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Photochemical reactions of Group 6 metal carbonyls in catalytic transformation of alkenes and alkynes

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Abstract

This review considers some results that illustrate one of the different categories of photocatalysis where light is used to generate a thermally active catalytic species C from a catalytically inactive precursor, the nominal catalyst N. In photocatalytic reactions presented here, the nominal catalyst N can be a Group 6 metal carbonyl, $M(CO)_6$, and substrates are alkenes or alkynes. This paper summarizes the most interesting approaches in each of three photocatalytic reactions: polymerization of alkynes; isomerization of alkenes; metathesis of alkenes. Special attention is given to catalytically active intermediate species formed in photocatalytic systems and to the reaction mechanism.

With the application of the low-temperature method formation of alkyne complexes of the type $[(\eta^2\text{-}RC{\equiv}CH)M(CO)_5]$, $[R(H)C{=}C{=}M(CO)_5]$ and $[(\eta^2\text{-}RC{\equiv}CH)M(CO)_4]$, intermediate compounds proposed for the photocatalytical polymerization of terminal alkynes have been shown.

The bis(alkene)tetracarbonyl complexes of tungsten are good prototypical catalysts for

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isomerization and metathesis of olefin. The rearrangement of these compounds to π-allyl hydrides was monitored by ^1H NMR.

The $[(CO)_4W(\mu\text{-}Cl)_3W(SnCl_3)(CO)_3]$ formed in the photochemical reaction of $W(CO)_6$ and $SnCl_4$ can be regarded as a prototypical catalyst for the metathesis of alkenes.

Keywords: Group 6 metal carbonyls; Alkene; Alkyne

1. Introduction

One of the different categories of photocatalysis, first named photoassisted reaction by Wrighton [1], then photogenerated catalysis by Salomon [2], and later photoinduced catalytic reaction by Hennig et al. [3], is defined as a situation where light is used to generate a thermally active catalytic species **C** from a catalytically inactive precursor, the nominal catalyst **N**. The photogenerated catalyst **C** promotes the transformation of a substrate **S** into a product **P** in a subsequent thermal process.

$$\text{NOMINAL CATALYST } (\mathbf{N}) \xrightarrow{h\nu} \text{CATALYST } (\mathbf{C}) \quad (1)$$

$$\text{SUBSTRATE } (\mathbf{S}) \xrightarrow{(\mathbf{C})} \text{PRODUCT } (\mathbf{P}) \quad (2)$$

In this class of photocatalysis, the nominal catalyst **N** is a coordination compound and the catalyst **C** can be a coordinatively unsaturated complex, a compound with metal in a higher oxidation state, or any other reactive species formed in the photochemical reaction (Eq. (1)). Catalysis in the ground state requires coordinative interaction between the catalyst and the substrate and the formation of a catalyst–substrate complex. The catalyst–substrate complex **C·S** transforms thermally into a catalyst–product complex **C·P**. The product may then be released to regenerate **C** or in another catalytic cycle product in complex with catalyst may be displaced by **S** to generate catalyst–substrate complex **C·S** directly. In photocatalytic reactions that we studied, the nominal catalyst **N** is a Group 6 metal hexacarbonyl and the substrates are alkenes or alkynes.

The role of transition-metal carbonyls, particularly those of Group 6 metals, in homogeneous photocatalytic and catalytic processes is a matter of considerable interest. UV irradiation of metal carbonyls is the method of choice for the generation of catalytically active species or for the synthesis of substituted derivatives in the presence of potential ligands. UV irradiation provides a simple and convenient method for the generation of thermally active coordinatively unsaturated catalysts for alkenes or alkynes transformation. By using tungsten and molybdenum carbonyl compounds as catalysts, alkynes and alkenes can be polymerized, isomerized, or metathesized [4].

The catalyst for alkynes polymerization can be generated photolytically in a hexane solution of $W(CO)_6$ and alkyne (Eq. (3)). This reaction was observed for the first time by Geoffroy and co-workers in 1985 [5].

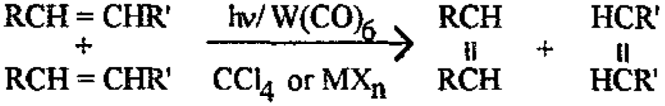
$$nRC\equiv CH \xrightarrow{h\nu/W(CO)_6} -\!\!(RC{=}CH)\!\!-_n \qquad (3)$$

Photocatalytic isomerization of alkenes in the presence of molybdenum and tungsten hexacarbonyls was observed by Wrighton et al. 20 years ago [6]. Carbonyl complexes of molybdenum and tungsten catalyse not only cis–trans isomerization of olefins but also promote double bond migration in terminal alkenes, which possess allylic hydrogen and from terminal alkene cis and trans internal alkenes are formed (Eq. (4)).

(4)

In our studies we observed enhanced catalytic activity of these complexes when reaction occurred in the presence of Lewis acids — metal halides [7].

Alkene metathesis catalyst can be photogenerated from $W(CO)_6$ in CCl_4 [7–10] or in the presence of Group 4, 13 or 14 metal halides, and in the last system even higher catalytic activity was observed than in CCl_4 [7,11] (Eq. (5)).



$$\begin{array}{c} RCH=CHR' \\ + \\ RCH=CHR' \end{array} \xrightarrow[CCl_4 \text{ or } MX_n]{h\nu/W(CO)_6} \begin{array}{c} RCH \\ \| \\ RCH \end{array} + \begin{array}{c} HCR' \\ \| \\ HCR' \end{array} \qquad (5)$$

In our studies we were interested in all these catalytic reactions, and the results presented here concern catalytically active intermediate species formed in photocatalytic polymerization of alkynes and isomerization and metathesis of alkenes. All these photocatalytic reactions are presumed to evolve initially through a complex of pentacarbonylalkene or alkyne. Such a complex is formed in photosubstitution of CO by organic substrate.

