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(Diimine)carbonyl Complexes of Chromium, Molybdenum, and Tungsten: Relationship between Resonance Raman Spectra and Photosubstitution Quantum Yields upon Excitation within the Lowest Metal to Diimine Charge-Transfer Band

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An explanation is given for the enhancement of Raman intensity of the (symmetrical) stretching mode of the carbonyl(s) cis with respect to L when complexes of the type $M(CO)_{4-x}L[P(OMe)_3]_x$ (M = Cr, Mo, W; $x = 0, 1$; L = 1,4-diazabutadiene, pyridine-2-carbaldehyde imine, 2,2′-bipyridine, 1,10-phenanthroline) are excited within the lowest MLCT band. The influence of the central metal atom, of the ligand L, and of the co-ligand is discussed in detail. Irradiation within the lowest MLCT band also causes photosubstitution of a cis carbonyl ligand with quantum yields varying from 10^{-5} to 10^{-2}. A relationship appears to exist between these photosubstitution quantum yields and the resonance enhancement of the carbonyl stretching mode.

Introduction

In recent articles[1–5] we reported the spectroscopic properties of a series of $M(CO)_4L$ complexes (M = Cr, Mo, W; L = dimine). Special attention was paid to the resonance Raman (RR) and magnetic circular dichroism (MCD) spectra of these compounds. Both the RR excitation profiles and MCD spectra showed the presence of at least three different electronic transitions within the first MLCT band, which could be assigned with the RR effect.

A remarkable RR effect observed during excitation within the MLCT band was the resonance enhancement of $\nu_s(\mathrm{CO^{cis}})$ $(A_1{}^2)$, the symmetrical stretching mode of the carbonyls cis with respect to the ligand L. This effect was explained by an interaction between virtual molecular orbitals having predominantly ligand $L\pi^*$ and $CO\pi^*$ character, respectively. In this article we shall discuss the origin of this RR effect of $\nu_s(\mathrm{CO^{cis}})$ $(A_1{}^2)$ in more detail and also report its dependence on the central metal M and on L. Also several complexes $M(CO)_3L[P(OMe)_3]$ are included.

The second part of this article is concerned with the photosubstitution reactivity of the $M(CO)_4L$ complexes, showing release of CO, upon irradiation within the MLCT band. The relationship which appears to exist between the photochemical quantum yield and the resonance enhancement of $\nu_s(\mathrm{CO^{cis}})$ $(A_1{}^2)$ will be discussed.[6]

The structure of one of the complexes is shown in Figure 1 while the different diimine ligands are presented in Figure 2. The following abbreviations will be used throughout the text for these ligands: bpy = 2,2′-bipyridine; phen = 1,10-phenanthroline; DAB-*p*-tol = 1,4-diazabutadiene (R_1 = *p*-tolyl, R_2 = H); DAB-*i*-Pr = 1,4-diazabutadiene (R_1 = isopropyl, R_2 = H); pyCa-*i*-Pr = pyridine-2-carbaldehyde imine (R_1 = isopropyl, R_2 = H); pyCaPh = pyridine-2-carbaldehyde imine (R_1 = phenyl, R_2 = H).

Experimental Section

All compounds were prepared by methods described earlier.[2,7,8] The electronic absorption spectra were recorded on a Cary 14 spectrophotometer.

RR spectra were measured on a Jobin-Yvon HG2S Ramanor, by using an SP Model 171 argon-ion laser and Models CR 490 and CR 590 tunable dye lasers with Rhodamine 6G, sodium fluorescein, and stilbene-3 in ethylene glycol as dyes and cyclooctatetraene as a photosensitizer. The spectra were recorded with a spinning cell from (2–6) × 10^{-4} M solutions in chloroform or benzene. Some chromium complexes were so unstable in the laser beam that their Raman spectra had to be taken very rapidly in a specially constructed spinning cell which could be cooled to −50 °C. Raman intensities were measured with a Hewlett-Packard Model 10 calculator with a 9864 A digitizer and corrected for the sensitivity of the spectrophotometer, absorption of the scattered light, and decomposition in the laser beam.

Photosubstitution quantum yields were measured at the maximum of the MLCT band by irradiating 4-mL stirred benzene solutions (~10^{-4} M) which were carefully degassed, in 40 × 10 × 10 mm quartz cells with a 50–100-mW laser beam. The photon flux was calculated from the laser power, which was measured by a Coherent Model 201 powermeter. Before calculation of the quantum yields, corrections were applied for reflections of the light within the cell, for transmission of the laser beam, and for absorption of the photoproduct. The equipment was tested with ferrioxalate actinometry.[9] The reactions, which only proceeded upon exposure to the light, were followed with a Cary 14 UV/Vis spectrophotometer.

The same photosubstitution quantum yields were obtained by following the product formation as by studying the disappearance of the starting complex. The tri- and dicarbonyl complexes formed were identified spectroscopically.

Results

Resonance Raman Spectra. The MLCT band for which the RR effect has been studied is the lowest energy band in the absorption spectra of the various complexes, its position varying from 500 to 650 nm in apolar solvents (see Figure 9). No reliable RR spectra could be obtained for $Cr(CO)_4(bpy)$ and $Cr(CO)_4(phen)$ because these complexes were photochemically too unstable in solution even at −50 °C. The case was similar for $W(CO)_3$(DAB-*i*-Pr)$[P(OMe)_3]$ which gave highly fluorescing decomposition products. The spectra of $Cr(CO)_4(pyCa)$ and $Cr(CO)_4$(DAB-*i*-Pr) could only be measured at −50 °C in the specially constructed spinning cell.

The complexes studied showed resonance enhancement of Raman intensity for all symmetrical metal–ligand stretching modes, $\nu_s(M{-}C)$ $(A_1{}^1)$, $\nu_s(M{-}C)$ $(A_1{}^2)$, and $\nu_s(M{-}N)$, respectively. The metal–carbon stretching modes have been assigned according to ref 10 and 11; the assignment of $\nu_s(M{-}N)$ has been discussed before.[1,2,4] Furthermore, several ligand vibrations and $\nu_s(\mathrm{CO^{cis}})$ $(A_1{}^2)$, the symmetrical stretching mode of the carbonyls cis with respect to L which has been assigned by Jernigan et al.,[12] were enhanced for all complexes with the

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

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

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[6] Some preliminary results have been published: R. W. Balk, D. J. Stufkens, and A. Oskam, *J. Chem. Soc., Chem. Commun.*, 604 (1979).

