Influence of Metal to Di-imine π-Backbonding on the Resonance-Raman Spectra of [M(CO)$_4$L], *fac*-[Re(CO)$_3$LCl], and [Ru(CO)$_3$L] Complexes (M = Mo or W; L = Di-imine)

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The resonance-Raman (r.R.) spectra of complexes [M(CO)$_4$L], *fac*-[Re(CO)$_3$LCl], and [Ru(CO)$_3$L] [M = Mo or W; L = 1,2-bis(arylimino)ethane or 1,2-bis(i-propylimino)ethane] obtained by excitation into the lowest-energy absorption band are reported. An increase of π-backbonding from the metal to the di-imine ligand appears to be accompanied by a decrease of the r.R. effect for the symmetrical stretching modes of the ligand with respect to the symmetrical metal–ligand stretching modes. At the same time, an increase of the r.R. effect is observed for vibrations of the aryl rings which are virtually inactive in the Raman spectra of the free ligands. This latter result is interpreted in terms of a distortion of the aryl rings in the metal-to-ligand charge transfer excited state.

IN a recent article[1] we discussed the influence which the valence of the central metal atom has on the properties of the lowest metal-to-ligand charge transfer (m.l.c.t.) state of [Re(CO)$_3$LX] and [M(CO)$_{4-x}$L{P(OMe)$_3$}$_x$] complexes (L = di-imine; X = Cl or Br; M = Cr, Mo, or W; x = 0 or 1) by comparing their resonance-Raman (r.R.) spectra. These r.R. spectra revealed that the lowest m.l.c.t. state of the rhenium complexes is mainly localized at the di-imine ligand. Besides, the same π* ligand orbital appeared to be involved in the intra-ligand (i.l.) and m.l.c.t. transition. In this article we report the r.R. spectra of the complexes [Re(CO)$_3$LCl], [M(CO)$_4$L], and [Ru(CO)$_3$L] (L = *p*-MeC$_6$H$_4$N=CHCH=NC$_6$H$_4$Me-*p* or 2,4,6-(Me)$_3$C$_6$H$_2$N=CHCH=NC$_6$H$_2$(Me)$_3$-2′,4′,6′; M = Mo or W).

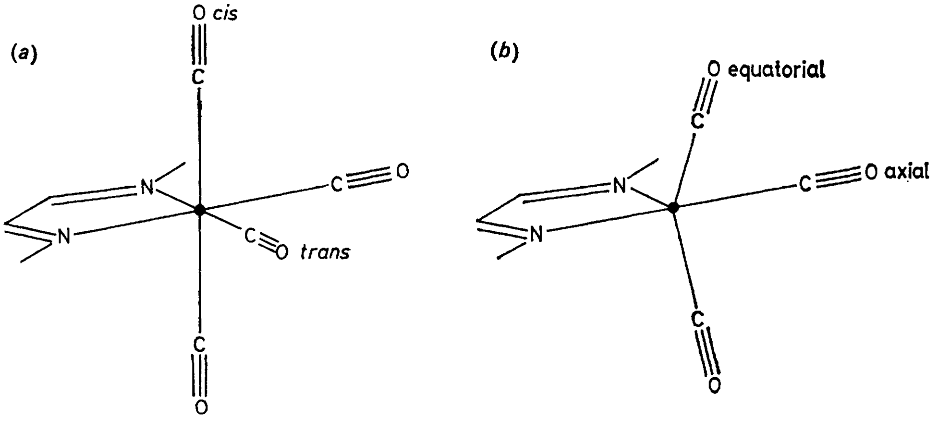

FIGURE 1 Structures of (*a*) the d^6 [M(CO)$_4$L] and (*b*) d^8 [M(CO)$_3$L] complexes (L = di-iminoethane)

Special attention is paid to the influence of π-backbonding from the metal to the di-imine ligand on these r.R. spectra. The structures of the [M(CO)$_4$L] and [Ru(CO)$_3$L] complexes are shown in Figure 1, although for [Ru(CO)$_3$L] a square-pyramidal structure cannot be excluded.[2,3] In these complexes the di-imine ligand is σ,σ-co-ordinated towards the d^6 and d^8 metal, as has been established by ^{1}H n.m.r.,[4–6] for example.

EXPERIMENTAL

The preparation of the ligands and of the d^6 transition-metal complexes has been described before.[9, 10] The complex [Ru(CO)$_3$(bmie)] [bmie = 1,2-bis(mesitylimino)ethane] was prepared according to ref. 6. This complex, which is rather sensitive to air in solution, was characterized by mass, ^{1}H n.m.r., and i.r. spectroscopy, with ν(CO) at 2 051, 1 988, and 1 976 cm^{-1}; this compares with *e.g.*, [Fe(CO)$_3${2,6-(Me)$_2$C$_6$H$_3$N=CHCH=NC$_6$H$_3$(Me)$_2$-2′,6′}] [2 041, 1 973, and 1 965 cm^{-1}; (both spectra taken from a n-hexane solution)]. Electronic absorption and r.R. spectra were recorded on a Cary 14 spectrophotometer and a Jobin Yvon HG 2S Ramanor, respectively. The Raman spectra were excited by a SP model 171 Ar$^+$ ion laser and a CR 490 tunable dye-laser with Rhodamine 6G, Rhodamine 110, and the sodium salt of fluorescein in ethylene glycol as dyes and with cyclo-octatetraene as photosensitizer. An Anaspec 300-S with a bandpass of 0.4 nm was used as a tunable pre-monochromator. Details of light detection and sampling techniques have been given before.[1] The spectra shown in Figures 3—7 have not been corrected for the spectral response of the Raman spectrophotometer.

RESULTS AND DISCUSSION

Contrary to the [Fe(CO)$_3$L]-complexes,[4,5] the mononuclear [Ru(CO)$_3$L] complexes (L = di-imine) can only be prepared for di-imine ligands possessing bulky substituents at the nitrogen atoms.[6] Thus, [Ru(CO)$_3$(bmie)] and [Ru(CO)$_3$(bipie)] [bipie = 1,2-bis(i-propylimino)ethane] could be isolated but not, for example [Ru(CO)$_3$(bptie)] [bptie = 1,2-bis(*p*-tolylimino)ethane]. In the latter case, di- or tri-nuclear ruthenium complexes were formed.

