Metal-to-ligand Charge-transfer Excited-state Photochemistry of $[Cr(CO)_5(C_4H_4N_2)]$ and $[Cr(CO)_4(NC_5H_4CH{=}NPr^i)]$.† The Difference between the Photochemical Behaviour of $[Cr(CO)_5(C_4H_4N_2)]$ in Solution at 243 K and in an Argon Matrix at 10 K

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Irradiation of $[Cr(CO)_4(NC_5H_4CH{=}NPr^i)]$ in solution within the lowest Cr-to-di-imine charge-transfer band causes photosubstitution of a *cis* carbonyl ligand. Free CO and *fac*-$[Cr(CO)_3(NC_5H_4CH{=}NPr^i)]$ are formed when the complex is irradiated within this absorption band in matrices at 10 K. On the other hand, irradiation of a solution of $[Cr(CO)_5(C_4H_4N_2)]$ within the Cr-to-pyridazine charge-transfer band mainly causes photosubstitution of pyridazine, whereas free CO and *cis*-$[Cr(CO)_4(C_4H_4N_2)]$ are formed upon irradiation of this complex in a matrix. These results are discussed in relation to the lifetimes of the metal-to-ligand charge-transfer excited states and to the resonance-Raman spectra of these complexes.

WRIGHTON *et al.*[1] have investigated the photosubstitution reactivity of a series of $[W(CO)_5L]$ complexes (L = substituted pyridine). In all cases they observed photosubstitution of L upon irradiation into the lowest-energy absorption band. The quantum yield of this photosubstitution reaction, however, appeared to be much lower when the lowest-energy excited state was metal-to-ligand charge-transfer (m.l.c.t.) (*ca.* 0.01) instead of ligand-field (*ca.* 0.60) in character. The same behaviour was observed for the photosubstitution of L in *cis*-$[W(CO)_4L_2]$ (L = substituted pyridine)[2] and of CO in $[W(CO)_4L']$ (L′ = di-imine) complexes.[3] For all these complexes the lowest m.l.c.t. state appeared to be virtually unreactive.

Quite recently however, we observed an increase in the m.l.c.t. photoreactivity of the $[M(CO)_4L']$ complexes (M = Cr, Mo, or W; L′ = di-imine) when W was replaced by Cr.[4] For example for $[Cr(CO)_4(phen)]$ (phen = 1,10-phenanthroline) a quantum yield of 6.6×10^{-2} was found for photosubstitution of CO, whereas Wrighton and Morse[3] measured 0.9×10^{-4} for the corresponding tungsten complex.

At the same time, we observed a resonance-Raman (r.R.) effect for the symmetrical stretching mode of the carbonyl ligands *cis* with respect to the di-imine $[\nu_s(CO^{cis})]$ [see Figure 1(*a*)], which also increased going from W to Cr in the $[M(CO)_4L']$ complexes.[4] This r.R. effect of $\nu_s(CO^{cis})$ was ascribed to a mixing of the m.l.c.t. excited state with a virtual molecular orbital localized at the *cis* carbonyl ligands. As a result of such a mixing charge will be transferred, not only to the di-imine ligand, but also to the *cis* carbonyls during the m.l.c.t. transition. Besides, a qualitative relationship was found between the relative r.R. intensity of $\nu_s(CO^{cis})$ and the quantum yield of photosubstitution of CO. Such a relationship is not unexpected since the charge transfer will cause a distortion of the *cis* carbonyl bonds and facilitate the photosubstitution of a *cis* carbonyl ligand in the m.l.c.t. excited state. This photosubstitution reaction could in principle also take place from a vibrational excited ground state after fast non-radiative decay from the m.l.c.t. state. This is however less probable in view of the fact that thermal substitution of a *cis* carbonyl ligand of $[Cr(CO)_4L']$ can only be performed at higher temperatures.

The corresponding $[Cr(CO)_5L]$ (L = imine) complexes, however, possess a rather weak Cr–L bond which can easily be broken at room temperature. For these complexes the reaction from a thermally activated ground state (release of L) is expected to compete with the reaction from the m.l.c.t. excited state.

The relative importance of these different types of photochemical reactions will depend on the actual lifetimes of the m.l.c.t. states, which are sensitive to changes in temperature and medium. It has been demonstrated that the phosphorescence lifetimes of the corresponding $[ReCl(CO)_3L']$ (L′ = 1,10-phenanthroline or related ligands)[5] and *fac*-$[ReX(CO)_3L_2]$[6] (X = Cl, Br, or I; L = 4-phenylpyridine or 4,4′-bipyridine) complexes drastically increase going from a fluid solution at room temperature to a rigid glass at 77 K. This means that the lifetimes of the triplet m.l.c.t. states of these complexes increase.

In agreement with this, photochemical reactions of $[Cr(CO)_5L]$ (L = imine) and $[Cr(CO)_4L']$ (L′ = di-imine) complexes with lowest m.l.c.t. states are expected to occur in rare-gas matrices directly from the m.l.c.t. states. On the other hand, reactions from a thermally activated ground state may become important for the $[Cr(CO)_5L]$ complexes in fluid solutions at room temperature.

