Temperature- and Wavelength-dependent Photochemistry of $[Cr(CO)_5(NMe_3)]$† in Argon and Xenon Matrices. Evidence for the Formation of $[Cr(CO)_5]$ and Novel $[Cr(CO)_4(NMe_3)]$ Complexes with Three Different Types of Symmetry

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Photolysis of $[Cr(CO)_5(NMe_3)]$ in Ar and Xe matrices at 10 K with λ = 229 and 254 nm results in nearly quantitative formation of $C_s[Cr(CO)_4(NMe_3)]$. The reaction can be reversed by irradiation with λ = 546 nm. At 40 K in Xe isomerization of $C_s[Cr(CO)_4(NMe_3)]$ into $C_{3v}[Cr(CO)_4(NMe_3)]$ or $C_{2v}[Cr(CO)_4(NMe_3)]$ has been detected. Long-wavelength photolysis with λ = 366, 405, and 436 nm results in release of the ligand NMe_3. Besides $Cr(CO)_5 \cdots X$ (X = Ar or Xe) a new species $Cr(CO)_5 \cdots NMe_3$ is obtained. The lifetime of the excited states of $[Cr(CO)_5(NMe_3)]$ appears to be longer than those for $[Cr(CO)_5(py)]$ and $[Cr(CO)_5(pyz)]$ (py = pyridine, pyz = pyrazine). An explanation is given for the observed influence of wavelength, matrix, ligand, and temperature on the photochemical behaviour. In several cases the structures of the photoproducts are determined by ^{13}CO labelling and force-field calculations.

DURING the last few years the photolability of substituted Group 6 carbonyls has received increasing attention. It appears to be very difficult to deduce the nature of the intermediates formed in solutions at room temperature during photochemical processes. In contrast, the matrix-isolation technique has proved to be an excellent tool for this purpose. Only a few substituted Group 6 carbonyls have been studied in a matrix. Poliakoff [1,2] reported the u.v. photolysis of $[M(CO)_5(CS)]$ (M = Cr or W) in several matrices and found evidence for the formation of both *cis*- and *trans*-$[M(CO)_4(CS)]$ complexes after photolysis with $\lambda = 300$ nm. No evidence was found for loss of CS under these conditions. Recently $[Cr(CO)_5(CSe)]$ was studied by Varetti *et al.*[3] in an Ar matrix at 20 K and the corresponding *cis*- and *trans*-$[Cr(CO)_4(CSe)]$ complexes were detected. Furthermore Varetti reported a release of CSe upon u.v. photolysis and at the same time reaction of $[Cr(CO)_5]$ with free CO resulting in $[Cr(CO)_6]$ formation.‡

Photochemistry of complexes with more bulky ligands were described by Rest and co-workers.[4] Photolysis of $[W(CO)_5L]$ (L = pyridine, 3-bromopyridine, or hydrogen sulphide) in several matrices at 10 K with $320 < \lambda < 390$ nm resulted in the formation of $[W(CO)_5]$, indicating that bulky ligands can also be generated in matrices.

The same results were found for $[M(CO)_5(PCl_3)]$ (M = Cr or W) in an Ar matrix at 10 K, as we reported earlier.[5-7] Photodetachment of PCl_3 was found by irradiation with λ = 229, 254, 280, 313, and 366 nm. Reco-ordination of PCl_3 was accomplished by irradiation with λ = 436 nm for $[W(CO)_5]$ and 546 nm for $[Cr(CO)_5]$. For the first time evidence was found for both CO and ligand rupture in matrix photoreactions of $[Cr(CO)_5(py)]$ and $[Cr(CO)_5(pyz)]$ (py = pyridine, pyz = pyrazine). Regeneration of the parent compounds was only partly effected due to isomerization of *cis*-$[Cr(CO)_4L]$ into *trans*-$[Cr(CO)_4L]$ (L = *N*-donor). The difference in photochemical behaviour between PCl_3 and nitrogen-donor ligand complexes was explained with the use of one-electron *d*-orbital energy diagrams.

In this article we describe the wavelength-dependent photoproduction of new species: $Cr(CO)_5 \cdots X$, $Cr(CO)_5 \cdots NMe_3$, and $Cr(CO)_4NMe_3 \cdots X$ with three different types of symmetry (X = Ar or Xe). A temperature dependence was observed for the obtained photoproducts. The reactions are reversed by long-wavelength irradiation. Attempts were made to find further evidence for all intermediates by ^{13}CO labelling and force-field calculations.

EXPERIMENTAL

Synthesis of $[Cr(CO)_5(NMe_3)]$.—The compound $[Cr(CO)_5(NMe_3)]$ was prepared under a nitrogen atmosphere by a method described by Koelle.[8]

A suspension of $ONMe_3$ (3.3 g, 4.4 mmol) in freshly distilled tetrahydrofuran (thf) (60 cm^3) was added at −50 °C to $[Cr(CO)_6]$ (4.8 g, 2.2 mmol). The reaction mixture was slowly warmed up, with stirring, over 10 h to room temperature. The green precipitate was filtered off and washed with n-hexane. The thf was removed from the precipitate at 0 °C under reduced pressure. Vacuum sublimination (0.1 Torr) § at room temperature yielded yellow crystals of $[Cr(CO)_5(NMe_3)]$. The purity of the complex was checked by i.r. spectroscopy.

Labelling of $[Cr(CO)_5(NMe_3)]$ *with* ^{13}CO.—Labelling of $[Cr(CO)_5(NMe_3)]$ was accomplished by irradiation for 3 h of a n-hexane solution of the complex with λ = 254 nm (Rayonet, preparative photochemical reactor, type RPR-208) under a ^{13}CO atmosphere. Cooling of the reaction mixture during photolysis to 5—10 °C prevented thermal decomposition. After removing the solvent, $[Cr(CO)_6]$ and $[Cr(CO)_{6-x}(^{13}CO)_x]$ were expelled by vacuum sublimination and recrystallization. This yielded a mixture of five isomers: $[Cr(CO)_5(NMe_3)]$, $[Cr(CO)_4(^{13}CO)(NMe_3)]$ (equatorial), $[Cr(CO)_4(^{13}CO)(NMe_3)]$ (axial), *fac*-$[Cr(CO)_3(^{13}CO)_2(NMe_3)]$, and *mer*-$[Cr(CO)_3(^{13}CO)_2(NMe_3)]$, which is in agreement with the results of Darensbourg and Murphy.[9]

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† Pentacarbonyl(trimethylamine)chromium(0).