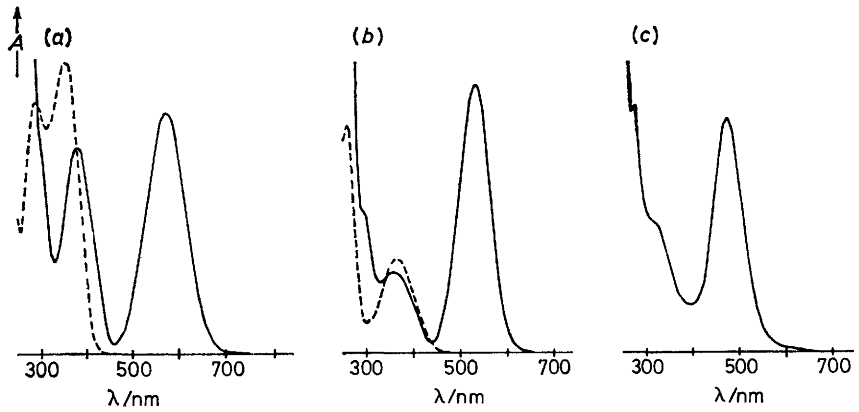

FIGURE 2 Absorption spectra of (a) [W(CO)$_4$(bptie)], (b) [W(CO)$_4$(bmie)], and (c) [Ru(CO)$_3$(bmie)] in cyclohexane. The solid curves represent the spectra of the complexes, the dotted curves are those of the ligands

Electronic Absorption Spectra.—The intense absorption band of [Ru(CO)$_3$(bmie)] at about 500 nm (Figure 2) is due to c.t. transitions in which the metal *d* orbitals and the lowest energy π^* level of the di-imine ligand are involved. In the spectra of the corresponding iron(0) complexes this band has also been observed and assigned to such transitions.[4,5] The band exhibits a very small negative solvatochromism, *i.e.* its position shifts to higher energy going from polar to apolar solvents. Assuming that π-backbonding towards the carbonyls is stronger than towards the di-imine ligand, this implies that the transition possesses a slight di-imine ligand-to-metal charge transfer (l.m.c.t.) character (excitation occurs parallel to the dipole moment).[11] This is in contrast to the corresponding absorption band of most d^6 complexes, which normally shows a positive solvatochromism and therefore belongs to a transition from the metal to the ligand (m.l.c.t.). The energy of the c.t. band of [Ru(CO)$_3$(bmie)] and of the corresponding iron(0) complexes [5,12] is rather high compared with the d^6 complexes (Table 1). For [Fe(CO)$_3$(bptie)] the band is observed at 19 600 cm^{-1} while the solvatochromism is zero, which implies that the energy of the transition is entirely due to overlap stabilization. For [W(CO)$_4$(bptie)], which also possesses a c.t. band without solvatochromism, the overlap stabilization causes a transition energy of 17 700 cm^{-1}. A direct comparison between the solvatochromism of the absorption bands of d^6 and d^8 complexes is not possible, since the dipole moments of these complexes will differ. This can, for example, be deduced from the frequency-lowering of ν(CO) for [M(CO)$_3$(di-imine)] (M = Fe or Ru) with respect to [M(CO)$_5$] (*ca.* 50 cm^{-1}), which is smaller than for [M(CO)$_4$(di-imine)] (M = Cr, Mo, or W) with respect to [M(CO)$_6$] (*ca.* 100 cm^{-1}).[11,13,14] Apart from the intense c.t. band, the absorption spectra of these complexes possess intra-ligand (i.l.) transitions. In the case of the bptie complexes these i.l. transitions can most easily be assigned because of their high intensity. These transitions are red-shifted with respect to the free ligand, this shift being largest for the rhenium complex and smallest for the iron compound. In the case of the complexes [M(CO)$_4$(bptie)] (M = Cr, Mo, or W) these i.l. transitions obscure the ligand-field (l.f.) transitions, which appear at about 370 nm in the spectra of the corresponding [M(CO)$_4$(bipie)] (M = Cr, Mo, or W) compounds and which have absorption coefficients of about 2 500 dm^3 mol^{-1} cm^{-1}.[11,15] Although the i.l. bands of bmie are much less pronounced in the spectra of the complexes because of their low absorption coefficients, they are expected to shift similarly going from the free to the complexed ligand. The shoulders at 385 and 275 nm, respectively, in the spectrum of [Ru(CO)$_3$(bmie)] are therefore assigned to i.l. transitions. The third shoulder at 315 nm will belong to l.f. transitions.[12,16,17]

TABLE 1

Electronic absorption spectral data of the complexes in benzene

Ligands	$10^{-3}\sigma$(c.t.) [a]/ cm^{-1}	$10^{-3}\Delta$ [b]/ cm^{-1}	$10^{-3}\sigma$(i.l.) [a]/ cm^{-1}
bptie			28.4 (18.0)
bmie			27.2 (4.4)
Complexes			
[Re(CO)$_3$(bptie)Cl]	19.4 (5.0)	2.2	25.0 (13.0)
[Re(CO)$_3$(bmie)Cl]	19.5 (6.6)	1.6	24.7 (3.4)
[Cr(CO)$_4$(bptie)]	16.2 (9.3)	0.6 [0.7]	26.9 (11.2) [c]
[Mo(CO)$_4$(bptie)]	16.7 (11.7)	1.0 [1.2]	26.7 (14.2) [c]
[Mo(CO)$_4$(bmie)]	17.3 (15.0)	0.7 [0.7]	27.0 (4.0) [c]
[W(CO)$_4$(bptie)]	17.7 (12.0)	0.1 [0.0]	26.6 (10.3) [c]
[W(CO)$_4$(bmie)]	18.4 (15.2)	0.0 [−0.4]	27.4 (3.4) [c]
[Fe(CO)$_3$(bptie)]	19.6	0.0 [0.0]	27.2
[Ru(CO)$_3$(bmie)]	21.1	−0.1 [−0.2]	26.0

[a] $10^{-3}\epsilon_{max.}$ (dm^3 mol^{-1} cm^{-1}) in parentheses. [b] $\Delta = \sigma_{CH_3CN}$(c.t.) $- \sigma_{C_6H_6}$(c.t.); $\Delta' = \sigma_{CH_3CN}$(c.t.) $- \sigma_{cyclohexane}$(c.t.) in square brackets. [c] Maximum of coinciding i.l. and l.f. bands, the l.f. band of [M(CO)$_4$(bipie)] is observed at about 27.0×10^3 cm^{-1} with $\epsilon_{max.} = 2\,500$ dm^3 mol^{-1} cm^{-1}.