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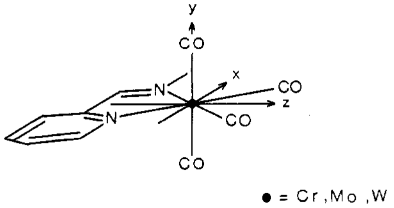

Figure 1. Structure of $M(CO)_4(pyCa)$.

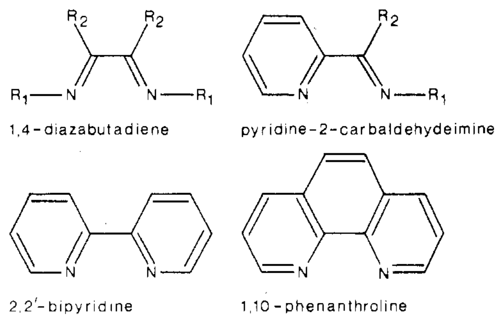

Figure 2. Different diimine ligands used: R_1 = isopropyl (*i*-Pr), *p*-tolyl (*p*-tol), or phenyl (Ph); R_2 = H.

exception of $W(CO)_4$(DAB-*p*-tol). For this latter compound $\nu_s(\mathrm{CO^{cis}})$ could not be observed. The enhanced ligand modes are ν_s(CN) of DAB,[1,4] ν(CN), ν(pyII), and ν(pyIII) of pyCa,[2,13-15] ν(pyI), ν(pyII), and ν(pyIII) of bpy,[15,16] and probably the same vibrations of phen. Although no progressions are observed in the RR spectra, we are most likely dealing with A-term or Franck–Condon emission,[17,18] because excitation takes place within strongly allowed electronic transitions. Furthermore, no resonance enhancement is observed for any asymmetric mode as would be expected in the case of vibronic interaction between the closely spaced electronic transitions, which have different symmetries (see ref 4). Normally, A-term Raman emission consists of a progression of one or more symmetric modes. From the fact that for these complexes resonance enhancement of a series of vibrations is observed instead of such progressions, it may be concluded that many bonds are slightly affected by the MLCT transitions.

The observation of resonance enhancement for the symmetrical metal–ligand stretching modes and for the diimine vibrations agrees with the MLCT character of this absorption band. The resonance enhancement of $\nu_s(\mathrm{CO^{cis}})$ ($A_1{}^2$), which is observed for nearly all complexes, is however quite remarkable. We have observed this effect before[1-4,8,19] and then proposed that the enhancement of $\nu_s(\mathrm{CO^{cis}})$ is caused by delocalization of the MLCT excited state over the cis carbonyl ligands.

However, since other effects such as oxidation of the central metal atom and decrease of π back-bonding can in principle also cause a resonance enhancement of $\nu_s(\mathrm{CO^{cis}})$, we found it necessary to get more information about the factors which influence the intensity of this mode.

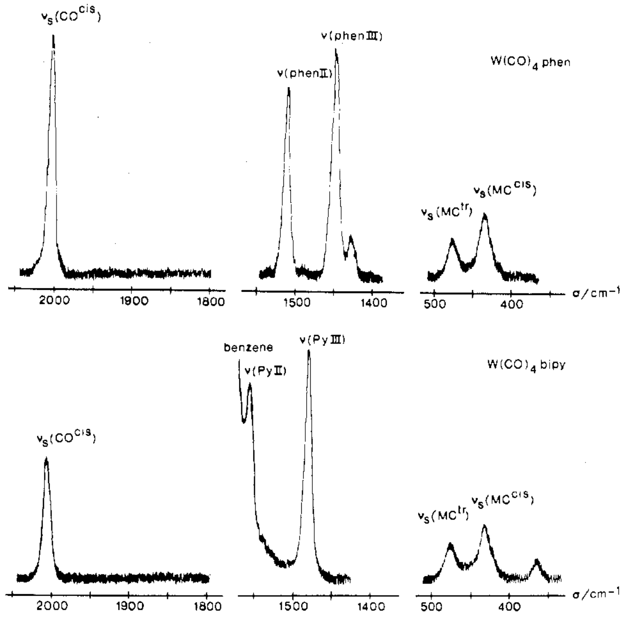

Figure 3. Metal–carbon, diimine ligand, and CO stretching modes of $W(CO)_4$(phen) and $W(CO)_4$(bpy) in C_6H_6.

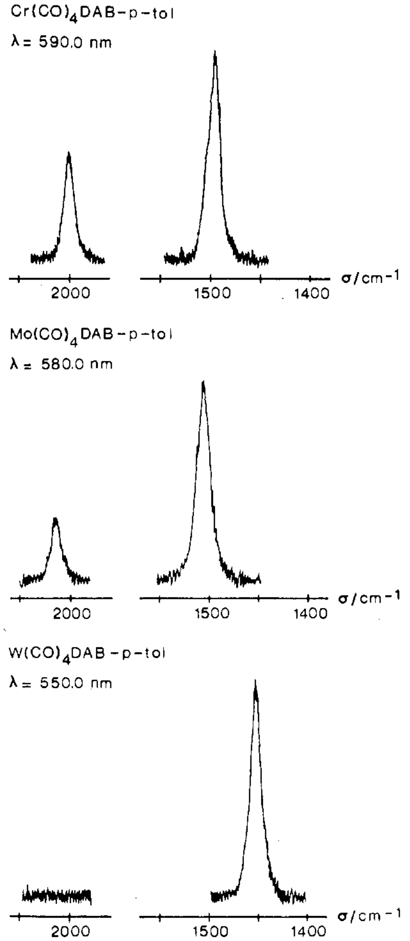

Figure 4. Resonance Raman bands of ν_s(CN) and $\nu_s(\mathrm{CO^{cis}})$ for $M(CO)_4$(DAB-*p*-tol) complexes (M = Cr, Mo, W) in $CHCl_3$.