‡ It seems more probable to us that the increase of a band at 1 990 cm^{-1} is not due to $[Cr(CO)_6]$ formation, but to the presence of *trans*-$[Cr(CO)_4(CSe)]$, which is confirmed by the intensity of the vibration at 2 084 cm^{-1} {A_1 of *trans*-$[Cr(CO)_4(CSe)]$}.

§ Throughout this paper: 1 Torr = (101 325/760) Pa.

Equipment.—The equipment to achieve cryogenic temperatures has been described in earlier papers.[5,7] The pulse technique of Rochkind[10] cannot be used for the $[Cr(CO)_5(NMe_3)]$ complex because of decomposition during the mixing with matrix gases. Normal vaporisation from an oven and co-condensation with the matrix was also prevented, due to the high volatility of the compound, giving broad-banded spectra and scattering matrices. (The vapour-pressure measurements of this compound are published elsewhere.)[11] Therefore a semi-pulse technique was developed by pumping off the sample compartment with a double-stage rotary pump and co-deposition with matrix gas by pulsing at the same time.

Temperature of the Displex never exceeded 10 K and the pressure of the sample compartment was less than 2 Torr (Ar pressure) during deposition. This technique resulted in transparent matrices after 100 to 150 pulses. Deposition times varied between 5 and 10 min and the vacuum of the Displex was better than 10^{-6} Torr. Matrix gases with purity 99.999% for Ar and 99.997% for Xe were employed. Infrared spectra were recorded on Beckman IR-7 and IR 4250 spectrometers and regularly calibrated with DCl and NH_3. U.v.-visible absorption spectra were recorded on a Cary-14 spectrophotometer with an extended sample compartment. Photolysis sources and filters have been reported elsewhere.[5,7] The photoelectron spectra were recorded on a Perkin-Elmer P.S.-18 spectrometer modified with an Helectros He(I)–He(II) source and calibration was performed before and after measurement.

TABLE 1

Infrared frequencies (cm^{-1}) of $[Cr(CO)_5(NMe_3)]$

	ν(C–O)					ν(^{13}C–O)	ν(N–C)	Free ligand ν(N–C)[a]
Assignments	A_1^2	B_1	E		A_1^1	E	A_1	A_1
Nujol mull, room temperature	2 065.9	1 965.5	1 931.9		1 914.5	1 901	830	827
n-Hexane, room temperature	2 067.5	1 967.1	1 935.2		1 918.7	1 903.4	829	
Ar matrix, 10 K	2 072.3	1 978.0	1 945.2	1 932.5	1 923.2[b]	1 906.2	831.2	823
			1 942.6	1 929.3	1 919.8			
			1 939.4[b]	1 927.5	1 918.2			
Xe matrix, 10 K	2 067.2	1 973.8	1 931.7[b]	1 925.8	1 913.7	1 899.9	835.9	
				1 921.9	1 908.3[b]			
Intensity	w	w	s		m	w	w	m

[a] Data from ref. 12. [b] Most intense band.

RESULTS

Infrared Spectra.—The matrix-isolation spectra of $[Cr(CO)_5(NMe_3)]$ are shown in Figures 1—5. For $[Cr(CO)_5(NMe_3)]$ with local C_{4v} symmetry, three fundamentals are expected in the i.r. CO stretching region, $2A_1$ and E. The influence of the matrix could be observed from the very weak B_1 mode, together with several matrix splittings. In going from an Ar to a Xe matrix fewer matrix splittings were detected.

The intensity pattern of $[Cr(CO)_5(NMe_3)]$ differed considerably from that found for $[Cr(CO)_5(py)]$ and for $[Cr(CO)_5(pyz)]$. The frequencies showed a good resemblance, however, as expected for compounds with almost the same σ-donor capability. The reason for the intensity differences is not yet clear.

For most $[Cr(CO)_5L]$ molecules slight decomposition cannot easily be prevented, but for $[Cr(CO)_5(NMe_3)]$ decomposition into $[Cr(CO)_6]$ and CO did not occur. Vibrations of the co-ordinated ligands were very weak. However, with signal expansion the ν(N–C) vibration was recorded. The assignment was made according to the method of Goldfarb and Khare.[12]

In Table 1 the influence of various media (Nujol mull, n-hexane, Ar-, and Xe matrices) is shown.

Ultraviolet-visible Spectra.—The u.v.-visible spectra of $[Cr(CO)_5(NMe_3)]$ in Ar and Xe matrices showed only two distinct absorptions at 246 and 419 nm (Ar matrix). The shift in going from Ar to Xe matrices was small and the bands were assigned to the $\pi^*(CO) \leftarrow Cr(3d)$ charge-transfer and ${}^1E_a(b_2^2e^3a_1^1) \leftarrow {}^1A_1(b_2^2e^4)$ ligand-field transitions respectively. Figures 6 and 7 show the u.v.-visible spectra of $[Cr(CO)_5(NMe_3)]$ in Ar matrices and Table 2 the data in Ar, Xe, and n-hexane.

Photochemistry.—*Argon matrix*, 10 K. Photolysis of $[Cr(CO)_5(NMe_3)]$ in an Ar matrix at 10 K with monochromatic light (λ = 229, 254, and 313 nm) resulted in a

$$[Cr(CO)_5(NMe_3)] \underset{\lambda = 546\,nm}{\overset{\lambda = 229,254\,nm}{\rightleftharpoons}} C_s[Cr(CO)_4(NMe_3)] + CO$$

decrease of parent bands and formation of $C_s[Cr(CO)_4(NMe_3)]$. The symmetries of the different $[Cr(CO)_4(NMe_3)]$ complexes were determined by ^{13}CO labelling. For $[Cr(CO)_4(NMe_3)]$ with C_s symmetry four i.r. active carbonyl bands are expected. At first sight only three new bands were detected (2 033.2, 1 906.0, and 1 891.4 cm^{-1}). The missing fourth band at 1 918.2 cm^{-1} was obscured by a parent band and could only be detected after 5 min irradiation with an unfiltered Hg lamp. This reduced the parent band totally. The bands showed a close similarity with those found for C_s $[Cr(CO)_4(py)]$. At the same time free

TABLE 2

U.v.-visible absorption bands (nm) of $[Cr(CO)_5(NMe_3)]$, $[Cr(CO)_5]$, and C_s $[Cr(CO)_4(NMe_3)]$

