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Photochemistry of $Cr(CO)_5PMe_3$ in Ar and CH_4 Matrices at 10 K

G. BOXHOORN, G. C. SCHOEMAKER, D. J. STUFKENS and A. OSKAM*

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

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Photolysis of $Cr(CO)_5PMe_3$ in argon and methane matrices at 10 K irradiated with the wavelengths 229–366 nm resulted in the formation of $Cr(CO)_4$-PMe_3 isomers and CO. The reaction is only partly reversed after irradiation with λ = 436, 546 and 578 nm because of isomerization of the $Cr(CO)_4PMe_3$ isomers. The photochemical behaviour is tentatively explained by means of a one electron d*-orbital energy diagram.*

Introduction

The solution photochemistry of $M(CO)_5N$-donor complexes has been extensively studied [1–3], whereas that of $M(CO)_5P$-donor complexes is only reported in a few articles [2, 4, 5]. Black *et al.* reported the formation of *cis*-$Mo(CO)_4(PCy_3)$(vacancy) and *trans*-$Mo(CO)_4(PCy_3)$(vacancy) (Cy = cyclohexyl) after irradiation (λ > 305 nm) of $Mo(CO)_5PCy_3$ in a hydrocarbon glass at 77 K [4]. Furthermore, photolysis with λ > 420 nm resulted in a conversion of the *trans*-isomer into the *cis*-isomer. In solutions at room temperature both efficient carbon monoxide release and phosphorus ligand substitution were detected for $W(CO)_5L$ (L = PPh_3, PBr_3, PH_3, $P(n\text{-}Bu)_3$) after photolysis with λ = 405 nm [2]. For $W(CO)_5PCl_3$ however, only efficient W–C bond rupture was observed with a low yield of PCl_3 substitution. No explanation was given for this different photochemical behaviour of the $W(CO)_5$-PCl_3 complex. Darensbourg *et al.* studied the substitution photolysis of $Mo(CO)_5PPh_3$ in the presence of ^{13}CO and both *cis* and *trans* labelled $Mo(CO)_4$-$(^{13}CO)PPh_3$ complexes were observed after photolysis with the wavelengths 313 and 366 nm [5]. A low quantum efficiency Ph_{366} = 0.11 was found for unique ligand loss. Besides this, photolysis of either pure *cis* or *trans* $Mo(CO)_4(PPh_3)_2$ afforded, in the presence of ^{13}CO primarily *cis*-$Mo(CO)_4(^{13}CO)PPh_3$, leading to the conclusion that the C_{4v} intermediate of $Mo(CO)_4PPh_3$ isomerizes to the C_s structure. In our laboratory the photochemical behaviour of $M(CO)_5L$ complexes (M = Cr, Mo, W: L = PCl_3, NMe_3, piperidine, pyridine and pyrazine) was studied in matrices at 10 K [6–10], as was also done by Rest [11]. Evidence was found for the wavelength dependent formation of $M(CO)_5$ and $M(CO)_4L$ complexes. The structure of this latter complex, proved by ^{13}CO labelling and force field calculations was found to be C_s [9].

In this article we present the photolysis of $Cr(CO)_5PMe_3$ in Ar and CH_4 matrices at 10 K with irradiation into the absorption bands of this pentacarbonyl complex at wavelengths 229, 254, 280, 313, 334 and 366 nm.

Experimental

$Cr(CO)_5PMe_3$ was prepared by adding $AgNO_3$-PMe_3 to $[Cr(CO)_5Cl]Et_4N$ in a CH_2Cl_2 solution, using the method of Connor [12]. The purity of the complex was checked by infrared spectroscopy and by elemental analysis. The equipment used to achieve the cryogenic temperatures has been described elsewhere, together with the photolysis sources and filters [6, 7, 9]. Infrared spectra were recorded on a Beckman IR-4250 spectrometer with a Ge filter in the sample beam. This filter was used to prevent photolysis by the Nernst glower and had a maximum transmittance between 2200 and 1800 cm^{-1}. UV–visible spectra were measured on a Cary 14 spectrometer. The complex was deposited slowly from a sample compartment in a stream of matrix gas, as was described by Rest [11]. The sample compartment was cooled to a temperature between –40 and –20 °C in order to prevent fast deposition, which would lead to bad isolation. In contrast to other $M(CO)_5L$ complexes no decomposition into $Cr(CO)_6$ was detected for the $Cr(CO)_5PMe_3$ complex. Argon with a purity of 99.9997% and methane with a purity of 99.9995% were employed.