2. Photoactivation of Group 6 metal hexacarbonyls

Interest in the photoactivation of transition-metal carbonyls stems in part from their potential use as photocatalysts [1–12]. Metal carbonyl complexes are among the most photoreactive transition metal complexes known. The photochemistry of Group 6 metal hexacarbonyls, $M(CO)_6$ ($M=Cr$, Mo, W), has been studied extensively during the past three decades [1,13–18]. The primary event upon irradiation of these complexes in solution, in low-temperature matrices, and in the gas phase, is the efficient loss of CO to give coordinatively unsaturated species, e.g. $M(CO)_5$ (Eq. (6)). This product is typically very short-lived in solution at ambient temperatures; in perfluoromethylcyclohexane solution flushed with CO at room temperature, the half-life of $Cr(CO)_5$ is only 13 ns [14] and in the same condition the half-life of $W(CO)_5$ is 20 ps [15].

$$M(CO)_6 \xrightarrow{h\nu} M(CO)_5 + CO \tag{6}$$

$$M(CO)_5 + S \rightarrow M(CO)_5S \tag{7}$$

M = Cr, Mo, W; S = solvent molecule

Transient absorption spectroscopy of these complexes in alkane solvents has provided evidence that formation of a solvated intermediate $M(CO)_5S$, where S is a solvent molecule, occurs within picoseconds (Eq. (7)). For the photochemical reaction of $Cr(CO)_6$ in cyclohexane, the formation of $[Cr(CO)_5(C_6H_{12})]$ has been found to occur with rate constants approaching those of diffusion control with a time constant of ca. 0.8 ps [16], while the formation of a solvatopentacarbonyl intermediate, $[W(CO)_5(C_7F_{14})]$, in perfluoromethylcyclohexane occurs with a first-order rate constant of $5 \times 10^{10}\ s^{-1}$ at 20 °C [17]. The hexacarbonyls of Cr, Mo, and W undergo high quantum yield (equal to or greater than 0.65) photosubstitution of CO by a suitable ligand and, in the case of $W(CO)_6$, the quantum yield is independent of the wavelength of irradiation [18]. The behaviour of $W(CO)_6$ appears to present a classical photochemical case that involves rapid internal conversion and efficient prompt intersystem crossing to the triplet with all substitutional reactivity originating in the ligand field (LF) triplet [12–18].

Detailed spectroscopic and structural information about metal carbonyl fragments has also been gained from photolytic decomposition of metal carbonyls in glassy hydrocarbon matrices at ca. 80 K [19] or in low-temperature matrices at 20 K [20,21]. The characterization of photolytic fragments penta-, tetra-, tri- and di-carbonyls in glassy hydrocarbon matrices by infrared spectroscopy at about 80 K was first reported by Sheline and co-workers over 30 years ago [19]. More recently, such photolytic fragments have been fully characterized by IR and UV–vis spectroscopy, and their interactions with matrix materials investigated, by Turner and co-workers with application of matrix-deposition techniques at about 20 K [20,21].

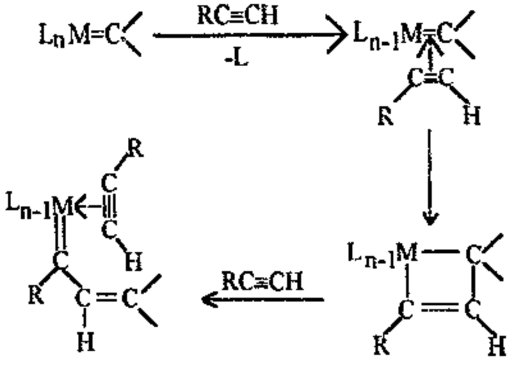
For investigation of intermediates formed in photocatalytic polymerization of alkynes, we have chosen matrix deposition techniques. The principle behind the low-temperature matrices method is as follows: when a chemical species is embedded at high dilution in a solid host at low temperature (a typical example being solid argon at 20 K), bimolecular reactions are suppressed and unimolecular decomposition is stopped for any process with an activation barrier larger than a few kilojoules per mole. The species is thus preserved. A stable precursor is trapped within the matrix and reactive species can be generated in situ by photolysis. The trapping of metal hexacarbonyls in a solid noble-gas matrix at low temperatures gives access to photochemically generated, normally very unstable $M(CO)_5$ or $M(CO)_4$ species only weakly perturbed and with an unlimited lifetime; under such conditions it may be characterized by IR and UV–vis spectroscopy.

The $\nu(CO)$ fundamentals of the $[M(CO)_5L]$ unit give rise to three IR absorptions, namely a weak feature at 2000–2100 cm^{-1} (a_1) of CO group trans to L and two more intense features between 1900 and 2000 cm^{-1} ($a_1 + e$). Depending upon the symmetry of the tetracarbonyl fragment, D_{4h} or C_{2v}, either one or four CO frequencies can be observed in IR spectra. Pentacarbonyl intermediates display a first LF band which may appear in the visible region if the ligand L is a sufficiently weak electron donor [1]. With this knowledge it has been possible to investigate matrices containing metal carbonyls, as well as reagents like alkyne, and so follow the reactions subsequently induced by photolysis. The matrix-isolation technique has proven extremely valuable as a means of identifying and characterizing unstable species formed in photochemical reactions [20,21]. It was, then, a logical application of this method to investigate the photochemical behaviour of molybdenum and tungsten hexacarbonyl in the presence of an organic substrate, alkyne molecules in our case. The questions raised then concern the intermediates formed in the photocatalytic polymerization of alkynes observed first by Geoffroy et al. 10 years ago [5].

3. Photocatalytic transformation of alkenes and alkynes in the presence of Group 6 metal carbonyls

3.1. Polymerization of alkynes

From earlier studies by Higashimura and co-workers [22] it is known that catalytic species in alkyne polymerization are carbene or alkylidene complexes. Coupling between the carbene and acetylene occurs through metallacyclobutene derivatives. The formation of carbene–alkyne intermediates is probably the first step in this mechanism, as is shown in Scheme 1.

