to different vibronic transitions. The same ligand modes are resonance enhanced upon excitation within both bands, while their relative intensities do not change much. This indicates that the same π^* level is involved in both transitions, as shown in Figure 7. This is supported by the observation that the excitation profiles of the ligand modes display strong constructive interference between the m.l.c.t. and i.l. maxima (see Figure 6).[2,3] The r.R. spectra of the corresponding $[Re(CO)_3(NC_5H_4CH{=}N\text{-}C_6H_4Me\text{-}p)Br]$ complex did not show such an effect (see next section). Enhancement of $RN{=}CHCH{=}NR$ ligand modes upon excitation within the i.l. band is 10 to 20 times larger than upon excitation within the m.l.c.t. band. On the other hand, the r.R. intensity of $\nu(CO^{cis})$ is only slightly larger when excitation occurs within the i.l. band than within the m.l.c.t. one. The larger r.R. effect induced by the i.l. transition shows that the ligand bonds are much more affected by a (bonding)$\pi\rightarrow$(antibonding)π^* transition than by a metal $d\rightarrow\pi^*$ transition.

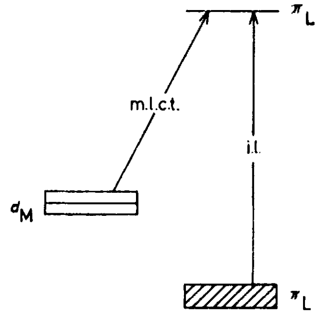

FIGURE 7 m.l.c.t. and i.l. transitions of $[Re(CO)_3(p\text{-}MeC_6H_4N{=}CHCH{=}NC_6H_4Me\text{-}p)Cl]$

The question remains why resonance enhancement is observed, although relatively weak, for $\nu(CO^{cis})$ upon excitation within the i.l. band. The r.R. effect for this mode upon excitation within the m.l.c.t. band has been explained with a delocalization of the m.l.c.t. excited state over the *cis* CO groups by ' through-space ' or ' through-metal ' interaction between orbitals having mainly π_L^* and $\pi_{CO_{cis}}^*$ character respectively. The i.l. transitions are most probably directed to the same π_L^* level (Figure 7) and resonance enhancement of $\nu(CO^{cis})$ is therefore also expected and observed for these transitions. However, no such large differences are expected between the r.R. effects of this CO stretching mode induced by the i.l. and m.l.c.t. transitions as have been found for the ligand modes. The excitation profiles show a sharp decrease of intensity below 430 nm. Although this might be due to destructive interference with l.f. (ligand field) transitions,[34] the maxima are too sharp and the l.f. transitions are expected at still shorter wavelengths (probably at *ca.* 300 nm: the l.f. transitions of the corresponding zerovalent tungsten complexes are found[2] below 400 nm). Furthermore, these maxima correspond with a low-energy shoulder of the i.l. band, which can just be observed in the absorption spectrum. We therefore ascribe them to a distinct $\pi\rightarrow\pi^*$ transition.

Resonance Raman Spectra of $[Re(CO)_3(NC_5H_4CH{=}NC_6H_4Me\text{-}p)\{Mn(CO)_5\}]$.—In order to obtain more information about the character of the lowest electronic transitions of the $[Re(CO)_3L\{Mn(CO)_5\}]$ complexes, we measured the r.R. spectra of $[Re(CO)_3(NC_5H_4CH{=}NC_6H_4Me\text{-}p)\{Mn(CO)_5\}]$ (see Figure 9). The exciting laser line was varied from 620 to 457.9 nm, thus covering the broad band which shows up in the absorption spectrum (Figure 8).

At room temperature the complex exhibits a very strong photosensitivity which has already been reported by Morse and Wrighton[10] for corresponding di-imine complexes. We therefore measured the r.R. spectra at *ca.* −170 °C in $K[NO_3]$ and KBr pellets, at which temperature the photosensitivity is sufficiently reduced to obtain reliable Raman spectra. Because these spectra could only be measured under direct reflection, a monochromator in combination with the laser had to be used. Under these circumstances we could not excite with wavelengths shorter than 457.9 nm, because the power of the dye laser with $PhCH{=}CHC_6H_4SO_3H\text{-}3$ as a dye was too low.