Results

Infrared and UV–Visible Spectra

The carbonyl region of the infrared spectra of $Cr(CO)_5PMe_3$ shows three main bands, both in

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*Author to whom correspondence should be addressed.

TABLE I. Infrared Frequencies of $Cr(CO)_5PMe_3$ in cm^{-1}.

Assignments	A_1^2	B_1	A_1^1	E	$\nu(^{13}CO)$
$Cr(CO)_5PMe_3$, n-hexane, RT	2066.2	--	1951.3	1939.0	1909.6
$Cr(CO)_5PMe_3$, Ar, 10 K	2067.9	1979.4	1955.4	1944.6 1941.4[a] 1931.0	1911.0
$Cr(CO)_5PMe_3$, CH_4, 10 K	2064.1	1976.3	1948.3	1942.4 1939.9 1936.8[a] 1930.3	1908.1

[a] Most intensive band.

solutions at room temperature and in matrices at 10 K. These bands at *ca.* 2070, 1950 and 1940 cm^{-1} are in agreement with the expectation for a compound with local C_{4v} symmetry and are assigned to A_1^2, A_1^1 and E respectively. Besides these main bands, several matrix splittings are detected in argon and methane matrices at 10 K, together with a weak band at about 1910 cm^{-1} due to the ^{13}CO complex in natural abundance. The data obtained from n-hexane solution and argon and methane matrices are compiled in Table I.

In the absorption spectra of $Cr(CO)_5PMe_3$ two intense bands are observed bewteen 220 and 250 nm. These bands are due to an intraligand and $M \rightarrow \pi^*(CO)$ transition respectively. Only one ligand field band was detected at about 330 nm. In Table II the data of the absorption spectra in n-hexane and in an argon matrix are tabulated.

TABLE II. UV–Visible Absorption Maxima of $Cr(CO)_5PMe_3$ in nm.

Assignments	Intraligand	$M \rightarrow \pi^*(CO)$	$d \rightarrow d$
$Cr(CO)_5PMe_3$, n-hexane, RT	224	248	333
$Cr(CO)_5PMe_3$, Ar, 10 K	219	245	329

Photochemistry

Photolysis of $Cr(CO)_5PMe_3$ both in argon and methane matrices at 10 K with the wavelengths 229, 254, 280, 313, 334 and 366 nm using an unfiltered mercury lamp always resulted in free CO and several new bands. By comparison with the $M(CO)_4$ N-donor complexes, we assign the 2034.6 (A′), 1931.0 (A′), 1917.1 (A″) and 1879.8 (A′) cm^{-1} bands (Ar matrix) to the formation of the $Cr(CO)_4PMe_3$ complex with C_s symmetry [7, 9] (see Table III). The number of separate bands in this region (> 6) excludes the formation of only one $Cr(CO)_4PMe_3$ species. At this moment we cannot definitely assign the other bands. However, after further photolysis with $\lambda = 436$ nm all bands of the $Cr(CO)_4PMe_3$ isomers in an argon matrix decreased, with the exception of the band at 1894.0 cm^{-1}. This band increased and we tentatively assign this latter band to the formation of the C_{4v} isomer of $Cr(CO)_4PMe_3$, in agreement with the results obtained for $Cr(CO)_4$ N-donor complexes. In a methane matrix the 1918.2 and 1872.4 cm^{-1} bands increased, ($\lambda = 436$), probably as a result of the formation of a $Cr(CO)_4PMe_3$ isomer with C_{2v} or C_{3v} symmetry. The same was found in an argon matrix after further photolysis with $\lambda = 546$ nm. Irradiation with this wavelength increased the parent bands, together with the bands at 2021.4, 1891.7 and 1871.7 (w) cm^{-1}. We intend to resolve the mechanism of the isomerization processes by ^{13}CO labelling. A similar isomerization behaviour was found for the $W(CO)_5PMe_3$ complex [14].

