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OLEFIN METATHESIS OF ALKENYLSILANES

II *. ON THE INITIATION OF OLEFIN METATHESIS WITH ORGANOSILANES

MATS BERGLUND, CARLAXEL ANDERSSON and RAGNAR LARSSON

Research group on catalysis, Inorganic Chemistry 1, Chemical Center, University of Lund, P.O.B. 124, S-221 00 Lund (Sweden)

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Summary

A study has been made of the cross-metathesis of alkenylsilanes $CH_2{=}CH(CH_2)_nSiX_3$ ($n = 1,2$; $X = CH_3$, Cl, OMe) with (*Z*)-2-pentene with WCl_6 as the catalyst precursor. For allyltrimethylsilane (ATMS; $n = 1$, $X = CH_3$) the reaction proceeds without added co-catalyst but with an induction period. The catalytically-active intermediate in this case is formed by allyl-group transfer from Si to W, as revealed by the formation of $ClSiMe_3$. Allyltrichlorosilane and allyltrimethoxysilane requires the addition of an alkylating co-catalyst, e.g. $SnMe_4$. Addition of a Lewis acid, e.g. $AlCl_3$ or $AlBr_3$, show that for ATMS removes the induction period and substantially raises the activity. The initial activity and the *E*/*Z*-stereoselectivity are affected in a very similar way by the addition of the Lewis acid. The results indicate that the Lewis acid participates in the initiating, propagating, and terminating steps of the reaction.

Introduction

Since the pioneering study in 1972 by Van Dam et al. [1] of the metathesis of functionalized olefins, e.g. methyloleate, this reaction has attracted considerable interest. This is because such reactions can give a range of different products, e.g. mono- or di-functionalized olefins and these products can be of considerable synthetic and economic value [2,3]. So far only a few systems, viz. $WCl_6/SnMe_4$ [1,4] and Re_2O_7/Al_2O_3 [5,6], have proved to be efficient catalysts for the metathesis of functionalized olefins; the difficulty lies in the deactivating effect of the polar substituents, which probably block the coordination sites of the catalyst. A recent paper [7] reports that properly designed metal carbenes can be used as catalysts for the reactions.

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* For Part I see Ref. 11.

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One type of functionalized olefins which has been little studied is alkenylsilanes [8,9]. Alkenylsilanes have become increasingly important reagents in organic synthesis [10], and so metathesis of silyl-olefins could become an important tool in the synthesis of organic rare and fine chemicals. With this in mind we have begun a study of suitable catalysts for this reaction. Another useful application of metathesis of organosilanes has been demonstrated by Streck [8], who synthezised polyalkenes bearing terminal reactive silyl groups; highly cross-linked polymers were obtained.

In most of the catalytic systems described above a co-catalyst is needed to activate the catalyst precursor. However, in the cross-metathesis of allyltrimethylsilane and (*Z*)-2-pentene [11] and in the ring-opening polymerization of cyclic olefins [12] it has been found that alkenylsilanes can act as catalyst activators.

Three main ways of making an active catalyst from WCl_6 can be distinguished: (i) treatment with alkylating agents [13], (ii) reaction with hydride donors [14], and (iii) electrochemical generation [15]. In a previous communication [11] we suggested that the activating power of allyltrimethylsilane is due to its ability to act as a mild alkylating agent, i.e. its use falls under category (i). In the present paper we report further studies on the activation of WCl_6 with organosilanes and also on the metathetical conversion of various alkenylsilanes. As a model reaction we chose the cross-metathesis of (*Z*)-2-pentene and some selected alkenylsilanes, since such reactions are known [6] to be a more sensitive indication of activity than self-metathesis.

