

## Differences in Photochemical Reactivity of $[M(CO)_4(\alpha\text{-di-imine})]$ ( $M = \text{Cr, Mo, or W}$ ) Complexes Explained by the Resonance Raman Effect

By ROELOF W. BALK, DERK J. STUFKENS,\* and AD OSKAM

(Anorganisch Chemisch Laboratorium, J. H. van 't Hoff Instituut, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands)

**Summary** It is shown that the Resonance Raman effect can elegantly explain differences in photochemical reactivity of  $[M(CO)_4(\alpha\text{-di-imine})]$  compounds when they are irradiated within the metal to  $\alpha\text{-di-imine}$  charge-transfer band.

NEARLY all studies of the photochemistry of  $[M(CO)_4L_2]$  and  $[M(CO)_4(L-L)]$  ( $M = \text{Cr, Mo, or W}$ ) have concerned complexes in which the lowest excited state is ligand-field excited. The only exceptions are  $[W(CO)_4(2\text{-Xpy})_2]$ ,  $[W(CO)_4(1,10\text{-phen})]$ , and  $[W(CO)_4(2,2'\text{-bipy})]$  ( $\text{py} = \text{pyridine}$ ,  $\text{phen} = \text{phenanthroline}$ ,  $\text{bipy} = \text{bipyridine}$ ) for which Wrighton<sup>1</sup> reported that the lowest excited state is charge-transfer in character and unreactive. However, during our investigation of the resonance Raman (RR) spectra of these and other  $[M(CO)_4(\alpha\text{-di-imine})]$  complexes with low-lying metal to  $\alpha\text{-di-imine}$  charge transfer (MLCT) transitions,<sup>2</sup> many of these compounds showed an unexpected release of CO when they were irradiated within the MLCT band. Addition of  $\text{PR}_3$  to the solution before irradiation resulted in the formation of  $[M(CO)_3\text{PR}_3(\alpha\text{-di-imine})]$ . The photochemical reactivity was largest for the Cr-complexes and for those possessing highly solvatochromic MLCT bands.

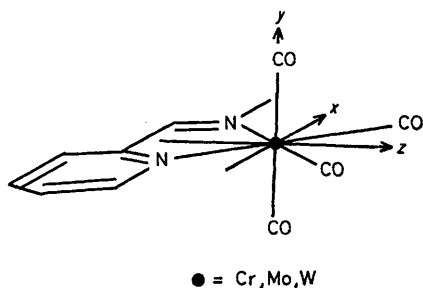


FIGURE 1. Structure of  $[M(CO)_4(\text{imp})]$ .

In order to find out whether the RR spectra could explain the photochemical reactivity of these compounds, we have compared these spectra with the rates of decomposition. For  $[M(CO)_4(\text{imp})]$  ( $M = \text{Cr, Mo, or W}$ ;  $\text{imp} = 2\text{-imino-methylpyridine}$ ) (see Figure 1) the results are presented in Figure 2. The left side of Figure 2 shows part of the RR spectra excited with a laser frequency which coincides with the maximum of the MLCT band. A large enhancement of Raman intensity was found for  $\nu_8(\text{M-N})$  at *ca.*  $240\text{ cm}^{-1}$ , for  $\nu(\text{PyII})$  ( $1549\text{ cm}^{-1}$ ),  $\nu(\text{PyIII})$  ( $1474\text{ cm}^{-1}$ ), and  $\nu(\text{CN})$  ( $1610\text{ cm}^{-1}$ ) of the di-imine ligand, and for the symmetrical stretching mode of the carbonyls which are *cis* with respect to impy [ $\nu_8(\text{CO}_{cis})$ ] at  $2023\text{ cm}^{-1}$ .<sup>3</sup> In contrast,  $\nu_8(\text{CO}_{trans})$  could not even be observed in the RR spectra which means that only the *cis*-carbonyls are strongly affected by the