Figure 3 shows the metal–carbon and CO stretching region of the RR spectra of $W(CO)_4$(phen) and $W(CO)_4$(bpy), excited close to the maximum of the MLCT band. These spectra, which have been corrected for absorption of the scattered light and for the sensitivity of the spectrophotometer, show that both symmetrical metal–carbon stretching modes

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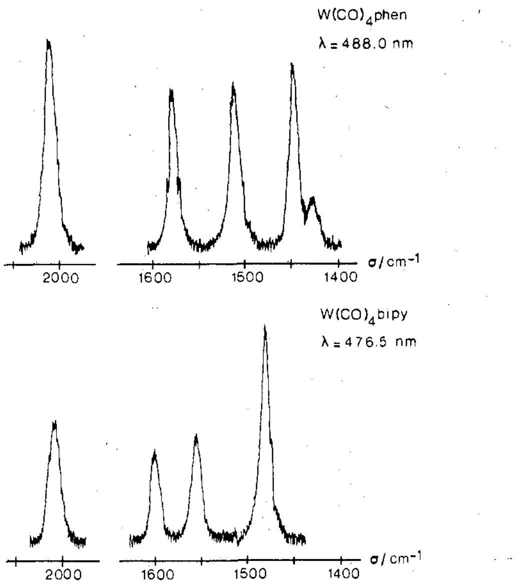

Figure 5. Part of the RR spectra of W(CO)$_4$L (L = phen, bpy) in CHCl$_3$.

are nearly equally enhanced in intensity although the RR effect is small. On the other hand, only ν_s(CO^{cis}) (A$_1$^{2}) shows a pronounced RR effect whereas ν_s(CO^{trans}) (A$_1$^{1}) cannot even be observed in the spectra. This appears to be a general property of these complexes because ν_s(CO^{trans}) has not been observed in the RR spectrum of any of these complexes, irrespective of the position of the exciting wavelength within the CT band. Furthermore, the intensity of ν_s(CO^{cis}) hardly changes with respect to the diimine vibrations if the exciting wavelength is shifted through the absorption band (see also Figure 5 in ref 4).

Figure 3 also shows that the intensity of ν_s(CO^{cis}) does not change in the same way as those of the symmetrical metal–carbon stretching modes.

Figure 4 shows that the size of the central metal atom in the complexes M(CO)$_4$(DAB-*p*-tol) (M = Cr, Mo) influences the relative intensity of ν_s(CO^{cis}) with respect to ν_s(CN) if the exciting line is close to the maximum of the MLCT band. When Cr is replaced by the larger Mo atom, a decrease of intensity is observed for ν_s(CO^{cis}) with respect to ν_s(CN). The same effect is observed for a series of pyCa complexes, where ν_s(CO^{cis}) also decreases in intensity with respect to the ligand modes when Cr is replaced by Mo (see Figure 8). A further decrease of relative intensity is observed for ν_s(CO^{cis}) in going from Mo to W. This effect can hardly be due to a difference in size since Mo and W do not differ much from each other. The disappearance of ν_s(CO^{cis}) will be primarily caused by a decrease of solvatochromism of the MLCT band in going from the Mo to the W complex (vide infra).

There appears to be also a dependence of the resonance enhancement of ν_s(CO^{cis}) on the electron distribution in the lowest excited state of the diimine ligand, which is demonstrated for W(CO)$_4$(phen) and W(CO)$_4$(bpy) (Figure 5). Both complexes have the same central metal atom, and their MLCT bands have nearly the same solvatochromism. However, the lowest π* orbital of bpy has less electron density at the N atoms,[20] which is reflected in a lower extinction coefficient of the MLCT band for all bpy complexes. Figure 5 shows that this difference between the two ligands also causes a decrease of relative intensity for ν_s(CO^{cis}) with respect to the ligand modes.

A third factor which influences the resonance enhancement of ν_s(CO^{cis}) is the mixing between metal and diimine orbitals.

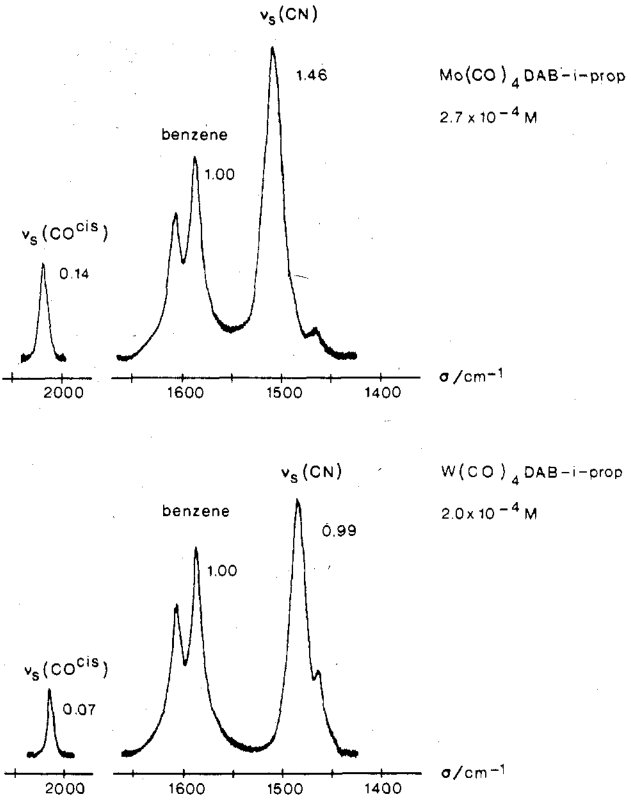

Figure 6. Part of the RR spectra of M(CO)$_4$(DAB-*i*-Pr) (M = Mo, W) in C$_6$H$_6$.

When this mixing is small, the MLCT transitions have predominant CT character and the solvatochromism Δ of the corresponding MLCT band is large. In that case the excited state will mainly be located at the diimine ligand. If the bonding interaction between metal and diimine increases, the excited state becomes less localized at the diimine ligand and the CT character and solvatochromism of the MLCT band decrease. Figure 6 shows the influence of this effect on the RR spectra. The MLCT transitions of Mo(CO)$_4$(DAB-*i*-Pr) have more CT character than those of W(CO)$_4$(DAB-*i*-Pr) because the solvatochromism Δ of the MLCT band is nearly twice as large for the former complex (Table I).

As a consequence the intensities of both ν_s(CO^{cis}) and ν_s(CN) decrease with respect to the 1600-cm^{-1} band of benzene when Mo is replaced by W. These spectra were excited close to the maximum of the MLCT band for solutions having the same optical density. The decrease of solvatochromism does, however, not influence the intensities of ν_s(CO^{cis}) and the diimine modes in the same way. The intensity of ν_s(CO^{cis}) decreases more than that of ν_s(CN), and this appears to be a general property of the Mo and W complexes containing the same diimine ligand. All these complexes show a decrease of relative intensity for ν_s(CO^{cis}) when the solvatochromism decreases. This is demonstrated by the spectra in Figures 4 and 8 and also by the data of Table I. The first columns of this table present the properties of the MLCT band (energy, solvatochromism, extinction coefficient). Photosubstitution quantum yields, which will be discussed hereafter, and relative Raman intensities are collected in the other columns. All corrected Raman intensities are related to the strongest ligand vibration. The assignment of the ligand modes of phen is uncertain. The data of this table show that an increase of bonding interaction between metal and diimine (decrease of Δ) causes a decrease of relative intensity of ν_s(CO^{cis}). This of course only holds if the complexes contain the same diimine ligand. Figure 7 shows what happens if two complexes have the same central metal atom but a different diimine ligand.