Besides the $Cr(CO)_4PMe_3$ isomers lower carbonyl fragments such as $Cr(CO)_3PMe_3$ were detected in the region between 1860 and 1830 cm^{-1}.

In an Ar matrix no $Cr(CO)_5$ was detected, except after extended photolysis (more than 1300 minutes) with light with the wavelength $\lambda = 254$ nm. Even then the most intense (E) mode of $Cr(CO)_5$, *i.e.* the 1966

TABLE III. Infrared Frequencies of $Cr(CO)_4PMe_3$ in cm^{-1}.

C_s $Cr(CO)_4PMe_3$, Ar	2034.6	1931.0	1917.1	1911 (sh)	1884 (sh)	1879.8
C_s $Cr(CO)_4PMe_3$, CH_4	2028.9	1926.7	1910.9	1908.2	1877.4	1873.3(sh)
C_{4v} $Cr(CO)_4PMe_3$, Ar					1894.0	
C_{4v} $Cr(CO)_4PMe_3$, CH_4					1889.5	
C_{2v} or C_{3v} $Cr(CO)_4PMe_3$, Ar	2021.4		1891.7(w)	1871.7(w)		
C_{2v} or C_{3v} $Cr(CO)_4PMe_3$, CH_4	2015.8	1918.2		1872.4		

cm^{-1} band, was very weak [13]. The intensity of this band was enhanced in a methane matrix after photolysis, but still remained very weak. No frequencies of Cr(CO)$_4$ were detected. In Figs. 1 and 2 the photolysis of Cr(CO)$_5$PMe$_3$ in an argon and in a methane matrix with an unfiltered mercury lamp is presented, together with the reverse reactions after irradiation with λ = 546 and λ = 436 nm respectively.

In the UV–visible absorption spectrum, the parent bands of the isolated Cr(CO)$_5$PMe$_3$ complex decreased after photolysis with an unfiltered mercury lamp. At the same time new bands were detected in the region between 380 and 650 nm. The bands were very broad and weak maxima were found at about 390, 440, 500

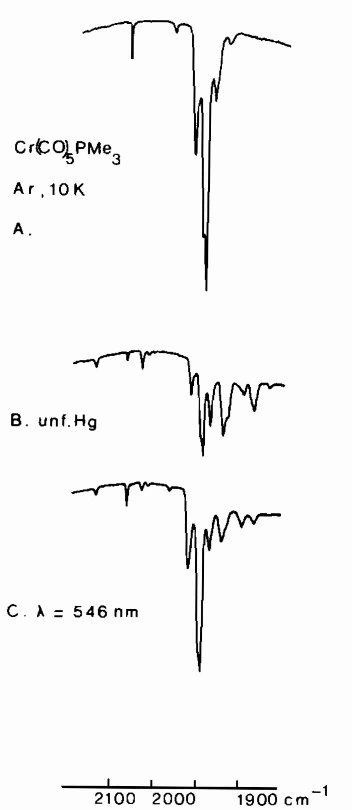

Fig. 1. Infrared spectrum of Cr(CO)$_5$PMe$_3$ in an Ar matrix at 10 K. A, after deposition; B, after 5 min. photolysis with an unfiltered Hg lamp; C, after 100 min. further photolysis with λ = 546 nm.

