Journal of Organometallic Chemistry, 451 (1993) C7–C9 C7

JOM 23615PC

Preliminary Communication

Influence of steric crowding at the heteroatom on the metathesis of functionalized olefins: the polymerization of alkylthiocyclooctenes catalyzed by a metallacyclic aryloxo(chloro)neopentylidenetungsten complex *

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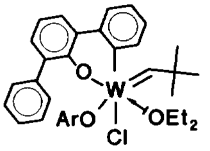
(Received December 22, 1992)

Abstract

The ring-opening metathesis polymerization of various alkylthiocyclooctenes was successfully carried out in the presence of a metallacyclic aryloxo(chloro)neopentylidenetungsten complex. The polymerization rates depend strongly on the steric crowding of the alkylthio substituent which confirms that coordination of the heteroatom to the metal is one of the important factors that govern the rate of the metathesis of this type of functionalized olefin.

The application of olefin metathesis to acyclic or cyclic olefins bearing functional groups remains one of the most promising uses of this reaction [1–3]. Unfortunately, with homogeneous Group 6 metal-based catalysts, the turnover rates are rather low in comparison with those obtained in the metathesis of ordinary olefins. This is true even for the recent well-defined alkylidene tungsten (or molybdenum) catalysts which are free of strong Lewis acid properties likely to cause interaction with functional groups [4–8]. A possible explanation of this loss of activity is a competition between the olefinic double bond and the heteroatom for coordination to the metal. Such an inhibiting (or stabilizing) effect of polar groups on metathesis catalysts has been discussed often for N-, O- or P-containing functionalities [1,9–14].

Recently we synthesized a metallacyclic aryloxo(chloro)neopentylidenetungsten complex (**1**) which has a rather high activity in the metathesis of olefinic esters such as ethyl oleate [6]. Complex **1** possesses two bulky aryloxide ligands and achieves coordinative saturation by complexing an Et_2O molecule, which also increases the steric shielding of the tungsten. The coordination sphere is also expected to be extremely rigid due to the metallacyclic structure. The high activity of complex **1** in the metathesis of oxygen-containing olefins led us to explore a new area, the metathesis of sulfur-containing olefins. We wish to report here the application of **1** in the ring-opening metathesis polymerization of various alkylthiocyclooctenes. We present evidence that the rate of the metathesis of functionalized olefins is governed, *inter alia*, by steric crowding at the heteroatom, confirming that complexation of this heteroatom to the metal is a crucial factor in this type of metathesis reaction.



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Complex **1**, an orange-brown powder, was prepared by reaction of $[WCl_3(CCMe_3)(dme)]$ [15] (dme = dimethoxyethane) with two equivalents of LiOAr (OAr $= OC_6H_3Ph_2$-2,6) in diethyl ether [6]. Various 5-alkylthiocyclooctenes (**2a–e**) were synthesized by radical addition of the appropriate thiol to cyclooctadiene [16]. Typically, the ring-opening metathesis polymerization reactions were performed by contact under argon and at 20°C of a solution of 0.025 mmol of **1** in 5 mL of C_6H_5Cl with 2.5 mmol of **2**. Under these conditions, after *ca.* 15–200 min of reaction (depending on the substrate), the conversion of the starting alkylthiocy-

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* Dedicated to Professor Gian Paolo Chiusoli in recognition of his important contributions to organometallic chemistry and its application in organic synthesis.

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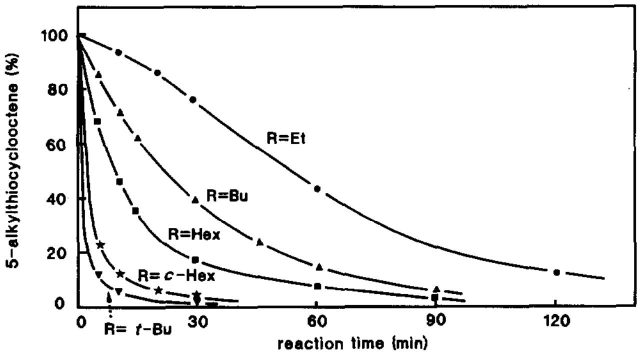
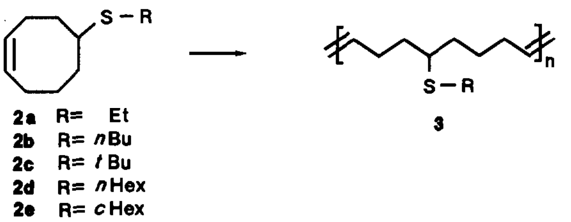


Fig. 1. Ring-opening metathesis polymerization of 5-alkylthiocyclooctenes (2) catalyzed by 1; 1: 0.025 mmol, 2: 2.5 mmol, C_6H_5Cl: 5 mL, reaction temperature: 20°C.



2a R= Et
2b R= *n*Bu
2c R= *t* Bu
2d R= *n*Hex
2e R= *c*Hex

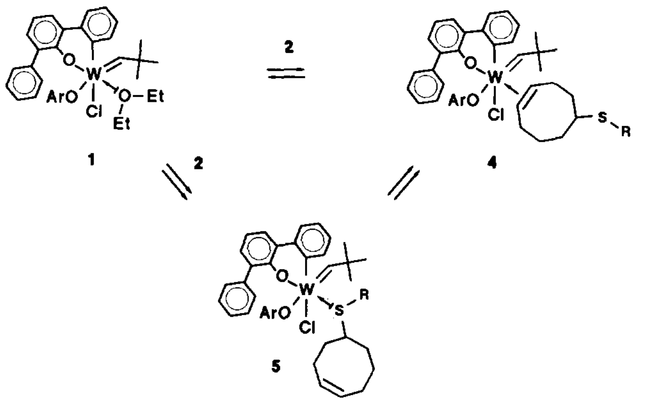
3

Scheme 1.

clooctene to the corresponding olefinic sulfur polymer 3[*] was nearly complete (Scheme 1).

