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Matrix photochemistry of the complexes (CO)₅M = C(OMe)Ph (M = Cr, W) having close-lying reactive MLCT and LF states

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Abstract

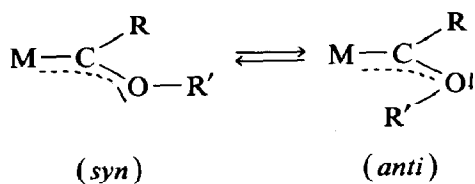
This article describes the photochemistry of (CO)₅M=C(OMe)Ph (M = Cr, W) in inert gas matrices as 10 K at different irradiation wavelengths. The reactions were studied by following the IR spectral changes in the carbonyl and carbene stretching region. Irradiation with visible light into the low-energy MLCT band resulted in complete conversion of the complexes from *anti*- into *syn*-configurations. A similar isomerization reaction occurred as the primary photoprocess upon irradiation into the LF band at ca. 350 nm but this reaction was followed by release of CO as a secondary photoprocess, and in the case of the W-complex a subsequent third photochemical reaction was also observed. The photoproduct of this last reaction appeared to be coordinatively saturated, although it still contained a W(CO)₄-moiety. In agreement with an earlier proposal based on flash-photolysis data, it is suggested that a C–H bond of the carbene methoxy group interacts with W via a two-electron, three-centre bond, thus occupying the open site at the metal.

Conclusions are drawn about the reactivity of the MLCT and LF states of the isomers.

Introduction

Transition metal complexes with an alkoxy-carbene ligand are known to exist in solution in two isomeric forms. Owing to the π -bond character of the C_{carbene}–C bond there is an equilibrium between *syn* and *anti* configurations, as follows:

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For complexes of the type $(\text{CO})_5\text{M}=\text{C}(\text{OMe})\text{R}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{R} = \text{alkyl or aryl}$) it has been shown that this isomerization takes place via rotation of the methoxy group around the carbene–O bond [1]. The *syn*:*anti* ratio in solution will depend on the metal, the R-group, and the environmental conditions (e.g. solvent and temperature). The *anti*-configuration is favoured energetically because of the electrostatic repulsion between the formally negative $\text{M}(\text{CO})_5$ -group and the oxygen lone pair in the *syn* isomer. This only applies, however, in the case of complexes with a rather long $\text{M}-\text{C}_{\text{carbene}}$ bond, since otherwise the steric interaction between the methoxy group and one of the *cis* carbonyl groups forces the equilibrium towards the *syn*-configuration. Thus, whereas $(\text{CO})_5\text{W}=\text{C}(\text{OMe})\text{R}$ occurs almost exclusively in the *anti*-configuration at RT, nearly equal amounts of both isomers are found for the Cr-analogue under these conditions. The ligand field (LF) photochemistry of the group 6 metal carbene carbonyl complexes has been frequently investigated [2–12]. The studies were mainly concerned with the photochemical reactions with alkenes or alkynes in order to provide a better insight into catalytic processes of these molecules (e.g. metathesis of alkenes) [13–16]. Irradiation into the LF band at 350 nm resulted in release of a carbonyl ligand *cis* to the carbene. Although there has been some controversy about the correct assignment of the reactive LF state [12], the available data suggest that it is the ${}^3\text{B}_2$ state related to the ${}^1\text{B}_2(\dots 3a_1^1 b_2^1) \leftarrow {}^1\text{A}_1(\dots b_2^2)$ transition in which the $d_{x^2-y^2}$ orbital is occupied. For most of these complexes the lower-energy ${}^1\text{B}_2(\dots 2a_1^1 b_2^1) \leftarrow {}^1\text{A}_1(\dots b_2^2)$ LF transition (population of d_{z^2}) is partly masked by the intense $\text{M} \rightarrow \text{carbene} (\pi^*)$ MLCT transition. However, for the complex $(\text{CO})_5\text{W}=\text{CPh}(\text{C}_6\text{H}_4\text{-}p\text{-OCH}_3)$ this lowest-energy LF transition was observed as an isolated band in its UV/Vis spectrum, positioned between the higher-energy LF band and the metal to carbene CT band [12].

