

Tungsten(II) chlorocarbonyls as alkene metathesis, arene alkylation and alkyne polymerization catalysts

Teresa Szymańska-Buzar *

Faculty of Chemistry, University of Wrocław, 50-383 Wrocław, Poland

Received 27 December 1996; accepted 22 February 1997

Abstract

Tungsten(II) chlorocarbonyl compound obtained by photochemical oxidation of $W(CO)_6$ with CCl_4 is an active alkene metathesis catalyst, free of any organometallic component. This indicates that the initially formed alkylidene ligand must come from the alkene. In toluene solution the same tungsten(II) compound also acts as a highly active catalyst for the transformation of alkenes to alkyltoluenes. Tungsten(II) compounds, which are formed in photochemical oxidation of $W(CO)_6$ with Group 14 tetrahalides, are extremely reactive at 25°C in phenylacetylene polymerization. The results reported here clearly demonstrate that the formation of tungsten(II) might be an important event in the creation by Lewis acids (Group 14 tetrachlorides) of the catalytic activity of tungsten(0) compounds.

Keywords: Tungsten(II) complexes; Polymerization; Metathesis; Alkylation

1. Introduction

In the course of our study of the catalytic activity of the tungsten(0) carbonyl–Lewis acid system, we have found that halocarbonyls of tungsten(II) are formed in the initial process and that those could act as catalyst in the metathesis, isomerization and polymerization of alkenes or alkynes [1–5]. One of the products formed in the photochemical reaction of $W(CO)_6$ and CCl_4 which was identified by the IR method was $[WCl_2(CO)_4]_2$ [1,6–8]. A similar photochemical oxidative addition reaction occurs between $W(CO)_6$ and $SnCl_4$ [9] or $GeCl_4$ [10]. However, the product $[(CO)_4W(\mu-Cl)_3W(SnCl_3)(CO)_3]$ has

been shown by X-ray studies to be a dimer containing three bridging chloride ligands and a tungsten–tin bond [9]. The most active cocatalyst in the system with $W(CO)_6/h\nu$ proved to be $ZrCl_4$. Also in this case the formation of a tungsten(II) compound was observed [2–5]. For these reasons we have become interested in the use of tungsten(II) complexes as catalysts for alkene metathesis and alkyne polymerization.

A number of tungsten(II) complexes has previously been shown to be effective catalysts for the metathesis of alkenes [4,5,8,11–15], in particular the complexes $[WCl_2(CO_3L_2)]$, $L =$ phosphine, arsine. However, these complexes require Lewis acid [4,5] or thermal activation [11–14] to be metathesis or polymerization catalysts.

* Tel.: +48-71-222348; e-mail: tsz@chem.uni.wroc.pl.

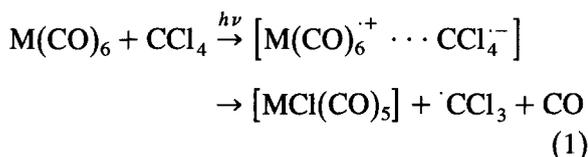
In this work, I report a new, surprisingly successful application of an alkene metathesis catalyst $[\text{WCl}_2(\text{CO})_4]_2$ to the synthesis of various alkylbenzenes and high molecular weight polyphenylacetylene.

2. Results and discussion

2.1. Synthesis of tungsten(II) compounds

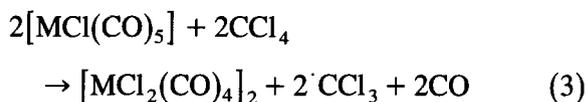
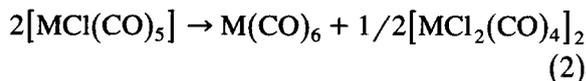
Tungsten(II) complexes can be prepared relatively simply in good yield in the photochemical reaction of $\text{W}(\text{CO})_6$ with CCl_4 , SnCl_4 or GeCl_4 according to the literature method [6,7,9,10]. Although the mechanism is unknown, in each case it is suspected that tungsten(0) is converted smoothly into tungsten(II) by a photochemical oxidative addition reaction.

The photochemical reaction of Group 6 metal hexacarbonyls $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) in CCl_4 has been studied extensively and a series of compounds afforded by the reactions has been identified [1,2,8,15–21]. Our studies revealed that the reaction proceeded according to the following scheme:



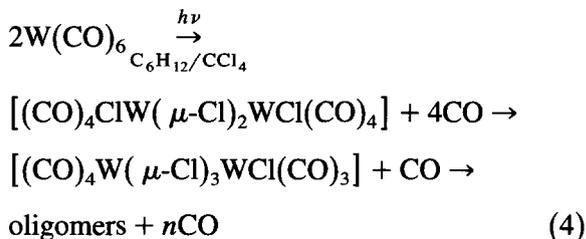
Such a course of reaction was supported by the identification of the trichloromethyl radical as the spin adduct with nitrosodurane in reaction with Cr, Mo and W hexacarbonyls. The organometallic radical $\text{MCl}(\text{CO})_5$ was simultaneously identified as the spin adduct with nitrosodurane in the case of chromium hexacarbonyl [1,19]. The transient formation of free $\cdot\text{CCl}_3$ was confirmed also in the present studies by reaction in cyclohexane, with CHCl_3 and hexyne products monitored by GC-MS. An attack by a trichloromethyl radical on $[\text{MCl}(\text{CO})_5]$ can lead to the compound $[\text{MCl}_2(\text{CO})_4]$ and dichlorocarbene. Another way to a compound

containing metal in the second oxidation state is Eq. (2) or Eq. (3).