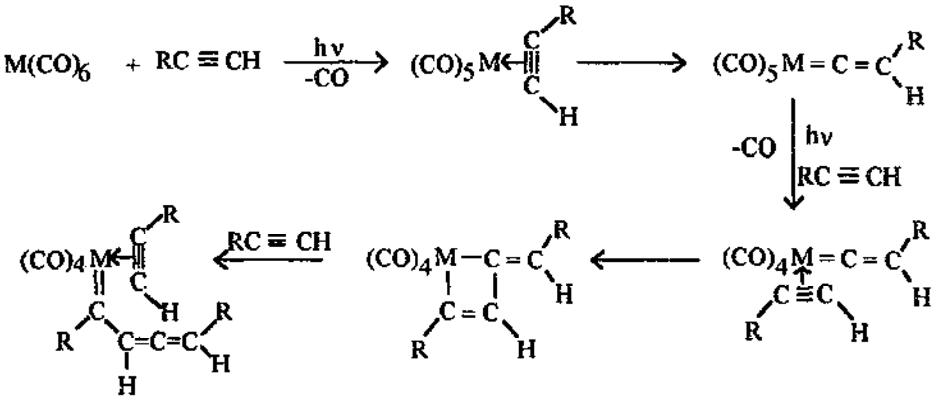


Scheme 1.

One question that still has not been answered satisfactorily concerns the origin of the initial alkylidene ligand in photocatalytic polymerization of alkynes catalysed by tungsten hexacarbonyl. Some version of vinylidene formation is one of the most attractive routes to the initial alkylidene complex [5,23–26].

The photocatalytic polymerization of 1-alkynes in the presence of $W(CO)_6$ proceeds, according to the proposal of Geoffroy et al. [5], as shown in Scheme 2.

Such a catalytic cycle involves the formation of a number of very labile intermedi-



Scheme 2.

ates: the first is a pentacarbonylalkyne complex, and the second a vinylidene complex which derives from the rearrangement of the alkyne complex. However, up to now, positive experimental evidence of this transformation is generally lacking, primarily because of the instability of such compounds. At the same time, there has been much interest in the rearrangement of a 1-alkyne to a vinylidene at a metal centre with d^6 configuration, which may well be the initiation step in the polymerization of 1-alkynes [5,23–26]. A coupling between the vinylidene and alkyne can occur through the metallacyclobutene derivatives and leads to a polymerization product, as in reaction with a carbene catalyst. To the best of my knowledge, up to now, no good proof has been given for the mechanism for polymerization of alkynes postulated by Geoffroy et al. [5], primarily because these intermediate species are too unstable.

Elucidation of the processes occurring in photochemical reactions is one of the main applications of the matrix-isolation technique [27]. It was the reason why we had chosen this technique for investigation of the metalhexacarbonyl–alkyne reaction [25,26].

In a typical experiment, a mixture of $M(CO)_6$:alkyne:$Ar(CH_4)$ in the ratio 1:100:2000 was deposited upon a window transparent to IR radiation, e.g. CsI held within a high vacuum shroud, and was then subjected to UV–visible photolysis. Depending on the type of experiment being performed, the photolysis may be at selected wavelengths. Photolysis products, penta- and tetracarbonyl species, can be observed by IR or UV–vis spectroscopies.

UV photolysis of a methane matrix containing $Mo(CO)_6$:ethyne:CH_4 in the molecular ratio 1:100:2000 leads to decarbonylation and formation of the corresponding pentacarbonyl, where the vacated coordination site is occupied by CH_4 or ethyne. This gave rise to the appearance and growth of two visible bands, one at 404 nm relatively more intense than the other at 368 nm. Both bands are attributable to the $b_2^2e^4a_1^0b_1 0 \rightarrow b_2^2e^3a_1^1b_1^0$ LF transition of the $Mo(CO)_5$ adduct, and the less intense band is characteristic of ethyne–pentacarbonyl complexes (Fig. 1(b)).