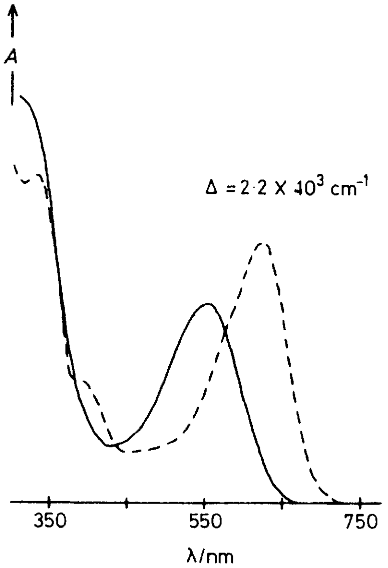

FIGURE 8 Electronic absorption spectra of $[Re(CO)_3(NC_5H_4CH{=}NC_6H_4Me\text{-}p)\{Mn(CO)_5\}]$ in CH_3CN (——) and cyclohexane (- - -)

The absorption spectra between 750 and 300 nm of a cyclohexane and an acetonitrile solution of $[Re(CO)_3(NC_5H_4CH{=}NC_6H_4Me\text{-}p)\{Mn(CO)_5\}]$ are shown in Figure 8. In cyclohexane, a strong band is observed at *ca.* 620 nm, which is strongly solvatochromic. This band resembles the m.l.c.t. band of the corresponding $[M(CO)_4(NC_5H_4CH{=}NPh)]$ complexes (M = Cr, Mo, or W).[6] The band possesses a shoulder at *ca.* 500 nm. The shoulder at *ca.* 400 nm seems also rather solvatochromic, although it is possible that it disappears under the broad band system at *ca.* 300 nm in acetonitrile. Deposition of the complex in KBr revealed an absorption spectrum which was only slightly shifted to longer wavelength with respect to the acetonitrile spectrum and a spectrum of the complex in K[NO$_3$] was not expected to deviate much from the KBr spectrum.

Parts of the r.R. spectrum obtained by excitation with 514.5 and 457.9 nm are shown in Figure 9. Although the complex exhibits luminescence upon irradiation at low temperatures, this luminescence occurs in the red region (*ca.* 700 nm),[10] so that the Raman spectra were not seriously obscured by this emission, even upon excitation at 600 nm.

Apart from the normal wavelength dependence of r.R. scattering, the r.R. spectra obtained by excitation with longer wavelengths than 514.5 nm remained essentially the same. In this wavelength region several di-imine ligand modes show enhancement of intensity, of which the most important ones are: ν(CN) at 1 620, ν(pyII) at 1 538, and ν(pyIII) at 1 478 cm^{-1}. In the low-frequency region of the r.R. spectra between 700 and 400 cm^{-1} several pronounced bands appeared, but between 400 and 50 cm^{-1} only some broad, very weak bands are observed (comparable with the weak 623 cm^{-1} band, measured in KBr). Apart from these modes, also a ν(CO) mode at 2 060 cm^{-1} is strongly enhanced in intensity.

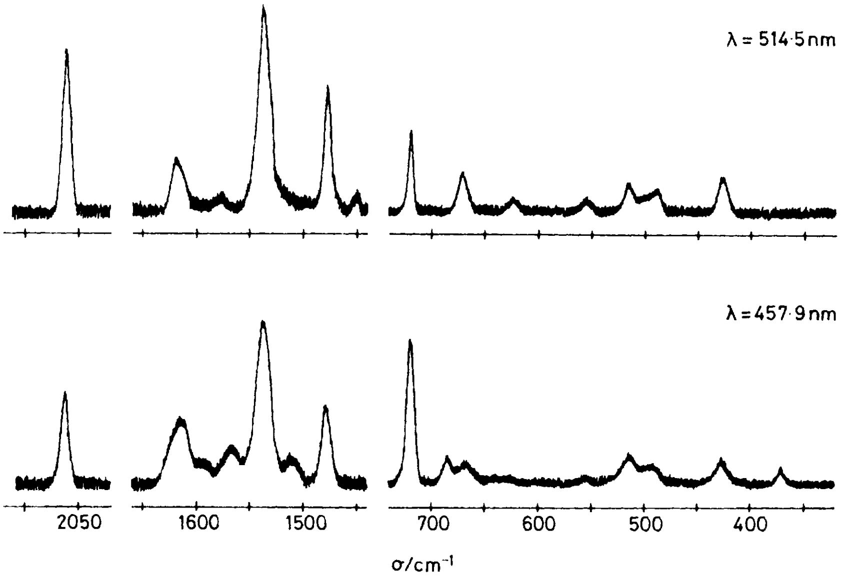

FIGURE 9 Parts of the r.R. spectra of [Re(CO)$_3$(NC$_5$H$_4$CH=NC$_6$H$_4$Me-*p*){Mn(CO)$_5$}] at *ca.* −170 °C in K[NO$_3$], excited with two different wavelengths. The 720 cm^{-1} band is a K[NO$_3$] band