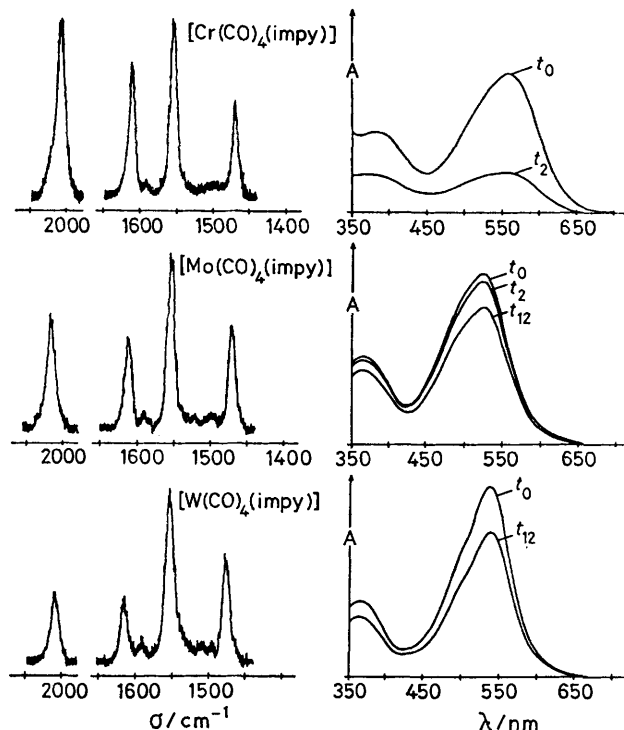


FIGURE 2. (left): High-frequency region of the RR spectra of  $[M(CO)_4(\text{imp})]$  in  $\text{CHCl}_3$ , (right): Comparison of the rates of decomposition by the decrease of absorption bands after 2 ( $t_2$ ) and 12 min ( $t_{12}$ ) of irradiation within the MLCT band.

MLCT transition. Depopulation of metal  $\pi\text{-d}$  orbitals or oxidation of the central metal as a result of the MLCT transition will affect both the *cis*- and *trans*-carbonyls and cannot explain the RR effect of  $\nu_8(\text{CO}_{cis})$ . We ascribe this RR effect to a mixing of  $\pi^*$ -orbitals of impy and the *cis*-carbonyls in the first excited state of these complexes.

In accordance with this explanation the intensity of  $\nu_8(\text{CO}_{cis})$  increases with respect to the di-imine modes when W is replaced by Mo or by the much smaller Cr atom. The smaller metal atom brings the CO and impy ligands closer to each other which causes a better 'through-space' overlap between the  $\pi^*$  orbitals of these ligands. The concomitant increase of intensity of  $\nu(\text{CN})$  with respect to the pyridine modes is most likely due to a better 'through space' overlap of the  $\pi^*$  orbitals of the carbonyls with the CN part of the impy ligand. This increase of overlap between the  $\pi^*$  orbitals of CO and impy appeared to stimulate the release of CO upon irradiation because a large increase of the rate of decomposition was observed (Figure 2). The Cr-complex was so unstable that RR spectra had to be taken very rapidly in a spinning cell cooled to  $-50^\circ\text{C}$ .

Similar results have been obtained for all  $[M(CO)_4L]$  complexes ( $M = Cr, Mo, or W$ ;  $L = 2,2'$ -bipy, 1,10-phen, impy, or dad = diazadiene). Apart from the size of the metal atom, however, the strengths of  $\pi$ -back-bonding between  $M$  and the  $\alpha$ -di-imine also influence the photochemical reactivity. An increase of  $\pi$ -interaction, demonstrated by a decrease of solvatochromism of the MLCT band, caused a decrease of reactivity while at the same time the Raman intensity of  $\nu_8(CO_{cis})$  decreased. Appar-

ently, strengthening of the metal-di-imine interaction in the ground- and excited-state diminishes the excited state interaction with the  $\pi^*$  orbitals of the CO ligands.

The existence of such a relation between photochemical reactivity and the RR effect represents a new and valuable application of this effect which will certainly not be restricted to the compounds reported here.

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<sup>1</sup> M. S. Wrighton and D. L. Morse, *J. Organometallic Chem.*, 1975, **97**, 405; H. B. Abrahamson and M. S. Wrighton, *Inorg. Chem.*, 1978, **17**, 3385.

<sup>2</sup> R. W. Balk, D. J. Stufkens, and A. Oskam, *Inorg. Chim. Acta*, 1978, **28**, 133; *ibid.*, 1979, **34**, 267; *J.C.S. Chem. Comm.*, 1978, 1016.

<sup>3</sup> R. J. Jernigan, R. A. Brown, and G. R. Dobson, *J. Co-ordination Chem.*, 1972, **2**, 47.