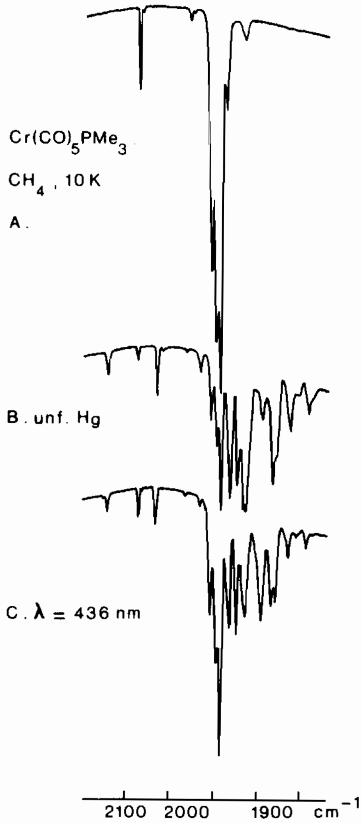

Fig. 2. Infrared spectrum of Cr(CO)$_5$PMe$_3$ in a CH$_4$ matrix at 10 K. A, after deposition; B, after 5 min. photolysis with an unfiltered Hg lamp; C, after 170 min. further photolysis with λ = 436 nm.

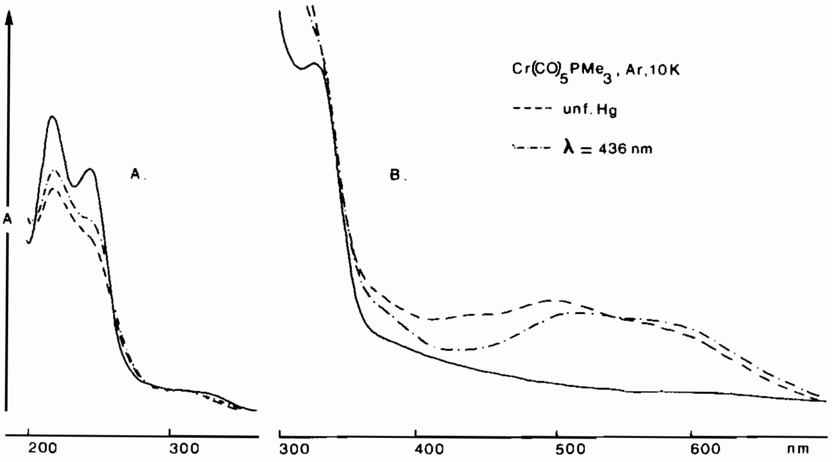

Fig. 3. UV–Visible absorption spectrum of Cr(CO)$_5$PMe$_3$ in an Ar matrix at 10 K. A, after a short deposition time; B, after a long deposition time (—— after deposition; – – – after photolysis with an unfiltered Hg lamp; – · – after photolysis with λ = 436 nm).

and 600 nm. Further photolysis with λ = 436 nm decreased the intensity of the 440 nm band and the 600 nm band increased simultaneously together with the parent bands. Assignments of these bands are not yet possible, but from the number of new absorption bands we can again conclude that more than one $Cr(CO)_4PMe_3$ isomer is formed. In Fig. 3 the UV–visible absorption spectrum of $Cr(CO)_5PMe_3$ in an argon matrix at 10 K is presented before and after photolysis, together with the reverse reaction.

Discussion

The photochemical behaviour of $Cr(CO)_5PMe_3$ in matrices at 10 K is to a certain extent comparable with the photolysis of $Mo(CO)_5PPh_3$ in tetrahydrofuran at room temperature [5]. For this latter complex a high quantum efficiency of CO loss was detected (Ph_{366} = 0.58), resulting in the formation of *cis* and *trans* complexes. Furthermore, a low quantum yield was measured for the unique ligand loss (Ph_{366} = 0.11). In contrast for $W(CO)_5PH_3$ the quantum yield for the formation of $W(CO)_6$ proved to be 0.65 in cyclohexane at room temperature [2]. These results show that general conclusions about the photochemical behaviour of $M(CO)_5L$ complexes cannot easily be drawn. Besides this, on going from solutions to hydrocarbon glasses at 77 K and to matrices at 10 K differences are found both in the photochemical behaviour [2, 6, 7, 10, 15] and in the radiative and non-radiative decays of the excited complexes [16]. These contradictions lead to the conclusion that every complex must be discussed separately.

For $Cr(CO)_5PMe_3$ formation of primarily the $Cr(CO)_4PMe_3$ isomers was detected, with a low yield of $Cr(CO)_5$. The results indicate that primarily the x- and y-axis are labilized, leading to the formation of C_s $Cr(CO)_4PMe_3$. The formation of the C_{2v}, C_{3v} or C_{4v} isomers of $Cr(CO)_4PMe_3$ is a result of either isomerization of the C_s isomer or of labilization along the z-axis. This labilization will generate $Cr(CO)_5$ as the main product, although C_{4v} $Cr(CO)_4PMe_3$ formation cannot be excluded.