The r.R. spectra closely resemble those of [M(CO)$_4$(NC$_5$H$_4$CH=NPh)],[3,6] both in the high-frequency (1 400—2 100 cm^{-1}) and in the low-frequency (100—700 cm^{-1}) region. Compared with the rhenium(I) complex, intensity enhancement of ν(pyI) is much weaker, while ν(CO) and the bands in the low-frequency region are much more intense. We tentatively assign the bands in the low-frequency region as follows, based upon our previous results for [M(CO)$_4$L] complexes: the 426 and 480 cm^{-1} (or 516 cm^{-1}) bands belong to ν(Re–C^{cis}) and ν_{sym}(Re–C^{trans}) respectively, the bands at *ca.* 623 and 670 cm^{-1} are δ(Re–C–O) modes. The 516 (or 480) and 555 cm^{-1} bands may be due to ν(M–C) modes of the Mn(CO)$_5$ moiety, which are enhanced in intensity by coupling with the corresponding modes of the Re(CO)$_5$ moiety.[17,35] The ν_{sym}(Re–N) mode expected at *ca.* 250 cm^{-1} is apparently not present in the spectrum, just as in the case of the [Re(CO)$_3$L(Cl,Br)] complexes. Also ν(Re–Mn), which is expected at *ca.* 110 cm^{-1},[36] could not be detected, even when excitation occurred at 457.9 nm.

The strong enhancement of intensity of the di-imine modes and the close analogy with other metal–di-imine complexes show that the lowest-energy band has to be assigned to a m.l.c.t. transition. Because of the fact that the ν(CO) mode at 2 060 cm^{-1} in K[NO$_3$] is strongly enhanced in intensity upon excitation within a metal-to-di-imine c.t. transition, we assign this band to a ν(CO^{cis}) mode (see structure on page 1124). This means that the m.l.c.t. excited state is delocalized over a CO group of the Re(CO)$_3$L moiety.

When excitation takes place with wavelengths shorter than 514.5 nm all ligand and low-frequency modes, with the exception of ν(CN) at 1 620 cm^{-1}, which are enhanced upon excitation within the low-energy c.t. band, show a decrease in intensity with respect to the 720 cm^{-1} band of K[NO$_3$]. Furthermore, several other bands appear, in the high-frequency as well as the low-frequency region. The new bands observed in the 457.9 nm spectrum are: 1 590 (sh), 1 575, 1 510, 686, and 371 cm^{-1}. Below 350 cm^{-1} no bands are found. The new bands between 1 700 and 1 400 cm^{-1} are assumed to be ligand modes, which are enhanced due to pre-resonance with an i.l. transition. In order to confirm this, we measured the pre-resonance Raman spectra of NC$_5$H$_4$CH=NC$_6$H$_4$Me-*p* in CHCl$_3$ by excitation at 457.9 and 514.5 nm. The former spectrum is shown in Figure 10. The electronic transitions of this ligand have higher energies than those of the corresponding p-MeC$_6$H$_4$N=CHCH=NC$_6$H$_4$Me-p ligand (see above) and the spectrum shown in Figure 10 is therefore measured for a solution which has a ten times higher concentration than the one used for the r.R. spectra of p-MeC$_6$H$_4$N=CHCH=NC$_6$H$_4$Me-p (Figure 3).

