

# Catalytically Active Intermediates in Photochemical Metathesis

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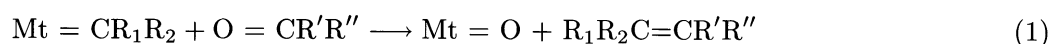
The nature of the active species in photocatalytic metathesis reaction was investigated. The formation of Wittig-type addition products with benzaldehyde indicates that catalytically active carbene is the product of olefin and tungsten hexacarbonyl under reaction conditions.

## Introduction

The photolysis of tungstenhexacarbonyl in carbon tetrachloride yields a catalytic mixture for olefin metathesis<sup>1</sup>. Many attempts have been made to characterize the reactive intermediates in this dark-colored heterogeneous mixture, and some species have been proposed mainly on the basis of some spectroscopic measurements<sup>3</sup>. Recently it has been shown that the metathesis reaction follows a heterogeneous pathway in this catalyst system, and some physical properties of the isolated precipitate have been reported<sup>4</sup>. Although the structure and the formation of the metathesis active intermediate are not yet clear, an intermediate transition metal carbene complex has long been believed to be active in metathesis reactions<sup>5</sup>. Because of this, well-characterized metal carbene complexes were prepared to metathesize olefins<sup>6</sup>. The carbene mechanism is now well accepted in the wide range of metathesis reactions.

According to the data in the literature, the formation of  $(CO)_4WCCl_2$ <sup>7</sup> and  $(CO)_3Cl_2W=CCl_2$  carbene complexes in the photocatalytic system has been postulated on the basis of the spectroscopic measurements. These dichlorocarbene tungsten complexes are believed to have catalytic properties.

It is also known that some metal-carbenes react with carbonyl compounds, as illustrated by equation 1<sup>8</sup>:



(Where  $R_1 =$  alkyl;  $R_2 =$  alkyl, H;  $R' =$  alkyl, aryl;  $R'' =$  alkyl, H)

In a system where metal-carbenes are present, the reaction (1) might be expected to take place. In this study, the relevant reactions of benzaldehyde in the photocatalytic metathesis are described.

## Experimental

### Materials

The  $W(CO)_6$  was purchased from Merck and used after sublimation. 1-octene (Merck), 2-octene and 4-octene (Sigma Chem. Company) were stored over  $CaH_2$  and then distilled under nitrogen. Cyclohexane (BDH), carbon tetrachloride (Merck) and benzaldehyde (Merck) were purified by fractional distillation in a nitrogen atmosphere.

### Typical reaction procedure

All reactions were carried out in a dry nitrogen atmosphere in 5-ml water-jacketed pyrex cells placed around a 150 W Hanau high-pressure mercury lamp. The system was first evacuated, and then filled with nitrogen. The cyclohexane solution (3.0 ml) containing  $W(CO)_6$  ( $8.80 \times 10^{-5}$  mol) and  $CCl_4$  (0.05 ml) was irradiated until the color turned to light yellow ( $\sim 12$  min), and then a mixture of olefin (0.5 ml; 1-octene, 2-octene, 4-octene) and benzaldehyde (0.1 ml) was added. Irradiation was continued for 2 hours more. Magnetic stirring was employed during irradiation.

### Analysis

GC-MS spectra of the reaction products were recorded on a combined system, HP 5890 GC, HP 5971 mass spectrometer connected to a HP 486/33 N computer preloaded with HP G 1034 C MS Chem. Station Software.

Column: 30 m, 0.2 mm internal diameter capillary, HP-1 % dimethylpolysiloxan gum.

Temperature : 50,250 °C, 10° C/min. Carrier gas: He 10 ml/min.

## Results and Discussion

For a comparative study of the effect of the carbonyl compound on the reaction, a series of experiments were carried out in the absence of the organic carbonyl compound. The formation of various types of chlorinated organic compounds associated with the metathesis products was observed in this case. Most were chlorinated derivatives of solvent cyclohexane (chlorocyclohexane) or substrate olefin (mono-or polychlorinated octenes). In addition on these side products, the formation of some other chloro-compounds (chloroform and hexachloroethane) and products of carbontetrachloride was observed. The formation of  $C_2Cl_6$  in the photocatalytic metathesis reaction has been reported previously<sup>9</sup>, but  $CHCl_3$  was observed in this study.