In this article we report the m.l.c.t. photochemistry of $[Cr(CO)_5(pydz)]$ (pydz = pyridazine) [Figure 1(*b*)] and $[Cr(CO)_4(ippyma)]$ [ippyma = isopropyl(2-pyridylmethylene)amine] [Figure 1(*a*)] both in solution at 243 K and in a matrix at 10 K. The results will be related to the r.R. spectra of these complexes. The complex $[Cr(CO)_5(pydz)]$ has been chosen because for this complex

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† Pentacarbonyl(pyridazine-*N*)chromium and tetracarbonyl-[isopropyl(2-pyridylmethylene)amine-*NN*′]chromium.

the lowest m.l.c.t. absorption band has a distinctly lower energy than the ligand-field band in non-polar media.

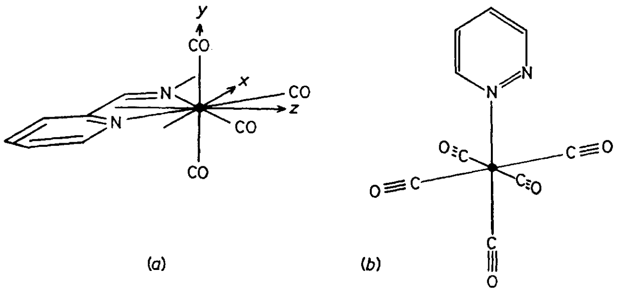

FIGURE 1 Structures of the complexes $[Cr(CO)_4(ippyma)]$ (*a*) and $[Cr(CO)_5(pydz)]$ (*b*)

EXPERIMENTAL

The u.v.–visible and i.r. spectrophotometers, the equipment to achieve cryogenic temperatures, and the photolysis sources used, have been described in previous articles.[4,7,8] The complexes were deposited on the cold window from an oven in a stream of matrix gas. For the pyridazine complex, the oven temperature was 35 °C, for the ippyma complex, *ca.* 80 °C. Argon and methane with a purity of 99.999% and 99.9995% respectively were employed. Resonance-Raman spectra were recorded with a Jobin–Yvon HG 2 S Ramanor using a SP model 171 argon ion laser and a model CR 490 tunable dye-laser with Rhodamine 6G in ethylene glycol as dye. The r.R. spectrum of $[Cr(CO)_4(ippyma)]$ was taken from a solution of the complex in $CHCl_3$ in a specially constructed spinning cell which could be cooled to −60 °C. The r.R. spectra of $[Cr(CO)_5(pydz)]$, which could not be taken in solution because of photodecomposition, were recorded from a dispersion of the complex in $K[NO_3]$ at *ca.* −170 °C in a device similar to that described by Clark and Turtle.[9] Corrections were applied for decomposition of the complexes in the laser beam.

Photosubstitution reactions of solutions of $[Cr(CO)_5(pydz)]$ in n-pentane and benzene and of $[Cr(CO)_4(ippyma)]$ in benzene were carried out by irradiating 4-cm^3 samples which were carefully degassed, with an excess of trimethyl phosphite or pyridazine (*ca.* 0.02 mol dm^{-3}). A CR 490 tunable dye-laser pumped by an SP 171 argon ion laser was used as the light source (10—100 mW). The reactions of the pyridazine complex with $P(OMe)_3$ had to be carried out at −30 °C in order to prevent the thermal substitution reaction. The reactions which were followed with a Cary 14 u.v.–visible spectrophotometer only proceeded during excitation. Determination of the quantum yields was only possible for the photosubstitution reaction of the ippyma complex and the method of calculation is described elsewhere.[4]

RESULTS

Infrared Spectra.—For $[Cr(CO)_5(pydz)]$ with local C_{4v} symmetry, three main i.r. bands are expected in the CO stretching region. These bands are indeed observed in the spectra of solutions. In matrices however, at least two intense bands are observed for the E mode. Since the relative intensities of the various i.r. bands still agree with local C_{4v} symmetry of the $[Cr(CO)_5]$ moiety, this effect is ascribed to matrix splittings. Similar large splittings have been observed for other $[M(CO)_5L]$ (M = Cr or W; L = imine or amine) complexes.[7,8] After deposition of $[Cr(CO)_4(ippyma)]$ in Ar and CH_4 matrices at 10 K four main bands are found at *ca.* 2 010, 1 920, 1 900, and 1 860 cm^{-1}. The positions of these bands and their relative intensities in the matrices are in agreement with the observed band pattern in solution at room temperature.[10] From this it can be concluded that the $[Cr(CO)_4]$ moiety of $[Cr(CO)_4(ippyma)]$ possesses C_{2v} symmetry both in solutions and matrices. Also for this latter complex, several matrix splittings were detected. The results are compiled in Table 1.

Electronic Absorption Spectra.—In Table 2 the electronic absorption spectral data of both complexes in solution at room temperature and in matrices at 10 K are presented. In the spectrum of $[Cr(CO)_5(pydz)]$ a $Cr(3d)\rightarrow\pi^*(CO)$ charge-transfer band is observed at *ca.* 240 nm and the $^1E_a(b_2e^3a_1)\leftarrow{}^1A_1(b_2{}^2e^4)$ ligand-field (l.f.) transition at *ca.* 410 nm. The m.l.c.t. band of this complex is found at *ca.* 460 nm in a n-hexane solution. The assignment of these bands is evident from the solvent dependence of the position of the 460 nm band [11] and from the positive A term observed for the 410 nm band in the magnetic circular dichroism (m.c.d.) spectrum.[12] The spectrum of $[Cr(CO)_4(ippyma)]$ in n-hexane shows a m.l.c.t. band at *ca.* 605 nm, while the l.f. band at *ca.* 400 nm partly overlaps with a c.t. transition from the metal to the second excited state of ippyma.[10]

Apart from small shifts, the spectra of the complexes are essentially the same in the matrix. These latter spectra are shown in Figures 2 and 3.