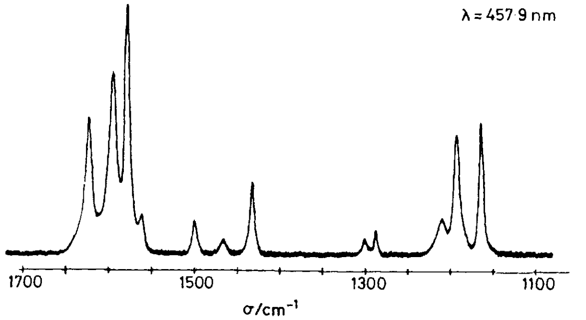

FIGURE 10 High-frequency region of the pre-resonance Raman spectrum of NC$_5$H$_4$CH=NC$_6$H$_4$Me-p in CHCl$_3$, excited at 457.9 nm. The 1 210 cm^{-1} band is a solvent band, while the 1 500 cm^{-1} solvent band is obscured by a ligand band. c = 2.7 × 10^{-2} mol dm^{-3}; slit width = 3 cm^{-1}

It is clear from a comparison of the r.R. spectra in Figures 9 and 10 that the new bands at 1 590 and 1 575 cm^{-1}, which appear in the r.R. spectrum of [Re(CO)$_3$(NC$_5$H$_4$CH=NC$_6$H$_4$Me-p){Mn(CO)$_5$}] upon excitation with λ = 457.9 nm, correspond to the strongest bands in the pre-resonance Raman spectrum of NC$_5$H$_4$CH=NC$_6$H$_4$Me-p. These modes will therefore certainly become enhanced by pre-resonance with an i.l. transition of the complexed ligand. The ν(CN) mode will also gain intensity from such a pre-resonance Raman effect and this may explain the fact that the intensity of this band does not decrease going from 514.5 to 457.9 nm excitation (Figure 9). Also the bands at 686 and 371 cm^{-1} (probably) belong to ligand modes, which become enhanced by pre-resonance with an i.l. transition.

The spectrum of Figure 10 shows that the excited state involved in the i.l. transition is extensively delocalized over the whole molecule, since vibrations of the C=N group, the pyridine ring, and the phenyl substituent are resonance enhanced. This agrees with an assignment of the ligand band to a π→π* transition. Contrary to p-MeC$_6$H$_4$N=CHCH=NC$_6$H$_4$Me-p (Figures 3 and 4) the relative intensities of the ligand modes enhanced by excitation within the m.l.c.t. band (Figure 9) strongly differ from those observed in Figure 10. This means that the π→π* transition of NC$_5$H$_4$CH=NC$_6$H$_4$Me-p has a very different influence on the ligand bonds than the metal d→π* transition.

TABLE 2

Assignment of the Raman bands of NC$_5$H$_4$CH=NC$_6$H$_4$Me-p in CHCl$_3$ [a]

	ν(CN)	ν(Ph)	ν(pyI)	ν(pyII)	ν(pyIII)	ν(pyIV)
NC$_5$H$_4$CH=NPr^i [b]	1 645		1 588	1 567	1 468	1 436
NC$_5$H$_4$CH=NC$_6$H$_4$Me-p	1 623s	1 595vs	1 579vs	1 560w	1 464vw	1 432m

[a] Wavenumbers in cm^{-1}; v = very, s = strong, m = medium, w = weak. [b] Values and assignments from ref. 2.

A comparison of the spectra of Figures 3 and 10 shows that ν(CN) of NC$_5$H$_4$CH=NC$_6$H$_4$Me-p is relatively weak with respect to the other ligand modes, where ν$_{sym}$(CN) of p-MeC$_6$H$_4$N=CHCH=NC$_6$H$_4$Me-p shows the strongest r.R. effect. This means that the C=N bond of NC$_5$H$_4$CH=NC$_6$H$_4$Me-p is much less influenced by the π→π* transition than the C=N bonds of p-MeC$_6$H$_4$N=CHCH=NC$_6$H$_4$Me-p.

The i.l. transitions of the NC$_5$H$_4$CH=NC$_6$H$_4$Me-p complex probably appear as a shoulder at *ca.* 330 nm in the absorption spectrum in cyclohexane (Figure 8). This is at about the same position as found for [Re(CO)$_3$(NC$_5$H$_4$CH=NC$_6$H$_4$Me-p)Br] and [M(CO)$_4$(NC$_5$H$_4$CH=NR)] (R = aryl) complexes (see above and ref. 3).

No clear r.R. effect could be ascribed as due to the electronic transition appearing as a shoulder at 400 nm in the cyclohexane spectrum. This may be due to its low intensity or to coincidence of this (solvatochromic) band with the much stronger i.l. band in K[NO$_3$].