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(20) R. W. Balk, to be submitted for publication.

Table I. Properties of the MLCT Band, Photosubstitution Quantum Yields, and Relative Raman Intensities for a Series of $M(CO)_4L$ and $M(CO)_3L[P(OMe)_3]$ Complexes

complex	$10^{-3} \times \sigma^{max}$ (c-C_6H_{12}),[a] cm^{-1}	$10^{-3} \times \Delta^{max}$,[b] cm^{-1}	λ^{max} (C_6H_6),[a] nm	ϵ^{max} (C_6H_6)	$10^4 \times \Phi_p^i$ [c]	relative Raman intensities[d]				
						ν_s-(CO^{cis})	ν(CN)	ν-(pyI)[e]	ν-(pyII)[e]	ν-(pyIII)[e]
$Cr(CO)_4$(DAB-*i*-Pr)[f]	17.1	2.0	560.0	8850	100	0.29	1.0			
$Cr(CO)_4$(DAB-*p*-tol)	16.1	0.7	617.0	9250	2.4	0.42	1.0			
$Cr(CO)_4$(pyCa-*i*-Pr)[f]	16.55	3.5	550.0	6050	130	1.0	0.65		1.0	0.53
$Cr(CO)_4$(pyCaPh)[f]	15.6	2.9	600.0	6300	16	0.62	0.35		1.0	0.47
$Cr(CO)_4$(phen)[g]	17.9[h]	3.8	514.5	4950	660					
$Cr(CO)_4$(bpy)[g]	17.5[h]	3.7	514.5	3400	540					
$Cr(CO)_3$(DAB-*i*-Pr)$[P(OMe)_3]$	17.0	1.4	582.5	10000	14	0.26[i]	1.0			
$Cr(CO)_3$(pyCa-*i*-Pr)$[P(OMe)_3]$	15.4	2.2	617.0	7550	5.0	0.51[i]	0.35		1.0	0.51
$Mo(CO)_4$(DAB-*i*-Pr)	17.8	2.2	535.0	11200	1.2	0.10	1.0			
$Mo(CO)_4$(DAB-*p*-tol)	16.5	1.2	600.0	10650	~0	0.13	1.0			
$Mo(CO)_4$(pyCa-*i*-Pr)	17.4	3.9	514.5	7200	1.5	0.59	0.47		1.0	0.58
$Mo(CO)_4$(pyCaPh)	16.4	3.5	564.0	6350	0.2	0.39	0.27		1.0	0.46
$Mo(CO)_4$(phen)	18.6[h]	4.0	488.0	6350	5.3	0.98		0.75	1.0	0.95
$Mo(CO)_4$(bpy)	18.5[h]	4.1	496.5	4500	2.7	0.40		0.29	0.41	1.0
$Mo(CO)_3$(DAB-*i*-Pr)$[P(OMe)_3]$	17.5	0.8	565.0	13100	0.0	0.08[i]	1.0			
$Mo(CO)_3$(pyCa-*i*-Pr)$[P(OMe)_3]$	16.4	2.7	575.0	8100	0.0	0.19[i]	0.23		1.0	0.44
$W(CO)_4$(DAB-*i*-Pr)	18.3	1.5		15600		0.06	1.0			
$W(CO)_4$(DAB-*p*-tol)	17.8	0.0		11950		0.0	1.0			
$W(CO)_4$(pyCa-*i*-Pr)	17.3	3.4		8250		0.30	0.24		1.0	0.49
$W(CO)_4$(pyCaPh)	16.4	2.8		8550		0.17	0.11		1.0	0.35
$W(CO)_4$(phen)	18.2[h]	4.0		8000		0.97		0.73	1.0	1.0
$W(CO)_4$(bpy)	18.0[h]	4.1		6200		0.42		0.34	0.47	1.0
$W(CO)_3$(DAB-*i*-Pr)$[P(OMe)_3]$[g]	18.9	−1.3		12300						
$W(CO)_3$(pyCa-*i*-Pr)$[P(OMe)_3]$	16.4	1.9		11550		0.07[i]	0.16		1.0	0.47

[a] $(\sigma, \lambda)^{max}$ = maximum of MLCT band. [b] $\Delta^{max} = \sigma^{max}(CH_3CN) - \sigma^{max}(c\text{-}C_6H_{12})$. [c] Φ_p^i = initial quantum yield of product formation ±10% (in C_6H_6). [d] Intensities relative to the strongest ligand mode. [e] Assignment uncertain for phen complexes. [f] Raman spectra measured at −50 °C. [g] No Raman data available. [h] Measured in CS_2. [i] $\nu(CO^{cis})$ instead of $\nu_s(CO^{cis})$.

These complexes also have a different solvatochromism for the MLCT band. Just as for the complexes in Figure 6, the decrease of solvatochromism going from the DAB-*i*-Pr to the DAB-*p*-tol compound, is accompanied by a decrease of intensity for both $\nu_s(CO^{cis})$ and ν_s(CN) with respect to the 1600-cm^{-1} band of benzene. At the same time, however, the relative intensity of $\nu_s(CO^{cis})$ increases which is in contrast with the behavior of the previous complexes.

Finally, the complexes containing the asymmetric pyCa ligand show a special behavior. For a series of these complexes the ligand stretching modes ν(pyIII) (~1470 cm^{-1}), ν(pyII) (~1550 cm^{-1}) and ν(CN) (~1600 cm^{-1}) together with $\nu_s(CO^{cis})$ are presented in Figure 8. These spectra were obtained by exciting close to the maximum of the MLCT band. The influence of the size of the metal (Cr, Mo) corresponds with the results of Figure 4. Furthermore, the decrease of solvatochromism going from the Mo to the W complexes and from the $M(CO)_4$(pyCa-*i*-Pr) to the $M(CO)_3$(pyCa-*i*-Pr)$[P(OMe)_3]$ complexes is accompanied by a decrease of relative intensity of $\nu_s(CO^{cis})$ just as for the DAB complexes (Figures 4 and 6). Besides, substitution of an alkyl group in the pyCa ligand by an aryl group has the same influence on the relative intensity of $\nu_s(CO^{cis})$ as it has for the DAB complexes. However, a decrease of relative intensity of $\nu_s(CO^{cis})$ appears to be accompanied by a decrease of intensity of ν(CN) with respect to the pyridine modes. The spectra show that this is a general property of these complexes and that the intensities of ν(CN) and $\nu_s(CO^{cis})$ are interrelated.