Resonance-Raman Spectra.—Parts of the r.R. spectra obtained by excitation within the lowest-energy m.l.c.t. transitions of $[Cr(CO)_5(pydz)]$ in $K[NO_3]$ at −170 °C and of

TABLE 1

Infrared frequencies of the complexes in Ar and CH_4 matrices at 10 K

Complex	Matrix	$\nu(CO)/cm^{-1}$					
		$A_1{}^2$	E	$A_1{}^1$	^{13}CO		
$[Cr(CO)_5(pydz)]$	Ar	2 073.2	1 948.9 1 940.3 1 926.8	1 917.1	1 903.8		
	CH_4	2 071.6	1 944.9 1 936.5	1 914.7	1 898		
		$A_1{}^2$	B_1	$A_1{}^1$	^{13}CO	B_2	^{13}CO
$[Cr(CO)_4(ippyma)]$	Ar	2 013.4	1 917.9	1 906.1 [a]	1 891.2	1 863.2	1 846.4
	CH_4	2 012.6	1 914.6 1 911.3	1 903.6		1 863.9 1 859.9 1 854.9 [b] 1 849.8	1 838.4

[a] In Ar this band is less intense. [b] Most intense band.

TABLE 2

Ultraviolet–visible spectral data (in nm) of the complexes [a]

Complexes	Conditions	M.l.c.t.		L.f.	$d \rightarrow \pi^*$(CO)
[Cr(CO)$_5$(pydz)]	n-Hexane, r.t.	464, 467 [b]		411, 405 [b]	244
	Ar, 10 K	450		395	239
	CH$_4$, 10 K	445		398	*c*
[Cr(CO)$_4$(ippyma)]	n-Hexane, r.t.	605	560 (sh)	398 [d]	*c*
	Ar, 10 K	588	540 (sh)	382 [d]	*c*

[a] r.t. = Room temperature, sh = shoulder. [b] After carrying out a Gaussian analysis on a Du Pont curve-resolver model 110. [c] Not measured. [d] This band is assigned to both a l.f. and a c.t. transition to a second excited state of the ippyma ligand (ref. 11).

[Cr(CO)$_4$(ippyma)] in CHCl$_3$ at −50 °C are shown in Figures 4 and 5, respectively. The pyridazine complex could only be measured in pre-resonance, because upon excitation with *e.g.* λ = 457.9 nm, the signal-to-noise ratio strongly decreased, probably as a result of destructive interference with l.f. transitions.[13]

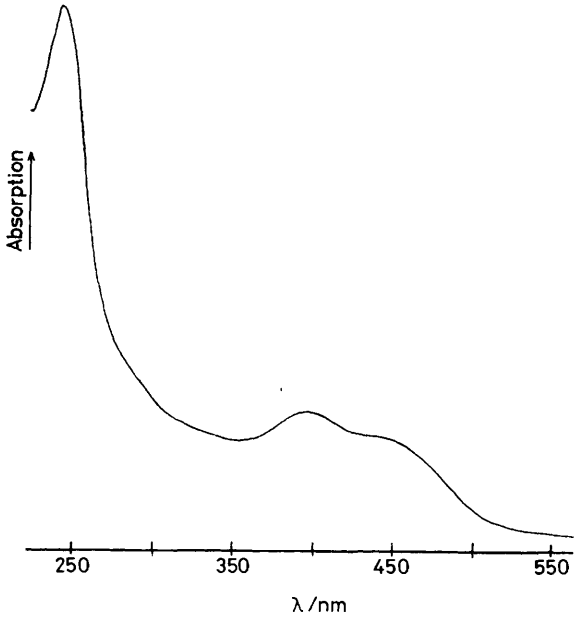

FIGURE 2 U.v.–visible absorption spectrum of [Cr(CO)$_5$(pydz)] in an Ar matrix at 10 K

In the low-frequency regions of the r.R. spectra of both compounds (150—700 cm^{-1}), which are not shown here, all symmetric metal–ligand modes are observed, but the r.R. effect for these vibrations is weaker than for the ligand modes. The assignment of the pyridazine modes which show a r.R. effect is given by Daamen *et al.*: [14,*] ν_{8a} at 1 580 cm^{-1}, ν_{19a} at 1 445 cm^{-1}, ν_{19b} at 1 419 cm^{-1}, and ν_1 at 966 cm^{-1}. For the ippyma complex strong enhancement of Raman intensity is found for ν(C=N) at 1 613 cm^{-1}, ν(pyII) at 1 556 cm^{-1}, and ν(pyIII) at 1 462 cm^{-1}.[4,†] For this complex, all ligand modes which show the r.R. effect are polarized. Apart from metal–ligand stretching modes, both complexes show strong enhancement of Raman intensity for the symmetrical stretching mode of the carbonyls *cis* with respect to the (di)-imine ligand ($A_1{}^2$) upon excitation within the metal-to-(di)-imine c.t. transitions. This effect, which is not observed for the symmetrical stretching mode of the *trans* carbonyls, has been discussed in previous articles [4,10,14,15] and ascribed to a delocalization of the m.l.c.t. excited state over the *cis* carbonyl ligands. This delocalization is presumably caused by a 'through-space' or 'through-metal' interaction between virtual molecular orbitals, mainly localized at the (di)-imine ligand and *cis* carbonyl groups, respectively.[4]

