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Preliminary communication

INITIATION OF OLEFIN METATHESIS FROM NON-ORGANOMETALLIC PRECURSORS

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Summary

Unidentified tungsten carbenes generated by the reaction of $W(CO)_3Cl_2$-$(AsPh_3)_2$ and norbornene can be activated with $AlCl_3$ to propagate the homometathesis of linear alkenes.

The metal carbene chain mechanism involving the transient formation of a metallacyclobutane is now generally accepted for olefin metathesis. The carbene-generating homogeneous catalyst systems are mainly of the Ziegler—Natta type. They are usually composed of either a transition metal halide and a non-transition metal organic compound or an organo-transition metal compound and a Lewis acid [1].

While the generation of the initiating carbenes by the interaction of a non-organometallic transition metal derivative and an olefinic substrate is widely used in the heterogeneous catalytic olefin metathesis since 1964 [2], the analogous processes in homogeneous systems are relatively new: transition metal halides such as WCl_6, $MoCl_5$, $ReCl_5$, etc. are known to initiate the ring-opening polymerization of norbornene, norbornadiene, and cyclopentene [3,4].

We have observed recently that $W(CO)_3Cl_2(AsPh_3)_2$ (I) is also a suitable catalyst for ring-opening polymerization of norbornene (NBE), norbornadiene, and for their cross-metathesis with alk-1-enes [5]. In the latter case the reaction is very selective: homometathesis products of the linear alkenes were not detected. This selectivity is destroyed by the addition of $AlCl_3$ and at the same time the activity of the catalyst in homometathesis of 2-pentene is considerably enhanced. The results are summarized in Table 1.

The conversion of 2-pentene into 2-butene and 3-hexene is readily achieved at 80°C in benzene solution containing catalytic amounts of I, NBE and $AlCl_3$ (1/4—8/6—12) (run 1—3). All the three components of this system are

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TABLE 1

RESULTS

(Catalyst: $W(CO)_3Cl_2(AsPh_3)_2$; Solvent: benzene; [2-pentene]: 3.7 mol l^{-1}; internal standard: n-pentane, 1.85 mol l^{-1}; Temperature: 80° C. Xp = conversion of 2-pentene, S: fraction of 2-pentene converted to butenes and hexenes)

Run	[Catalyst] (mmol l^{-1})	Cocatalyst (mmol l^{-1})		[NBE] (mmol l^{-1})	Reaction time (min)	Xp (%)	S (%)
1	5.0	$AlCl_3$	20	200	15	56	68
2	5.0	$AlCl_3$	20	30	15	26.7	64
3	5.0	$AlCl_3$	40	60	15	43	93
					60	57	75
4	5.0	—	0	200	60	15	20
5	5.5	$AlCl_3$	24	0	60	40	10
6	0	$EtAlCl_2$	20	200	60	26	0.7
7	4.0	$EtAlCl_2$	20	200	60	62	67
8	5.0	$AlCl_3$	60	100	60	1	70 [a]
9A	3.3	$AlCl_3$	30	60	5	21	93 [a,b]
9B	3.3	—	0	60	60	0	0 [a,b]

[a] Temperature: 20° C. [b] Carbene solution made at 80° C, see text.

essential for producing a fast-acting combination. Reactions catalyzed by the two-component systems give very low yields (run 4,5,6).

The structures of the chain carrying complexes of this novel catalyst system are probably identical with that for the well known I/$EtAlCl_2$ combination [6]. This is supported by the fact that the replacement of $AlCl_3$ by $EtAlCl_2$ does not change the main features of the catalyst (run 7).

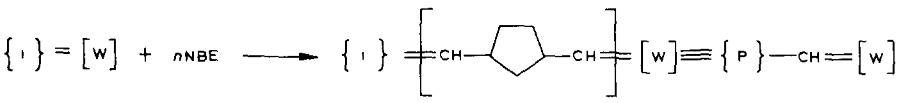
The mixture of the catalyst components is ineffective if prepared at room temperature (run 8). The generation of the carbenes and their activation with the Lewis acid can be carried out separately. Thus solution of NBE and I (18/1) was incubated at 80° C in benzene solution for 2 min then the resulting homogeneous yellow solution was cooled to room temperature and aliquots were added to a 2-pentene/n-pentane (2/1) solution. On addition of $AlCl_3$ the metathesis of 2-pentene started without any induction period at room temperature (run 9A). Parallel experiments without an added cocatalyst did not lead to detectable amounts of butenes or hexenes (run 9B).

Our results demonstrate that an initiating metallacarbene $\{i\}=[W]$ is formed very rapidly by the reaction of NBE and I at elevated temperature (eq. 1) and

$$\mathrm{NBE} + W(CO)_3Cl_2(AsPh_3)_2 \xrightarrow{80^\circ C} \{i\}=[W] \qquad (1)$$

the benzene solution containing the "living" carbene can be handled and stored at room temperature.

This carbene is able to propagate the ring-opening polymerization of NBE forming a new carbene $\{P\}—CH=[W]$ with a polymeric chain on it (eq. 2).



(2)

The propagation comes to an end when the monomer is consumed, or terminated in a reaction with 2-pentene to form a polymer molecule and one of the two possible chain transferring carbenes (eq. 3).

$$\{P\}\text{—}CH{=}[W] + CH_3CH{=}CHCH_2CH_3 \longrightarrow \begin{array}{c} \{P\}\text{—}CH{=}CHCH_3 + CH_3CH_2CH{=}[W] \\ \text{or} \\ \{P\}\text{—}CH{=}CHCH_2CH_3 + CH_3CH{=}[W] \end{array} \quad (3)$$

These chain transferring carbenes can initiate the ring-opening polymerization of NBE, but they are virtually inactive in a productive metathesis of 2-pentene such as shown in eq. 4, unless a Lewis acid activator is added to the system to

$$CH_3CH_2CH{=}[W] + CH_3CH_2CH{=}CHCH_3 \rightleftharpoons CH_3CH_2CH{=}CHCH_2CH_3 + [W]{=}CHCH_3 \quad (4)$$

increase the electrophilic character of the carbene moieties. Studies of the telomers and other organic derivatives formed in the initiation steps is in progress.

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