Assignments	$d\pi \rightarrow {}^*$(CO)	$d \rightarrow d$	$d \rightarrow d$
$[Cr(CO)_5(NMe_3)]$			
n-Hexane, room temperature	250	428	
Ar matrix, 10 K	246	419	
Xe matrix, 10 K	251	420	
$[Cr(CO)_5]$			
Ar matrix, 10 K	238	533	
Xe matrix, 10 K	245	494	
$C_s[Cr(CO)_4(NMe_3)]$			
Ar matrix, 10 K	239	346	*ca.* 506
Xe matrix, 10 K	246	346	480—500

TABLE 3

Infrared frequencies (cm^{-1}) of the photolysis products of [Cr(CO)$_5$(NMe$_3$)]

Assignments	ν(C–O) A_1	A'	E	A_1	A'	A'	A''
Cr(CO)$_5$ · · · Ar	2 092		1 966.0	*a*			
Cr(CO)$_5$ · · · NMe$_3$	*b*		1 959.5	*a*			
Cr(CO)$_5$ · · · Xe	2 085.6		1 957.9	*a*			
			1 954.0				
Cr(CO)$_5$ · · · NMe$_3$	*b*		1 951.0	*a*			
C_s Cr(CO)$_4$NMe$_3$ · · · Ar		2 033.2			1 918.2 [a]	1 906.0	1 891.4
C_s Cr(CO)$_4$NMe$_3$ · · · Xe		2 027.4			1 913.3 [a]	1 899.5	1 884.4
C_{4v} Cr(CO)$_4$NMe$_3$ · · · Ar	*b*		1 909.4				
C_{4v} Cr(CO)$_4$NMe$_3$ · · · Xe	*b*		1 900.6				
C_{3v} Cr(CO)$_4$NMe$_3$ · · · Xe [c]	2 014.6		1 892.5	1 874.7			
or C_{2v} Cr(CO)$_4$NMe$_3$ · · · Xe			1 889.0				

[a] Coinciding with parent bands. [b] Not observed. [c] Assignment dependent of the structure.

CO appeared at 2 138 cm^{-1} and in the region between 850 and 750 cm^{-1} only small intensity changes took place.*

In the u.v.–visible spectrum new absorptions were found for C_s [Cr(CO)$_4$(NMe$_3$)] at 239, 346, and 506 nm (see Figure 6). The latter band was not detected for the corresponding [Cr(CO)$_4$(py)] and [Cr(CO)$_4$(pyz)] complexes, because it was obscured by an absorption of [Cr(CO)$_5$] at 540 nm.[7]

The reaction was reversed by long-wavelength irradiation with λ = 546 nm and only partly with λ = 436 nm, which is in agreement with ref. 1. Table 3 gives the i.r. frequencies of the photolysis products of [Cr(CO)$_5$(NMe$_3$)].

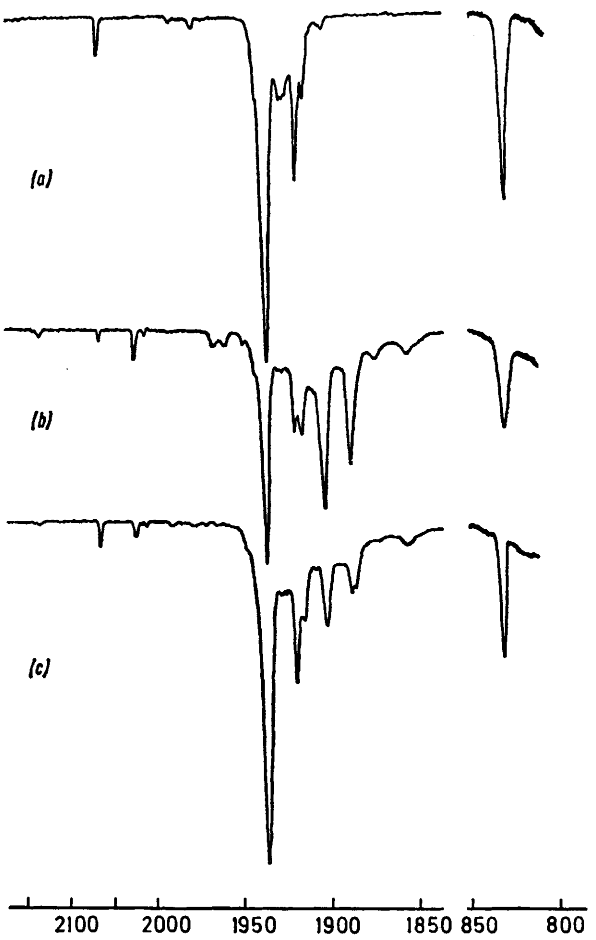

FIGURE 1 Infrared spectrum of [Cr(CO)$_5$(NMe$_3$)] in an Ar matrix at 10 K. (*a*) After deposition, (*b*) after 195 min photolysis with λ = 254 nm, and (*c*) after further photolysis with λ = 546 nm for 150 min

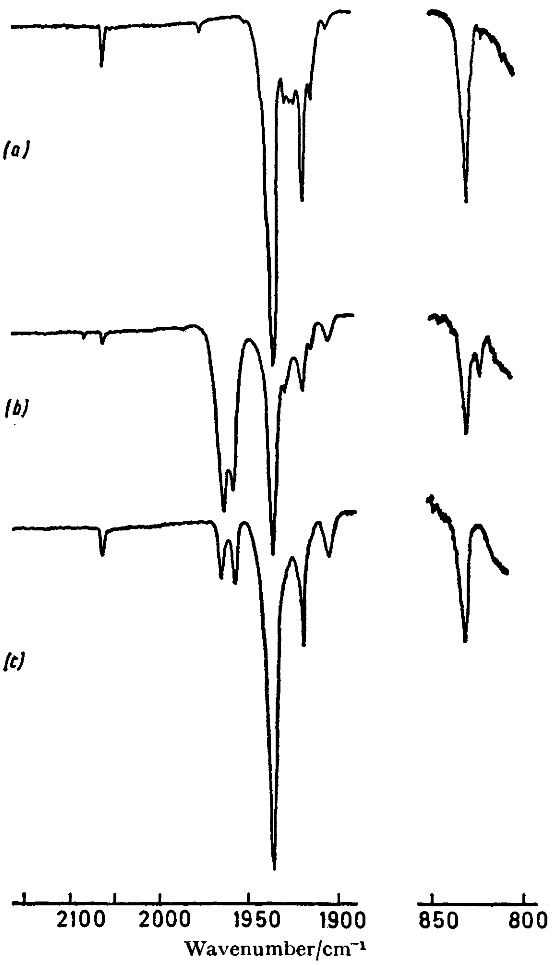

FIGURE 2 Infrared spectrum of [Cr(CO)$_5$(NMe$_3$)] in an Ar matrix at 10 K. (*a*) After deposition, (*b*) after 60 min photolysis with λ = 436 nm, and (*c*) after further photolysis with λ = 546 nm for 30 min

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* Very small [Cr(CO)$_5$] absorptions were detected near 1 960 cm^{-1} and besides these, weak bands were found at 1 877.7, 1 859, and in the region 1 810—1 830 cm^{-1}. These latter bands were due to lower carbonyl formation such as [Cr(CO)$_3$(NMe$_3$)] and [Cr(CO)$_2$-(NMe$_3$)] and were not attributed to [Cr(CO)$_4$] or [Cr(CO)$_3$] (ref. 13).