Photosubstitution Reactivity. Wrighton and co-workers described the photosubstitution reactivity in solution of a series of $W(CO)_4L_2$ and $W(CO)_4L$ complexes all possessing a lowest CT excited state.[21,22] For these complexes which included $W(CO)_4$(phen) and $W(CO)_4$(bpy), they reported a regular decrease of photosubstitution reactivity when the wavelength of the irradiating Hg source was varied up to 436 nm. It was concluded that the lowest CT excited state of these complexes is unreactive showing no photosubstitution of CO.

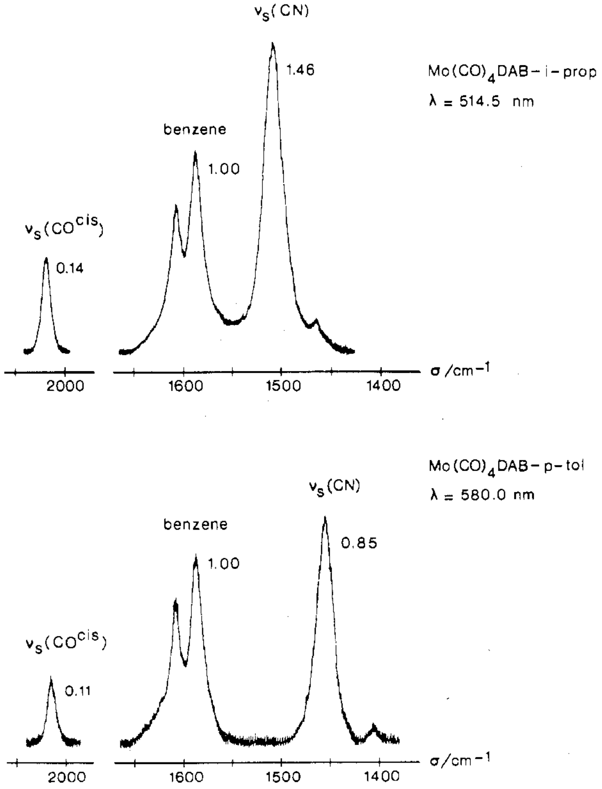

Figure 7. Part of the RR spectra of $Mo(CO)_4L$ (L = DAB-*i*-Pr, DAB-*p*-tol) in C_6H_6.

During our RR measurements on these and similar complexes with exciting lines coinciding with the MLCT band,

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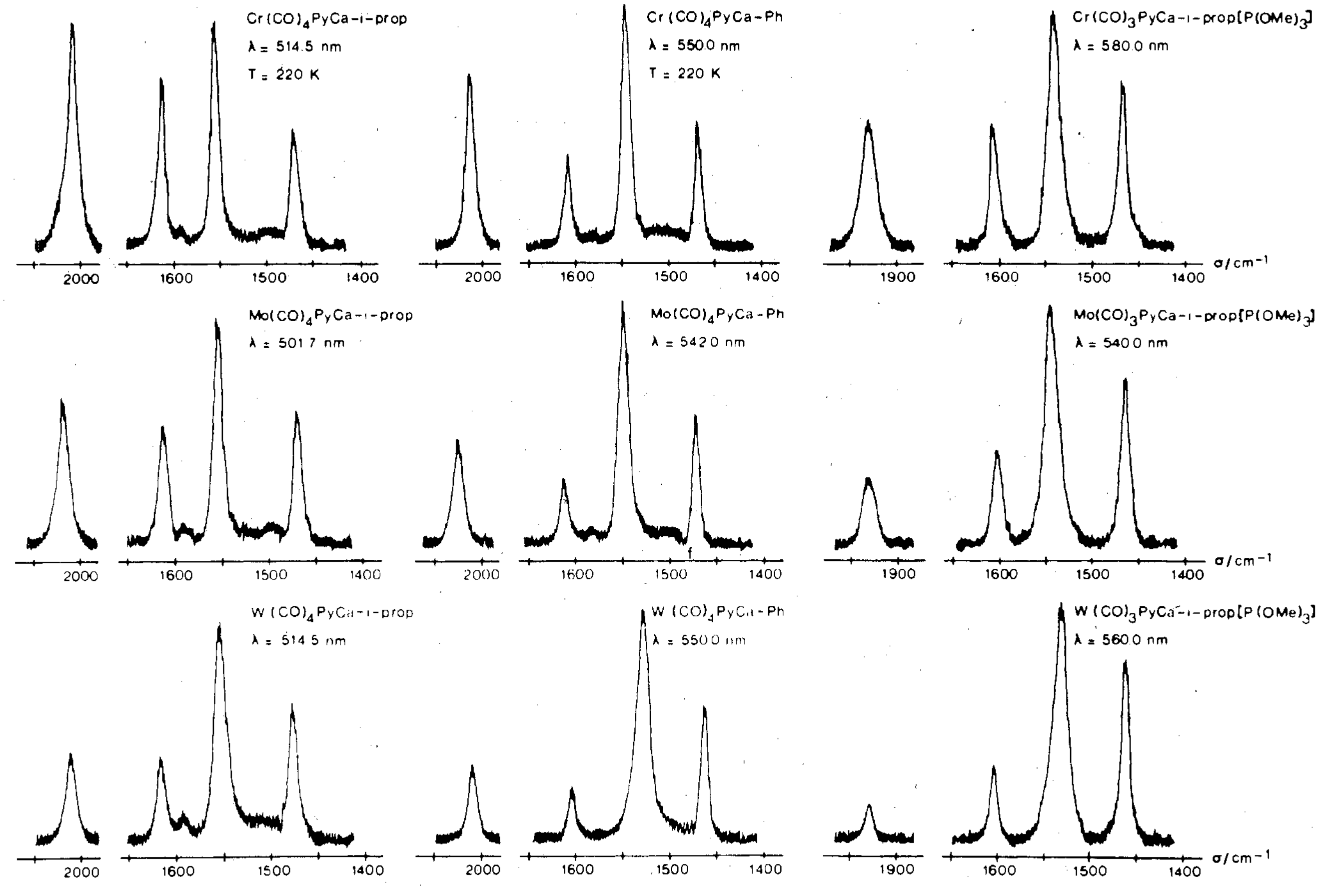