The MLCT states of these carbene complexes have so far been reported to be photochemically inert in solution at room temperature. Normally, such complexes having a lowest-energy MLCT state are only photoreactive when irradiation leads to occupation of a reactive LF state at higher energy. The MLCT states themselves are normally not reactive [17], and only recently have reactions from such states been observed [18,19]. Irradiation of $(\text{CO})_5\text{W}=\text{C}(\text{OMe})\text{X}$ ($\text{X} = \text{Ph}, \text{Me}$) with 405 nm in the presence of CO has been shown to lead to photosubstitution of the carbene ligand by CO with low quantum yields ($\phi < 10^{-2}$ mol/einstein) [5]. In this case also the reaction does not occur from the lowest MLCT state but from the lowest LF state, in which the metal–carbene bond is weakened by occupation of the d_{z^2} -orbital.

This study is concerned with the elucidation of the reactions from the various LF and MLCT states in these complexes under conditions in which occupation of higher-energy reactive states can be excluded. For this purpose inert-gas matrices at 10 K were chosen as media since they have been successfully used for the identification of reactive intermediates in inorganic photochemistry [20–23].

This article describes the photochemistry of the complexes $(\text{CO})_5\text{M} = \text{C}(\text{OMe})\text{Ph}$ ($\text{M} = \text{Cr}, \text{W}$) in Ar, CH_4 and CO matrices at 10 K by irradiation into the LF band at ca. 350 nm and into the 405 nm transition, which is mainly MLCT in character.

Experimental

Preparations and spectra

The $(\text{CO})_5\text{M} = \text{C}(\text{OMe})\text{Ph}$ ($\text{M} = \text{Cr}, \text{W}$) complexes were synthesized by published procedures [24] and were carefully purified before use.

A Nicolet 7199B FT-IR interferometer with a liquid-nitrogen-cooled MCT-detector (32 scans, resolution 1.0 cm^{-1}) was used for recording the IR spectra. The resonance Raman (rR) spectra were recorded on a Jobin Yvon HG 2S Ramanor instrument using an SP Model 171 Ar^+ laser. An Anaspec 300-S filter with a band-pass of $\sim 0.4 \text{ nm}$ was used as premonochromator. The rR spectra were recorded under direct reflection from a CH_4 -matrix at 10 K.

Photochemistry

An SP Model 171 Argon ion laser and a medium pressure Hg-lamp provided with an interference filter or a sodium glass cut-off filter were used as light sources for the photochemical reactions. The matrix isolation equipment, provided with a modified Air Products Displex Model CSW-202B closed-cycle helium refrigerator, was used as described before [25]. The complexes were sublimed onto a NaCl sample window kept at a temperature of 10 K during the deposition under a vacuum of $< 10^{-6}$ Torr. Argon, methane and carbon monoxide, with purities of 99.999, 99.9995 and 99.997%, respectively, were employed as matrix gases.

Results and discussion

The photochemical reactions discussed below were all monitored by the IR spectral changes in the CO- and carbene-stretching region. Table 1 presents these IR data for both the parent compounds and their photoproducts.

Initially, $(\text{CO})_5\text{W} = \text{C}(\text{OMe})\text{Ph}$ (**1**) was irradiated in a CO-matrix at 10 K with the visible radiation from a medium pressure Hg-lamp. All CO-stretching vibrations were shifted to higher frequencies by $1\text{--}3 \text{ cm}^{-1}$. At the same time significant shifts occurred in the carbene vibrations in the $700\text{--}1500 \text{ cm}^{-1}$ region (see Fig. 1).

The strong bands of **1** at 1235 , 990 and 876 cm^{-1} , which were assigned by Fischer et al. [26] to $\nu(\text{C}_{\text{carbene}}\text{--O})$, $\nu(\text{H}_3\text{C}\text{--O})$ and $\nu(\text{C}_{\text{carbene}}\text{--C}_{\text{Ph}})$, respectively, are characteristic of the *anti*-configuration, which is the expected structure of tungsten carbene complexes (vide supra). The photoproduct of the above reaction is most likely *syn*- $(\text{CO})_5\text{W} = \text{C}(\text{OMe})\text{Ph}$, since its carbene frequencies closely correspond to those of other *syn*-carbene complexes, such as *syn*- $\text{M}_2(\text{CO})_9(\text{carbene})$ ($\text{M} = \text{Mn}, \text{Tc}, \text{Re}$) [27]. A nearly complete *anti* \rightarrow *syn* conversion was achieved by irradiation of **1** in Ar, CO as well as in CH_4 matrices. During none of these experiments was release of CO observed.