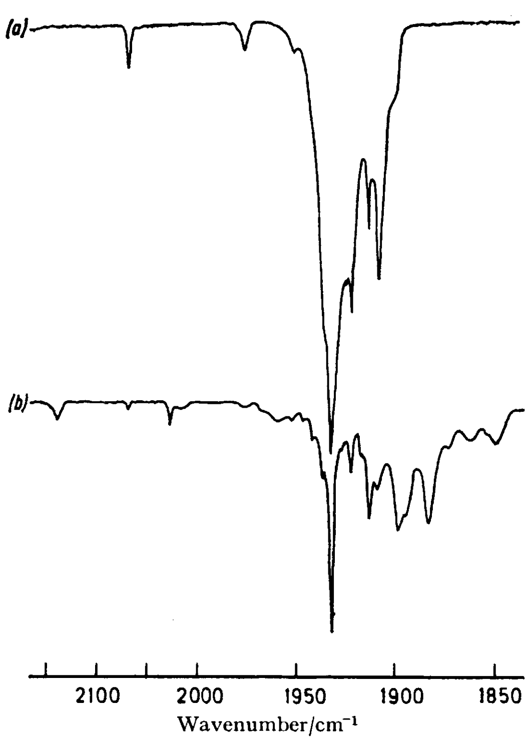


FIGURE 3 Infrared spectrum of [$Cr(CO)_5(NMe_3)$] in a Xe matrix at 10 K. (*a*) After deposition and (*b*) after 1 320 min photolysis with λ = 254 nm

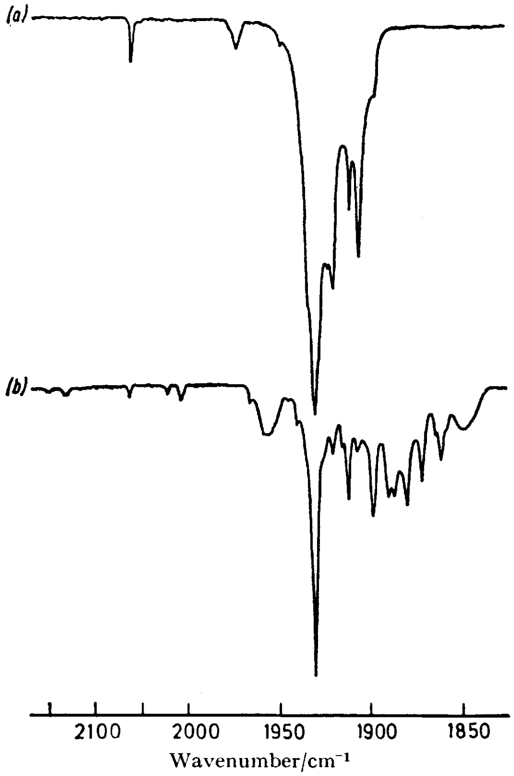


FIGURE 4 Infrared spectrum of [$Cr(CO)_5(NMe_3)$] in a Xe matrix at 40 K. (*a*) After deposition and (*b*) after 1 200 min photolysis with λ = 254 nm

Quite different results were obtained after irradiation with the wavelengths 366, 405, and 436 nm. Corresponding to the bands found for [$Cr(CO)_5$] after irradiation of [$Cr(CO)_6$] [14] three new bands were expected. However,

$$[Cr(CO)_5(NMe_3)] \underset{\lambda = 546\,nm}{\overset{\lambda = 366, 405, 436\,nm}{\rightleftharpoons}} [Cr(CO)_5] + NMe_3$$

two new CO vibrations could be observed at 2 092 and 1 966 cm^{-1}, of which the latter band was split. This splitting is caused by an interaction at the vacant coordination site (see below). The band at 1 936 cm^{-1} could not be detected because of overlapping bands.

Free NMe_3 could also be detected from a band at 824 cm^{-1} which appeared under signal-expansion conditions.

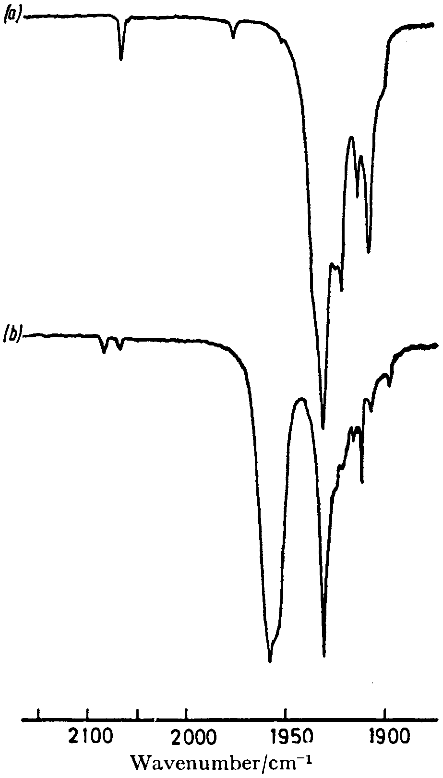


FIGURE 5 Infrared spectrum of [$Cr(CO)_5(NMe_3)$] in a Xe matrix at 40 K. (*a*) After deposition and (*b*) after 60 min photolysis with λ = 436 nm

A small band at 1 909.4 cm^{-1} closely corresponds to the band found for C_{4v} [$Cr(CO)_4(py)$] and is assigned to the formation of C_{4v} [$Cr(CO)_4(NMe_3)$]. The [$Cr(CO)_5$] bands disappeared completely after photolysis with λ = 546 nm. At the same time the 1 909.4 cm^{-1} band increased.