Figure 8. Part of the RR spectra of $M(CO)_{4-x}(pyCaR)[P(OMe)_3]_x$ complexes in $CHCl_3$ (M = Cr, Mo, W; x = 0, 1; R = *i*-Pr, Ph).

we also observed a very low photosubstitution reactivity for the tungsten–diimine complexes. The corresponding Cr and Mo compounds, however, are much more photoreactive. If $P(OMe)_3$ is added to a solution of a diimine complex of these metals, reaction 1 occurs upon irradiation within the MLCT band. Figure 9a shows the change of the absorption spectrum after irradiation of $Cr(CO)_4$(pyCa-*i*-Pr) in the presence of $P(OMe)_3$. The spectrum after 4 min of irradiation corresponds to that of $Cr(CO)_3$(pyCa-*i*-Pr)$[P(OMe)_3]$ which confirms that reaction 1 actually takes place. Also a second carbonyl ligand can be replaced by $P(OMe)_3$, but in that case the photoreactivity is much smaller because complete conversion according to reaction 2 can only be accomplished after irradiating for a long time (Figure 9b). The factors which influence the quantum yields for the photosubstitution reaction will be discussed in the next section.

$$M(CO)_4L + P(OMe)_3 \rightarrow M(CO)_3L[P(OMe)_3] + CO \quad (1)$$

$$M(CO)_3L[P(OMe)_3] + P(OMe)_3 \rightarrow M(CO)_2L[P(OMe)_3]_2 + CO \quad (2)$$

No quantum yields are reported in the table for the tungsten compounds, because on the one hand they are very low, but on the other the type and rate of reaction seems to depend on the substituting ligand for these tungsten complexes. If PPh_3 is added to a solution of $W(CO)_4$(phen), normal photosubstitution according to reaction 1 is observed upon irradiation at different positions within the MLCT band ($\phi_p{}^i = 0.2 \times 10^{-4}$ at 501.7 nm). If however pyridine is used instead of PPh_3, the photosubstitution reaction has a quantum yield which is about 4 times larger and side reactions seem also to occur. The photooxidation is even much faster. In the case of $P(OMe)_3$ normal photosubstitution of CO is only observed upon irradiation with wavelengths up to 488 nm. Irradiation with longer wavelengths does not cause a shift of the MLCT band which is characteristic for the formation of the tricarbonyl compound (isosbestic points at 527 and 382 nm), but instead a decrease and broadening of the MLCT band is observed with isosbestic points at 547 and 372 nm.

If these tungsten compounds are, however, irradiated within the LF band with λ = 436 nm, a normal photosubstitution of CO by the ligands is observed with only small differences between the photosubstitution quantum yields.

For the photochemical reaction of $W(CO)_4$(phen) with pyridine, Wrighton and co-workers calculated a photosubstitution quantum yield $\phi_p{}^i = 0.9 \times 10^{-4}$.[21] Our quantum yield for the same reaction appears to be twice as large. This discrepancy is presumably due to the fact that in our calculations absorption of the photoproduct has been taken into account.

The dependence of the photosubstitution quantum yields on the nucleophilic substituents may be related to the photochemical results of Gray and co-workers for the tungsten hexaisocyanides.[23,24] These authors deduced an associative mechanism for substitution of the isocyanide upon irradiation within the lowest tungsten to isocyanide CT band. In the case of Cr and Mo the mechanism appeared to be mainly dissociative.

This deviating behavior of the tungsten complexes upon irradiation within the MLCT band will be the subject of further investigation.

Discussion

During a metal to diimine CT transition the metal will be oxidized, and as a result all metal–ligand bonds will be af-

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(23) K. R. Mann, H. B. Gray, and G. S. Hammond, *J. Am. Chem. Soc.*, **99**, 306 (1977).

(24) H. B. Gray, K. R. Mann, N. S. Lewis, J. A. Thich, and R. M. Richman, *Adv. Chem. Ser.*, **No. 168**, 44 (1978).