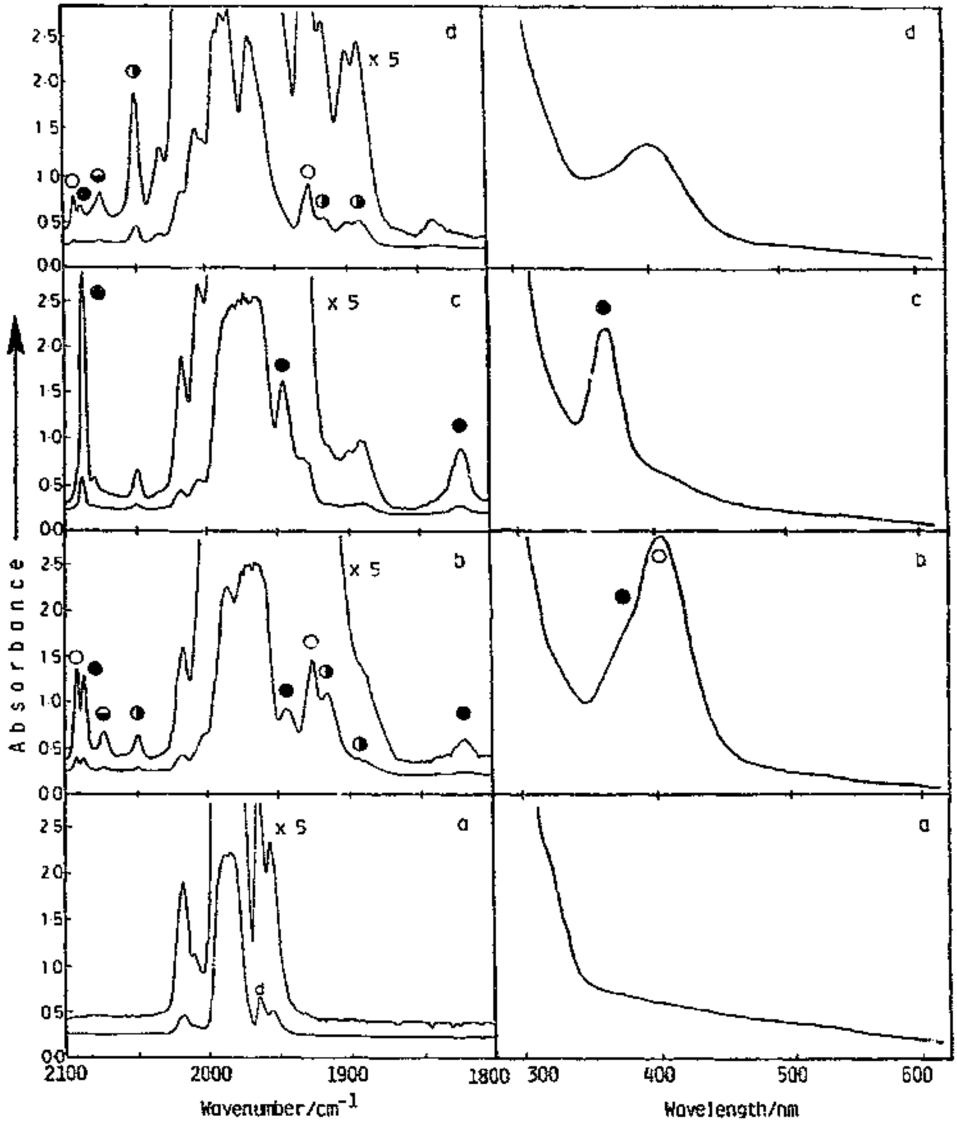


Fig. 1. IR absorption spectrum in the region 1800–2100 cm^{-1} and UV–vis absorption spectrum in the region 300–600 nm displayed by a solid CH_4 matrix containing $Mo(CO)_6$ and C_2H_2 with the composition $Mo(CO)_6$:C_2H_2:CH_4 of ca. 1:100:2000 at 20 K showing the effects of short-term photolysis at different wavelengths. (a) Spectra of the matrix after deposition. (b) Spectra after photolysis at λ=313 nm. (c) Spectra after photolysis at λ=445 nm. (d) Spectra after photolysis at λ=369 nm. Bands are labelled as follows: ○ [CH_4···$Mo(CO)_5$]; ● [(η^2-C_2H_2)$Mo(CO)_5$]; ◒ [H_2C=C=$Mo(CO)_5$]; ◑ $Mo(CO)_4$; 'd' [HC≡CH]$_2$. (Reproduced with permission from Ref. [25]).

On the left side of Fig. 1 we can see the changes in the IR spectra of photolysed CH_4 matrices containing $Mo(CO)_6$ and alkyne. After the photolysis of a matrix with radiation having $\lambda \approx 313$ nm, the IR spectrum witnessed a decay of the absorption due to $Mo(CO)_6$, to the accompaniment of the appearance and growth of new absorptions at 2142 and 2137 cm^{-1} (due to photo-ejected CO), and the appearance and growth of new absorptions at 2093, 1966, and 1926 cm^{-1} (due to the ν(CO) modes of the adduct $[CH_4 \cdots Mo(CO)_5]$ and bands characteristic of a pentacarbonylethyne complex at 2088, 1969, and 1945.5 cm^{-1}. A broad weak band centred near 1820 cm^{-1} is attributable to the $\nu(C{\equiv}C)$ mode of coordinated alkyne molecule. The irradiation of the mixture of these products into a band belonging to the $[CH_4 \cdots Mo(CO)_5]$ adduct results in the enrichment of the matrix in the [ethyneMo(CO)5] complex while $[CH_4 \cdots Mo(CO)_5]$ almost disappears. In the IR spectrum we observed an increase of bands characteristic of ethyne complexes, e.g. at 2088 cm^{-1} attributable to CO trans to the coordinated alkyne (a_1), and at 1969, 1945.5 cm^{-1} ($a_1 + e$), and an increase in intensity of the ν(CC) band due to vibration of the coordinated alkyne. Also, in the visible spectra we observed only the band attributable to the lowest-energy spin-allowed LF transition of the alkyne complex at 368 nm. Irradiation into this band with photolysing light having $\lambda = 369$ nm causes further decarbonylation and depletion of the matrix in the alkyne complex, regeneration of the pentacarbonylmethane adduct, and also increases in intensity of other bands. A band in the IR spectra at ca. 2052 cm^{-1} was identified as one of four bands belonging to tetracarbonyl alkyne species of the type $[Mo(CO)_4LL']$, where L and L′ represent any two of the same or different ligands from CH_4, C_2H_2, or $=C=CH_2$. Another band at 2074 cm^{-1} was identified as one of three ν(CO) bands belonging to the pentacarbonylvinylidene species, formed in photochemical isomerization of the alkyne complex. The rearrangement of an alkyne to a vinylidene occurs only under the influence of higher energy light, that is 313 nm or 369 nm. It is understood that the vinylidene complex can form only in a photochemical reaction of coordinated terminal alkyne, like ethyne or propyne, but in photochemical reactions of internal alkynes such as 2-butyne we observed only penta- and tetracarbonylalkyne complexes. Another observation is that coordination to an alkyne molecule photosensitizes the pentacarbonyl fragment to a further loss of CO, giving rise presumably to $Mo(CO)_4$ derivatives. This is most conspicuous in near-UV photolysis, $\lambda = 369$ nm, which causes the tetracarbonyl concentration to rise, reach a maximum, and slowly decrease with the simultaneous appearance of another new product. On the evidence of its IR spectrum and of the effects of deuteration or ^{13}C-enrichment, this is probably $[(\eta^2\text{-RCCH})Mo(CO)_4]$ (R,R′=H,H or Me,Me) in which the alkyne is acting formally as a four-electron donor [25].