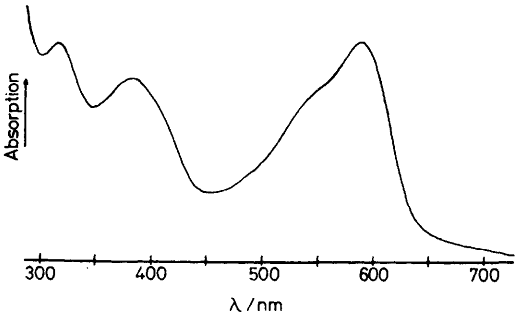

FIGURE 3 U.v.–visible absorption spectrum of [Cr(CO)$_4$(ippyma)] in an Ar matrix at 10 K

Photochemistry in Solution.—[Cr(CO)$_4$(ippyma)]. When a benzene solution of [Cr(CO)$_4$(ippyma)] and P(OMe)$_3$ is irradiated within the m.l.c.t. band, which is at much lower energy than the lowest l.f. band (see Figure 3), *fac*-[Cr(CO)$_3$(ippyma){P(OMe)$_3$}] is formed with a quantum yield $\Phi_p{}^i$ = 0.013‡ at λ = 550 nm (maximum of the m.l.c.t. band). When this product is irradiated within its m.l.c.t. band ($\lambda_{max.}$ = 617 nm in benzene), substitution of a second CO group occurs with a much lower quantum yield ($\Phi_p{}^i$ = 0.0005 at λ = 617 nm).[4] The complex formed, [Cr(CO)$_2$(ippyma){P(OMe)$_3$}$_2$], is stable in the laser beam. Figure 6 shows the r.R. spectral changes which accompany these processes. The spectra were obtained on excitation with λ = 600 nm and the photoreaction was studied by irradiation with the same wavelength. The r.R. spectrum at *t* = 0 therefore shows already some features of the photoproduct. After four minutes of irradiation with a 100-mW laser beam, conversion to the tricarbonyl is nearly complete [Figure 6(*c*)], because ν_s(CO^{cis}) at 2 018 cm^{-1} of the tetracarbonyl compound has nearly disappeared. Resonance Raman enhancement is observed for ν(CO^{cis}) of the tricarbonyl photoproduct at 1 933 cm^{-1}, for ν(pyII) at 1 532 cm^{-1}, and for ν(pyIII) at 1 460 cm^{-1} [ν(C=N) at 1 607 cm^{-1} is obscured by the 1 600 cm^{-1} solvent band]. The relative intensities of these bands are much larger than those of the tetra- and di-carbonyl .complexes [Figure 6(*a*) and 6(*e*) respectively], because the exciting laser line nearly coincides with the maximum of the m.l.c.t. band of this complex. This is not the case for the two other compounds, because the m.l.c.t. band shifts to lower energy when the *cis* CO

[*] Nomenclature from R. C. Lord, A. L. Marston, and F. A. Miller, *Spectrochim. Acta*, 1957, **9**, 113.

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

[‡] $\Phi_p{}^i$ = Initial quantum yield of product formation.

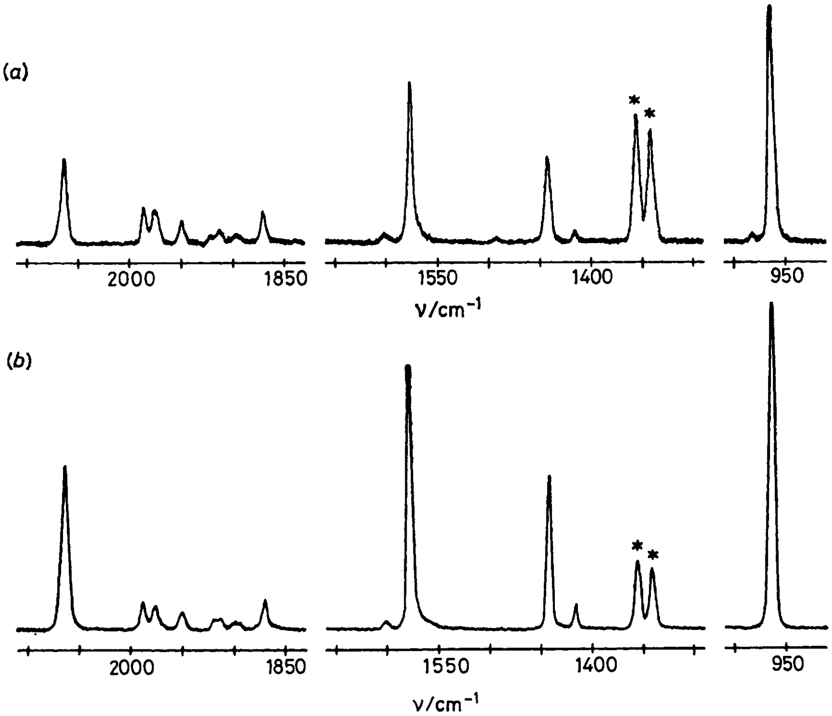

FIGURE 4 Parts of the r.R. spectra of $[Cr(CO)_5(pydz)]$ in $K[NO_3]$ at −170 °C, excited at (*a*) $\lambda = 589.3$ and (*b*) $\lambda = 514.5$ nm. The bands indicated with an asterisk belong to the nitrate ion

