Journal of Organometallic Chemistry, 128 (1977) 339—344

FORMATION OF METAL—CARBENE COMPLEXES IN THE REACTION OF TRIMETHYLSILYL(GERMYL)METHYLLITHIUM WITH WCl_6. USE OF THIS REACTION FOR INITIATION OF CYCLOOLEFIN POLYMERIZATION

B.A. DOLGOPLOSK, I.A. ORESHKIN, K.L. MAKOVETSKY *, E.I. TINYAKOVA, I.Ya. OSTROVSKAYA, I.L. KERSHENBAUM and G.M. CHERNENKO

Institute of Petrochemical Synthesis of the U.S.S.R., Academy of Sciences, Moscow (U.S.S.R.)

(Received September 9th, 1976)

Summary

In a study of the reaction of WCl_6 with $LiCH_2ZMe_3$ (Z = Si or Ge) evidence for metal—carbene intermediates emerged. The main products of Me_3ZCH_2 group conversion were trimethylchlorosilane(germane) and tetramethylsilane-(germane). The breaking of the W—CH_2ZMe_3 bond with a "throwing-off" of the methylene fragment as a complex with tungsten is believed to account for the formation of Me_3ZCl compounds. Further decomposition of the tungsten—methylene complex leads to the production of ethylene and propylene. It has been shown that Me_4Z formation is not associated with homolytic splitting of the W—C bond. A possible reaction scheme for this involves the metal—carbene species. WCl_6 and trimethylsilylmethyl derivatives of Li, Mg and Ti proved to be effective catalysts for ring-opening polymerization of cycloolefins.

Introduction

According to current ideas carbene complexes of some transition metals (W, Mo, etc.) are the active centres in olefin metathesis and cycloolefin ring-opening polymerization. Recently it has been shown possible to initiate cycloolefin ring-opening by metal—carbene complexes produced during the decomposition of aliphatic diazo-compounds with tungsten halides [1,2]. The pathways of the metal—carbene active centres formation in commonly used catalytic systems may vary, e.g., α-elimination of hydride from transition metal alkyls, isomerization of π-olefin complexes, etc. Below we describe some results of a study of the new catalytic system effective for cycloolefin ring-opening polymerization, where the intermediate formation of the metal—carbene species can be traced by analysis of the products obtained in the interaction of the catalyst components.

TABLE 1

YIELDS OF SOME PRODUCTS FORMED IN THE REACTION OF WCl_6 WITH $LiCH_2ZMe_3$ (Z = Si OR Ge) (Yields shown based on LiR or WCl_6)

(WCl_6 concentration 0.02 mole/l, temperature 20°C, solvent: benzene)

Reagents	Molar ratio Li : W	Yields of products (GLC data) (mole %)							
		Me_3SiCl		Me_4Si		Me_3GeCl		Me_4Ge	
		LiR	WCl_6	LiR	WCl_6	LiR	WCl_6	LiR	WCl_6
$WCl_6 + LiCH_2SiMe_3$	1 : 1	31.5	31.5	17.0	17.0				
$WCl_6 + LiCH_2SiMe_3$	2 : 1	23.5	47.0	23.5	47.0				
$WCl_6 + LiCH_2SiMe_3$	3 : 1	8.0	24.0	22.0	66.0				
$WCl_6 + LiCH_2SiMe_3$	4 : 1	5.5	22.0	27.0	108.0				
$WCl_6 + LiCH_2SiMe_3$	5 : 1	0	0	21.0	105.0				
$WCl_6 + LiCH_2SiMe_3$ [a]	1 : 1	27.5	27.5	n/d					
$WCl_6 + LiCH_2GeMe_3$	1 : 1					43.5	43.5	11.3	11.3
$WCl_6 + LiCH_2GeMe_3$	2 : 1					34.5	69.0	24.0	48.0

[a] In this experiment the reaction was carried out in the presence of cyclopentene (10 mols C_5H_8 : 1 mol WCl_6).

Results and discussion

The reaction of WCl_6 with organolithium compounds of general formula $LiCH_2ZMe_3$ (Z = Si or Ge) proceeds very fast in a hydrocarbon medium at room temperature. According to PMR data the interaction of equimolar amounts of these reagents leads to the complete disappearance of the organolithium compound from the solution after 10—15 min. Organometallic derivatives of tungsten produced by alkylation of WCl_6 decompose rapidly under the conditions employed giving some reduced form of tungsten and different products of Me_3ZCH_2 group conversion. The products were identified on the basis of GLC, PMR and mass-spectral data. Table 1 shows the yields of the two principal reaction products, Me_3SiCl (or Me_3GeCl) and Me_4Si (Me_4Ge), obtained at different molar ratios of Li : W.