Oxidation to $[\text{WCl}_2(\text{CO})_4]_2$ then occurs according to a stoichiometry which remains unknown. The formation of a compound of the type $[\text{WCl}_2(\text{CO})_4]_2$ was evidenced only by the IR method ($\nu(\text{CO})$ in KBr: 2096 (w), 2020 (vs), 1940 (s,br) cm^{-1}). The first halocarbonyl of tungsten(II) to have its structure determined [22] was $[\text{WBr}_2(\text{CO})_4]_2$, the product of the reaction between $\text{W}(\text{CO})_6$ and Br_2 . It is a dimer in which seven-coordinate tungsten atoms are bridged by two bromine ligands. The $\nu(\text{CO})$ frequencies for this compound were observed in CH_2Cl_2 solution at 2095 (w), 2020 (s) and 1935 (m) cm^{-1} [22]. The CO loss leads to an asymmetrical molecule with three bromine bridges $[(\text{CO})_4\text{W}(\mu\text{-Br})_3\text{WBr}(\text{CO})_3]$ [22].

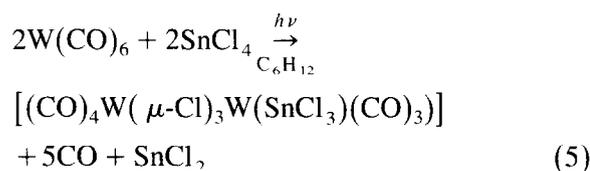
The precipitate which is formed at the time of the photolysis of $\text{W}(\text{CO})_6$ in CCl_4 or $\text{C}_6\text{H}_{12}/\text{CCl}_4$ solution is brown, insoluble in hydrocarbons, slightly soluble in CH_2Cl_2 and CCl_4 , and extremely sensitive to air. The ligands Cl bridge between metals and therefore lead to relatively insoluble and poorly characterized oligomers or polymers (Eq. (4)).



The resulting product can be dissolved in coordinate solvents such as acetonitrile or acetone; however, such solvents as other nucleophiles $\text{L} = \text{dppe}, \text{bpy}, \text{PPh}_3$, etc., give the corresponding monomeric seven-coordinate com-

plexes $[\text{WCl}_2(\text{CO}_3\text{L}_2)]$ [6,7]. A bis(acetonitrile) compound appears to be very unstable and difficult to characterize. This may be attributable to loss of CO and association, probably dimerization, with the formation of chlorine bridges. In acetone solution very fast decarbonylation and formation of a compound with the characteristic $\nu(\text{W}=\text{O})$ band at 970 cm^{-1} was observed.

To obtain more tractable products, the investigation of photochemical reactions of $\text{W}(\text{CO})_6$ and metal tetrachlorides SnCl_4 [9] or GeCl_4 [10] was carried out. In that reaction, we observed the formation of a bimetallic, dimeric tungsten(II) compound. X-ray structure investigation revealed the formation of a tungsten–tin bond between tungsten and the trichlorostannate radical. The mechanism for the formation of $[(\text{CO})_4\text{W}(\mu\text{-Cl})_3\text{W}(\text{SnCl}_3)(\text{CO})_3]$ is not known but the reaction can be summarized as follows (Eq. (5)) [9].



A similar product is formed in the reaction of $\text{W}(\text{CO})_6$ with GeCl_4 [10]. In contrast to

$[\text{WCl}_2(\text{CO})_4]_2$ both heterobimetallic tungsten(II) compounds are well soluble in aromatic and halogenated hydrocarbons. On the basis of the similarity of reactions of Group 14 tetrahalides, we can postulate the formation of a similar chlorine-bridged dinuclear complex (Eq. (5)) also in reactions with tetrachlorocarbon (Eq. (4)). However, we could not obtain evidence for the coordination of a trichlorocarbon radical or a dichlorocarbene ligand to tungsten.

2.2. Catalytic polymerization of phenylacetylene (PA)

Investigation into the possibility of the polymerization of PA by well-defined halo carbonyls of tungsten(II) initially focused on the compound $[\text{WCl}_2(\text{CO})_4]$ formed in the photochemical reaction of $\text{W}(\text{CO})_6$ with CCl_4 . Such a species is insoluble in hydrocarbons and poorly soluble in CH_2Cl_2 but reacts rapidly at room temperature with an excess of phenylacetylene to yield red poly(phenylacetylene) (PPA) in high yield. In toluene the reaction is completed in 2 h at room temperature. This is quite interesting since if toluene or no solvent at all is used the reaction mixture is not homogeneous but polymerization of PA occurs rapidly. The solubility

Table 1
Polymerization of PA catalyzed by chlorocarbonyls of tungsten(II) at room temperature ^a

Catalyst	Conversion (%)		Yield (%) ^b	$10^{-3} M_w$	DPBD			$(\text{PA})_2$	Other products, (%) ^c		
	1 h	24 h			—	—	—		1,2,3-TPB	1,2,4-TPB	1,3,5-TPB
$[\text{WCl}_2(\text{CO})_4]_2$ ^{d,e}	60	100	72	27	0.2	—	0.6	1.3	4.1	42.4	44
$[\text{WCl}_2(\text{CO})_4]_2$ ^e	57	100	83	50	—	—	—	5.0	3.6	34.6	39.3
$[(\text{CO})_4\text{W}(\mu\text{-Cl})_3\text{W}(\text{SnCl}_3)(\text{CO})_3]$	24	63	62	44	—	2.2	1.6	2.5	—	44.5	32.3
$[(\text{CO})_4\text{W}(\mu\text{-Cl})_3\text{W}(\text{GeCl}_3)(\text{CO})_3]$	67	95	51	20	3.8	5.2	3.0	—	—	20.0	8.7
$[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$ ^f	7	7.5	7.3	5	—	4.5	3.0	4.5	—	35.5	23.5
$[\text{WCl}(\text{GeCl}_3)(\text{CO})_3(\text{NCMe})_2]$	11	39	26	10	5.6	3.2	11.1	8.8	—	18.3	10.9

^a The reaction mixture contained 0.05 mmol of catalyst and 5 mmol of PA in 5 cm³ of toluene.