In the particular case of 5-*n*-butylthiocyclooctene (**2b**), we determined the kinetic parameters of the reaction. The polymerization was found to be first-order both with respect to the monomer and with respect to the catalyst. The apparent activation energy was found to be 7.9 kcal mol^{-1} (33 kJ mol^{-1}) in the temperature range 0–75°C. This can be compared to 5.2 kcal mol^{-1} found for the polymerization of unsubstituted cyclooctene catalyzed by the multi-component metathesis catalyst $WCl_6/EtOH/EtAlCl_2$ [17].

Comparison of the kinetic curves obtained at 25°C for the various monomers shows a strong influence of the nature of the alkyl substituent at sulfur on the rate of polymerization (Fig. 1).



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4

5

Scheme 2.

The most reactive monomers are those with branched alkyl substituents on the sulfur atom, **2c** and **2e**. For example, with 5-tert-butylthiocyclooctene (**2c**) the polymerization was roughly complete within 15 min, with an initial turnover rate higher than 1000 h^{-1}. Nevertheless, it should be noted that under the same conditions, quantitative polymerization of unsubstituted cyclooctene is obtained in 2 min (initial turnover rate > 5000 h^{-1}; 86% conversion in 1 min). Thiocyclooctenes with *n*-alkyl substituents are less reactive. In this family there is a significant effect of the chain length of the alkyl group; the longer it is, the faster the polymerization. In the limiting case of ethyl-substituted thiocyclooctene, an induction period of ca. 30 min was observed.

Figure 1 indicates unambiguously that an increase of the steric demands of the alkylthio substituent leads to an increase of the polymerization rate. This suggests that bulky substituents around the sulfur atom could decrease the inhibiting effect induced by a possible coordination of the sulfur to the tungsten atom. These results are interpreted on the basis of a coordination competition between the molecule of diethyl ether present in the starting complex **1**, the olefinic C=C double bond of the cyclooctene moiety and the thioether functionality. One can envisage three equilibria between the three species **1**, **4** and **5**, depicted in Scheme 2[**]. For a given type of olefinic substrate, the rate of the metathesis reaction would depend on the respective concentrations of species **4** and **5**[†]. Obviously, the concentration of **4** reaches a maximum in the case of unsubstituted cyclooctene resulting in a high reaction rate. With alkylthio-substituted cyclooctenes, the formation of **5** would lead to a decrease of the concentration of **4**. One can assume that the

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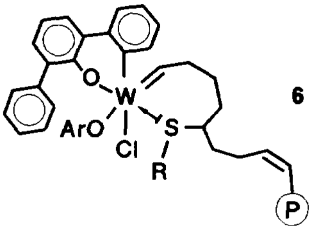
[*] The polymers were isolated as sticky solids by dilution of the reaction medium with THF and precipitation with methanol. Elemental analyses and NMR spectra (^{1}H and ^{13}C in $CDCl_3$) of these polymers were in accord with formula **3**. In particular, the ^{1}H NMR spectrum showed that the double bond is not lost during the reaction, thus proving this to be a ring-opening metathesis polymerization. For example, the ^{1}H NMR spectrum of poly-5-*t*-butylthiooctene, **3c** (300 MHz, $CDCl_3$, 25°C) contains a multiplet at δ 5.32 arising from the protons at the acyclic C=C double bonds compared to δ 5.65 from the corresponding protons on the monomer, **2c**. A polymerization experiment with **2c** at 25°C in the absence of solvent gave 65% yield of recovered polymer with $M_w = 140000$, $M_N = 39700$, $T_g = -26$°C.

[**] The equilibria of Scheme 2 concern the alkylidenes involved in the initiation process but the same equilibria can also be considered in the case of the propagating alkylidene species.

lower the steric crowding at the sulfur atom, the higher the stability of **5** and the lower the concentration of **4**, the consequence being a lower metathesis rate.

Another explanation of the results involves a possible intramolecular rather than intermolecular coordination of the sulfur function [9,13]. In fact, if we consider the propagating species **6**, there is a possibility of a retro-coordination of the sulfur atom of the alkylidene chain to the tungsten, resulting in the stabilization of an inactive species. In this case, an increase of the steric crowding at the sulfur atom would also lead to a weaker coordination of the sulfur and would facilitate the coordination of a new substrate molecule.



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In summary, we have obtained evidence that the rate of the metathesis of functionalized olefins such as olefinic thioethers is affected by the coordination of the heteroatom to the catalyst metal centre. One of the parameters that strongly influences this coordination is the steric crowding at the heteroatom. It is likely that these steric effects are particularly pronounced in the case of the metathesis catalyst **1**, which is sterically crowded at the tungsten and is very rigid due to the metallacyclic structure.

Acknowledgements

The authors express their thanks to the Société Nationale Elf-Aquitaine and to the Commission of the European Communities for support.

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[†] In principle, the metathesis rate can also be governed by the equilibrium between **1** and **4**, which probably depends on the reactivity of the olefinic C=C double bond with the metal centre. One can assume that this reactivity will be influenced by steric and electronic parameters correlated with the nature of this olefinic double bond: cyclic or acyclic, mono-, di-, tri- or tetra-substituted, conjugated or non-conjugated, with or without a heteroatom in the vicinity, *etc.*