Experimental

Chemicals

WCl_6 was purified by vacuum sublimation. Analytical grade chlorobenzene was dried over CaH_2 and distilled under nitrogen before use. (*Z*)-2-pentene (Fluka), tetramethyltin (Fluka) and allyltrimethylsilane (Jansen Chimica) were distilled, and stored over molecular sieves under nitrogen. Allyltrichlorosilane [17], allyltrimethoxysilane [18] and 3-butenyltrimethylsilane [19] were prepared by known procedures. $AlBr_3$ and $AlCl_3$ (Jansen Chimica) were used as received and solutions of the appropriate concentration made up in chlorobenzene. All catalyst manipulations were carried out under oxygen-free nitrogen.

Analysis

The product mixtures from the olefin methathesis experiments were analyzed with a Perkin–Elmer F17 Gas Chromatograph equipped with a computing integrator (LCI-100). Two columns were used, viz. 10% OV-17 on Chromosorb WHP and 10% SE-30 on Chromosorb WHP. The products obtained were identified by mass spectrometry and by comparison of their retention times with those of authentic samples. Relative response factors were determined for authentic samples or were in some cases calculated by the Scanlon and Willis method [16].

Olefin methathesis experiments

The metathesis experiments were carried out in a stirred glass vessel at room temperature as described previously [11,20]. The following general conditions were used: Solvent: Chlorobenzene. $C(WCl_6)$ 1.0×10^{-2} M, $C((Z)\text{-2-pentene}) = C(\text{alkenylsilane}) = 0.5$ M. Samples were quenched with pyridine except when analysis for chlorotrimethylsilane was involved.

The term cross products used in the figure legends is defined as the sum of the products $CH_3CH{=}CH(CH_2)_nSiX_3$ and $CH_3CH_2CH{=}CH(CH_2)_nSiX_3$.

Results and discussion

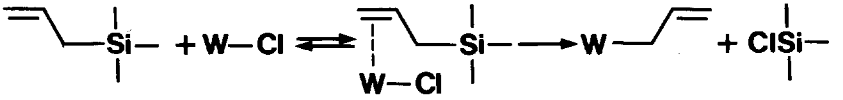
Catalyst activation

The presently accepted mechanism of the metathesis reaction involves the initial formation of a metal carbene complex. This carbene can be formed from conventional alkylating agents, e.g. SnR_4, BuLi or $EtAlCl_2$ by successive alkyl group transfer to the metal followed by an α-hydrogen elimination [21].

In an catalyst system free from an alkylating co-catalyst the substrate itself must be able to initiate the carbene formation. For tetraorganosilanes the capacity for transfer of the organic group to WCl_6 has been found to depend on the nature of this group [22]. E.g., the reaction of R_4Si and R_3SiPh with WCl_6 has been found to give 16 and 63% conversion respectively, at equimolar metal to silane ratio; furthermore with R_3SiPh it was the Si–Ph bond that was predominantly broken. The low reactivity of tetraalkylsilanes has also been demonstrated in metathesis experiments [23]. Allyltrimethylsilane (ATMS), on the other hand, is more prone to undergo Si–C bond cleavage, as observed in the reaction with WCl_6 [24] and with Pd^{II} and Hg^{II} salts [25]. In the latter case stable π-allyl complexes of Pd^{2+} and Hg^{2+} could be isolated. For WCl_6, however, only chlorotrimethylsilane and decomposition products such as propene and 1,5 hexadiene have been observed; these are probably derived from an intermediate tungsten allyl complex.

As pointed out in the Introduction, ATMS has a dual role under cross-metathesis conditions; since it acts both as a co-catalyst, generating the active catalyst, and as a substrate. The plot of Fig. 1 (Al/W = 0) reveals an induction period of 5 min. Since we have observed that premixing of WCl_6 and ATMS for 5 min before the addition of (Z)-2 pentene result in the immediate formation of cross products the induction period probably represents the time needed to produce the initial carbene.