^b After 24 h reaction, dissolving in methylene chloride, precipitating with methanol and drying.

^c Other products in the residue obtained after separation of PPA.

DPBD – three different isomers of diphenylbutadiene with retention time 14.2, 14.8, 15.4, respectively; $(\text{PA})_2$ – dimer of PA detected by MS as 1*H*-indene-1-(phenylmethylene) with retention time 14.5; TPB – isomers of triphenylbenzene, with retention time 17.3, 19.8, 23.0, respectively.

^d Reaction in neat PA.

^e Heterogeneous system.

^f The same results were obtained with toluene or CH_2Cl_2 as solvent.

of the tungsten(II) compound does not appear to be an important factor. The compound is highly active even when it is insoluble. Polymerization in neat PA gave a material with properties typical of PPA obtained in solution (Table 1).

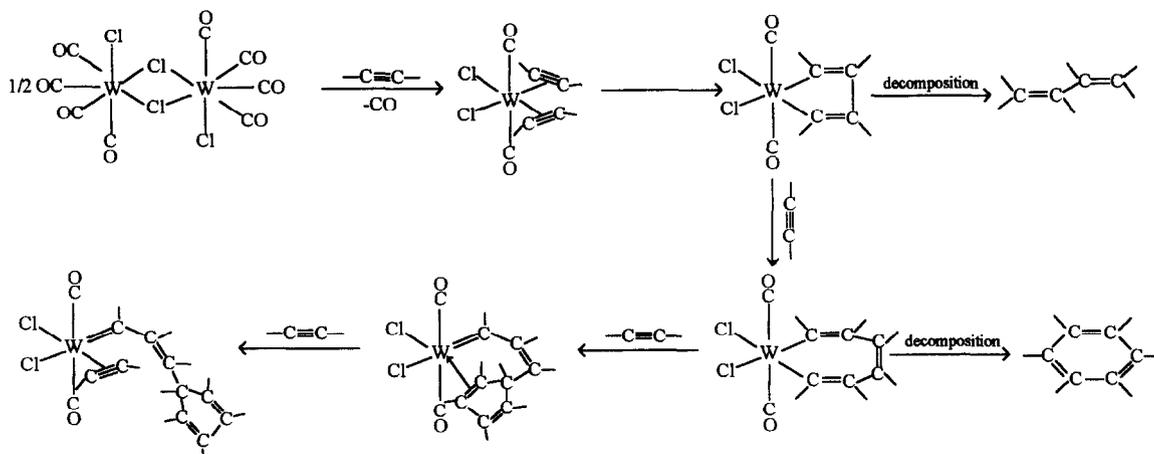
The data in Table 1 show that the yields of PPA depend on the used tungsten(II) compound. The dimeric compounds $[\text{WCl}_2(\text{CO})_4]_2$, $[(\text{CO})_4\text{W}(\mu\text{-Cl})_3\text{W}(\text{SnCl}_3)(\text{CO})_3]$ and $[(\text{CO})_4\text{W}(\mu\text{-Cl})_3\text{W}(\text{GeCl}_3)(\text{CO})_3]$ all polymerize PA at comparable rates that qualitatively are very fast. The monomeric tungsten(II) compounds $[\text{WCl}(\text{GeCl}_3)(\text{CO})_3(\text{NCMe})_2]$ and $[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$ obtained in reactions of the above dimers with acetonitrile have much more lower catalytic activity (Table 1). The composition of the residue obtained after the separation of PPA from the reaction mixture is also different. In reactions catalyzed by bis(acetonitrile) compounds the amount of formed dimers: diphenylbutadienes (DPBD) and $(\text{PA})_2$ in comparison to triphenylbenzenes (TPB) is much bigger than in reactions with dimeric tungsten compounds. The $(\text{PA})_2$ having formula $\text{C}_{16}\text{H}_{12}$ was identified by MS as 1*H*-indene-1-(phenylmethylene).

The PPA formed is from dark red to orange with molecular weight (M_w) from 1 to 5×10^4 , air-stable and totally soluble in aromatic and halogenated hydrocarbons. The structure of PPA was determined according to the method of Simionescu et al. [23] using IR and ^1H NMR spectroscopies and was identified as *trans*. A typical absorption at about 740 cm^{-1} characteristic of the *cis*-PPA is very low intensity or completely absent in the IR spectrum obtained here for the PPA samples. The signals in ^1H NMR spectra characteristic of stereoregular PPA are broad.

In studies of the polymerization reaction mechanism, the most difficult problem is to explain how the catalytically active intermediate can be formed in catalyst systems that do not contain an organometallic component and the initially formed catalytic species must come from the alkyne complex.