The corresponding complex $(\text{CO})_5\text{Cr} = \text{C}(\text{OMe})\text{Ph}$ (**2**), present in the matrix in both isomeric forms, showed the same isomerization reaction. Thus, the following

Table 1
IR spectral data of (CO)₂M=C(OMe)Ph (M = Cr, W) and their photoproducts in matrices at 10 K.

Complex	$\nu(\text{CO})$	$\nu(\text{C}_{\text{carbene}}-\text{O})$	other carbene vibrations
(CO) ₂ W=C(OMe)Ph (1)			
<i>anti</i> -isomer ^a	2072 s, 1985 w, 1948 s, 1933 sh	1235 s ^b	1221 m, 1152 m, 990 m $\nu(\text{H}_3\text{C}-\text{O})$ ^b , 876 m $\nu(\text{C}_{\text{carbene}}-\text{C}_{\text{Ph}})$ ^b , 770 w
<i>syn</i> -isomer ^a	2073 s, 1987 w, 1949 s, 1936 sh	1271 s ^c	1194 s, 1150 s, 1145 s, 938 m, 919 m, 878 w, 762 s
(CO) ₂ Cr=C(OMe)Ph (2)			
<i>anti</i> -isomer ^d	2065 m, 1990 w, 1942 s	1234 s	1221 sh, 1149 m, 988 m $\nu(\text{H}_3\text{C}-\text{O})$ ^b , 876 m $\nu(\text{C}_{\text{carbene}}-\text{C}_{\text{Ph}})$ ^b , 765 w
<i>syn</i> -isomer ^d	2068 m, 1995 w, 1945 s	1271 s	1194 s, 1144 s, 1130 m, 938 s, 916 m, 878 w, 760 s
<i>syn</i> -(CO) ₂ Cr=C(OMe)Ph ^e	2034 m, 1889 br /	^g	1194 m, 1186 m, 1144 s, 1129 m, 937 s, 916 m, 877 w, 759 s
<i>syn</i> -(CO) ₂ W=C(OMe)Ph ^e	2040 m, 1948 s, 1876 /	1263 sh ^g	1192 s, 1143 s, 1131 m, 937 m, 918 m, 878 w, 758 m
Prod X ^e	2022 m /	-	1111 m, 1100 m, 759 m

^a CO matrix. ^b Assignment taken from ref. 26. ^c Ar matrix. ^d CH₄ matrix. ^e Other bands (partly) obscured by unreacted parent compound. ^g (Partly) obscured by strong CH₄ vibration in this region.