In the case of a photochemical reaction of tungsten hexacarbonyl with an alkyne in low temperature argon or methane matrices, the formation of vinylidene complexes as well as tetracarbonyl species is characterized by significantly greater yield (Fig. 2). Tungsten alkyne complexes appear to be more photosensitive than molybdenum [26]. After irradiation with UV light, a higher concentration of vinylidene complexes was achieved than of alkyne complexes (Fig. 2). Two bands in the visible region, at 370 and 460 nm, are characteristic of the vinylidene complex. Irradiation

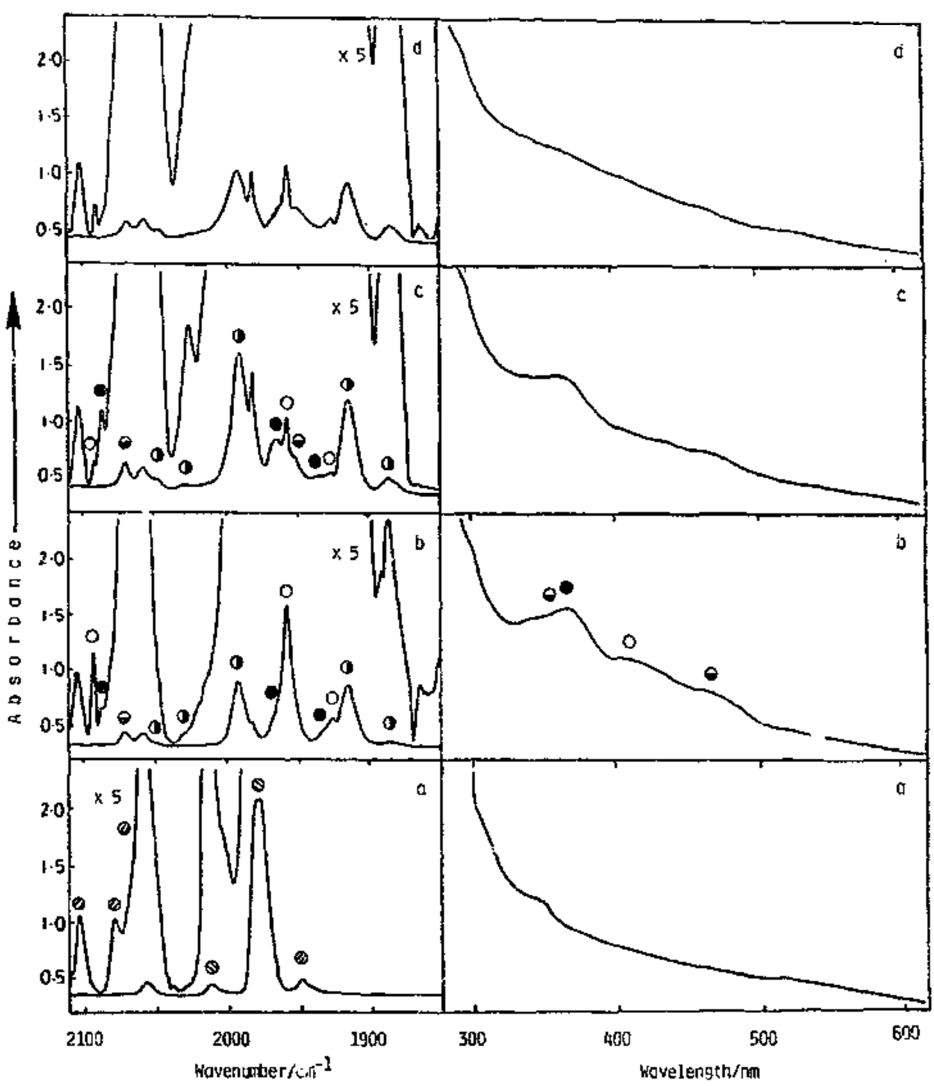


Fig. 2. IR absorption spectrum in the region 1850–2100 cm^{-1} and UV–vis absorption spectrum in the region 300–600 nm displayed by a solid CH_4 matrix containing $W(CO)_6$ and $MeC{\equiv}CH$ with the composition $W(CO)_6{:}MeC{\equiv}CH{:}CH_4$ of ca. 1:250:5000 at 20 K showing the effects of short-term photolysis at different wavelengths. (a) Spectra of the matrix after deposition. (b) Spectra after photolysis at $\lambda = 313$ nm. (c) Spectra after photolysis at $\lambda = 445$ nm. (d) Spectra after photolysis at $\lambda = 369$ nm. Bands are labelled as follows: ○ $[CH_4 \cdots W(CO)_5]$; ● $[(\eta^2\text{-}MeC{\equiv}CH)W(CO)_5]$; ◓ $[Me(H)C{=}C{=}W(CO)_5]$; ◑ $W(CO)_4$ species; ⊘ free [MeCCH] or $[MeCCH]_n$; and ⊗ $[W(CO)_6]$. (Reproduced with permission from Ref. [26]).

with green light leads to disappearance of $[CH_4 \cdots W(CO)_5]$ but does not influence vinylidene species. Photolysis with higher energy UV light leads to CO loss and formation of tetracarbonylalkyne species (Fig. 2).

The characterization of alkyne complexes of the type $[(\eta^2\text{-RC}\equiv\text{CH})\text{M(CO)}_5]$, $[\text{R(H)C}=\text{C}=\text{M(CO)}_5]$ and $[(\eta^2\text{-RC}\equiv\text{CH})\text{M(CO)}_4]$ is noteworthy because the formation of such compounds must surely be the first three stages in the mechanism proposed to account for the photocatalytical polymerization of terminal alkynes as mediated by Group 6 metal carbonyl compounds. In this way the mechanism for alkyne polymerization postulated by Geoffroy et al. [5] has been proven.