Reactivity investigations of $[(\text{CO})_4\text{W}(\mu\text{-Cl})_3\text{W}(\text{SnCl}_3)(\text{CO})_3]$ [24,25] and an analogous W–Ge [10] compound have shown that chlorine bridge-breaking and substitutions of a CO group by an organic substrate occur very easily and alkyne compounds $[\text{WCl}_2(\text{CO})_2(\text{RC}\equiv\text{CR}')_2]$ and $[\text{WCl}(\text{MCl}_3)(\text{CO})_2(\text{RC}\equiv\text{CR}')_2]$, M = Sn, Ge; R = R' = Ph, Et; R = Ph, 'Bu, R' = H are formed. In reaction with terminal alkynes at first formed complexes are very unstable and rearrange initiating polymerization reactions. The bis(phenylacetylene) complexes have the characteristic $\nu(\text{CO})$ vibration at about 2100 cm^{-1} but we have not yet been able to completely characterize these complexes, owing to their extreme lability [25]. In the reaction of $[\text{WCl}_2(\text{CO})_4]_2$ and the diphenylacetylene compound $[\text{WCl}_2(\text{CO})_2(\text{PhC}\equiv\text{CPh})_2]$ was identified by ^{13}C NMR spectra with characteristic carbon signals at δ 201.38 (CO), 187.86 ($\equiv\text{CPh}$) and 171.93 ($\equiv\text{CPh}$) ppm. This kind of compound could be formed also in the reaction of $[\text{WCl}_2(\text{CO})_4]_2$ with phenylacetylene but attempted characterization of this alkyne complex failed probably because of low conversion of the starting material and high reactivity of formed alkyne compound. In the reaction of the bis(acetonitrile) complex the formation of a PA complex with the characteristic $\nu(\text{CO})$ band at about 2100 cm^{-1} has also been observed.

In the polymerization of PA studied here the first intermediate is undoubtedly a bis(alkyne) complex. The bis(alkyne) tungsten(II) complexes whose structure was resolved by X-ray investigation have the *cis* configuration of two alkyne ligands [25,26]. The most probable mechanism for alkyne polymerization contains at first the coupling of two *cis* alkynes and metallacycle formation. The next step is the insertion of an alkyne into the metal–carbon bond as shown in Scheme 1. The metallacycle formed with four molecules of PA can then rearrange to an alkylidene ligand as was observed by Yeh et al. [27] in reaction of $\text{W}(\text{CO})(\text{PhC}\equiv\text{CPh})_3$ with an excess of diphenylacetylene. The small amounts of PA dimers



Scheme 1.

(PA)₂, diphenylbutadienes (DPBD) and triphenylbenzenes (1,3,5-TPB and 1,2,4-TPB), detected by GC-MS in a residue obtained after separation of PPA with methanol (Table 1), confirm the formation of metallacyclopentadiene and metallacycloheptatriene as intermediate compounds (Scheme 1).

2.3. Metathesis of 2-pentene

Recently we have been studying the role of Lewis-acids as catalyst activators, particularly for tungsten(0) metathesis catalysts. The most effective catalysts were found to be those in which tungsten(0) is converted to a tungsten(II) compound [3–5]. A great deal of knowledge concerning the mechanism of the formation of the possible catalytic intermediates has been accumulated and published; however, in almost all cases the nature of the catalytically active species is not well defined [1–5,28,29].

When chlorocarbonyl of tungsten(II) obtained in the photochemical oxidation of W(CO)₆ by CCl₄ is suspended in toluene and 2-pentene is added, a very fast metathesis reaction occurs and an equilibrium mixture of alkenes (50% of 2-pentene, 25% of 2-butene and 25% of 3-hexene) is achieved after a few minutes. However, in toluene solution alkene

metathesis products, as well as starting alkenes, rearrange to alkyltoluenes, which were detected by GC-MS as shown in Fig. 1. In this way it was possible to detect not only the initially formed alkenes but also their metathesis and cometathesis products.

When the reaction of [WCl₂(CO)₄]₂ occurred in neat 2-pentene, besides metathesis products,

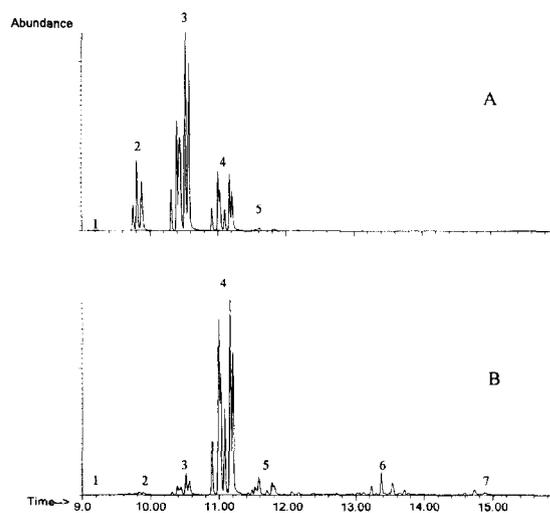
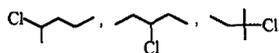


Fig. 1. GC-MS analysis of toluene alkylation products formed in a catalytic system consisting of [WCl₂(CO)₄]₂ and 2-pentene (A), 3-hexene (B). The group of signals denoted by 1 are isomers of propyltoluene, 2 – butyltoluene, 3 – pentyltoluene, 4 – hexyltoluene, 5 – heptyltoluene, 6 – octyltoluene, 7 – nonyltoluene.

the formation of a small amount ($\sim 5\%$) of chloropentanes, three isomeric forms:



in the ratio 1:0.9:0.7, respectively, was observed. Such a product can be formed after the insertion of an olefin into a W–Cl bond giving an alkyl ligand which after reductive elimination (abstraction of a proton from another compound) would produce chloropentane in a side reaction.