Resonance-Raman Spectra.—(1) *Pre-resonance-Raman spectra of the ligands.* The Raman spectra of the free di-imine ligands are shown in Figure 3. Even if excitation takes place at long wavelength (*e.g.*, λ = 600 nm), the Raman spectra are dominated by bands showing a pre-resonance-Raman (pre-r.R.) effect upon excitation with shorter wavelength. Recently, we reported the pre-r.R. spectra of p-MeC$_6$H$_4$N=CHCH=NC$_6$HM$_4$e-p in CHCl$_3$.[1]

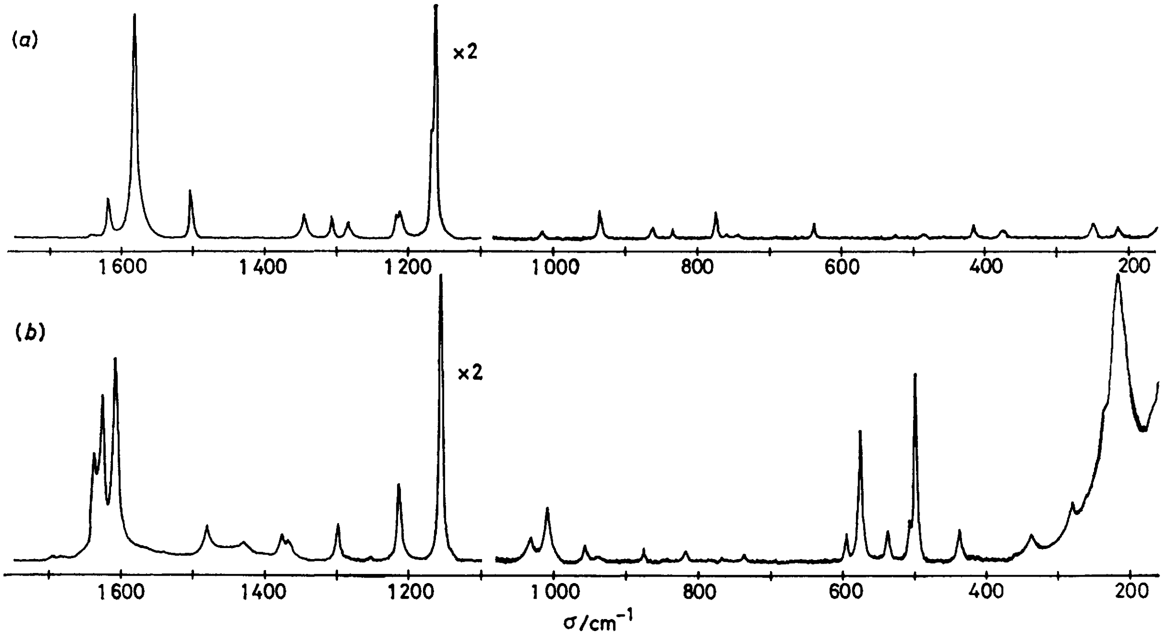

FIGURE 3 Part of the Raman spectra of two di-imine ligands excited with λ = 595.5 nm. The spectrum of (*a*) bptie is measured with a slit width of 300 μm, that of (*b*) bmie with a slit width of 400 μm

On approaching the low-lying $\pi\rightarrow\pi^*$ transition of the ligand a pre-r.R. effect was observed for bands between 1 100 and 1 700 cm^{-1}, all being polarized. ν_{sym}(CN) at 1 580 cm^{-1} and two bands at about 1 170 cm^{-1} showed a strong r.R. effect. ν(Ph) at 1 618 cm^{-1} and a band at 1 500 cm^{-1} showed a weak pre-r.R. effect while a very small enhancement of intensity was observed for the three bands at about 1 300 cm^{-1}. The Raman spectrum of the ligand bmie differs in several aspects from that of bptie. First of all, several low-frequency vibrations of the former ligand are much more intense with respect to the high-frequency ones. Also ν(Ph), which is assigned to the doublet at 1 626 and 1 638 cm^{-1} (comparable with the doublet at about 1 600 cm^{-1} in the Raman spectra of benzene and toluene) is enhanced in intensity with respect to ν_{sym}(CN) at 1 600 cm^{-1}. Furthermore, the absorption coefficient of the lowest i.l. transition is much smaller in the case of bmie and the same holds for the pre-r.R. effects observed for the high-frequency modes of this ligand. These results indicate that the conjugation between the phenyl ring and the N=CHCH=N moiety is reduced in the bmie ligand.[18] This effect is undoubtedly due to steric hindrance between the methyl groups at the *ortho* positions of the ring and the protons of the di-imine group, which forces the phenyl ring out of the plane of the N=CHCH=N group.