groups are successively replaced by $P(OMe)_3$ (tetracarbonyl: $\lambda_{max.} = 550$ nm; tricarbonyl: $\lambda_{max.} = 617$ nm; dicarbonyl: $\lambda_{max.} = 670$ nm). Irradiation of $[Cr(CO)_4(ippyma)]$ with shorter wavelengths *e.g.* $\lambda = 457.9$ nm also gives substitution of a *cis* carbonyl group. The photosubstitution quantum yield of formation of the tricarbonyl complex is $\Phi_p{}^i = 0.04$, but when *ca.* 50% of the tetracarbonyl is converted to the tricarbonyl complex, formation of the dicarbonyl compound already becomes important. This behaviour differs from that observed at $\lambda = 600$ nm since irradiation at this latter wavelength resulted in nearly 100% formation of the tricarbonyl complex before the dicarbonyl compound was formed (see Figure 6). This change in the relative photosensitivities of the tetra- and tri-carbonyl complexes is most likely due to the fact that at $\lambda = 457.9$ nm excitation partly occurs into the l.f. band of both complexes.

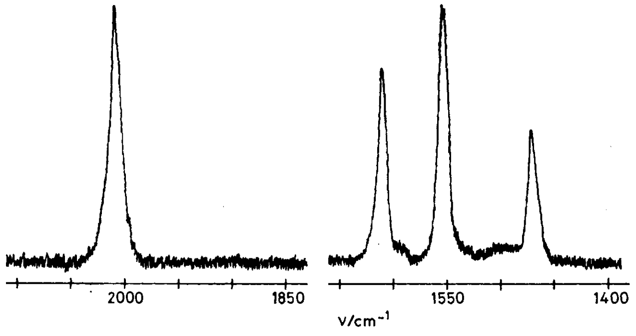

FIGURE 5 Part of the r.R. spectrum of $[Cr(CO)_4(ippyma)]$ in $CHCl_3$ at −53 °C and $\lambda = 514.5$ nm

$[Cr(CO)_5(pydz)]$. The photochemistry of $[Cr(CO)_5(pydz)]$ in solution was studied by adding an excess (0.02 mol dm^{-3}) of $P(OMe)_3$. The reaction in n-pentane had to be carried out at lower temperatures (*ca.* −30 °C) because substitution of pyridazine by $P(OMe)_3$ already occurs thermally at room temperature. The complex was irradiated within the m.l.c.t. band at 514.5 nm. At this wavelength the l.f. transition does not absorb (Figure 2). This irradiation resulted in an intensity decrease of both the l.f. and m.l.c.t. bands (at 410 nm and 440 nm respectively). At the same time, however, the l.f. band showed a small shift to shorter wavelength ($\lambda = 395$ nm), whereas the m.l.c.t. band shifted to longer wavelength ($\lambda = 470$ nm). This result points to the formation of both $[Cr(CO)_5\{P(OMe)_3\}]$ (disappearance of l.f. and m.l.c.t. bands) and $[Cr(CO)_4(pydz)\{P(OMe)_3\}]$ (shifts of l.f. and m.l.c.t. bands). The amount of $[Cr(CO)_4(pydz)\{P(OMe)_3\}]$, however, was small and the i.r. spectrum of the photoproduct in solution only showed the vibrations of $[Cr(CO)_5\{P(OMe)_3\}]$.

These results show that the m.l.c.t. photochemistry of $[Cr(CO)_5(pydz)]$ in solution is different from that of $[Cr(CO)_4(ippyma)]$. The latter compound only shows photosubstitution of CO and no replacement of the di-imine ligand, whereas replacement of pyridazine is much more important than photosubstitution of CO in the case of $[Cr(CO)_5(pydz)]$. In order to study the photosubstitution of CO in the case of $[Cr(CO)_5(pydz)]$, this reaction was favoured by adding an excess of pyridazine to a solution of the complex instead of $P(OMe)_3$. In that case photosubstitution of pyridazine does not give a new product. Benzene had to be used instead of n-pentane because of the poor solubility of the photoproduct in non-polar solvents. Irradiation with $\lambda = 514.5$ nm then gives a decrease of intensity for both the l.f. and m.l.c.t. band while at the same time a new m.l.c.t. band appears at longer wavelength (Figure 7). This band belongs to the lowest-energy m.l.c.t. transition of $[Cr(CO)_4(pydz)_2]$ which is shifted to lower energy with respect to $[Cr(CO)_5(pydz)]$ as a result of the