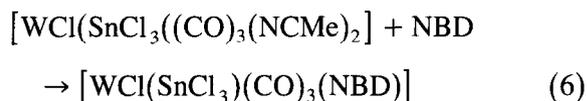
If the reaction of tungsten(II) compound occurs with 2-pentene being the mixture of isomers: *trans* (79.6%), *cis* (18.3%) and 1-pentene (2.3%), isomerization takes place as well as metathesis. In an equilibrium mixture of metathesis products, e.g. butene, pentene and hexene, an increase of *trans* isomers and decrease of terminal olefin with time was observed. The isomerization and metathesis are two parallel reactions and it seems plausible that the key step in both reactions is analogous, e.g. π -allyl hydride.

In contrast to many other olefin metathesis catalysts the system $[\text{WCl}_2(\text{CO})_4]_2$ does not lose its activity. The solid remaining after the removal of the reagents retains its catalytic activity. Reaction with olefin did not cause its decomposition as gauged by the lack of change in the IR spectra. This suggests that only a small part of the starting compound rearranges to catalytic active species. The unknown tungsten(II) chlorocarbonyl species therefore appears to be the active catalyst.

It is now accepted that in the case of olefin metathesis the alkylidene complexes are catalytically active species [30]. The question then arises: how are these intermediates formed from the known tungsten(II) complexes, $[\text{WCl}_2(\text{CO})_4]_2$ and an alkene?

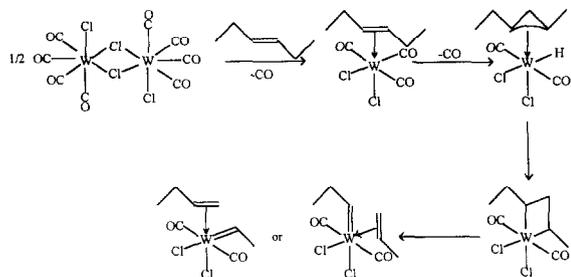
Several possible intermediates could arise through reactions of the tungsten(II) complex and the alkene, depending on whether the W–

Cl–W bridge-breaking and coordination of alkene, or alkene insertion into W–Cl bond is the preferred reaction channel. The results presented here suggest that the formation of active sites involves the removal of chloride ligands from the coordination sphere of the tungsten by chlorine bridge splitting, thus providing coordination sites for the incoming olefinic ligands like as in reactions with nitrogen or phosphorus containing ligands [24] or alkynes [25]. Therefore, it can be proposed that a six-coordinate alkene complex $[\text{WCl}_2(\text{CO})_3(\text{alkene})]$ or $[\text{WCl}_2(\text{CO})_2(\text{alkene})_2]$ is the first product formed in the reaction between $[\text{WCl}_2(\text{CO})_4]_2$ and the alkene. The compound $[\text{WBr}_2(\text{CO})_2(\text{NBD})]$, analogous to that proposed, was obtained in the reaction of $[\text{WBr}_2(\text{CO})_4]_2$ and norbornadiene (NBD) [31]. However, in a reaction of the substitution of the acetonitrile by norbornadiene [32] (Eq. (6)) a seven-coordinated tungsten(II) complex is formed; therefore the formation of a seven-coordinated alkene complex in the reaction of $[\text{WCl}_2(\text{CO})_4]_2$ and the alkene could not be excluded.



While I am not prepared at this time to propose a detailed mechanism for the generation of an alkylidene ligand from the coordinated alkene it is possible to speculate on some feasible mechanisms based on the findings of the first-formed alkenes in the metathesis products.

The simple alkene complexes of tungsten(II) are normally unstable. The coordinated alkene can rearrange to a π -allyl hydride and next to a cyclobutane ligand as was proposed by Green and coworkers [33–36] and Sherman and Schreiner [37]. The intermediate tungstenacyclobutane complex can rearrange to give a new alkene and alkylidene ligand (Scheme 2). Although no metallacycles are observed, the expected new alkenes (propene from 2-pentene; propene and butene from 3-hexene) have been



Scheme 2.

observed (Scheme 2). It is difficult to image a different way in which propene or butene can be formed from 3-hexene than metallacycle splitting.

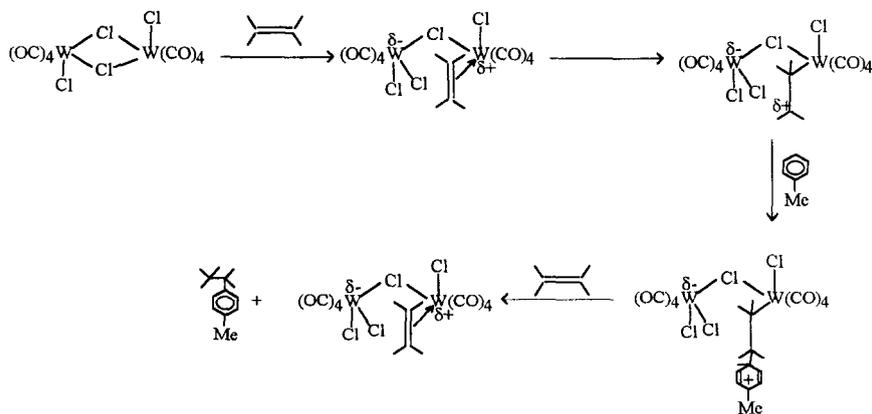
These observations are consistent with the proposition that the key step in metathesis catalyzed by $[\text{WCl}_2(\text{CO})_4]_2$ is the addition of an olefin to tungsten giving an unstable π -allyl hydride and next a metallacyclobutane ring which splits to carbene and alkene.