(2) *Resonance-Raman spectra of the rhenium, molybdenum, and tungsten complexes.* The r.R. spectra of the complexes, shown in Figures 4 and 5, were excited close to the maximum of the m.l.c.t. band. Although no progressions are observed, we are most likely dealing here with *A*-term or Franck-Condon emission,[19,20] since excitation takes place into allowed electronic transitions ($\varepsilon_{max.}$ 5 000—15 000 dm^3 mol^{-1} cm^{-1}) and all Raman bands are polarized. From the fact that resonance enhancement is observed for a large number of vibrations without any progressions, we deduce that many bonds are slightly affected by the m.l.c.t. transition. Several r.R. bands below 700 cm^{-1} belong to metal–ligand vibrations. The band at about 275 cm^{-1} in the spectra of the [M(CO)$_4$-(bptie)] complexes is assigned to ν_{sym}(M–N). The corresponding vibration of [Mo(CO)$_4$(MeN=CHCH=NMe)] has been assigned by ^{15}N enrichment to a band at 220 cm^{-1}.[21] The shift to higher frequency is caused by the increase of π-backbonding, going from the alkyl- to the aryl-di-imine complex. From the two bands observed for [Re(CO)$_3$(bptie)Cl] in this frequency region, the band at 290 cm^{-1} has been shown to be absent in the r.R. spectrum of [Re(CO)$_3$(bipie)Br].[1] This band will therefore belong to ν(Re–Cl) and the band at 270 cm^{-1} to ν_{sym}(Re–N).

For [Re(CO)$_3$(bmie)Cl] only one band is observed at 282 cm^{-1}, which is assigned to both ν(Re–Cl) and ν_{sym}(Re–N). The corresponding complexes [M(CO)$_4$(bmie)] (M = Mo and W) show a strong r.R. band for ν_{sym}(M–N) at about 290 cm^{-1}. The bands at *ca.* 325 and 525 cm^{-1} in the spectra of the bmie complexes are assigned to vibrations of the complexed ligand. The band at 325 cm^{-1} is not present in the spectra of the corresponding bptie complexes, whereas the band at 178 cm^{-1} is observed only in the spectra of the bptie complexes. Assignment of the 178 cm^{-1} band to a δ(C–M–C) vibration is rejected since such a mode is expected between 50 and 120 cm^{-1}.[13] For the band at 525 cm^{-1} the assignment is based on the fact that the r.R. effect of this band strongly differs from the other (metal–ligand) vibrations in this frequency region. The symmetrical metal–carbon stretching modes of some of these complexes have been observed in the r.R. spectra

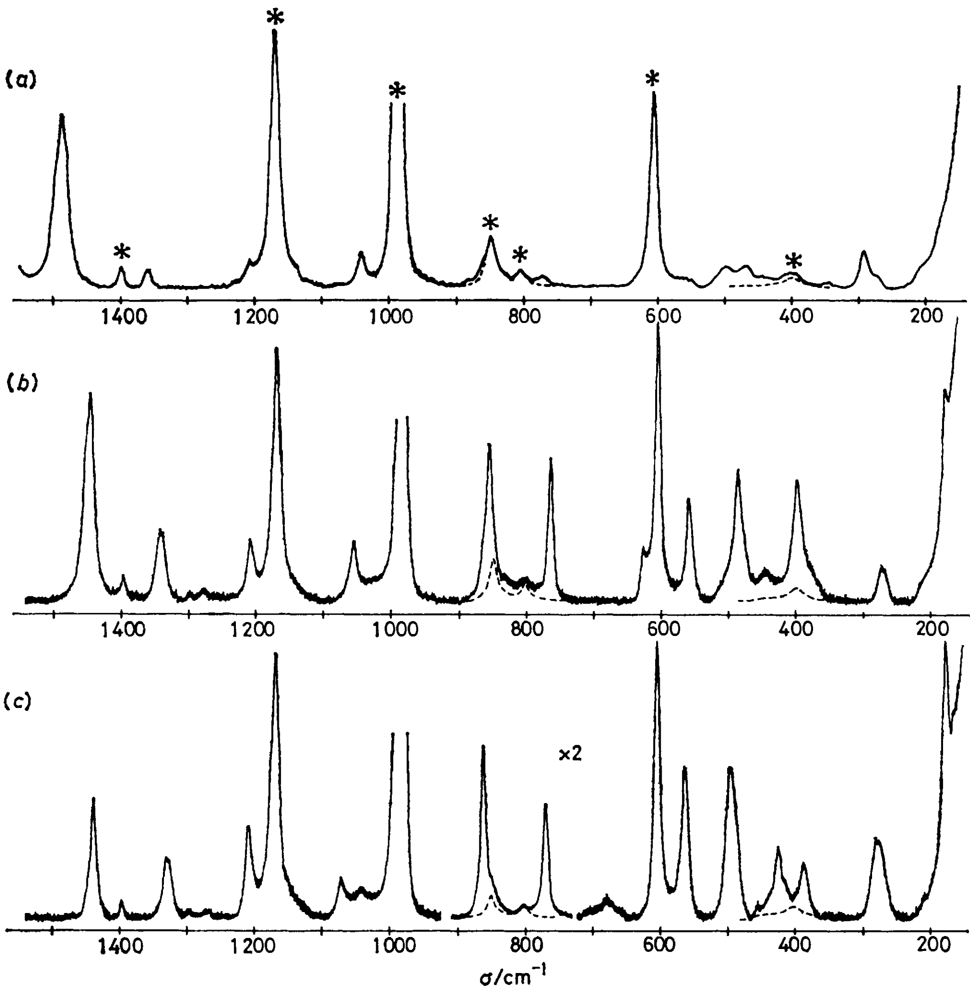

FIGURE 4 Part of the r.R. spectra of the complexes (*a*) [Re(CO)$_3$LCl], (*b*) [Mo(CO)$_4$L], and (*c*) [W(CO)$_4$L] (L = bptie) in C_6H_6. The solvent bands, indicated with an asterisk, are, in a few cases, represented by a dotted curve. The optical density at the excitation wavelength was 4.6 (514.5 nm) for the rhenium complex, 2.5 (595.5 nm) for the molybdenum complex, and 3.5 (595.5 nm) for the tungsten complex (in a 1-cm cell)

between 400 and 500 cm^{-1}.[21] The two bands at *ca.* 400 and 500 cm^{-1} in the spectra of the complexes [M(CO)$_4$(bmie)] are assigned to these vibrations (see Table 2).