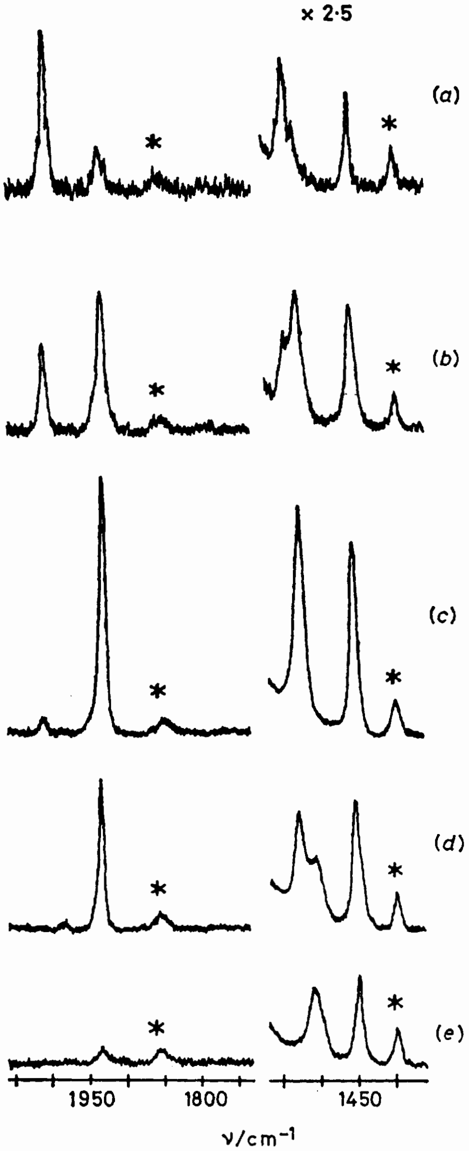

FIGURE 6 Part of the r.R. spectral changes of $[Cr(CO)_4(ippyma)]$ in C_6H_6 after t minutes of irradiation with $\lambda = 600$ nm and laser power p (mW) in the presence of $P(OMe)_3$: (a) $t = 0$, $p = 100$; (b) $t = 1$, $p = 100$; (c) $t = 4$, $t' = 0$, $p = 200$; (d) $t' = 40$, $p = 200$; (e) $t' = 160$, $p = 200$ ($t' = 0$ corresponds to the point where the laser power was changed). The spectra were also excited with $\lambda = 600$ nm, spectrum (a) with 20-mW laser power, (b)—(e) with 100 mW. Solvent bands are indicated with an asterisk

substitution of a carbonyl ligand by pyridazine. The absorption spectrum shows an isosbestic point until a reasonable amount of the photoproduct is formed. Upon further irradiation with $\lambda = 514.5$ nm this latter compound decomposes in the laser beam. This decomposition of the photoproduct prevented the determination of the photosubstitution quantum yield.

Irradiation of a n-pentane solution of $[Cr(CO)_5(pydz)]$ with excess of $P(OMe)_3$ within the l.f. band with the u.v. lines of an argon ion laser ($\lambda = 351.1$, 363.8 nm) gave $[Cr(CO)_5\{P(OMe)_3\}]$ as the main product (decrease of l.f. and m.l.c.t. bands). However, a fairly small amount of $[Cr(CO)_4(pydz)\{P(OMe)_3\}]$ was formed at the same time.

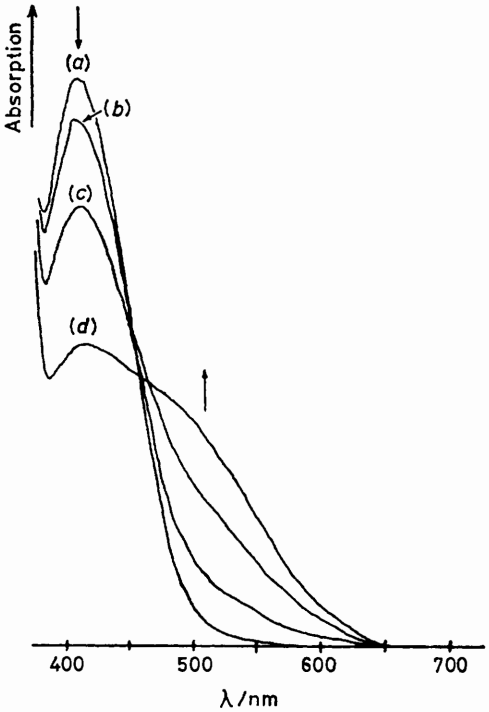

FIGURE 7 U.v.–visible spectral changes of a benzene solution of $[Cr(CO)_5(pydz)]$ after t minutes of irradiation in the presence of pyridazine (ca. 0.02 mol dm^{-3}): (a) $t = 0$, (b) $t = 0.25$, (c) $t = 1$, (d) $t = 5$; $T = 293$ K; $\lambda = 514.5$ nm; $p = 50$ mW

Photochemistry in Matrices.—$[Cr(CO)_4(ippyma)]$. Photolysis of $[Cr(CO)_4(ippyma)]$ in Ar and CH_4 matrices at 10 K into the m.l.c.t. band at 610 nm resulted in the formation of free CO with a frequency of *ca.* 2 140 cm^{-1} and of a new species with three i.r. bands in the CO stretching region (see Figure 8). The positions of these bands at 1 930, 1 842, and