2.4. Catalytic alkylation of toluene

The alkylation of aromatic compounds by alkenes is not nearly as well-known as the alkylation of aromates by alkyl halides (Friedel–Crafts reaction), which is a fundamental process in organic chemistry. It was previously noted that the olefin metathesis catalyst, which has a strong Lewis acidity, promotes a secondary cationic reaction such as alkylation of

the aromatic solvent. Such a reaction can even mask completely the metathesis reaction [38–40]. With $[\text{WCl}_2(\text{CO})_4]_2$ as catalyst the alkylation and metathesis are two parallel reactions; however, the relative rate of metathesis reactions is much higher than the alkylation. In the metathesis reaction the equilibrium mixture of alkenes is achieved after 5 min, but 100% conversion of olefins to alkyltoluenes was observed after 24 h reaction time. A metathesis process should be lower in energy than an alkylation one. Activation energy of 6–8 kcal/mol was found for the metathesis reaction [41] and 10–16 kcal/mol is generally accepted for the alkylation of benzene by secondary carbenium ions [42].

It seems plausible that the key step in alkylation of toluene might be analogous to alkene metathesis. It seems reasonable to view the reaction as consisting of the coordination of alkene to the electrophilic metal center formed after asymmetrical chlorine bridge splitting, followed by nucleophilic attack by toluene on the strongly positively polarized olefin carbon atom (Scheme 3). Tungsten(II) alkene complexes could be polarized $\text{M}(\delta^+) - \text{C}(\delta^-) - \text{C}(\delta^+)$ and toluene could interact with the positive carbon of the coordinated alkene. The subsequent reductive elimination of the alkyltoluene involves the reconstruction of the chlorine bridge and regeneration of the starting tungsten(II) com-



Scheme 3.

plex. The coordinated alkene can rearrange as shown in Scheme 3.

The formation of the alkyltoluenes, confirmed by GC-MS, occurred in quantitative yield. Thus, rapid stirring of a mixture of $[\text{WCl}_2(\text{CO})_4]_2$ and 3-hexene in toluene at room temperature gives 78% conversion to hexyltoluene (GC-MS) after 24 h. The six isomers of hexyltoluene having the molecular formula $\text{C}_{13}\text{H}_{20}$ were observed (Fig. 1B). At this time no alkene remains, the other major products being butyl (3.2%) and pentyltoluenes (6.8%). A small amount of propyl (0.2%), heptyl (6.4%), octyl (3.2%) and nonyltoluene (2.2%) was also observed (Fig. 1B). In the reaction of 2-pentene, the metathesis products: propene, butene, hexene, and heptene, as well as pentene, produced alkyltoluenes (Fig. 1A).

One of the features of the Friedel–Crafts reaction promoted by Lewis-acids is that in substitution reactions on aromatic systems containing *ortho*–*para* directing substituents the product is predominantly the *para* isomer. It is a pity that it was impossible to identify isomers of alkyltoluenes, but without a doubt the ratio of the three regioisomers of butyltoluene is always the same, 1:3:2.6, the six isomers of pentyltoluene are in the ratio: 1:2.8:2.5:1.8:5.6:4.8 and the hexyltoluenes ratio is 1:2.5:2.1:1.1:2.7:2.3 (Fig. 1).

3. Conclusion

The irradiation of $\text{W}(\text{CO})_6$ in an alkane/ CCl_4 solution leads to a compound which was identified by the IR method as $[\text{WCl}_2(\text{CO})_4]_2$. This compound, free of any organometallic cocatalyst, is a highly active and selective reagent for the catalysis of alkene metathesis. Catalytically active species must come from the olefin complex.

The mechanism proposed for alkylidene formation is consistent with the key step being addition of an olefin to tungsten to give an unstable metallacyclobutane ring.

In the presence of terminal alkynes the tungsten(II) compound rearranges to an alkyne polymerization catalyst.

Of particular interest is the use of an alkene as the alkylating agent of toluene in a reaction catalyzed by chlorocarbonyls of tungsten(II).

Based upon these results, it seems likely that the formation of the tungsten(II) might be an important step in creating catalytic activity of tungsten(0) compounds by Lewis acids (Group 14 tetrachlorides).

4. Experimental

All operations were carried out in an inert atmosphere with standard Schlenk techniques. Photochemical reactions were carried out in a glass reactor with a Pyrex window. A high-pressure mercury lamp HBO 200 was used as the light source.

The analysis of the catalytic reaction products was performed on a Hewlett Packard GC-MS system. IR spectra were recorded on a FT-IR Impact 400, a Nicolet instrument.

4.1. Synthesis of tungsten(II) compounds

Tungsten(II) complexes can be prepared in the photochemical reaction of $\text{W}(\text{CO})_6$ with CCl_4 , SnCl_4 or GeCl_4 according to the literature method [6,7,9,10].