In the u.v.-visible absorption spectra two bands were detected, the 238 nm band assigned to the $\pi^*(CO) \leftarrow Cr(3d)$ charge-transfer transition and the 533 nm band due to a *d–d* transition (see Figure 7). While short-wavelength photolysis (λ = 229 and 254 nm) showed the formation of C_s [$Cr(CO)_4(NMe_3)$] and long-wavelength photolysis (λ = 366, 405, and 436 nm) yielded [$Cr(CO)_5$] and C_{4v} [$Cr(CO)_4(NMe_3)$] (small quantities), the intermediate wavelengths (313 and 334 nm) gave both. In this case the results differ from those found for [$Cr(CO)_5(py)$] and [$Cr(CO)_5(pyz)$], since for these complexes a ' turning point ' was found between 313 and 334 nm and for $[Cr(CO)_5(NMe_3)]$ this point lies between 334 and 366 nm.

Xenon Matrix, 10 *and* 40 K.—Photolysis of $[Cr(CO)_5(NMe_3)]$ in a Xe matrix at 10 K does not differ much from the photolysis in Ar matrices. For C_s $[Cr(CO)_4(NMe_3)]$ four new bands are found after short-wavelength photolysis with $\lambda = 229$ and 254 nm (2 027.4, 1 913.3, 1 899.5, and 1 884.4 cm^{-1}). Apart from these bands very small absorptions of lower co-ordinated complexes were detected at 1 864.5, 1 853, and in the region between 1 825 and 1 800 cm^{-1}. Ejection of the ligand NMe_3 only occurred in a small percentage of the sample, which is deduced from the weak bands of $[Cr(CO)_6]$ at about 1 958 cm^{-1}. In going from Ar to Xe the quantum yields decreased by a factor of three to four. The same holds for the reverse reaction with $\lambda = 546$ nm (as in ref. 1).

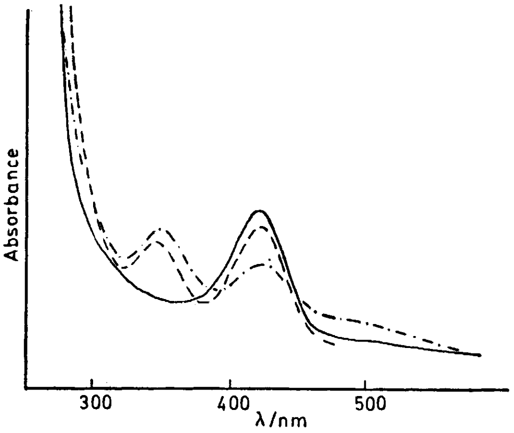


FIGURE 6 U.v.-visible absorption spectrum of $[Cr(CO)_5(NMe_3)]$ in an Ar matrix at 10 K. After deposition (—), after 90 min photolysis with $\lambda = 229$ nm (— • —), and after further photolysis with $\lambda = 546$ nm for 75 min (— — —)

However, when the temperature of the Xe matrix was raised to 40 K, a completely different species was obtained after irradiation with $\lambda = 229$ and 254 nm. New bands were detected at 2 014.6, 1 890.7,* 1 874.7, 1 864.5, and 1 853 cm^{-1}. The latter two were also detected after irradiation at 10 K. These bands cannot be due to lower carbonyl formation such as $[Cr(CO)_4]$ and $[Cr(CO)_3]$ after ejection of both CO and NMe_3. In a separate experiment $[Cr(CO)_6]$ was photolyzed with $\lambda = 229$ nm in a Xe matrix. Comparing these photoproduct bands with the bands found after photolysis of $[Cr(CO)_5(NMe_3)]$ we concluded that those at 1 864.5 and 1 853 cm^{-1} are not due to $[Cr(CO)_4]$ or $[Cr(CO)_3]$. We tentatively attribute these bands to the formation of $[Cr(CO)_3(NMe_3)]$ and $[Cr(CO)_2(NMe_3)]$. The unassigned bands at 2 014.6, 1 890.7, and 1 874.7 cm^{-1} will be discussed below. Photolysis of $[Cr(CO)_5(NMe_3)]$ with u.v. light in Xe at 40 K not only resulted in the formation of a new species, but also a considerable increase in quantum yield for $[Cr(CO)_5]$ formation.

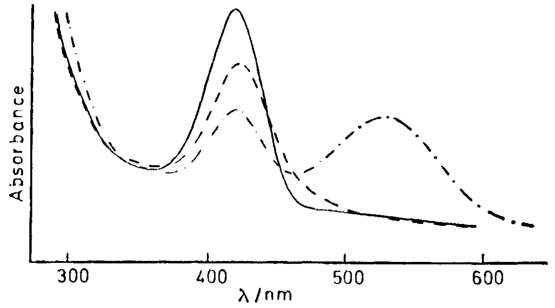
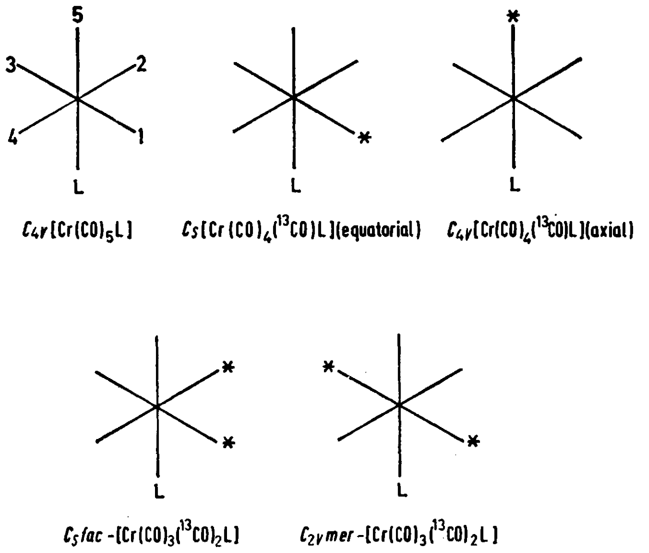


FIGURE 7 U.v.-visible absorption spectrum of $[Cr(CO)_5(NMe_3)]$ in an Ar matrix at 10 K. After deposition (—), after 90 min photolysis with $\lambda = 405$ nm (— • —), and after further photolysis with $\lambda = 546$ nm for 95 min (— — —)

The reverse reaction was slowly accomplished by irradiation with $\lambda = 436$ and $\lambda = 546$ nm.