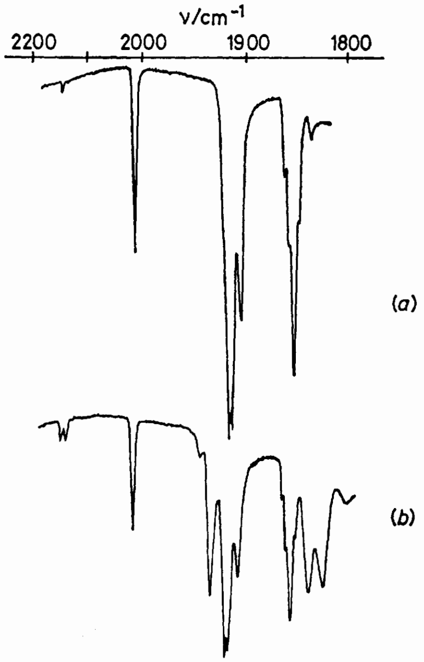

FIGURE 8 Infrared spectrum of $[Cr(CO)_4(ippyma)]$ in a CH_4 matrix at 10 K. (a) After deposition, (b) after 64 h photolysis with $\lambda = 610$ nm

TABLE 3

Infrared frequencies of two photofragments in Ar and CH_4 matrices at 10 K

Fragment	Matrix	$\nu(CO)/cm^{-1}$			
		A'	A'	A'	A''
cis-$[Cr(CO)_4(pydz)]$ [a]	Ar	2 022.8	*b*	1 923.4	1 886.2
	CH_4	2 021.9	*b*	1 916.3	1 875.5
		A'	A'	A''	
fac-$[Cr(CO)_3(ippyma)]$	Ar	1 929.9	1 842.1	1 834.2	
	CH_4	1 929.5	1 838.8 1 831.7	1 825.7	

[a] Besides the *cis*-$[Cr(CO)_4(pydz)]$ frequencies, frequencies of *fac*-$[Cr(CO)_3(pydz)]$ were measured. [b] Obscured by parent bands.

1 834 cm^{-1} (Ar matrix) are in close agreement with those of the i.r. bands found for *fac*-$[Cr(CO)_3(ippyma)L']$ complexes (L′ = *P*-donor or isocyanide) in solution [10,15] and with the bands found for $[W(CO)_3(PPr^i_3)_2]$ and $[Mo(CO)_3\{P(C_6H_{11})_3\}]$ in glasses [16] (see Table 3). From this result and from the observation of free CO, we conclude that after photolysis of $[Cr(CO)_4(ippyma)]$ into the m.l.c.t. band, *fac*-$[Cr(CO)_3(ippyma)]$ is formed. The same product is generated after irradiation into the $Cr(3d)\rightarrow\pi^*(CO)$ transition with the wavelength $\lambda = 229$ nm. After photolysis, several new bands are observed in the electronic absorption spectra at 370 nm and 510 nm and one above 625 nm. Attempts to reverse the reaction failed, probably because of overlapping parent and product absorption bands.

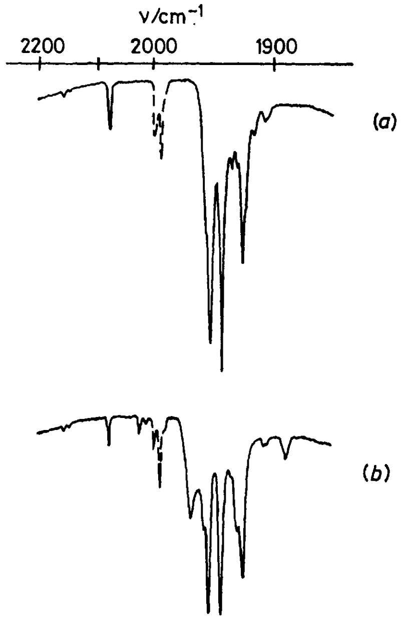

FIGURE 9 Infrared spectrum of $[Cr(CO)_5(pydz)]$ in an Ar matrix at 10 K, $[Cr(CO)_6]$ (— — —). (*a*) After deposition, (*b*) after 16 h photolysis with $\lambda = 436$ nm

$[Cr(CO)_5(pydz)]$. Photolysis of $[Cr(CO)_5(pydz)]$ both in argon and methane matrices at 10 K with short wavelength ($\lambda = 254$ nm) radiation resulted in the formation of primarily $[Cr(CO)_4(pydz)]$ and free CO. The positions of the bands of $[Cr(CO)_4(pydz)]$ and their relative intensities show that this fragment has C_s symmetry, in agreement with other $[Cr(CO)_4L]$ species (L = NMe_3, piperidine, pyridine, or pyrazine) [7,8,17] (see Table 3). Photolysis of $[Cr(CO)_5(pydz)]$ with longer wavelengths (*i.e.* $\lambda = 366$ and 436 nm) resulted in the formation of both $[Cr(CO)_5]$ and *cis*-$[Cr(CO)_4(pydz)]$ (Figure 9). The yield of *cis*-$[Cr(CO)_4(pydz)]$ is high compared with the results for other $[Cr(CO)_5(N\text{-donor})]$ complexes.[7,8,17]

Photolysis of $[Cr(CO)_5(pydz)]$ into its m.l.c.t. band yielded free CO and *cis*-$[Cr(CO)_4(pydz)]$ (Figure 10).