4.1.1. Photochemical reaction of $\text{W}(\text{CO})_6$ with CCl_4

$\text{W}(\text{CO})_6$ (1 g, 2.8 mmol) was dissolved in 100 cm^3 of CCl_4 or in a mixture of $\text{C}_6\text{H}_{12}/\text{CCl}_4$ 10:1, with continuous stirring under a stream of argon. The mixture was irradiated for 2 h. The amorphous, brown precipitate that settled down was filtered off, washed repeatedly with heptane to remove soluble side products and any unreacted $\text{W}(\text{CO})_6$. The relatively insoluble dark brown compound was dried under reduced pressure (yield = 1.2 g). The IR spectra of the isolated precipitate showed $\nu(\text{CO})$ bands charac-

teristic of $[\text{WCl}_2(\text{CO})_4]_2$ at 2096 (w), 2022 (vs) and 1940 (s,br) cm^{-1} . Analysis for carbon and chloride found: C 10.42% and Cl 19.88% (but changed in time even in an argon atmosphere); calculated for $[\text{WCl}_2(\text{CO})_4]_2$: C 13.1%, Cl 19.33% and for $\text{W}_2\text{Cl}_4(\text{CO})_7$: C 11.75%, Cl 19.82%.

4.1.2. Reactivity of $[\text{WCl}_2(\text{CO})_4]_2$

4.1.2.1. *Reaction with acetone.* $[\text{WCl}_2(\text{CO})_4]$ dissolving in acetone gives a dark brown solution; however, after a few minutes the solution becomes deep blue. The blue solid which is formed after evaporation of acetone is characterized by the absence of $\nu(\text{CO})$ bands and the presence of a strong $\nu(\text{W}=\text{O})$ band at 970 cm^{-1} in the IR spectrum.

4.1.2.2. *Reaction with acetonitrile.* $[\text{WCl}_2(\text{CO})_4]_2$ was dissolved in NCMe and the solution was stirred for 60 min. Filtration, followed by removal of the solvent in vacuo gave the brown $[\text{WCl}_2(\text{CO})_3(\text{NCMe})_2]$. IR: $\nu(\text{CO})$ 2030 (s) and 1940 (s); $\nu(\text{CN})$ 2320 (w) and 2290 (w) cm^{-1} .

4.1.2.3. *Reaction with PPh_3 .* $[\text{WCl}_2(\text{CO})_4]$ was dissolved in CH_2Cl_2 and a solution of PPh_3 in CH_2Cl_2 was added. Filtration followed by removal of the solvent in vacuo which gave the yellow powder, which was recrystallized from $\text{CH}_2\text{Cl}_2/\text{heptane}$, giving pure $[\text{WCl}_2(\text{CO})_3(\text{PPh}_3)_2]$. IR $\nu(\text{CO})$ at 2015 (s), 1935 (vs) and 1990 (s) cm^{-1} and other data agreed with those discussed elsewhere [6,7].

4.1.2.4. *Reaction with $\text{PhC}\equiv\text{CPh}$.* A solution of $\text{PhC}\equiv\text{CPh}$ was added to $[\text{WCl}_2(\text{CO})_4]$ dissolved in CH_2Cl_2 , and the mixture was stirred for 24 h. Filtration to remove the insoluble substrate and removal of the solvent in vacuo gave brown $[\text{WCl}_2(\text{CO})_2(\text{PhC}\equiv\text{CPh})_2]$, which was recrystallized from $\text{CH}_2\text{Cl}_2/\text{heptane}$. ^{13}C NMR δ (ppm) 201.38 (CO), 187.86 ($\equiv\text{C}$), 171.93 ($\equiv\text{C}$).

4.2. Catalytic reaction procedure

The procedures for metathesis, alkylation and polymerization are similar. The catalytic reactions were carried out in a 50 cm^3 glass reactor provided with a septum through which liquid reactants were introduced and removed by a syringe. The reactions were run in a 5 ml overall volume of solution containing about 5 mmol of the catalyst and 500 mmol of 2-pentene or PA. The solution was stirred and gas-samples were removed with a syringe and injected into the PORA PLOT-Q, 15 m, column of the chromatograph fitted with a flame ionisation detector. For reactions in which the product could not be resolved by GLC, the GC-MS was used in addition (HP5, 25 m, column).

4.3. Catalytic polymerization of phenylacetylene (PA)

In a typical reaction, the toluene solution of PA and the internal chromatographic standard (*ortho*-xylene) was added to the catalyst and the conversion of PA was monitored by chromatography.

For the analysis of PA reaction products, reactions were continued for 24 h and then methanol was added. The polymer was collected, recrystallized from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$, dried in vacuo and analyzed by ^1H NMR, IR spectroscopy and gel-permeation chromatography. Molecular weights of the PPA were measured using toluene solutions, a refractive index monitor and a Plgel 10 μ MIXED-B column. The values recorded are the weight of polystyrene that would exhibit the chromatograms observed.

The filtrate obtained after the precipitation of the polymers was evaporated to dryness and the CH_2Cl_2 solution of the residue was investigated by GC-MS. Analysis showed mainly diphenylbutadienes and triphenylbenzenes.

4.4. Metathesis of 2-pentene

In a typical reaction, the solution of alkene and internal chromatographic standard cy-

clopentane was added to a catalyst. The suspension was stirred at 25°C and gas-samples were removed with a syringe and injected into the column of chromatograph fitted with a flame ionisation detector.

4.5. Alkylation of toluene

The toluene solution of alkene and $[\text{WCl}_2(\text{CO})_4]_2$ was stirred at 25°C for 24 h. After that time the analysis by GLC did not indicate the presence of alkenes. The toluene was removed by distillation under reduced pressure and the residue was identified by mass spectrometry to be a mixture of alkyltoluenes in 100% yield.

Acknowledgements

This work was supported by a grant from the Polish State Committee for Scientific Research (KBN No. 3T09A 094 10).