Photolysis of $[Cr(CO)_5(NMe_3)]$ in a Xe matrix with $\lambda = 436$



C_{4v}[Cr(CO)$_5$L] C_s[Cr(CO)$_4$(^{13}CO)L](equatorial) C_{4v}[Cr(CO)$_4$(^{13}CO)L](axial)

C_s*fac*-[Cr(CO)$_3$(^{13}CO)$_2$L] C_{2v}*mer*-[Cr(CO)$_3$(^{13}CO)$_2$L]

FIGURE 8 Observed $[Cr(CO)_x(^{13}CO)_{5-x}L]$ complexes (L = NMe_3, * = ^{13}CO)

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* Split band: high resolution spectrum 1 892.5 and 1 889.0 cm^{-1}.

nm at 10 K and 40 K resulted in the ejection of NMe_3 and the formation of $[Cr(CO)_5]$, concluded from the new ν(CO) stretching bands at 2 085.6 and 1 957.9 cm^{-1}.

^{13}CO *Labelling Force-field Calculations*.—When ^{13}CO was allowed to react with the short-wavelength photolysis products of $[Cr(CO)_5(NMe_3)]$ a mixture of five isomers were found after purification: $[Cr(CO)_5(NMe_3)]$, $[Cr(CO)_4(^{13}CO)(NMe_3)]$ (equatorial), $[Cr(CO)_4(^{13}CO)(NMe_3)]$ (axial), *fac*-$[Cr(CO)_3(^{13}CO)_2(NMe_3)]$, and *mer*-$[Cr(CO)_3(^{13}CO)_2(NMe_3)]$. The latter two were obtained in a much lower yield (see Figure 8).

TABLE 4

Observed and calculated frequencies (cm^{-1}) of $[Cr(CO)_x(^{13}CO)_{5-x}(NMe_3)]$ in Ar at 10 K [a]

Molecule					
$[Cr(CO)_5(NMe_3)]$	2 072.3	1 978.0	1 939.4	1 939.4	1 923.2
	(2 071.9)	(1 978.3)	(1 939.4)	(1 939.4)	(1 922.5)
$[Cr(CO)_4(^{13}CO)(NMe_3)]$	2 063.4	1 972.0	1 939.4 [b]	1 924.6	1 907.6
(equatorial)	(2 063.8)	(1 971.3)	(1 939.3)	(1.923.9)	(1 908.9)
$[Cr(CO)_4(^{13}CO)(NMe_3)]$	*c*	1 978.0 [d]	1 939.4 [b]	1 939.4 [b]	1 881.5
(axial)	(2 068.8)	(1 978.4)	(1 939.4)	(1 939.4)	(1 882.4)
fac-$[Cr(CO)_3(^{13}CO)_2(NMe_3)]$	2 054.0	1 966.0	1 924.6 [d]	1 910.2	1 907.6 [d]
	(2 054.3)	(1 966.1)	(1 925.2)	(1 909.7)	(1 907.8)
mer-$[Cr(CO)_3(^{13}CO)_2(NMe_3)]$	2 054.0 [d]	*c*	1 939.4 [b]	1 918.4 [d]	1 896.1
	(2 055.6)	(1 953.1)	(1 939.3)	(1 918.9)	(1 895.9)

The refined force constants are: $k_1 = 1\ 583.1$, $k_5 = 1\ 512.8$, $k_{12} = 33.3$, $k_{15} = 33.2$, and $k_{13} = 64.1$ Nm^{-1}.

[a] Calculated values are given in parentheses. [b] Coinciding bands. [c] Not detected. [d] Obscured band.

$[Cr(CO)_5(NMe_3)]$. To assign the observed i.r. frequencies of this mixture force-field calculations have to be performed. The frequencies of $[Cr(CO)_5(NMe_3)]$ were used to calculate the frequencies of the possible isomers. Initial force constants were chosen with the approximation that $k_{12} = \frac{1}{2}\ k_{13}$. This set of force constants predicted most bands within one wavenumber. The initial force constants were refined with the aid of the observed wavenumbers of all isotopes and an iterative computer program. Least-squares refinement yielded the final set of force constants as given in Table 4.

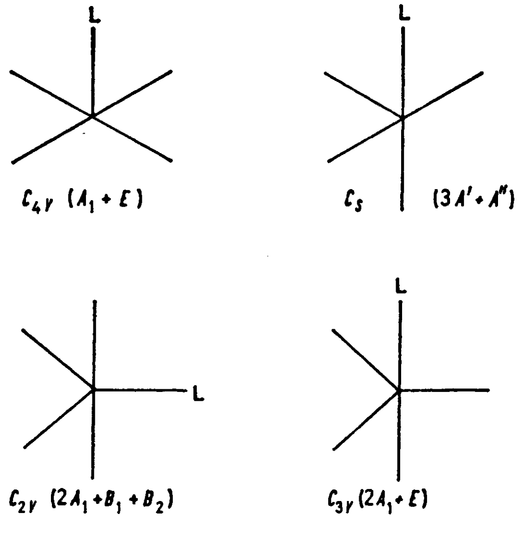

FIGURE 9 Possible structures for $[Cr(CO)_4L]$ complexes: square-pyramidal structures C_{4v} and C_s, trigonal-bipyramidal structures C_{2v} and C_{3v} (L = NMe_3)

$[Cr(CO)_4(NMe_3)]$. Short-wavelength photolysis (λ = 229 nm) of the labelled $[Cr(CO)_5(NMe_3)]$ complexes in Ar at 10 K yielded a mixture of different $[Cr(CO)_4(NMe_3)]$ species. Figure 9 shows the possible structures for unlabelled $[Cr(CO)_4(NMe_3)]$ complexes.