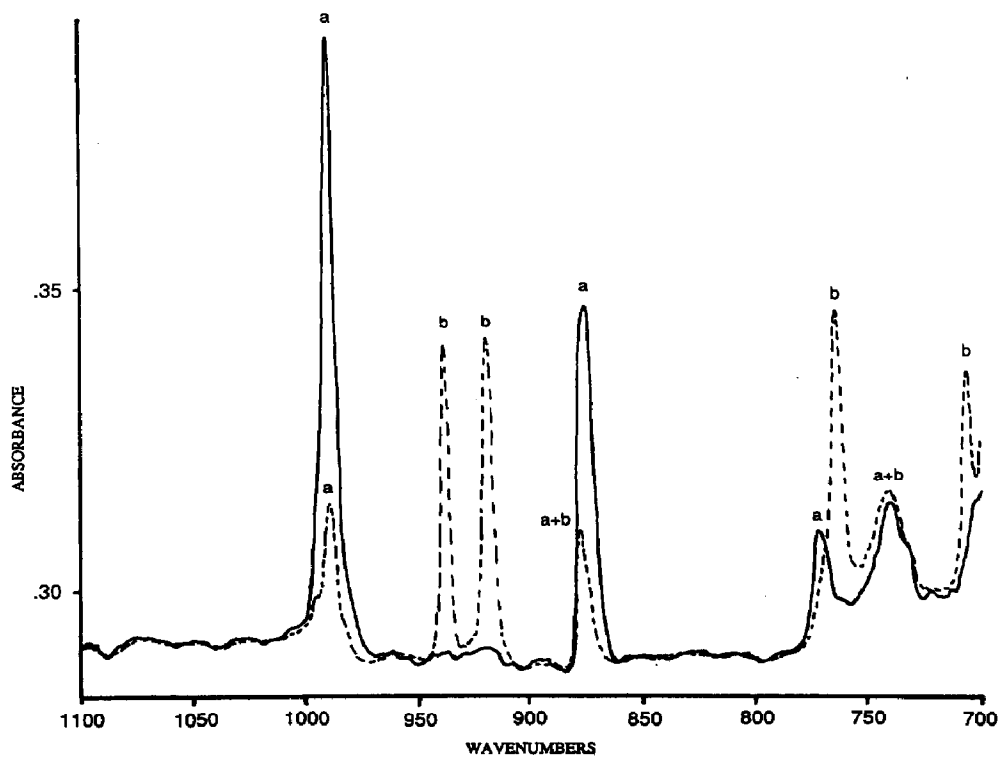
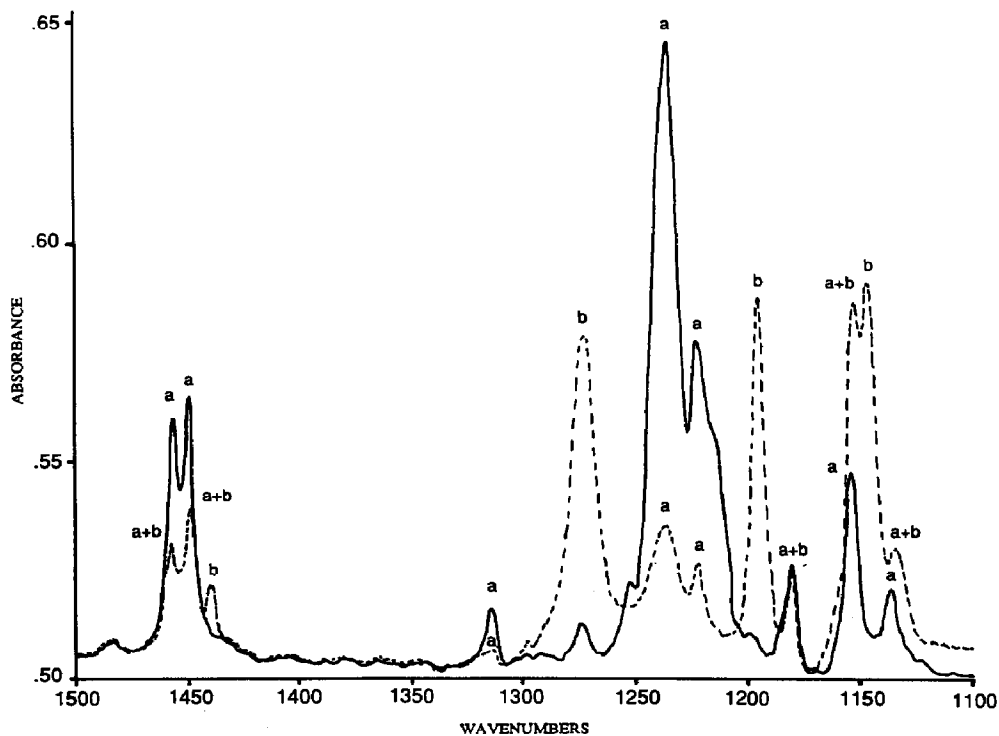


Fig. 1. Infrared spectra (top = 1100–1500 cm^{-1} , bottom = 700–1100 cm^{-1}) recorded before irradiation of *anti*-1 (a) in a CO matrix at 10 K (—) and after its ca 80% photochemical conversion into *syn*-1 (b) (-----).