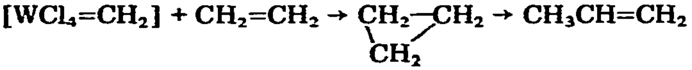
In addition to the major components listed in Table 1 the reaction mixture also contained Me_3SiCH_2Cl (or Me_3GeCH_2Cl) and $(Me_3SiCH_2)_2$, the expected decomposition products of the alkyl derivatives of transition metals.

The formation of significant amounts of Me_3SiCl(Me_3GeCl) can be considered as the most important fact. The only reasonable explanation of their production seems to be the "throwing-off" of the methylene fragment from the Me_3ZCH_2 group of the organotungsten compound obtained in the alkylation stage. A possible reaction scheme involves the metal—carbene intermediate (I):

$$\begin{aligned} &Me_3ZCH_2Li + WCl_6 \rightarrow Me_3ZCH_2WCl_5 + LiCl \\ &Me_3ZCH_2WCl_5 \rightarrow Me_3ZCl + \underset{(I)}{[CH_2{=}WCl_4]} \end{aligned} \qquad (1)$$

The energetically advantageous formation of the Si(Ge)—Cl bond as well as a certain carbene stabilization by complexation may be invoked to account for the observed mode of decomposition. The ensuing breakdown of the intermediate I results in the formation of ethylene and propylene (Table 2).

As seen from the Table 2 data, at molar ratio Li : W = 1, up to 58% methylene fragments may be converted to ethylene. A reduction in the amount of ethylene with the increase of the Li : W ratio correlates with the fall of Me_3SiCl yields and the simultaneous increase of Me_4Si yields (cf. also Table 1). The formation of propylene may be attributed to isomerization of the intermediate cyclopropane (eq. 2):



$$[WCl_4{=}CH_2] + CH_2{=}CH_2 \rightarrow \text{cyclo-}(CH_2)_3 \rightarrow CH_3CH{=}CH_2 \qquad (2)$$

The presence of trace amounts of cyclopropane was established by GLC analysis. It is noteworthy that norcarane and some other cyclopropane derivatives, as has been shown in our laboratory, are readily subject to isomerization to olefins in the presence of metathesis catalysts.

Both ethylene and propylene were practically absent in the reaction mixture when the reaction between $LiCH_2SiMe_3$ and WCl_6 was carried out in the presence of cyclopentene (Table 2). The disappearance of these olefins may be related to the participation of the metal—carbene intermediate I in the initiation of cycloolefin polymerization, so far as the yield of Me_3SiCl (Table 1) is nearly independent of the presence of the cycloolefin.

TABLE 2

ETHYLENE AND PROPYLENE FORMATION IN THE INTERACTION OF WCl_6 WITH $LiCH_2SiMe_3$

Molar ratio Li : W	Yield (mol %) [a]	
	Ethylene	Propylene
1 : 1	58	trace
2 : 1	17	8.5
1 : 1 [b]	0	trace
2 : 1 [b]	trace	trace

[a] Based on intermediate I formation according to eq. 1. [b] Reaction was carried out in the presence of cyclopentene (100 mol C_5H_8 : 1 mol WCl_6).

The formation of Me_4Si and Me_4Ge might be a result of a homolytical cleavage of the W—CH_2ZMe_3 bond with the production of the $^{\cdot}CH_2ZMe_3$ free radical followed by hydrogen abstraction from the solvent. However, the mass-spectra showed that neither Me_4Si not other conversion products contained deuterium atoms when the reaction was conducted in deuterated solvents ($CD_3C_6H_5$ or C_6D_{12}). The production of Me_4Si could be accounted for by a peculiar disproportionation reaction of the dialkyltungsten derivatives:

$$\begin{aligned} &2\,Me_3SiCH_2Li + WCl_6 \rightarrow (Me_3SiCH_2)_2WCl_4 + LiCl \\ &(Me_3SiCH_2)_2WCl_4 \rightarrow Me_4Si + \underset{(II)}{[Me_3SiCH{=}WCl_4]} \end{aligned} \tag{3}$$

If that is the case, reaction 3 is very similar to the reaction of neopentyllithium with tris(neopentyl)tantalum dichloride affording neopentane and an alkylcarbene complex of tantalum [3]. We had not been able hitherto to trace the formation of the assumed complex II. But the increase of the $Me_4Si(Me_4Ge)$ yields at high Li : W molar ratios (Table 1) may be interpreted as circumstantial evidence in favour of the suggested reaction scheme. The formation of dialkyltungsten derivatives in the equimolar interaction of the reagents would then be related to the associated state of the organolithium reagent.

The catalysts produced from WCl_6 and trimethylsilylmethyl derivatives of the Group I—IV metals are very effective for cycloolefin ring-opening polymerization, as shown in Table 3. Cyclopentene may be polymerized by the system WCl_5—$LiCH_2SiMe_3$ in a wide temperature region. High conversions of polypentenamer are attained in reasonable times even at —78° C. Although the lithium compound seems to be the most active as a component of the catalysts of this type, sufficiently high activity is inherent also for magnesium and titanium derivatives, as illustrated in Table 3. The catalysts containing organomagnesium and organolithium compounds exert anionic character and avoid therefore side reactions of the Friedel—Crafts type which constitute a serious drawback of the common metathesis catalysts based on the organoaluminium compounds.