Matrix splittings in the spectra of the unlabelled species could be excluded, since the bands were too separated. In this case the number of bands points to two possible structures, C_s and C_{2v}. The set of initial force constants for the C_s isomer were chosen according to Poliakoff [1] with $k_{23} = k_{25} = k_{35} = \frac{1}{2}k_{24}$ (see Figure 10). With these assumptions the wavenumbers for the labelled C_s $[Cr(CO)_4(NMe_3)]$ complexes were predicted and compared with the observed frequencies. Least-squares refinement including all the isotopic frequencies gave the set of force constants and the predicted frequencies as compiled in Table 5. Although force-constant calculations on the C_{2v} structure could also fit the observed frequency data, we could conclude on arguments of the intensities of the bands, that the C_s species is the product of the short-wavelength photolysis of $[Cr(CO)_5(NMe_3)]$.*

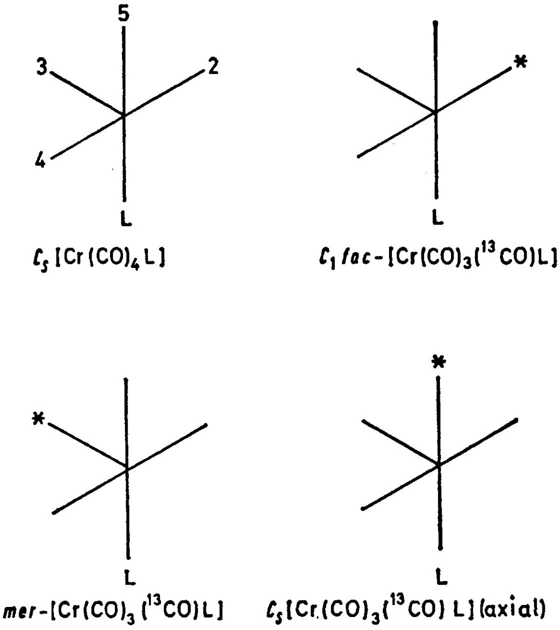

FIGURE 10 Observed $[Cr(CO)_3(^{13}CO)L]$ complexes (L = NMe_3, * = ^{13}CO). Bis labelled complexes were not detected

The same procedure was used for the data obtained in Xe

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* Predicted order of intensities for C_{2v} structure: A_1(w), B_1(s), A_1(mw), B_2(s); C_s structure: A'(w), A'(mw), A'(s), A''(m).

matrices at 10 K for labelled $[Cr(CO)_5(NMe_3)]$ and C_s $[Cr(CO)_4(NMe_3)]$. At 40 K in Xe however, new bands were detected after short-wavelength photolysis at 2 014.6, 1 890.7 (split into 1 892.5 and 1 889.0), and 1 874.7 cm^{-1}. From the number of bands no conclusions could be drawn about one of the two other possible structures, C_{2v} $(2A + B_1 + B_2)$ and C_{3v} $(2A_1 + E)$. Our hope, that ^{13}CO labelling could distinguish between these structures, was not fulfilled because of the many isotopes of $[Cr(CO)_5(NMe_3)]$ and the low quantum yields in Xe. Proof of this structure has to wait for experiments with $[Cr(CO)_5(pip)]$ (pip = piperidine), since with this compound more stereospecific labelling is possible.[9]

At this point it is worth noticing that in Ar small traces of C_{2v} or C_{3v} $[Cr(CO)_4(NMe_3)]$ were also detected, as evident from the very weak 2 021.5 cm^{-1} band.

TABLE 5

Observed and calculated frequencies (cm^{-1}) of C_s $[Cr(CO)_3(^{13}CO)(NMe_3)]$ in Ar at 10 K [a]

Molecule				
C_s $[Cr(CO)_4(NMe_3)]$	2 033.2	1 918.2	1 906.0	1 891.4
	(2 033.2)	(1 918.3)	(1 906.3)	(1 891.4)
C_1 *fac*-$[Cr(CO)_3(^{13}CO)(NMe_3)]$	2 020.9	*b*	1 891.4 [c]	1 878.8
	(2 020.6)	(1 916.2)	(1 891.4)	(1 877.7)
C_s *mer*-$[Cr(CO)_3(^{13}CO)(NMe_3)]$	2 027.7	*b*	1 906.0 [c]	1 860.5
	(2 027.9)	(1 911.8)	(1 906.5)	(1 860.5)
C_s $[Cr(CO)_3(^{13}CO)(NMe_3)]$ (axial)	2 027.7 [c]	1 910.2 [c]	1 906.0 [c]	*d*
	(2 028.0)	(1 910.1)	(1 906.4)	(1 862.0)

The refined force constants are: $k_2 = 1\,541.1$, $k_3 = 1\,492.2$, $k_5 = 1\,494.4$, $k_{23} = 42.8$, $k_{24} = 73.1$, $k_{25} = 41.4$, and $k_{35} = 48.3$ Nm^{-1}.

[a] Calculated values are given in parentheses. [b] Obscured bands. [c] Coinciding bands. [d] Not detected.

DISCUSSION

The explanation of the photochemistry of Group 6 substituted carbonyls has until now only been possible using a one-electron *d*-orbital energy diagram, which has proved to be successful.[5,7] From the photoelectron spectra (p.e.s.) of $[Cr(CO)_5(NMe_3)]$ the energy difference $\Delta\pi$ between the occupied orbitals b_2 and e is measured as 2 500 cm^{-1}. The u.v.–visible absorption spectrum shows the lowest energy *d–d* transition at 23 900 cm^{-1} (419 nm). There has been some controversy about the nature of this transition. Magnetic circular dichroism (m.c.d.) spectra[15-17] showed however, that the lowest unoccupied orbital has predominant d_{z^2} character. This means that the *d–d* transition is ${}^1E_a(b_2{}^2e^3a_1{}^1)\leftarrow{}^1A_1(b_2{}^2e^4)$. From p.e.s. and u.v.–visible data we deduced that $\Delta\sigma = \Delta(d_{x^2-y^2} - d_{z^2})$ increases going from pyridine and pyrazine to NMe_3. Besides, we found that the rate of non-radiative decay from $d_{x^2-y^2}$ to d_{z^2} is related to $\Delta\sigma$,[5,7] so a faster decay is expected for the pyridine and pyrazine complexes than for $[Cr(CO)_5(NMe_3)]$. In accordance with this, different photochemical behaviour is detected for pyridine and pyrazine to that of NMe_3. For $[Cr(CO)_5(py)]$ and $[Cr(CO)_5(pyz)]$ a mixture of $[Cr(CO)_5]$ and C_s $[Cr(CO)_4L]$ (L = *N*-donor) is always observed, whereas $[Cr(CO)_5(NMe_3)]$ is converted into either $[Cr(CO)_5]$ or C_s $[Cr(CO)_4(NMe_3)]$, depending on the wavelength of excitation.