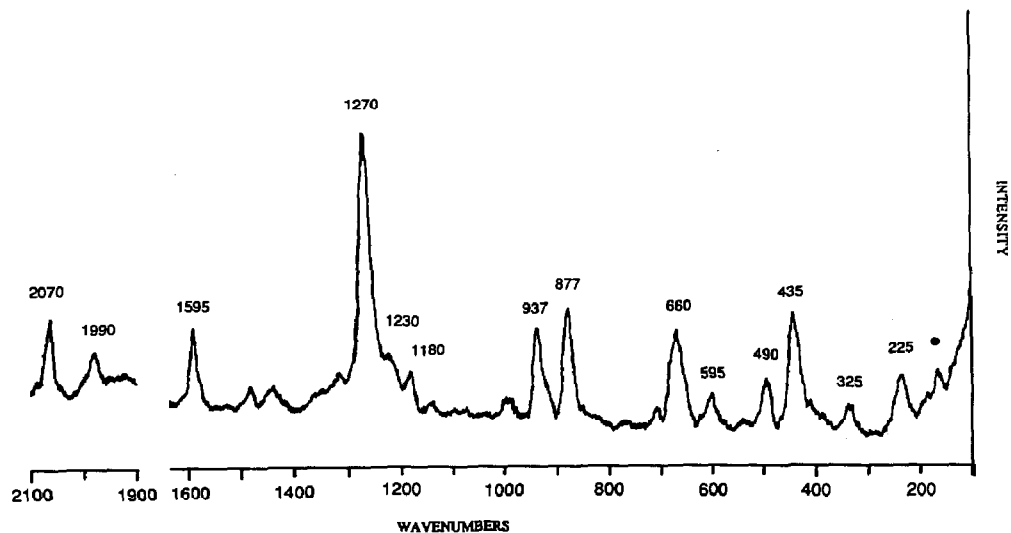


Fig. 2. Resonance Raman spectrum of complex **1** in a CH_4 matrix at 10 K obtained by excitation with 457.9 nm (● = plasma band).

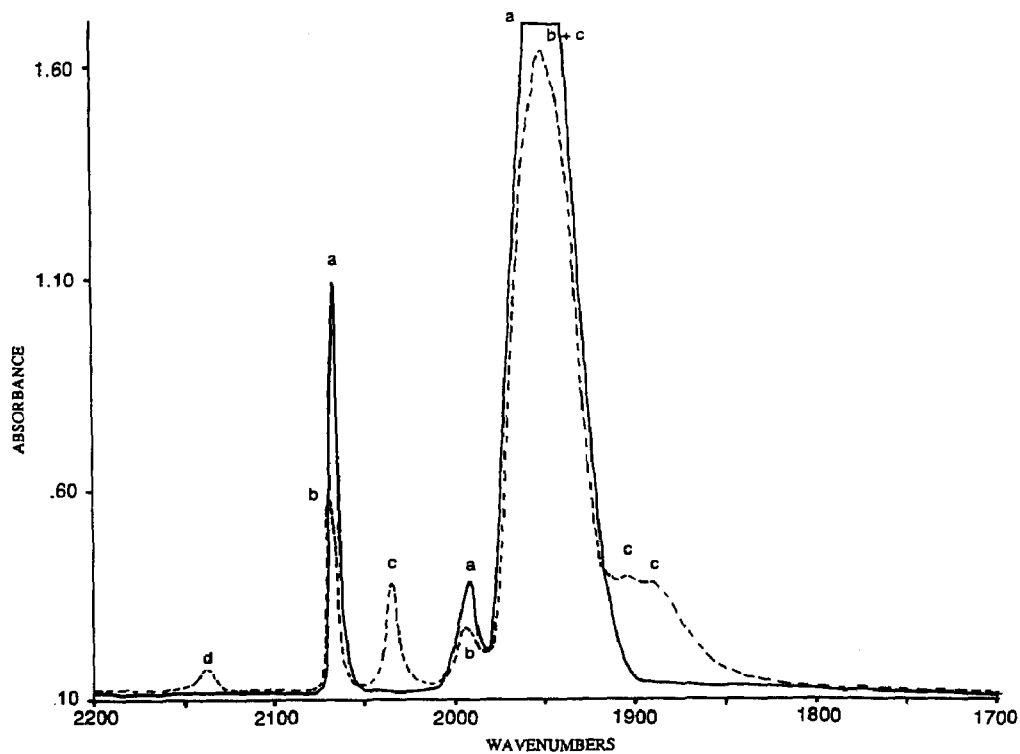
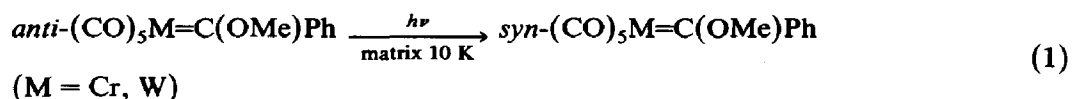


Fig. 3. Infrared spectra (CO-stretching region) recorded before (—) and after (----) irradiation of **2** (a = *anti*, b = *syn*) in a CH_4 matrix at 10 K with the 366 nm line of a medium pressure mercury lamp (c = CO-loss product $(\text{CO})_4\text{Cr}=\text{C}(\text{OMe})\text{Ph}$, d = free CO).

reaction had occurred for both complexes upon irradiation into the lowest-energy absorption band:



This absorption band contains both a metal–carbene (MLCT) transition and the lowest-energy LF transition. Although occupation of the LF state will weaken both the metal–CO and metal–carbene bonds along the *z*-axis of the complex, the weakest of these, the metal–carbene bond, will be preferentially broken. This reaction is not observed in the matrices however, because the bulky carbene ligand cannot escape from the matrix cage and therefore re-unites with the $\text{M}(\text{CO})_5$ fragment to reform the parent compound. As a consequence only the less efficient isomerization reaction is observed, which most probably occurs from the lowest MLCT state. This assumption is supported by the resonance Raman (rR) spectrum of complex **1**, shown in Fig. 2.