3.2. *Isomerization of alkenes*

Photolysis of a solution of Cr, Mo, and W carbonyls in excess of alkenes results in the olefin complex and olefin isomerization products [1–4,6,7]. Apart from the formation of olefin complexes, little is known regarding the details of the key steps in an actual olefin reaction. Photodissociation of CO from M(CO)_6 is known to lead to photosubstitution by an alkene. Often, the resulting metal alkene complex is regarded as a catalyst of alkene isomerization, which may occur thermally or may require further photoactivation [6]. During our continuing study of the photocatalytic system containing W(CO)_6 and an alkene, we set out to prepare bis(alkene)tetracarbonyl tungsten complexes which can be the prototypical catalyst for many catalytic reactions of olefins [28]. As compounds of this kind are thermally unstable, we chose the photolytical method of synthesis. Extended photolysis of tungsten hexacarbonyl in the presence of a 20-fold alkene excess in *n*-hexane at room temperature leads to the formation of the corresponding bis(alkene)tetracarbonyl compounds via the less stable $[(\eta^2\text{-alkene})\text{W(CO)}_5]$ complexes (Eq. (8)), as is shown in Fig. 3.

$$\text{W(CO)}_6 \xrightarrow[\text{alkene}]{h\nu/-\text{CO}} \text{W(CO)}_5\text{(alkene)} \xrightarrow[\text{alkene}]{h\nu/-\text{CO}} \text{W(CO)}_4\text{(alkene)}_2\text{alkene}$$

$$= \text{unsubstituted acyclic } (\text{C}_5\text{–C}_{10}) \text{ and cyclic } (\text{C}_5\text{–C}_8) \text{ olefins} \qquad (8)$$

The ν(CO) fundamentals of the W(CO)_5 unit give rise to three IR absorptions, namely a weak feature at 2083–2073 cm^{-1} (a_1) and two more intense features at 1933–1967 cm^{-1} (a_1+e) (Fig. 3). As expected, continued irradiation under such conditions resulted in the loss of a second molecule of CO with the appearance and growth of IR bands due to a bis(alkene)tetracarbonyl complex. The bis(alkene)tetracarbonyl compounds are stable enough to be characterized by IR, UV–vis and NMR spectra. A trans structure of these compounds has been assigned on the basis of the IR spectra. In the IR spectrum of these compounds, one strong band appears in the carbonyl stretching region at about 1940 cm^{-1}, as is expected for D_{4h} local symmetry of W(CO)_4 moiety [28].

Our new observations concerning the reactivity of those compounds shed considerable light on the nature and method of formation of the catalytic species and provided some evidence on the mechanism of the isomerization and metathesis reaction of alkenes. The reactivity investigation of terminal alkene compounds reveals that a thermal and photochemical reaction of bis(alkene) compounds leads to the formation of alkene isomerization products — an internal alkene. In the case

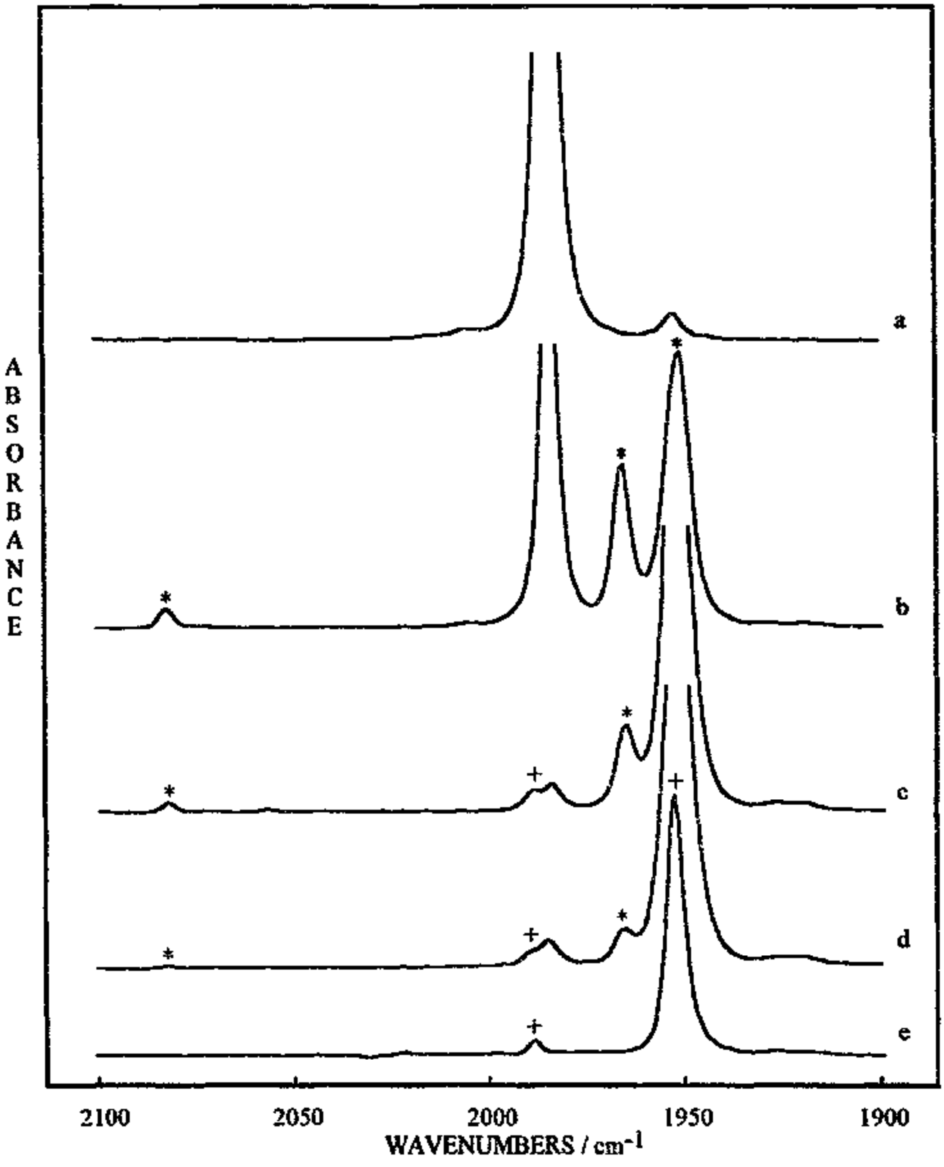
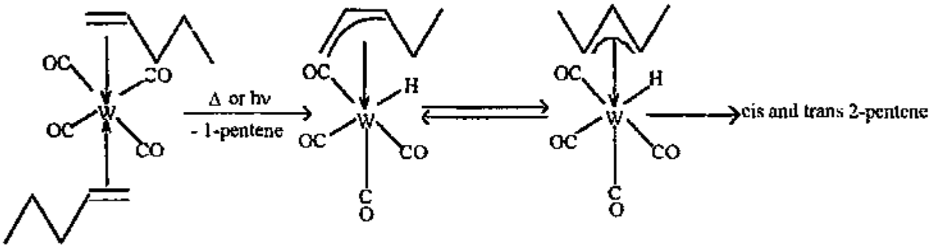