The question remains from which metal orbital the m.l.c.t. transition responsible for the low-energy solvatochromic band originates. The band has been assigned by Morse and Wrighton [10] to a transition from the metal-to-metal bonding orbital to the lowest π* orbital of the di-imine ligand L ($\sigma_b \rightarrow \pi_L^*$). Thus, during excitation depopulation of the orbital responsible for the metal-to-metal single bond takes place, giving rise to a cleavage of this bond.[10] However, depopulation of such a σ_b level is expected to cause a r.R. effect for ν(Re–Mn) upon excitation within the m.l.c.t. band [32] and such an effect is not observed. The ν(Re–Mn) mode could not even be detected in the r.R. spectra.

In agreement with our r.R. results and recently reported absorption spectral data of a series of [M(CO)$_3$(RN=CHCH=NR){Mn(CO)$_5$}] complexes (M = Mn or Re),[11] we assign this low-energy band to a metal $d_\pi \rightarrow \pi_L^*$ c.t. transition. This assignment is in accordance with the expected position of this m.l.c.t. band with respect to the corresponding one of [Re(CO)$_3$(NC$_5$H$_4$CH=NC$_6$H$_4$Me-p)Br] if the difference in charge of the rhenium metal in these complexes is taken into account. Normally, a shift of the m.l.c.t. bands of *ca.* 1 eV † to higher energy is found going from a complex with a zerovalent metal to one with a monocationic central metal atom.[37] Such a shift is *e.g.* observed going from [W(CO)$_4$] to [Re(CO)$_3$Br] [6] and also for [Re(CO)$_3${Mn(CO)$_5$}] with respect to [Re(CO)$_3$Br].

The shoulder at 400 nm has been assigned by Morse and Wrighton [10] to the metal $d_\pi \rightarrow \pi_L^*$ transition and by Staal *et al.*[11] to a transition from a metal d orbital to the second excited state of the di-imine ligand ($d_\pi \rightarrow \pi_L{}^*{}_2$). We do

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† Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J.

not agree with these assignments. The energy of this band is too high and the intensity too low for the $d_\pi \rightarrow \pi_L^*$ transition, while our results for $[M(CO)_{4-x}L(PR_3)_x]$ complexes (M = Cr, Mo, or W; $x = 0, 1,$ or 2)[2] and the molecular-orbital calculations[3,38] do not agree with a $d_\pi \rightarrow \pi_L{}^*{}_2$ transition. Although the latter assignment cannot fully be excluded in the case of $[Re(CO)_3(NC_5H_4CH{=}NC_6H_4Me\text{-}p)\{Mn(CO)_5\}]$, it does not explain the occurrence of a similar band in the spectrum of the corresponding RN=CHCH=NR complexes.[11] The ligand RN=CHCH=NR (R = Pr^i, Bu^t, or C_6H_4Me-*p*) does not possess a low-lying second π^* level. We assign this 400 nm shoulder tentatively to the $\sigma_b \rightarrow \pi_L^*$ transition. The low intensity of the shoulder is in accordance with the small transition probability expected for such a transition.

Morse and Wrighton[10] have shown that the metal-to-metal bond is broken upon irradiation within the lowest-energy m.l.c.t. band. They ascribed this photoreaction to a weakening of the metal-to-metal bond during the $\sigma_b \rightarrow \pi_L^*$ c.t. transition. The r.R. spectra, however, do not show a r.R. effect for ν(Re–Mn) which means that this bond is hardly affected by the m.l.c.t. transition. We therefore ascribe the breaking of this bond to a fast deactivation of the m.l.c.t. excited state to a thermally activated ground state in which the metal-to-metal bond is broken.

Conclusions.—It has been shown in this study that the r.R. effect of the $[Re(CO)_3L(X)]$ complexes [L = di-imine; X = halide or $Mn(CO)_5$] can be used to: (*i*) discriminate between the different bands in the absorption spectra of the complexes, (*ii*) characterize m.l.c.t. and i.l. transitions and excited states, (*iii*) obtain detailed information about the changing character of the lowest-lying m.l.c.t. states on going from a complex with a zerovalent central metal atom to one with a monocationic central metal atom.

We are indebted to Dr. L. H. Staal for his gifts of $[Re(CO)_5Br]$ and $[Re(CO)_3(p\text{-}MeC_6H_4N{=}CHCH{=}NC_6H_4Me\text{-}p)Cl]$, to Mr. J. Tromp for preparing the binuclear rhenium–manganese complex, and to Mr. Th. Snoeck for his assistance during the r.R. experiments.

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