The strongest rR effect is observed for $\nu(\text{C}_{\text{carbene}}-\text{O})$, which means that especially the $\text{C}_{\text{carbene}}-\text{O}$ bond is affected by the MLCT transition. As a result, the rotation of the methoxy group around this bond will be facilitated, giving rise to the isomerization [1]. The observation of a band at 1270 cm^{-1} for this vibration shows that the isomerization had already taken place during the rR measurements.

The matrix photochemistry of **1** and **2** was also studied by irradiation into the LF band at ca. 350 nm. Again isomerization of the parent compound according to reaction 1 appeared to be the primary photoprocess, although the reaction was followed in this case by photochemical loss of CO. Figure 3 shows the IR spectral changes in the CO-stretching region upon irradiation of **2**, in a CH_4 matrix, by the 366 nm line of a medium pressure Hg-lamp.

After irradiation for a short time the bands of the parent compound had shifted slightly to higher frequencies, indicating the conversion of **2** into its *syn* isomer (*syn-2*). After prolonged irradiation IR bands belonging to a tetracarbonyl complex appeared, together with the 2137 cm^{-1} band of free CO. The carbene ligand in this photoproduct is still in the *syn*-configuration, as indicated by the characteristic bands in the $700\text{--}1500\text{ cm}^{-1}$ region (see also Table 1).

When, after completion of the photochemical reaction, the matrix was annealed to 40 K, the tetracarbonyl species re-united with CO to give *syn-2*. The same reaction was observed after subsequent irradiation with the 457.9 nm laser line. Such a photochemical regeneration of the starting complex has been observed before for many other CO-loss products [28–30]. In view of these results, the secondary photoproduct is assumed to be the coordinatively unsaturated species $\text{syn}-(\text{CO})_4\text{Cr}=\text{C}(\text{OMe})\text{Ph}$.

A similar reaction took place upon irradiation of **1** with the 353/365 nm lines of an Ar^+ laser. In this case, however, irradiation caused transformation of the secondary photoproduct $\text{syn}-(\text{CO})_4\text{W}=\text{C}(\text{OMe})\text{Ph}$ into another tetracarbonyl complex, denoted subsequently as product X. X has its highest CO-stretching vibration at 2022 cm^{-1} , compared to 2040 cm^{-1} for the corresponding vibration of $\text{syn}-(\text{CO})_4\text{W}=\text{C}(\text{OMe})\text{Ph}$. The formation of X is accompanied by the disappearance of the characteristic *syn*-carbene vibrations and the appearance of two new bands at 1111 and 1100 cm^{-1} , respectively (see Fig. 4)