There is a marked difference in the photochemical behaviour of $Cr(CO)_5PMe_3$ and $Cr(CO)_5PCl_3$ in argon matrices at 10 K. After irradiation into the absorption bands, the latter compound yielded only $Cr(CO)_5$ and PCl_3. This different behaviour can be explained by the d-orbital energy diagram of $M(CO)_5L$ complexes, which is derived from the combination of PES, UV–visible absorption and MCD (magnetic circular dichroism) data [6, 7, 9, 10, 17–19]. In the PE-spectrum of $Cr(CO)_5PCl_3$ no splitting of the occupied b_2 and e orbitals was detected [17] in contrast to $Cr(CO)_5PMe_3$ for which a splitting of 1129 cm^{-1} was observed [20]. Furthermore, there is a marked difference between the MCD spectra of these two complexes [19]. Whereas the MCD spectrum of $Cr(CO)_5PMe_3$ shows a positive A-term for the metal to π^*(CO) CT transition at 245 nm, the corresponding transition of $Cr(CO)_5PCl_3$ at 226 nm shows a negative B-term, just like $Cr(CO)_6$. From these PES and MCD results it can be concluded that the metal d-orbitals of $Cr(CO)_5PCl_3$ have (nearly) octahedral symmetry. The unoccupied a_1 and b_1 orbitals will therefore (nearly) coincide as well and from this result the wavelength independence of the photochemical release of PCl_3 can be understood [6, 7].

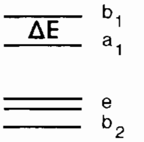

Fig. 4. d-Orbital energy diagram of $M(CO)_5L$ complexes.

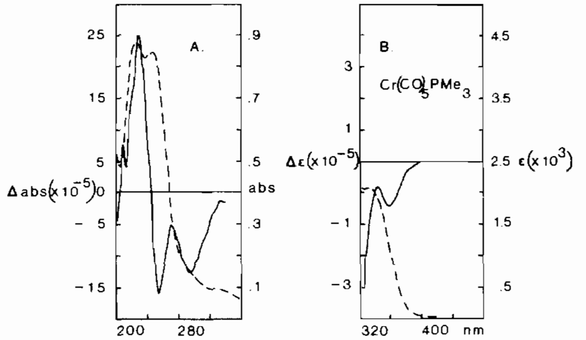

Fig. 5. MCD (——) and absorption (– – –) spectra of $Cr(CO)_5PMe_3$ in n-hexane. A, between 200 and 340 nm; B, between 325 and 400 nm.

If PCl_3 is replaced by the electron donating ligand PMe_3 all metal d-orbitals are raised in energy and according to the PES results the e-level more (7.58 eV) than b_2 (7.72 eV). The different behaviour of these two levels is caused by the stabilizing influence of π-backbonding on e. The a_1 (d_{z^2}) orbital strongly interacts with the lone pair of the trimethylphosphine ligand and will therefore be raised more in energy than the other metal orbitals. This is in fact observed in the UV–visible absorption spectra, because the LF transition from e to a_1 is shifted appreciably to higher energy going from $Cr(CO)_5PCl_3$ to $Cr(CO)_5PMe_3$.

$Cr(CO)_5PMe_3$ shows release of CO and formation of $Cr(CO)_4PMe_3$ after irradiation, which points to a destabilization along the x- and y-axis in the lowest excited state. Such a destabilization is indeed expected for complexes such as $Cr(CO)_5PMe_3$: occupation of the d_{z^2}-orbital after high energy irradiation will lead to a fast non-radiative decay to the $d_{x^2-y^2}$ orbital and as a result only $Cr(CO)_4PMe_3$ and CO are generated. This explanation of the photochemical behaviour is still at a speculative stage and further experiments with M(CO)$_5$P-donor complexes are in progress.

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