References

- [1] D. Borowczak, T. Szymańska-Buzar, J.J. Ziółkowski, *J. Mol. Catal.* 27 (1984) 355.
- [2] T. Szymańska-Buzar, J.J. Ziółkowski, *J. Mol. Catal.* 43 (1987) 161.
- [3] T. Szymańska-Buzar, *J. Mol. Catal.* 48 (1988) 43.
- [4] T. Szymańska-Buzar, *J. Mol. Catal.* 68 (1991) 177.
- [5] T. Szymańska-Buzar, *J. Mol. Catal.* 93 (1994) 137.
- [6] T. Szymańska-Buzar, *Inorg. Chim. Acta* 145 (1988) 231.
- [7] T. Szymańska-Buzar, *J. Organomet. Chem.* 375 (1989) 85.
- [8] P.G.M. Schilder, D.J. Stufkens, A. Oskam, J.C. Mol, *J. Organomet. Chem.* 426 (1992) 351.
- [9] T. Szymańska-Buzar, T. Głowiak, *J. Organomet. Chem.* 489 (1995) 207.
- [10] T. Szymańska-Buzar, in preparation.
- [11] L. Bencze, K.J. Ivin, J.J. Ronney, *J. Chem. Soc., Chem. Commun.* (1980) 834.
- [12] L. Bencze, A. Kraut-Vass, *J. Mol. Catal.* 28 (1984) 369.
- [13] L. Bencze, A. Kraut-Vass, *J. Organomet. Chem.* 270 (1984) 211.
- [14] L. Bencze, A. Kraut-Vass, L. Prókai, *J. Chem. Soc., Chem. Commun.*, (1985) 911.
- [15] A. Agapiou, E. McNeils, *J. Organomet. Chem.* 99 (1975) C47.
- [16] A. Agapiou, E. McNeils, *J. Chem. Soc., Chem. Commun.* (1975) 187.
- [17] P. Krausz, F. Garnier, J.E. Dubois, *J. Am. Chem. Soc.* 97 (1975) 437.
- [18] P. Krausz, F. Garnier, J.E. Dubois, *J. Organomet. Chem.* 108 (1976) 197.
- [19] T. Szymańska-Buzar, M. Gyor, A. Rockenbauer, L. Sümegi, *React. Kinet. Catal. Lett.* 32 (1986) 407.
- [20] T. Szymańska-Buzar, A.J. Downs, T.M. Greene, M.A.K. Wood, *J. Organomet. Chem.* 419 (1991) 151.
- [21] F. Garnier, P. Krausz, H. Rudler, *J. Organomet. Chem.* 186 (1980) 77.
- [22] F.A. Cotton, L.R. Falvello, J.H. Meadows, *Inorg. Chem.* (1985) 514.
- [23] C.J. Simionescu, V. Percec, S. Dumitrescu, *J. Polym. Sci. Polym. Chem.* 15 (1977) 2497.
- [24] T. Szymańska-Buzar, *J. Organomet. Chem.* 492 (1995) 241.
- [25] T. Szymańska-Buzar, T. Głowiak, *J. Organomet. Chem.* 523 (1996) 63.
- [26] E.M. Armstrong, P.K. Baker, M.G.B. Drew, *J. Organomet. Chem.* 336 (1987) 377.
- [27] W.-Y. Yeh, S.-M. Pengband, G.-H. Lee, *J. Chem. Soc. Chem. Commun.* (1993) 1056.
- [28] M. Jaroszewski, T. Szymańska-Buzar, M. Wilgocki, J.J. Ziółkowski, *J. Organomet. Chem.* 509 (1996) 19.
- [29] T. Szymańska-Buzar, M. Jaroszewski, M. Wilgocki, J.J. Ziółkowski, *J. Mol. Catal.* 112 (1996) 203.
- [30] R.R. Schrock, *J. Organomet. Chem.* 300 (1986) 249, and references therein.
- [31] F.A. Cotton, J.H. Meadows, *Inorg. Chem.* 23 (1984) 4688.
- [32] T. Szymańska-Buzar, T. Głowiak, *Polyhedron* 16 (1997) 1599.
- [33] M. Ephritikine, M.L.H. Green, R. MacKenzie, *J. Chem. Soc., Chem. Commun.* (1976) 619.
- [34] M. Ephritikine, M.L.H. Green, *J. Chem. Soc., Chem. Commun.* (1976) 926.
- [35] N.J. Cooper, M.L.H. Green, *J. Chem. Soc., Chem. Commun.* (1974) 76.
- [36] G.J.A. Adam, S.G. Davies, K.A. Ford, M. Ephritikine, P.F. Todd, M.L.H. Green, *J. Mol. Catal.* 8 (1980) 15.
- [37] F.O. Sherman, P.R. Schreiner, *J. Chem. Soc., Chem. Commun.* (1978) 223.
- [38] M. Nagasawa, K. Kikukawa, M. Takagi, T. Matsuda, *Bull. Chem. Soc. Jpn.* 51 (1978) 1291.
- [39] L. Hocks, A.J. Hubert, P. Teyssie, *Tetrahedron Lett.* 29 (1973) 2719.
- [40] L. Hocks, A. Noels, A.J. Hubert, P. Teyssie, *J. Org. Chem.* 41 (1976) 1631.
- [41] W.B. Hughes, *J. Am. Chem. Soc.* 92 (1970) 532.
- [42] G.A. Olah, P.R. Schleyer, *Carbonium Ions*, vol. II, Interscience, New York, N.Y., 1968, p. 774.