The new type of decomposition reactions discussed above may be considered as an example of a redox reaction generating metal—carbene complexes since the formation of the latter are accompanied by the transition of tungsten(VI) to tungsten(IV) in a single chemical act.

TABLE 3

CYCLOOLEFIN POLYMERIZATION BY THE CATALYSTS BASED ON WCl_6 AND $M(CH_2ZMe_3)_n$ COMPOUNDS (M = Li, Mg, OR Ti; Z = Si OR Ge) IN TOLUENE

Cycloolefin	$M(CH_2ZMe_3)_n$	Molar ratios		Concentration of COL (vol %)	Temperature (°C)	Time (h)	Polymer yield (%)	*cis*-Unit content (%)
		M : W	*COL*[a] : W					
Cyclopentene	$LiCH_2SiMe_3$	1	2000	50	20	0.25	83	22
Cyclopentene	$LiCH_2SiMe_3$	1	1000	20	20	1.0	66	30
Cyclopentene	$LiCH_2SiMe_3$	1	1000	60	−30	0.5	41	53
Cyclopentene	$LiCH_2SiMe_3$	1	1000	60	−78	0.5	35	67
Cyclopentene	$LiCH_2GeMe_3$	2	1000	55	20	0.5	39	44
Cyclopentene	$Mg(CH_2SiMe_3)_2$	0.5	500	40	20	1.0	72	37
Cyclopentene	$Ti(CH_2SiMe_3)_4$	1	1000	60	20	0.25	44	32
Cyclooctadiene-1,5	$LiCH_2SiMe_3$	1	1000	50	20	1.0	82	77
Cyclooctadiene-1,5	$Mg(CH_2SiMe_3)_2$	0.5	500	50	20	0.75	18	83

[a] COL = cycloolefin.

Experimental

All experiments were performed under carefully purified argon. Tungsten hexachloride was purified by sublimation of volatile impurities (mostly $WOCl_4$) at 200°C in an argon stream, and was dissolved in dry toluene or an other hydrocarbon solvent to form 0.02—0.05 *M* solution. Solvents and cycloolefins employed in this study were purified by conventional methods, distilled under Ar atmosphere and stored over sodium wire or in the presence of ethyllithium.

Trimethylsilylmethyllithium was prepared by the reaction of Li metal with Me_3SiCH_2Cl in benzene at 60°C by a somewhat modified procedure of Lewis and Brown [4]. A similar method was used for the synthesis of Me_3GeCH_2Li. Bis(trimethylsilylmethyl)magnesium was synthesized by the interaction of Mg turnings with Me_3SiCH_2Cl in absolute ether followed by symmetrization with dioxan. Tetrakis(trimethylsilylmethyl)titanium(IV) was prepared from $TiCl_4$ and $LiCH_2SiMe_3$ in hexane at 0—4°C according to the method reported in [5] with some modification. Organometallic compounds were used as 0.01—0.04 *M* solutions in hydrocarbons.

The reactions of $LiCH_2SiMe_3$ (or its germanium analog) with WCl_6 was carried out in sealed glass tubes. After 15 min at 20°C all volatile products were distilled off and analysed by GLC. Analyses of the silicon and germanium derivatives were performed using a 3 m × 3 mm column with 10% squalane on Chromosorb W operated at 50°C, n-hexane being used as an internal standard. For ethylene and propylene analysis 4.5 m × 3 mm column with 10% squalane on Chromaton N operated at 20°C was employed.

Polymerization runs were carried out in 30 ml glass bottles. The charge order was: monomer, WCl_6 solution, additional amount of solvent, and after 10—15 min, solution of organometallic compound. Sealed bottles were transfered to the proper constant temperature bath. Polymerization was terminated with methanol, and the polyalkenamers obtained were analyzed by the usual methods.

References

1 B.A. Dolgoplosk, T.G. Golenko, K.L. Makovetsky, I.A. Oreshkin, and E.I. Tinyakova, Dokl. Akad. Nauk SSSR, 216 (1974) 807; Eur. Polym. J., 10 (1974) 901.
2 T.G. Golenko, B.A. Dolgoplosk, K.L. Makovetsky, I.Ya. Ostrovskaya, Dokl. Akad. Nauk SSSR, 220 (1975) 863.
3 R.R. Schrock, J. Amer. Chem. Soc., 96 (1974) 6796.
4 H.L. Lewis, T.L. Brown, J. Amer. Chem. Soc., 92 (1970) 4664.
5 M.R. Collier, M.F. Lappert, J. Chem. Soc. Dalton, (1973) 445.