Fig. 3. IR absorption spectrum displayed by solution containing $W(CO)_6$ (3 mmol) and 1-hexene (62 mmol) in n-hexane (20 cm^3) showing the effects of photolysis. (a) Spectra before irradiation. (b) Spectra after 2 min photolysis. (c) Spectra after 10 min photolysis. (d) Spectra after 30 min photolysis. (e) Spectrum of *trans*-[$W(CO)_4(\eta^2$-1-hexene$)_2$] in n-hexane after separation from reaction mixture. Bands are labelled as follows: * 2082, 1951, 1965 cm^{-1} [$W(CO)_5(\eta^2$-1-hexene)]; + 1988, 1952 *trans*-[$W(CO)_4(\eta^2$-1-hexene$)_2$]. (Reproduced with permission from Ref. [28]).

of 1-pentene, *cis*- and *trans*-2-pentene are formed. In the presence of Lewis acid, the formation of metathesis products, ethylene, propylene and 1-butene, was observed. The formation of π-allylic hydrides is a key step in the catalytic isomerization of olefins and also in the metathesis of olefins [1,6,7,12]. After the thermal or photochemical loss of an alkene molecule, the formation of π-allylic hydride derivatives of tungsten can be imagined (Scheme 3).



Scheme 3.

In the presence of Lewis acids, the π-allylic hydride formed can rearrange to a metallacyclobutene derivative to initiate the metathesis of alkenes [7].

Evidence for the formation of π-allylic hydride intermediates was obtained from ^{1}H NMR investigation. In the ^{1}H NMR spectrum of bis(1-pentene)tetracarbonyl tungsten solution after heating, we not only observed the appearance of free 1-pentene, *cis*- and *trans*-2-pentene, but also signals characteristic of hydrides coordinated to tungsten. Two new signals appeared at about -3 ppm [29]. The distinctive high-field position of the hydride resonance and a definite, albeit small, ca. 17 Hz J(W–H), coupling is consistent with tungsten–hydrogen bond formation. To the best of my knowledge this is the first evidence for transformation of a coordinated alkene to a π-allylic hydride.

3.3. *Metathesis of alkenes*

Alkene metathesis catalysts can be photogenerated from $W(CO)_6$ in CCl_4 [8–11] or in the presence of Lewis acids — Group 4, 13, and 14 metal halides [7,11]. The photochemical reaction of Group 6 metal hexacarbonyls $M(CO)_6$ ($M=Cr$, Mo, W) in CCl_4 has been studied extensively and a series of compounds afforded by the reactions has been identified [4,7–11]. Our studies revealed that the reaction proceeded according to the following scheme.

$$M(CO)_6 + CCl_4 \xrightarrow{h\nu} [M(CO)_6^{\cdot +} \cdots CCl_4^{\cdot -}] \rightarrow [M(CO)_5Cl] + {}^{\cdot}CCl_3 + CO \tag{9}$$

Such a course of reaction was supported by the identification of the trichloromethyl radical as the spin adduct with nitrosodurane in reaction with Cr, Mo and W hexacarbonyls. The organometallic radical $M(CO)_5Cl$ was simultaneously identified as the spin adduct with nitrosodurane only in the case of chromium hexacarbonyl

($a_N = 8.346$ G; $a_{Cr} = 18.456$ G, $g = 1.985$) [11,30]. It was also observed that the radical $^{\cdot}CCl_3$ formed disappeared in the presence of metal hexacarbonyls at a rate depending on the kind of metal and decreasing in the order: W > Mo > Cr. Thus, it could be concluded that in the presence of metal hexacarbonyls, radicals formed in the first stage undergo secondary reactions depending on the kind of metal. An attack by $^{\cdot}CCl_3$ on the $[M(CO)_5Cl]$ can lead to an M^{II} compound $[M(CO)_4Cl_2]$ and dichlorocarbene. Another way to an M^{II} compound is a disproportionation reaction shown in Eq. (10).

$$2[M(CO)_5Cl] \rightarrow M(CO)_6 + 1/2[M(CO)_4Cl_2]_2 \qquad (10)$$

The formation of a compound of the type $[W(CO)_4Cl_2]_2$ was indicated by the IR method (νCO: 2100w, 2010s and 1940m cm^{-1} [31]). The photochemical oxidation reaction of $W(CO)_6$ to $[W(CO)_4Cl_2]_2$ with CCl_4 was applied in the synthesis of W^{II} compounds, $[WCl_2(CO)_3(PPh_3)_2]$ [31] and $[WCl_2(CO)_3bipy]$ [32].