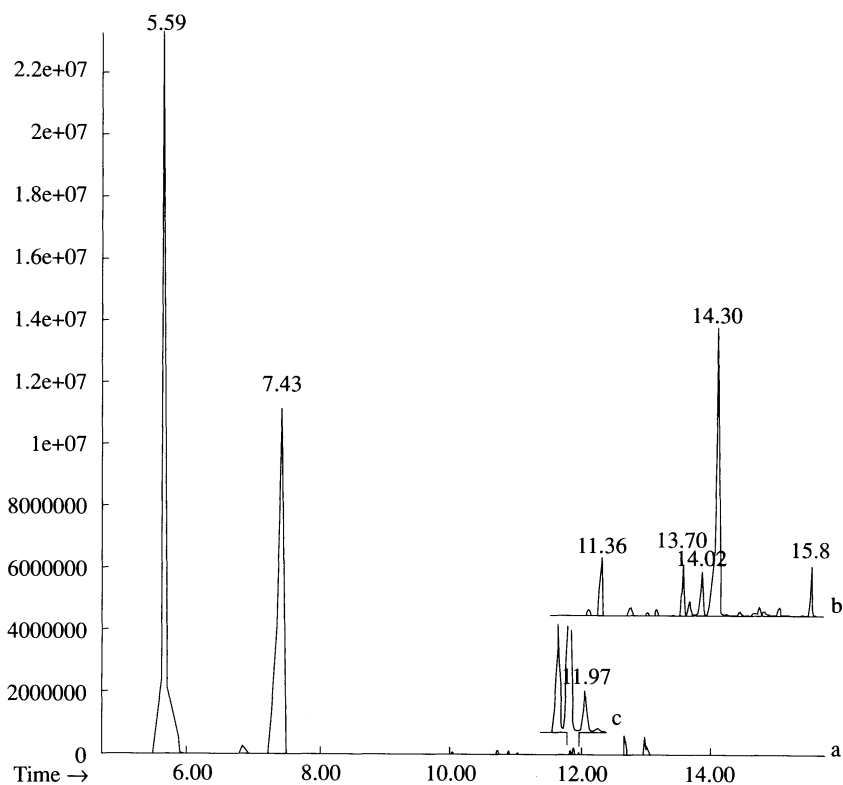
These chlorinated compounds, particularly  $C_2Cl_6$  and  $CHCl_3$ , clearly indicate the formation of  $CCl_3$  radicals when  $W(CO)_6$  is irradiated in the presence of  $CCl_4$ .

In order to determine whether a tungstendichlorocarbene complexes takes part in photocatalytic metathesis, benzaldehyde was added to the irradiated solution of  $W(CO)_6$  and  $CCl_4$  in cyclohexane. The possible product 1,1-dichloro, 2-phenyl-ethylene was not detected.

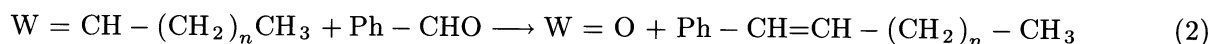
When similar experiments were carried out in the presence of olefins, the products shown in the Table were observed. When the  $W(CO)_6/CCl_4$  system was first irradiated for 10 minutes and the olefin and benzaldehyde were then added, there was no metathesis, but instead a very small amount of Wittig-type addition products (Figure) was detected.

**Table 1.** The Wittig-type addition compounds produced in the photochemical olefin metathesis when benzaldehyde was added.

Olefin	Wittig-Type Addition Product
1-Heptene	1phenyl-1-heptene
1-Octene	1-phenyl-1-octene
2-Octene	1-phenyl-1-heptene
4-Octene	1-phenyl-1-pentene

**Figure 1.** GC of the reaction mixtures, (a) photolysis of the  $W(CO)_6/CCl_4$  with 1-octene and benzaldehyde, (b) without benzaldehyde, (c) magnification of the indicated range.

The formation of phenyl substituted olefins may be expressed as follows:



Where  $n=2$  for 4-octene,  $n=4$  for 2-octene,  $n=5$  for 1 octene and  $W$  denotes the metal site with the ligands attached. The amounts of coupling products were not sufficiently large for isolation and further characterization.

The detailed GC-MS study of the reaction products showed no traces of terminal dichloro olefins. For this reason, it is difficult to attribute the catalytic properties of the  $W(CO)_6/CCl_4$  system to tungsten-dichlorocarbene complexes.

As reported by Brothers and Roper<sup>10</sup>, the combination of an oxidized tungsten fragment and a triplet state dichlorofragment should not be expected to give a stable carbene. Also the catalyst system shows higher activity when  $CCl_4$  is replaced by  $ZrCl_4$  or  $TiCl_4$ <sup>11</sup>. Therefore it is possible to assume the role of  $CCl_4$  to be that of reactant rather than a cocatalyst. These results lead us to propose an alternative

explanation for the formation of active species: the trichloromethyl radical formed in the photochemical system abstracts allylic hydrogen from the coordinated olefin and generates  $\text{CHCl}_3$  and the allyl-tungsten complex, which in turn may yield the expected metal-carbene by various routes.

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