From the results presented in Figs. 1–3 it is clear that the induction period is also affected by the presence of Lewis acids, e.g. AlX_3 (X = Cl, Br) or Lewis bases, e.g. diethyl ether. Irrespective of whether $AlBr_3$ or $AlCl_3$ was used the qualitative picture was the same. Even at a very low Al/W ratio no induction period was observed (Figs. 1, 3). Addition of diethyl ether to the system resulted in an increased induction period, the more so the greater the ether concentration (Fig. 2). These effects of Lewis bases and acids can be explained if we assume, by analogy to the reaction between Pd^{2+} or Hg^{2+}, that the formation of a W-π-olefin complex is the initial step in a reaction sequence leading to the active carbene (eq. 1).



(1)

By abstracting a chloride ligand from WCl_6 the Lewis acid creates a stronger electrophile, viz. WCl_5^+ and so the ease of olefin coordination is increased. The Lewis base on the other hand has the opposite effect; it competes with the silylolefin for the coordination site of the metal. This competition will, of course, be more pronounced at higher ether concentrations.

The decrease of the induction period on AlX_3 treatment can, however, also be

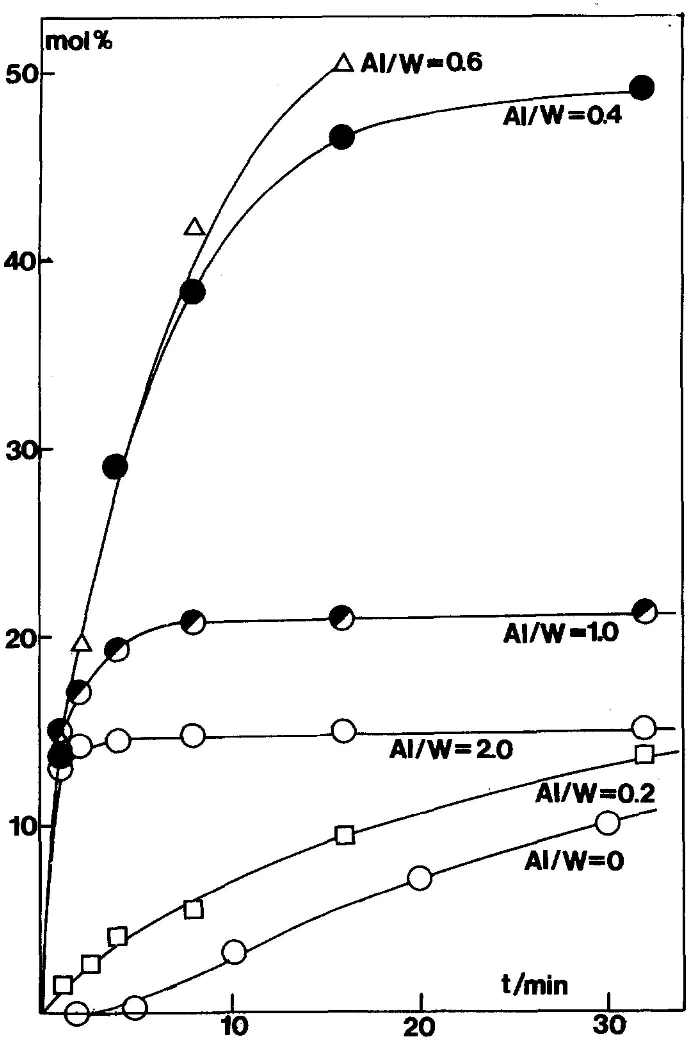
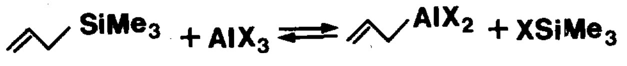


Fig. 1. Effect of $AlBr_3$ addition. The yield of cross-products in the cross-metathesis of allyltrimethylsilane and (*Z*)-2-pentene vs. *t* at various $AlBr_3/WCl_6$ molar ratios.

related to the formation of an allyl-Al compound in the reaction system. This reaction produces a stronger alkylating agent which reacts more readily with the tungsten compounds (eqs. 2–4). Participation of an analogous intermediate has been proposed for the redistribution of benzyltrimethylsilane catalyzed by $AlCl_3$ [26].