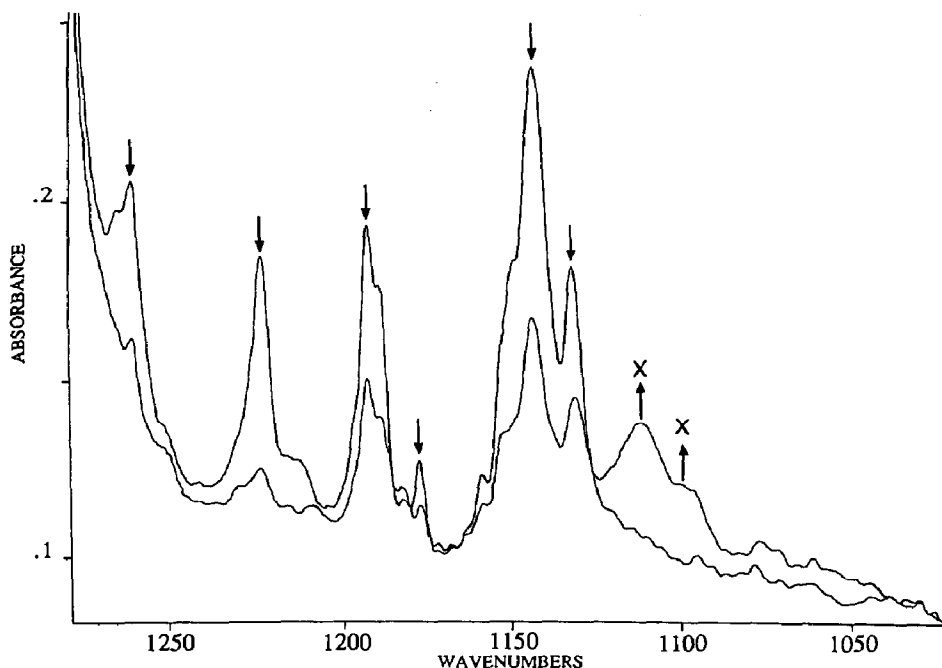
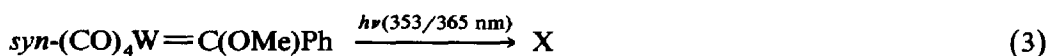
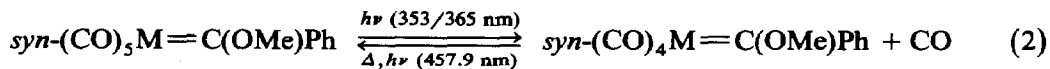


Fig. 4. IR spectral changes in the 1000–1300 cm^{-1} region accompanying the photochemical formation of X according to reactions 2 and 3.

Syn-(CO)₄W=C(OMe)Ph was converted both thermally (annealing) and by irradiation with the 457.9 nm laser line into *syn*-1. X appeared to be (photo) stable under these conditions, which means that the two tetracarbonyl species do not undergo interconversion as e.g. in the case of the two structural isomers of W(CO)₄CS [30].

Thus, when irradiation of 1 or 2 takes place into the 350 nm LF band, reaction 1 is followed by reaction 2, which is not observed upon photolysis with visible light. Furthermore, in the case of complex 1 a third photochemical reaction (reaction 3) was observed.



These reactions show that, remarkably, irradiation of the *anti*-isomers of 1 and 2 with UV excitation gives rise to isomerization (reaction 1), whereas the *syn*-isomers undergo release of CO (reaction 2). This difference in behaviour is probably due to a difference in energy between the LF and MLCT states of these isomers.

Irradiation of *anti*-1 and *anti*-2 into the 350 nm band will give rise to population of the $^{1,3}B_2(\dots 3a_1^1 b_2^1)$ LF states which are reactive with respect to release of an equatorial CO ligand. Since this reaction is not observed, even though CO is small enough to escape from the matrix cage, it can be concluded that fast non-radiative decay occurs to the lowest MLCT state from which the isomerization reaction takes place. Since the corresponding *syn*-isomers react instead from their LF states according to reaction 2, it may be concluded that the LF and MLCT states are so close in energy that they both react from the more reactive LF state. Support for

such a shift in the lowest MLCT state upon going from the *anti*- to the *syn*-isomers of 1 and 2 comes from the observation that the *syn*-isomers are not transformed photochemically into their *anti*-isomers upon irradiation with visible light (*vide supra*). Unfortunately, no further evidence for this effect could be obtained from the absorption spectral changes since no reliable UV/Vis spectra could be recorded for the matrices.

The question remains of whether product X can be identified from the present data. First of all, this complex is formed photochemically from *syn*-(CO)₄W=C(OMe)Ph without loss or take up of CO, which means that it still contains the (CO)₄W-moiety. On the other hand, neither annealing the matrix to 40 K nor irradiation with visible light induces a back-reaction with CO to give *syn*-(CO)₅W=C(OMe)Ph. Product X is therefore most likely a coordinatively saturated species.