That the position of the d_{z^2} orbital is shifted to lower energy in going from pyridine and pyrazine to NMe_3 is confirmed by the shift of the 'turning point' {$[Cr(CO)_5(NMe_3)]$ between 334 and 366 nm, $[Cr(CO)_5(py)]$ or $[Cr(CO)_5(pyz)]$ between 313 and 334 nm}. The influence of $\Delta\sigma$ is also apparent from the quantum yield of C_s $[Cr(CO)_4L]$ at short-wavelength excitation, which is largest for L = NMe_3. The same holds for the quantum yield after long-wavelength irradiation; for L = NMe_3 the formation of $[Cr(CO)_5]$ is increased. This is in accordance with the solution results of Wrighton[18] who found an increase of luminescence lifetime going from $[W(CO)_5(py)]$ to $[W(CO)_5L]$ (L = amine). This long lifetime of $[Cr(CO)_5(NMe_3)]$ explains the occurrence of small quantities of C_{4v} $[Cr(CO)_4(NMe_3)]$. Normally NMe_3 rupture is far more favoured than CO *trans* ejection. If the lifetime of the excited state is long, the chances of detecting C_{4v} $[Cr(CO)_4(NMe_3)]$ as well is increased. In co-operation with Dr. A. J. Rest attempts will be made to measure the emission spectra and to calculate the lifetimes of various $[M(CO)_5L]$ complexes (M = Cr, Mo, or W; L = *N*-donor or *P*-donor).[19]

Matrix Effects.—After photolysis of $[Cr(CO)_5(NMe_3)]$ with λ = 366, 405, or 436 nm in an Ar matrix not only one broad *E* band of $[Cr(CO)_5]$ was detected but a splitting into two frequencies 1 966.0 and 1 959.5 cm^{-1}. This splitting was not detected after photolysis of $[Cr(CO)_5(PCl_3)]$, $[Cr(CO)_5(py)]$, and $[Cr(CO)_5(pyz)]$.

The diameter of Ar atoms is *ca.* 3.76 Å.[20] From crystallographic data[21] a 'diameter' for NMe_3 can be estimated and is calculated to be 5.1 Å. In comparison with pyridine and pyrazine, NMe_3 can more easily occupy a substitutional site in the matrix and therefore two forms of $[Cr(CO)_5]$ are generated, $Cr(CO)_5 \cdots Ar$ (1 966.0) and $Cr(CO)_5 \cdots NMe_3$ (1 959.5). In a Xe matrix (size 4.3 Å) this effect is also seen at 10 K, $Cr(CO)_5 \cdots Xe$ (1 957.9) and $Cr(CO)_5 \cdots NMe_3$ (1 951.0). At 40 K almost a single band was detected, probably caused by a decrease of the rigidity at higher temperatures, making it possible for NMe_3 to occupy sites in the second co-ordination sphere of the complex. It is worth noting that there are two values found for $Cr(CO)_5 \cdots NMe_3$ in Ar and Xe. This effect was also seen in mixed-matrix experiments:[22] Ne doped with 2% Xe : 1 966 cm^{-1} due to $Cr(CO)_5 \cdots Xe$; Ar doped with 2% Xe : 1 963 cm^{-1} due to $Cr(CO)_5 \cdots Xe$, which shows, that the second co-ordination sphere of the chromium complex also plays a role in the frequency shifts of the complexes.

Furthermore, a *d–d* transition in the absorption spectrum due to $Cr(CO)_5 \cdots NMe_3$ was expected. We found, however, that this band did not have a Gaussian form, indicating the presence of more than one $[Cr(CO)_5]$ fragment.

Quantum yields are lower in a Xe matrix than in an Ar one at the same temperature. Luminescence studies [23] have shown, that heavy atoms such as Xe are able to quench the fluorescence by external spin–orbit coupling; lifetimes of the excited states are decreased and this is a possible explanation for the lower quantum yields in Xe compared to Ar. The work of Gibson and Rest [24] on C_6H_6 in several matrices supports this.

Temperature Effects.—Photolysis of $[Cr(CO)_5(NMe_3)]$ in Xe at 40 K with $\lambda = 229$ and 254 nm resulted in the formation of a new $[Cr(CO)_4(NMe_3)]$ species, the C_{2v} or C_{3v} isomer. When C_s $[Cr(CO)_4(NMe_3)]$ isomerizes into C_{2v} or C_{3v} symmetry a small bending of CO groups has to occur. This bending is hindered at 10 K, because then only very small bands of C_{2v} or C_{3v} were found.

Short-wavelength irradiation of $[Cr(CO)_5(NMe_3)]$ at 40 K in Xe not only yielded new complexes but also an increase in pentacarbonyl formation. This effect is both explained by a rigidity decrease and by a probable increase of internal conversion between the excited $d_{x^2-y^2}$ and d_{z^2} states.

Formation of C_{4v} $[Cr(CO)_4(NMe_3)]$.—When $[Cr(CO)_5(NMe_3)]$ is irradiated with $\lambda = 366$, 405, or 436 nm in Xe or Ar not only $[Cr(CO)_5]$ is detected, but also a weak band, which is assigned to C_{4v} $[Cr(CO)_4(NMe_3)]$ formation. Reversing the reaction with $\lambda = 546$ nm, not only causes an increase in parent bands, but also a small increase in the C_{4v} $[Cr(CO)_4(NMe_3)]$ photoproduct. In the $[Cr(CO)_5(py)]$ and $[Cr(CO)_5(pyz)]$ complexes irradiation with $\lambda = 546$ nm resulted in isomerization of the *cis* complex, but this effect was not detected with $[Cr(CO)_5(NMe_3)]$. Therefore the small increase of C_{4v} $[Cr(CO)_4(NMe_3)]$ is not due to isomerization but involves another mechanism. Because of the long lifetime of the excited state, the possibility of detecting both $[Cr(CO)_5]$ and C_{4v} $[Cr(CO)_4(NMe_3)]$ is increased. When the reaction is reversed as the result of subsequent long-wavelength irradiation, softening of the matrix occurs permitting diffusion of CO and hence more C_{4v} $[Cr(CO)_4(NMe_3)]$.

Conclusions.—Photolysis of $[Cr(CO)_5L]$ complexes in which L is a good σ donor with no π-acceptor capabilities results in high quantum yields of C_s $[Cr(CO)_4L]$, after short-wavelength photolysis.

Temperature-dependent photochemistry is a new aspect in matrix-isolation photolysis, leading to formation of new complexes and different relative quantum yields.

The difference in quantum yields between $[Cr(CO)_5(NMe_3)]$ and $[Cr(CO)_5(py)]$ or $[Cr(CO)_5(pyz)]$ after photolysis points to a decrease of excited-state lifetimes in going from NMe_3 to pyridine or pyrazine.

In going from Ar to a Xe matrix the lifetimes of the excited states decrease.

Luminescence studies at various temperatures both in solution and matrices are necessary to explain the different photochemical behaviour in solution and in matrices.

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