TABLE 2

Resonance enhanced metal–ligand modes

Complex	Raman wavenumbers (cm^{-1}) and assignments		
	ν_{sym}(M–N)	ν_{sym}(M–C)	δ(M–C–O)
[Mo(CO)$_4$(bipie)] [a]	231	407, 464	591, 635
[Mo(CO)$_4$(bptie)] [b]	274	400, 488	560, 628
[W(CO)$_4$(bptie)] [b]	277	424, 496	565, 678
[Mo(CO)$_4$(bmie)] [b]	292	400, 500	582, 668
[W(CO)$_4$(bmie)] [b]	293	417, 492	586, 680
[Ru(CO)$_3$(bmie)] [b,c]	200	334, 377	453, 508, 536

[a] Frequencies from ref. 15, measured in cyclohexane. [b] Measured in benzene. [c] Excited at 514.5 nm.

The bands at 400 and 488 cm^{-1} in the spectrum of [Mo(CO)$_4$(bptie)] will belong to the same type of vibrations. In the case of [W(CO)$_4$(bptie)] the assignment is less straightforward, since two bands are observed around 400 cm^{-1} (387 and 424 cm^{-1}). In agreement with the spectra of [W(CO)$_4$(bmie)] we assign the band at 424 cm^{-1} to ν_{sym}(W–C) and the band at 387 cm^{-1} to a ligand vibration. The band at 496 cm^{-1} is assigned to the other symmetrical metal–carbon stretching mode of [W(CO)$_4$(bptie)]. The high intensity and broadness of this band indicate however that this metal–carbon stretching mode coincides with a ligand vibration. The metal–carbon vibrations of the corresponding rhenium complexes can not easily be assigned. The bands between 550 and 700 cm^{-1} are assigned to δ(M–C–O) vibrations. The remaining bands in the spectra will belong to di-imine vibrations. The rather strong band between 1 440 and 1 500 cm^{-1} is assigned to ν_{sym}(CN). This vibration is shifted by about 90 cm^{-1} to lower frequency upon complexation of the ligand to Re. For the Mo and W complexes this vibration is further lowered in frequency as a result of increasing π-backbonding. The band in the region 1 000—1 070 cm^{-1} corresponds to the ring–ring stretching vibration of bipyridine [22] and is therefore assigned to ν_{sym}(CC). This assignment is in agreement with the

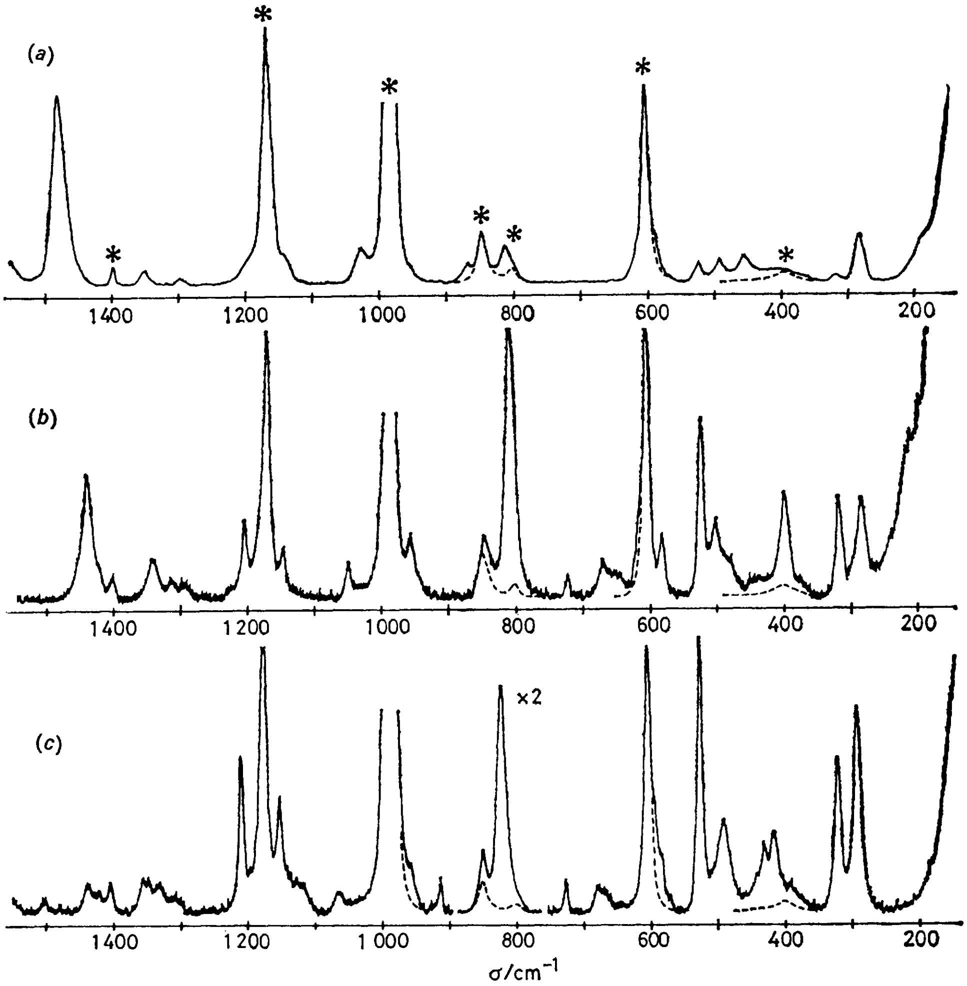

FIGURE 5 Part of the r.R. spectra of the complexes (*a*) [Re(CO)$_3$LCl], (*b*) [Mo(CO)$_4$L], and (*c*) [W(CO)$_4$L] (L = bmie) in C_6H_6. The solvent bands, indicated with an asterisk are, in a few cases, represented by a dotted curve. The optical density at the excitation wavelength was 4.6 (514.5 nm) for the rhenium complex, 2.5 (580.0 nm) for the molybdenum complex, and 3.5 (550.0 nm) for the tungsten complex (in a 1-cm cell)

frequency increase of this vibration going from the Re to the Mo and W complexes. The π-backbonding increases in this order, which means that the π* level of the di-imine ligand becomes more involved in the ground state of the complex. This π* level is antibonding with respect to the C=N bonds but bonding with respect to the C–C bond of the N=CHCH=N group of the di-imine ligand. As a result, a frequency decrease is observed for ν_{sym}(CN) and an increase for ν_{sym}(CC) when the π-backbonding increases.