In order to establish the route by which these W^I and W^{II} halocarbonyl intermediates are formed, and to gain an understanding of the overall reaction mechanism, experiments in low-temperature matrices have been done [33]. The photolysis of $W(CO)_6$ molecules isolated in CCl_4-doped Ar matrices at ca. 20 K or in solid CCl_4 matrices at ca. 70 K results in photodissociation of CO and formation of the unsaturated C_{4v} molecule $W(CO)_5$ which weakly binds a molecule of CCl_4. The complex $[W(CO)_5CCl_4]$ exhibits a UV–vis absorption band at 380 nm and three ν(CO) frequencies: 2088, 1973, and 1943 cm^{-1}. Attempts to chart the course of subsequent photochemical changes stemming from the primary product $[W(CO)_5CCl_4]$, and linking with the results of solution studies at ambient temperatures, have failed so far to produce any clear evidence of other products [33]. The identity of the catalytically active entity in this system remains unknown. A suggestion has been made [34] that it is an unstable dichlorocarbene complex of type $[Cl_2C{=}WCl_2(CO)_3]$.

To obtain more stable products, the investigation of photochemical reactions of $W(CO)_6$ and metal tetrahalides $SnCl_4$ [35] and $GeCl_4$ [36] was carried out. In that reaction, we observed the formation of bimetallic, dimeric tungsten(II) compounds. X-ray structure investigation revealed the formation of a tungsten–tin bond between tungsten and the trichlorostannate radical (Fig. 4). A similar product is formed in reaction with $GeCl_4$ [36]. The reaction mechanism for the formation of $[(CO)_4W(\mu\text{-}Cl)_3W(SnCl_3)(CO)_3]$ is not known, but the reaction can be summarized as follows [35]:

$$2W(CO)_6 + 2SnCl_4 \xrightarrow[C_6H_{12}]{h\nu} [(CO)_4W(\mu\text{-}Cl)_3W(SnCl_3)(CO)_3] + 5CO + SnCl_2 \qquad (11)$$

Reactivity investigations of halocarbonyltungsten–tin compounds have shown that substitutions of the CO group by an organic substrate occur very easily and compounds initiate the polymerization of terminal alkynes [37].

On the basis of similarity of reaction of Group 14 tetrahalides, we can postulate

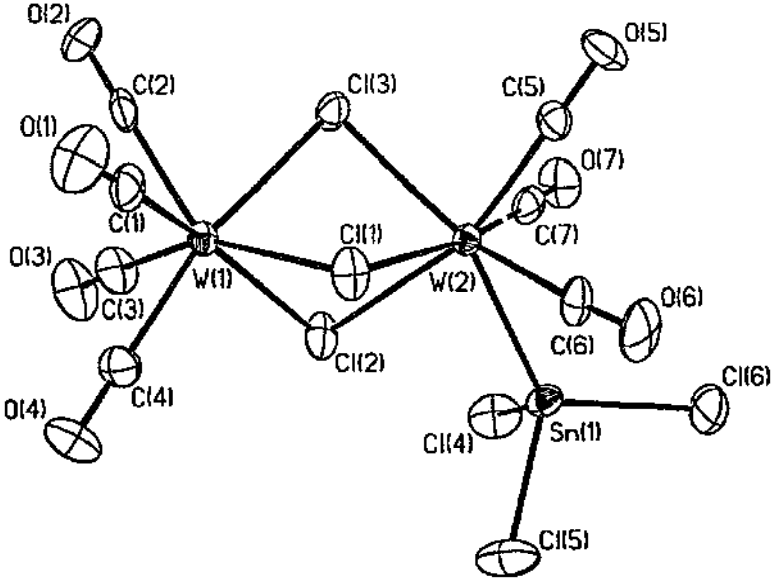
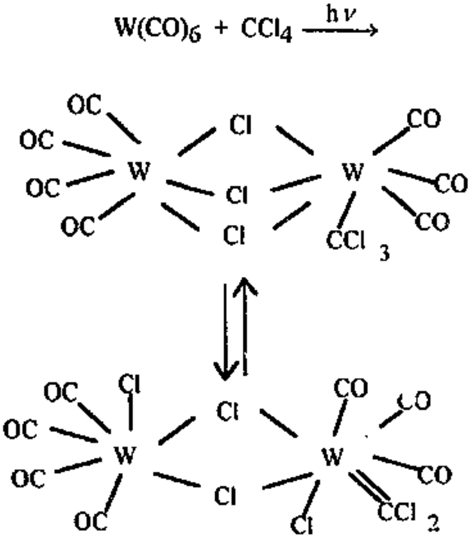


Fig. 4. *X*-ray crystal structure of the $[(CO)_4W(\mu\text{-Cl})_3W(SnCl_3)(CO)_3]$. (Reproduced with permission from Ref. [35]).

the formation of a similar halogen-bridged dinuclear complex also in reaction with carbon tetrahalide (Scheme 4). A trichlorocarbon radical coordinated to tungsten can rearrange to dichlorocarbene ligand. Dichlorocarbene complex can initiate the catalytic metathesis of alkenes.



Scheme 4.

4. Conclusion

Matrix isolation is an excellent method for monitoring the photosubstitution reaction of Group 6 hexacarbonyls. UV photolysis of low-temperature argon or methane matrices containing $M(CO)_6$ and an alkyne results in photodissociation of CO and the formation of alkyne complexes of the type $[(\eta^2\text{-RC}{\equiv}\text{CH})M(CO)_5]$, $[R(H)C{=}C{=}M(CO)_5]$ and $[(\eta^2\text{-RC}{\equiv}\text{CH})M(CO)_4]$. The formation of such compounds must surely be the first three stages in the mechanism proposed to account for the photocatalytical polymerization of terminal alkynes as mediated by Group 6 metal carbonyl compounds. In this way the mechanism for alkyne polymerization postulated by Geoffroy et al. [5] has been proven.

The bis(alkene)tetracarbonyl complexes of tungsten are good prototypical catalysts for the isomerization and metathesis of olefins. The rearrangement of these compounds to π-allyl hydrides was monitored by ^{1}H NMR.

The identification of $[(CO)_4W(\mu\text{-Cl})_3W(SnCl_3)(CO)_3]$, the product of the photochemical reaction of $W(CO)_6$ and $SnCl_4$, helps to explain the mechanism for the formation of dichlorocarbene — the catalytically active species in metathesis of olefin catalysed by the $W(CO)_6$–CCl_4 system.

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