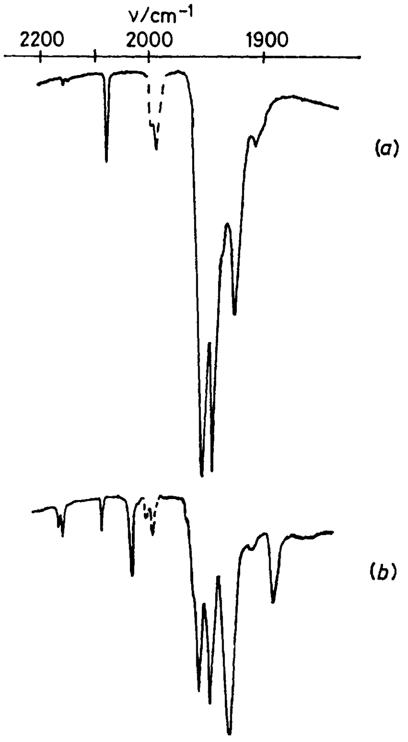

FIGURE 10 Infrared spectrum of $[Cr(CO)_5(pydz)]$ in an Ar matrix at 10 K, $[Cr(CO)_6]$ (— — —). (*a*) After deposition, (*b*) after 90 h photolysis with $\lambda = 520$ nm

DISCUSSION

Although the m.l.c.t. photoreactivity of $[Cr(CO)_4(ippyma)]$ in the matrix is small (65 h of irradiation), the dissociative loss of a *cis* carbonyl ligand is evident from the i.r. spectrum. This result and the r.R. data (see below) implicate that the photosubstitution of CO by $P(OMe)_3$ in solution is also most likely to occur *via* release of a *cis* carbonyl ligand and not of a *trans* carbonyl group followed by a rearrangement of the intermediate.[18] This reaction will take place in the m.l.c.t. excited state because non-radiative relaxation processes are less effective in the matrix. Furthermore, in contrast to other metal carbonyls,[19] the complexes under study do not luminesce in a matrix. The photosubstitution of CO by $P(OMe)_3$ in solution is also assumed to occur in the m.l.c.t. excited state and not in a thermally activated ground state, since the reaction cannot be performed thermally at room temperature. This result agrees with our previous interpretation of this photochemical reaction which was based on the relationship between the m.l.c.t. photoreactivity of these complexes and the r.R. effect of $\nu_s(CO^{cis})$.[4] Now, if a certain Raman band shows a strong r.R. effect, the equilibrium conformation of the complex will be distorted along this normal coordinate going from the ground state to the electronic excited state.[20] This distortion can even be so large that it initiates a photochemical reaction in the excited state, which is apparently the case for the *cis* carbonyl ligands of $[Cr(CO)_4(ippyma)]$. Consequently, r.R. spectra can be used to investigate what kind of photochemical reactions are expected to occur in the electronic excited state and whether a certain reaction takes place in the electronic excited state or in a thermally activated ground state. In this respect the photochemistry of $[Re(CO)_3L'\{Mn(CO)_5\}]$ (L' = 1,10-phenanthroline) is of interest. This complex possesses a Re–Mn bond which is broken upon irradiation within the Re→L' c.t. band.[21] The Raman spectra however, do not show a r.R. effect for ν(Re–Mn), which means that the Re–Mn bond is hardly affected by this m.l.c.t. transition.[22] It is therefore most likely that this metal–metal bond is broken in a thermally activated ground state and not in the m.l.c.t. excited state.

There is a close analogy between the r.R. spectra of $[Cr(CO)_4(ippyma)]$ and $[Cr(CO)_5(pydz)]$. Both complexes show a strong r.R. effect for the symmetrical stretching mode of the carbonyls *cis* with respect to L(L') (Figures 4 and 5). This analogy also holds for the photochemical behaviour in the matrix, both complexes showing release of CO upon irradiation within the m.l.c.t. band. This means that also $[Cr(CO)_5(pydz)]$ releases CO in the m.l.c.t. excited state.

In solution, however, these complexes behave differently. For $[Cr(CO)_5(pydz)]$ photosubstitution of pyridazine by PR_3 is the main reaction, whereas a CO ligand is replaced in the case of $[Cr(CO)_4(ippyma)]$. The former reaction differs from that in the matrix and will now take place in a thermally activated ground state instead of in the m.l.c.t. excited state. The same reaction already takes place thermally at room temperature. The occurrence of these two different reactions depending on the medium and temperature is most likely due to a change of lifetime of the m.l.c.t. excited state (see above). This explanation of the m.l.c.t. photochemistry of $[Cr(CO)_5(pydz)]$ differs from that given by Wrighton *et al.*[1] for $[W(CO)_5L]$ (L = 4-substituted pyridine). These authors ascribe the photosubstitution of L upon irradiation within the m.l.c.t. band to the photoreactivity of the m.l.c.t. excited state.

Upon irradiation of $[Cr(CO)_5(pydz)]$ within the l.f. band, both pyridazine and to a smaller extent CO is released in the matrix. The same result has been obtained for L = pyridine and pyrazine. The corresponding $[Cr(CO)_5L]$ complexes with L = NMe_3 or piperidine, however, only showed release of L upon irradiation within the l.f. band.[7,8,17] This deviating behaviour of the imine complexes with respect to the amine ones, is most certainly due to the near coincidence of the l.f. and m.l.c.t. excited states.

Conclusion.—It is shown that a different m.l.c.t. photochemistry can be achieved for $[Cr(CO)_5(pydz)]$ by variation of medium and temperature and that the r.R. effect can be used to decide whether a photochemical reaction occurs in an electronic excited state or in a thermally activated ground state.

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