The increase of π-backbonding to the di-imine ligand not only influences the frequencies of ν_{sym}(CN) and ν_{sym}(CC) but also their r.R. intensities. A large decrease of intensity is observed for these vibrations, whereas at the same time ν_{sym}(M–N) is strongly enhanced in intensity. These intensity changes are caused by the decrease of c.t.

TABLE 3

Resonance enhanced di-imine ligand modes of the complexes in benzene

	Raman wavenumbers (cm^{-1}) and assignments							
Complex	ν_{sym}(CN)		$\omega_x(\omega_3)$ [b]	ω_x'	ν_{sym}(CC)	$\omega_x(\omega_5)$ [b]	$\gamma_{CH}(\omega_{14})$ [b]	$\gamma_x(\omega_{16})$ [b]
[Mo(CO)$_4$(bipie)] [a,c]	1 500				1 150			
[Re(CO)$_3$(bptie)Cl]	1 493	1 365	1 216		1 050	863	770	
[Mo(CO)$_4$(bptie)]	1 455	1 349	1 216		1 063	856	765	178 [d]
[W(CO)$_4$(bptie)]	1 445	1 334	1 214		1 076	862	769	178 [d]
[Re(CO)$_3$(bmie)Cl]	1 487	1 359			1 035	815	527	325
[Mo(CO)$_4$(bmie)]	1 447	1 350	1 213	1 153	1 056	810	525	325
[W(CO)$_4$(bmie)]	1 440	1 354	1 209	1 152	1 062	822	529	331
[Ru(CO)$_3$(bmie)]	1 482	1 305	1 212		1 066	842	472	

[a] Values from ref. 28. [b] Notation from ref. 24. [c] Measured in $CHCl_3$. [d] Partly obscured by Rayleigh scattering.

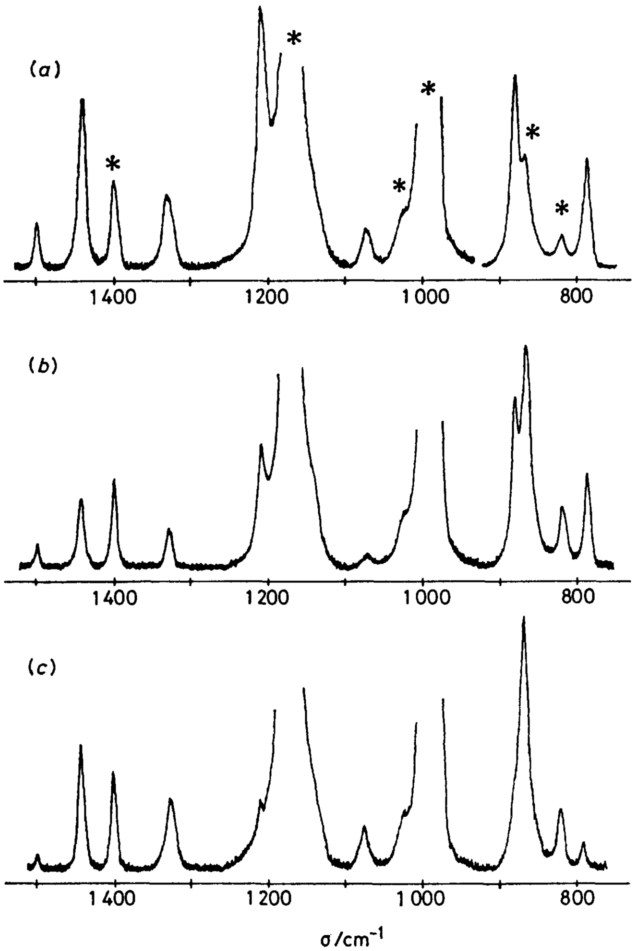

FIGURE 6 Part of the r.R. spectra of [W(CO)$_4$(bptie)] in C_6H_6, excited with different laser lines: (*a*) λ = 514.5, (*b*) 488.0, (*c*) 457.9 nm. The bands, indicated with an asterisk, are solvent bands. Some weak bands of benzene are omitted

character of the m.l.c.t. transition as a result of the increase of π-backbonding. A similar effect is observed for several bipie complexes.[15] If less charge is transferred to the ligand, the ligand bonds will be less affected by the m.l.c.t. transition and as a result the intensities of ν_{sym}(CN) and ν_{sym}(CC) will decrease. At the same time, the m.l.c.t. transition will obtain more metal–ligand bonding $(d_\pi + \pi^*) \longrightarrow$ metal–ligand antibonding $(\pi^* - d_\pi)$ character and this will cause the enhancement of r.R. intensity observed for ν_{sym}(M–N).

A remarkable effect is observed for the bands at about 1 215, 860, 770, and 178 cm^{-1} of the *p*-MeC_6H_4N=CHCH=NC_6H_4Me-*p* complexes and for the bands at about 1 210, 1 150, 815, 525, and 325 cm^{-1} of the bmie complexes. These bands, which are not present in the r.R. spectra of the corresponding alkyl di-imine complexes, arise from conjugation of the aryl rings with the N=CHCH=N group and from vibrations of the aryl rings. Contrary to the behaviour of ν_{sym}(CN) and ν_{sym}(CC) these bands show a strong enhancement of intensity going from the Re to the W complexes. Apparently, the increase of π-backbonding towards the di-imine ligand has a strong influence on the aryl groups of the ligands. The assignment of these bands, given in Table 3, is mainly based on the results of Brandmüller [23,24] and of Harrand.[25] The band at *ca.* 1 210 cm^{-1} in the spectra of these complexes is assigned to an ω_x mode (see ref. 24 for notation). This band is also present in the Raman spectra of methyl- and *p*-dimethyl-substituted benzenes. For the bmie complexes the extra band at *ca.* 1 150 cm^{-1} is assigned to an $\omega_{x'}$ mode (x′ denotes the 2,6-methyl groups). The substituted benzenes possess two types of modes in the 700—900 cm^{-1} region, namely ω_x and γ_{CH} vibrations. For the bptie complexes two bands are observed at about 860 and 770 cm^{-1}. The bmie complexes, however, only show one band at about 820 cm^{-1}. Apparently, the mode belonging to the bands at 860 and 820 cm^{-1} is rather independent of substituents at the *ortho* positions of the ring and these bands are therefore assigned to an ω_x mode (ω_5 for *p*-xylene). The band at *ca.* 770 cm^{-1} in the spectra of the bptie complexes will belong to a γ_{CH} mode (ω_{14} for *p*-xylene). This mode, which is only observed in the i.r. spectra of various *p*-substituted benzenes,[26] shifts by 200 cm^{-1} going from benzene to *p*-xylene. It is expected to undergo a similar shift going from *p*-xylene to 1,2,4,6-tetramethylbenzene. Thus, we ascribe the band at 530 cm^{-1} of the bmie complexes also to this γ_{CH} mode. Brandmüller *et al.* calculated a value of 183.5 cm^{-1} for the lowest frequency mode of *p*-xylene, which is γ_x, an i.r.-active mode. Accordingly, we assign the band at