The formation of X is accompanied by drastic changes in the carbene stretching region. Only two new bands showed up at ca. 1100 cm⁻¹ and no other carbene vibrations of either a *syn*- or *anti*-configuration were observed. These new bands around 1100 cm⁻¹ closely correspond to the 1105 cm⁻¹ resonance Raman (rR) band reported recently by Bell et al. for a transient photoproduct of 1 [31]. These authors performed a time-resolved rR study by irradiating 1 at room temperature both into its ¹B₂(...3a₁¹b₂¹) and ¹B₂(...2a₁¹b₂¹) LF state. The transient thus formed had a solvent-dependent lifetime of 3–25 μs. However, its time-resolved rR spectrum showed not only a band at 1105 cm⁻¹ but also several carbene stretching vibrations which we were able to identify from our IR matrix spectra as belonging to a *syn*-carbene complex. This means that Bell et al. probably observed the rR bands of two transients, one of them being the *syn*-(CO)₄W=C(OMe)Ph photoproduct of reaction 2. Indeed, Bell et al. suggested that their transient formed from this photoproduct by a rearrangement reaction in which a two-electron, three-centre bond was formed between the metal and one of the methoxy C–H bonds. A similar rearrangement could very well have taken place during reaction 3 in the matrix. The two IR bands of X around 1100 cm⁻¹ then have their counterpart in the 1105 cm⁻¹ rR band. Moreover, such a two-electron, three-centre bond will prevent the back-reaction of X with CO to give *syn*-1 upon annealing the matrix or irradiating with visible light (*vide supra*).

In order to achieve such a two-electron, three-centre bond, the photoproduct *syn*-(CO)₄W=C(OMe)Ph of reaction 2 must, however, first be transformed into its *anti*-isomer. It is therefore suggested that this light-induced isomerization is that shown in equation 3, and is followed by the two-electron, three-centre bond formation, as depicted in Fig. 5.

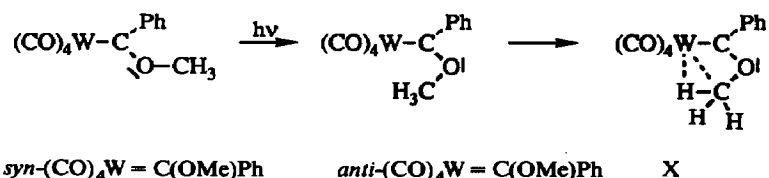


Fig. 5. Photochemical formation of product X according to reaction 3.

There is still a clear discrepancy between the photoreaction of **1** observed by Bell et al. at room temperature and our low-temperature matrix results. Bell et al. did not observe any difference between the reactions of **1** with 355 and 405 nm excitation; in both cases product X was formed. They concluded that 405 nm excitation into the lowest LF transition gives rise to *trans* CO loss and to formation of the *trans*-isomer of *syn*-(CO)₄W=C(OMe)Ph. This photoproduct would then undergo a fast *trans* to *cis* interconversion, necessary for the formation of X. Irradiation with 355 nm leads to *cis* CO loss from the second LF state and formation of the *cis*-isomer of *syn*-(CO)₄W=C(OMe)Ph. Alternatively, this isomer may have been formed out of its *trans*-isomer, which was in turn produced by *trans* CO loss from the lowest LF state after fast internal conversion from the second LF state. If this explanation were correct, visible excitation of **1** in the matrix at 10 K would also give rise to *trans* CO loss and formation of the *trans*-isomer of *syn*-(CO)₄W=C(OMe)Ph or possibly of the *cis*-isomer after a *trans* to *cis* interconversion, but we did not observe this reaction. Instead, irradiation with visible light gave rise only to photoisomerization of **1** from the lowest MLCT state. Apparently, *trans* CO loss from the lowest LF state of **1**, as proposed by Bell et al., is not an efficient photoprocess.

A more plausible explanation for their results might be that irradiation of **1** at room temperature with 405 nm light also gives rise to *cis* CO loss by thermal occupation of the second LF state. In the matrix at 10 K thermal occupation of this LF state will be prevented. As a result, visible excitation of **1** in a matrix gives rise only to *anti* to *syn* photoisomerization from the MLCT state.

Conclusions

The results of this matrix IR study show that the photochemical reactions of **1** and **2** all proceed via an *anti* → *syn* isomerization of the carbene moiety, probably from the lowest ³MLCT state. Whereas irradiation into the MLCT band results only in this isomerization (reaction 1), photodissociation of CO occurs from the ^{1,3}B₂(... 3a₁¹b₂¹) LF state, to give the coordinatively unsaturated *syn*-(CO)₄M=C(OMe)Ph (M = Cr, W) complexes. From the tungsten carbene complex a second tetracarbonyl species was formed photochemically (reaction 3) in which the carbene ligand had a changed character. This product X probably involves a two-electron, three-centre interaction between the metal and a C–H bond of the carbene methoxy group. Work is in progress to verify this suggestion.

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