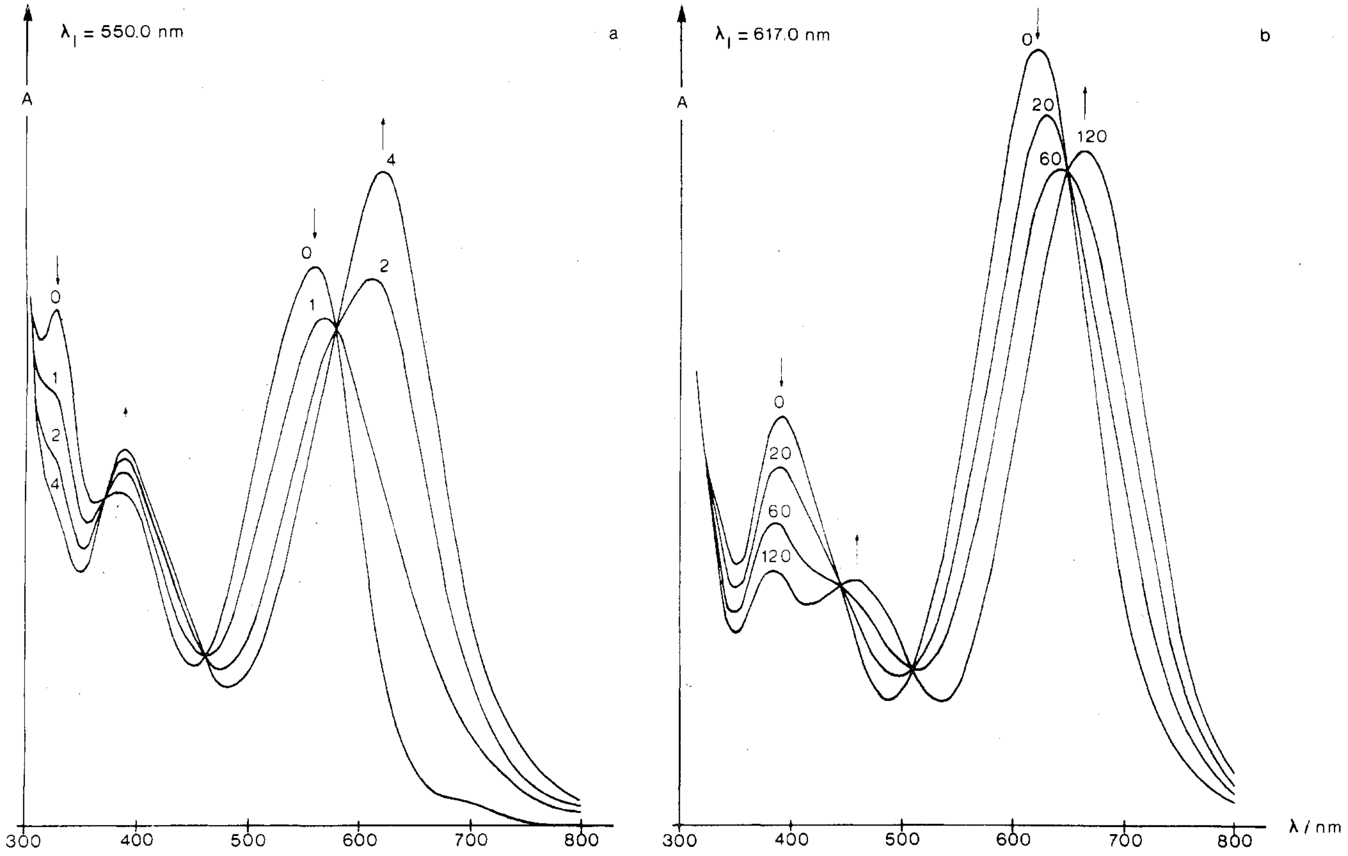

Figure 9. UV–visible spectral changes of benzene solutions of (a) $Cr(CO)_4(pyCa\text{-}i\text{-}Pr)$ and (b) $Cr(CO)_3(pyCa\text{-}i\text{-}Pr)[P(OMe)_3]$ after minutes of irradiation within the maximum of the MLCT band in the presence of $P(OMe)_3$.

fected. This can cause a RR effect for all symmetrical metal–ligand stretching modes. The RR effect of the symmetrical diimine stretching modes will be caused by the change of bond lengths of the ligand as a result of the negative charge transferred to it. On the other hand, such a MLCT transition will also diminish the π back-bonding from the metal to the carbonyls. This effect can be responsible for part of the RR effect of the symmetrical metal–carbon stretching modes, but it can also influence the carbonyl bonds and cause a RR effect for the symmetrical carbonyl stretching modes. However, all spectra show the remarkable feature that only $\nu_s(CO^{cis})$ is resonance enhanced, whereas $\nu_s(CO^{trans})$ cannot even be observed in the spectra. This behavior is observed for all diimine complexes. Oxidation of the metal will equally influence the cis and trans carbonyls and cannot be responsible for this RR effect of $\nu_s(CO^{cis})$. It is also unlikely that the resonance enhancement of $\nu_s(CO^{cis})$ is caused by a change of π back-bonding during the MLCT transition.

First of all, π back-bonding to the cis carbonyls is smaller than to the trans carbonyls as a result of the relatively small π back-bonding to the diimine ligand. Accordingly, the stretching modes of the trans carbonyls have lower frequencies. Furthermore, molecular orbital calculations[20] show that all three metal d orbitals which are involved in the MLCT transitions have π back-bonding to the carbonyls. They have however different π back-bonding capacities with respect to the cis and trans carbonyls and one of the orbitals can only have π back-bonding to the trans carbonyls. In contrast with this, $\nu_s(CO^{trans})$ does not show up in any of the RR spectra even if the exciting line is varied within the absorption band from one MLCT transition to another. At the same time, the relative intensity of $\nu_s(CO^{cis})$ hardly changes. Finally, there appears to be no relationship at all between the degree of π back-bonding between the metal and the cis carbonyls, which is reflected in the frequencies of the stretching modes of these ligands, and the relative intensity of $\nu_s(CO^{cis})$.

All these data and trends make an explanation in terms of π back-bonding unlikely. We prefer to assign the resonance enhancement of $\nu_s(CO^{cis})$ to a delocalization of the MLCT excited state over the cis carbonyls. Such a delocalization can result from a "through-space" overlap between virtual molecular orbitals mainly localized at the diimine ligand and the cis carbonyls, respectively. It can also be caused by a "through-metal" interaction between these orbitals. Although this latter interaction cannot be excluded, the large influence of the size of the central metal atom upon the relative intensity of $\nu_s(CO^{cis})$ points to a "through-space" overlap. As a result of such a delocalization negative charge will also be transferred to the cis carbonyls during the MLCT transition, and this effect can be responsible for the RR effect of $\nu_s(CO^{cis})$. It will be shown now that the observations discussed in the previous section are in agreement with this explanation.

First of all, Figure 3 shows that different mechanisms are responsible for the RR effect of $\nu_s(CO^{cis})$ and of the symmetrical metal–carbon stretching modes, respectively. The intensities of $\nu_s(MC^{cis})$ and $\nu_s(MC^{trans})$ hardly change going from $W(CO)_4(phen)$ to $W(CO)_4(bpy)$ whereas the intensity of $\nu_s(CO^{cis})$ shows a large decrease. Figure 5 shows a similar decrease of intensity for $\nu_s(CO^{cis})$ with respect to the diimine stretching modes of these complexes. Phenanthroline has more electron density at the N atoms in the lowest π* orbital than bipyridine,[20] and it is therefore expected that the π* orbitals of the cis carbonyls will better overlap, "through-space" or "through-metal", with phen than with bpy. This agrees with the higher relative intensity of $\nu_s(CO^{cis})$ observed for the phen complex. The same result is observed for the corresponding Mo complexes (Table I).

The decrease of intensity of $\nu_s(\mathrm{CO^{cis}})$ with respect to ν_s(CN) when Cr is replaced by Mo in the M(CO)$_4$(DAB) complexes (Figure 4) indicates a decrease of delocalization of the MLCT excited state over the cis carbonyls. Such an effect is of course expected when the central metal atom becomes larger.