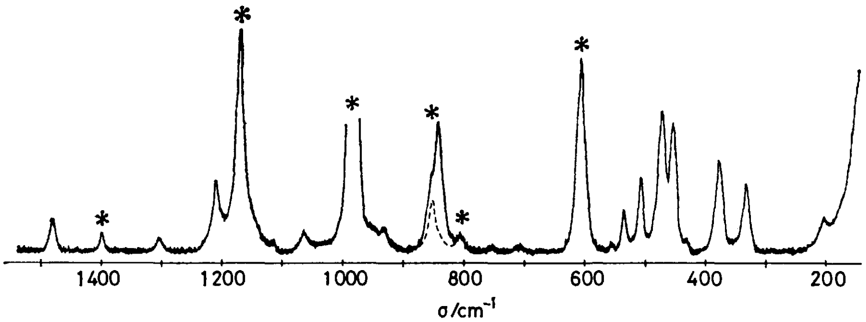

FIGURE 7 Part of the r.R. spectrum of [Ru(CO)$_3$(bmie)] in C_6H_6, excited at 514.5 nm. The bands, indicated with an asterisk, are solvent bands and in a few cases indicated by a dotted curve. The band at 400 cm^{-1} of benzene has been omitted. The optical density at this wavelength is about 9.0 (in a 1-cm cell)

178 cm^{-1} of the bptie complexes to such a γ_x vibration (ω_{16} for *p*-xylene). Because of the correspondence between the r.R. spectra of the di-imine complexes, we assign the 325 cm^{-1} band of the bmie complexes to this γ_x vibration, which is expected to be very sensitive to substitution in the aryl ring. The high r.R. intensities of these γ_{CH} and γ_x out-of-plane bending modes and of other vibrations of the aryl rings show that these rings become severely distorted in the m.l.c.t. excited state. This, however, only occurs for those complexes which have a very strong metal-to-di-imine π-backbonding. The m.l.c.t. excited state is then strongly antibonding between the metal and the di-imine ligand (see above). Apparently, this antibonding character causes a shift of negative charge to the aryl rings, away from the co-ordinating nitrogen atoms. As a result of this extra charge the aryl rings become distorted, losing their planar conformation.

Raman spectra of some of these complexes have also been measured by excitation close to the lowest i.l. transition of the complexed di-imine ligand, which is observed at *ca.* 375 nm (see Figure 2). Upon approaching the i.l. band with the exciting laser line a regular decrease of r.R. intensity is observed for the bands at 1 214, 862, and 769 cm^{-1} in the case of the complex [W(CO)$_4$(bptie)] (see Figure 6) and also for the bands below 600 cm^{-1}. On the other hand, the bands at 1 445 cm^{-1} [ν_{sym}(CN)], 1 334 and 1 076 cm^{-1} [ν_{sym}(CC)] become enhanced in intensity going from 488.0 to 457.9 nm excitation. This means that although the bonds of the bptie ligand and especially those of the N=CHCH=N group are affected by the i.l. transition, the aryl rings are not distorted during this transition as they are by the m.l.c.t. transition.

(3) *Resonance-Raman spectrum of* [Ru(CO)$_3$(bmie)].—The r.R. spectrum of this complex, excited close to the lowest energy absorption band (Figure 2), is shown in Figure 7. A weak r.R. effect is observed for ν_{sym}(CN) at 1 482 cm^{-1}, whereas the bands below 600 cm^{-1}, mainly belonging to metal–ligand vibrations, are much more enhanced in intensity. This kind of r.R. effect agrees with our observation that the c.t. band only shows a very small negative solvatochromism and therefore belongs to a transition which is mainly bonding ⟶ antibonding in character. In this respect this complex resembles the corresponding tungsten compound. There are, however, two major differences between the r.R. spectra of these two complexes. First of all, ν_{sym}(CN) has a frequency of 1 482 cm^{-1} in the case of [Ru(CO)$_3$(bmie)] and of 1 440 cm^{-1} for [W(CO)$_4$(bmie)]. This means that the π-backbonding to the di-imine ligand is weaker for the ruthenium complex. [Fe(CO)$_3$(bptie)] also shows a relatively high frequency of 1 492 cm^{-1} for ν_{sym}(CN).[27] A second feature is the much lower intensity of the aryl vibrations of the ruthenium complex at 1 212, 842, and 472 cm^{-1} with respect to the corresponding bands at 1 209, 822, and 529 cm^{-1} of the tungsten complex. Apparently, the aryl rings are much less distorted in the m.l.c.t. excited state of the ruthenium complex than of the tungsten one as a result of the weaker π-backbonding. Figure 8 shows the wavelength dependence of the low-frequency region. All bands, with the exception of that at 472 cm^{-1}, show the same r.R. effect. They are therefore assigned to the same kind of vibrations. The band at 200 cm^{-1} is assigned to ν_{sym}(Ru–N), the bands at 334 and 377 cm^{-1} to symmetrical metal–carbon stretching modes, and the bands at 453, 508, and 536 cm^{-1} to δ(M–C–O) vibrations. The band at 472 cm^{-1}, showing a much stronger r.R. effect, is assigned to a ligand mode. The corresponding band at about 525 cm^{-1} in the r.R. spectra of the d^6 complexes also shows a stronger r.R. effect than the metal–ligand vibrations.