If the solvatochromism of the MLCT band increases, the corresponding transitions have more CT character. As a result more charge is transferred to the diimine ligand and also to the cis carbonyls if the MLCT excited state is delocalized. This explains the intensity increase of both $\nu_s(\mathrm{CO^{cis}})$ and ν_s(CN) when the solvatochromism becomes larger (Figure 6). However, this figure also shows that the relative intensity of $\nu_s(\mathrm{CO^{cis}})$ increases when the CT character of the transition increases. This means that a decrease of interaction between metal and diimine (increase of Δ) is accompanied by an increase of the interaction between diimine and carbonyl orbitals in the CT excited state. This behavior is observed for all complexes containing the same diimine ligand. The question remains why the intensity of $\nu_s(\mathrm{CO^{cis}})$ is larger with respect to ν_s(CN) for the DAB-*p*-tol than for the DAB-*i*-Pr complexes (Figure 7) although the solvatochromism of the CT band is smaller for the DAB-*p*-tol complex. Molecular orbital calculations of the DAB ligands show[20] that in the lowest excited state the electron density at the CN groups decreases when an isopropyl group is replaced by a *p*-tolyl substituent. This effect will mainly be responsible for the observed decrease of intensity of ν_s(CN) with respect to $\nu_s(\mathrm{CO^{cis}})$ in going to the DAB-*p*-tol complex. The same effect is observed for the pyCa complexes shown in Figure 8, when pyCa-*i*-Pr is replaced by pyCaPh. In the lowest excited state the electron density at the CN group is less for pyCaPh. As a result the RR effect of $\nu_s(\mathrm{CO^{cis}})$ increases with respect to ν(CN) at about 1600 cm^{-1} [4] although the solvatochromism of the pyCaPh complexes is smaller than for the corresponding pyCa-*i*-Pr ones. With respect to the pyridine modes of the pyCa ligand, a normal behavior is observed for $\nu_s(\mathrm{CO^{cis}})$ when the solvatochromism of the complex changes. However, the spectra of Figure 8 even show differences in the relative intensity of ν(CN) with respect to the pyridine modes when the complexes contain the same ligand, e.g., if the central metal atom is replaced or if a carbonyl ligand is substituted by P(OMe)$_3$. The intensity of ν(CN) increases with respect to the pyridine modes when the intensity of $\nu_s(\mathrm{CO^{cis}})$ becomes larger. This relationship between ν(CN) and $\nu_s(\mathrm{CO^{cis}})$ is presumably caused by a better overlap of the carbonyl orbitals with the CN part of the pyCa ligand. MO calculations of these ligands[4,20] show that the electron density in the lowest excited state of pyCa is higher at the N atom of the CN group than at the corresponding atom of the pyridine ring.

It has been mentioned in the previous section that these complexes decompose in the laser beam when they are irradiated within the MLCT band. If P(OMe)$_3$ is added to a solution of a complex, photosubstitution of a cis carbonyl ligand by the phosphite takes place with quantum yields $\phi_p^{\,i}$ which are highest for the Cr complexes (see Table I).

There appears to be a direct relationship between the photochemical reactivity of these complexes and their RR effect. First of all, complexes are only photochemically reactive if $\nu_s(\mathrm{CO^{cis}})$ shows resonance enhancement of Raman intensity. Furthermore, although quantum yields will be determined by many factors, they appear to be qualitatively related to the intensity of $\nu_s(\mathrm{CO^{cis}})$ in the RR spectra (see Table I). Apparently, the same factors which determine the RR effect of $\nu_s(\mathrm{CO^{cis}})$ also influence the quantum yield $\phi_p^{\,i}$. E.g., replacement of Cr by Mo or of phen by bpy causes a decrease of both the quantum yield and the RR intensity of $\nu_s(\mathrm{CO^{cis}})$. The same effect is observed when the solvatochromism of the MLCT band is diminished, e.g., in going from M(CO)$_4$L to M(CO)$_4$L[P(OMe)$_3$].

An exception to this relationship seems to be the change of $\phi_p^{\,i}$ which is observed when DAB-*i*-Pr is replaced by DAB-*p*-tol. The decrease of $\phi_p^{\,i}$ is then accompanied by an increase of the relative intensity of $\nu_s(\mathrm{CO^{cis}})$. We have shown however that, although the intensity of $\nu_s(\mathrm{CO^{cis}})$ increases with respect to ν_s(CN) when an isopropyl group of DAB is replaced by a *p*-tolyl substituent, the intensity of this mode decreases with respect to a solvent band (see Figure 7). Thus, the decrease of $\phi_p^{\,i}$ is yet accompanied by a decrease of the RR effect of $\nu_s(\mathrm{CO^{cis}})$.

From this relationship between photosubstitution reactivity and RR effect of $\nu_s(\mathrm{CO^{cis}})$ we conclude that the MLCT excited state has to be delocalized over the cis carbonyls in order that a cis CO group can be released. The negative charge transferred to the cis carbonyls during the MLCT transition will reduce the π back-bonding from the metal to the cis carbonyls and destabilize the metal cis carbonyl bonds.

Conclusions

A detailed investigation of the factors which influence the RR effect of $\nu_s(\mathrm{CO^{cis}})$ of the complexes under study shows that the change of π back-bonding or the oxidation of the metal during the MLCT transition cannot be responsible for this effect. All results support an explanation in terms of delocalization of the MLCT excited state over the cis carbonyls. This same delocalization of the MLCT excited state is assumed to be responsible for the release of CO upon irradiation within the MLCT band because a qualitative relationship exists between the photosubstitution quantum yields and the RR effect of $\nu_s(\mathrm{CO^{cis}})$.

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Registry No. Cr(CO)$_4$(DAB-*i*-Pr), 74219-90-2; Cr(CO)$_4$(DAB-*p*-tol), 74219-91-3; Cr(CO)$_4$(pyCa-*i*-Pr), 36100-10-4; Cr(CO)$_4$(pyCaPh), 36100-13-7; Cr(CO)$_4$(phen), 14168-63-9; Cr(CO)$_4$(bpy), 15668-63-0; Cr(CO)$_3$(DAB-*i*-Pr)[P(OMe)$_3$], 74219-92-4; Cr(CO)$_3$(pyCa-*i*-Pr)[P(OMe)$_3$], 74219-93-5; Mo(CO)$_4$(DAB-*i*-Pr), 31027-19-7; Mo(CO)$_4$(DAB-*p*-tol), 31021-59-7; Mo(CO)$_4$(pyCa-*i*-Pr), 36100-15-9; Mo(CO)$_4$(pyCaPh), 36100-16-0; Mo(CO)$_4$(phen), 15740-78-0; Mo(CO)$_4$(bpy), 15668-64-1; Mo(CO)$_3$(DAB-*i*-Pr)[P(OMe)$_3$], 74219-95-7; Mo(CO)$_3$(pyCa-*i*-Pr)[P(OMe)$_3$], 74219-96-8; W(CO)$_4$(DAB-*i*-Pr), 57344-61-3; W(CO)$_4$(DAB-*p*-tol), 57304-44-6; W(CO)$_4$(pyCa-*i*-Pr), 36107-20-7; W(CO)$_4$(pyCaPh), 36107-21-8; W(CO)$_4$(phen), 14729-20-5; W(CO)$_4$(bpy), 15668-66-3; W(CO)$_3$(DBA-*i*-Pr)[P(OMe)$_3$], 74219-97-9; W(CO)$_3$(pyCa-*i*-Pr)[P(OMe)$_3$], 74219-98-0.