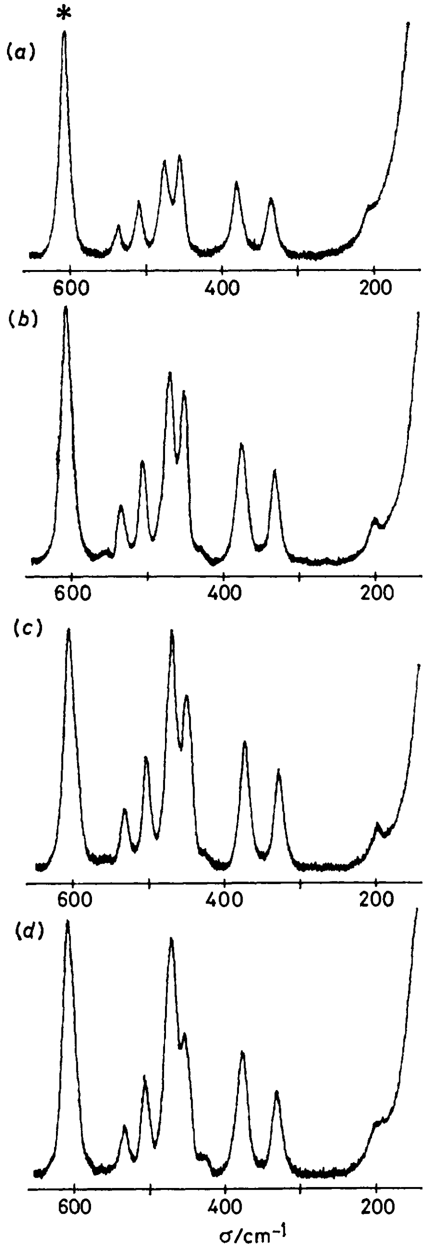

FIGURE 8 Parts of the r.R. spectra of [Ru(CO)$_3$(bmie)] in C$_6$H$_6$, excited at different wavelengths: (*a*) λ = 540.0, (*b*) 514.5, (*c*) 488.0, (*d*) 457.9 nm. The solvent band at 606 cm^{-1} is indicated with an asterisk, while that at 400 cm^{-1} has been omitted

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REFERENCES

[1] R. W. Balk, D. J. Stufkens, and A. Oskam, *J. Chem. Soc., Dalton Trans.*, 1981, 1124.

[2] O. S. Mills and G. Robinson, *Acta Crystallogr.*, 1963, **16**, 758.

[3] F. A. Cotton, M. D. La Prade, B. F. G. Johnson, and J. Lewis, *J. Am. Chem. Soc.*, 1971, **93**, 4626.

[4] S. Otsuka, T. Yoshida, and A. Nakamura, *Inorg. Chem.*, 1967, **6**, 20.

[5] H. tom Dieck and A. Orlopp, *Angew. Chem.*, 1975, **87**, 246.

[6] L. H. Staal, L. H. Polm, K. Vrieze, F. Ploeger, and C. H. Stam, *Inorg. Chem.*, in the press.

[7] D. Leibfritz and H. tom Dieck, *J. Organomet. Chem.*, 1976, **105**, 255.

[8] L. H. Staal, L. H. Polm, and K. Vrieze, *Inorg. Chim. Acta*, 1980, **40**, 165.

[9] H. Bock and H. tom Dieck, *Chem. Ber.*, 1967, **100**, 228.

[10] L. H. Staal, A. Oskam, and K. Vrieze, *J. Organomet. Chem.*, 1979, **170**, 235.

[11] R. W. Balk, D. J. Stufkens, and A. Oskam, *Inorg. Chim. Acta*, 1978, **28**, 133.

[12] G. Boxhoorn, M. B. Cerfontain, D. J. Stufkens, and A. Oskam, *J. Chem. Soc., Dalton Trans.*, 1980, 1336.

[13] D. M. Adams, 'Metal–Ligand and Related Vibrations,' Edward Arnold, London, 1967.

[14] J. R. Moss and W. A. G. Graham, *J. Chem. Soc., Dalton Trans.*, 1977, 95.

[15] R. W. Balk, D. J. Stufkens, and A. Oskam, *Inorg. Chim. Acta*, 1981, **48**, 105.

[16] M. Dartiguenave, Y. Dartiguenave, and H. B. Gray, *Bull. Soc. Chim. Fr.*, 1969, 4223.

[17] H. Daamen and A. Oskam, *Inorg. Chim. Acta*, 1978, **26**, 81.

[18] E. D. Schmid, P. Schlenker, and R. R. M. Brand, *J. Raman Spectrosc.*, 1977, **6**, 314.

[19] R. J. H. Clark and B. Stewart, *Struct. Bonding (Berlin)*, 1979, **36**, 1.

[20] J. M. Friedman, D. L. Rousseau, and V. E. Bondybey, *Phys. Rev. Lett.*, 1976, **37**, 1610.

[21] L. H. Staal, D. J. Stufkens, and A. Oskam, *Inorg. Chim. Acta*, 1978, **26**, 255.

[22] E. Castelucci, L. Angeloni, N. Neto, and G. Sbrana, *Chem. Phys.*, 1979, **43**, 365.

[23] E. W. Schmid, J. Brandmüller, and G. Nonnenmacher, *Z. Elektrochem.*, 1960, **64**, 726.

[24] E. W. Schmid, J. Brandmüller, and G. Nonnenmacher, *Z. Elektrochem.*, 1960, **64**, 940.

[25] M. Harrand, *J. Raman Spectrosc.*, 1975, **4**, 53.

[26] 'Catalogue of Raman and infrared spectral data,' Sadtler Research Laboratories Inc., Philadelphia, 1976.

[27] M. W. Kokkes, unpublished work.

[28] R. W. Balk, Th. Snoeck, D. J. Stufkens, and A. Oskam, *Inorg. Chem.*, 1980, **19**, 3015.