(2)

(3)

$$AlX_2Cl + XSiMe_3 \rightleftharpoons AlX_3 + ClSiMe_3 \qquad (4)$$

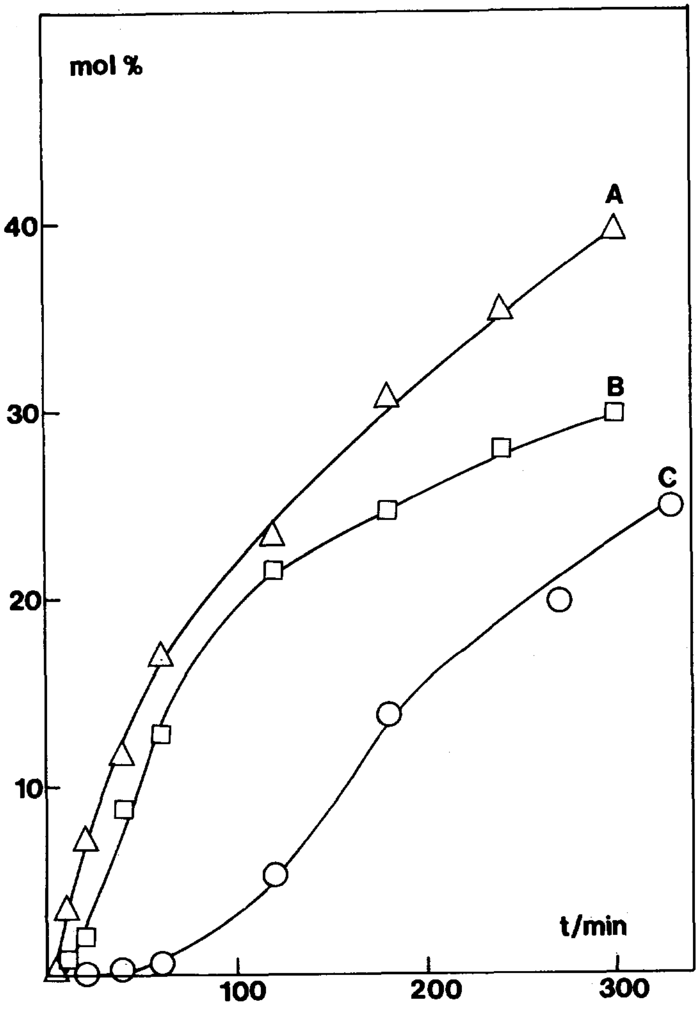


Fig. 2. Effect of diethyl ether addition. The yield of cross-products in the cross-metathesis of allyltrimethylsilane and (*Z*)-2-pentene vs. *t*. A: WCl_6, B: $WCl_6 + Et_2O$, C: $WCl_6 + 2Et_2O$.

The Lewis acid may in certain cases be bound to the metal atom via halide bridges, which can facilitate the formation of a carbene [27]. This is yet another way by which the presence of AlX_3 could lower the induction period.

The initiation was in all cases accompanied by formation of $ClSiMe_3$ as shown in Table 1. Two conclusions can be drawn from the data in Table 1. First, since WCl_6 is the only source of chlorine the degree of chloro ligand transfer from WCl_6 to Si is reflected in the amount of $ClSiMe_3$ formed on the initiation; this reaches a limiting value of 3.4 equiv. at an Al/W ratio of 0.4. Second, since no formation of $BrSiMe_3$ was detected, reaction 4 must be included in the overall reaction scheme.

The process of generating the active intermediate from WCl_6 is generally believed to involve initial reduction to a WCl_4 species [28]. The reduction can be achieved by the successive transfer of two alkyl groups from an alkylating co-cata-

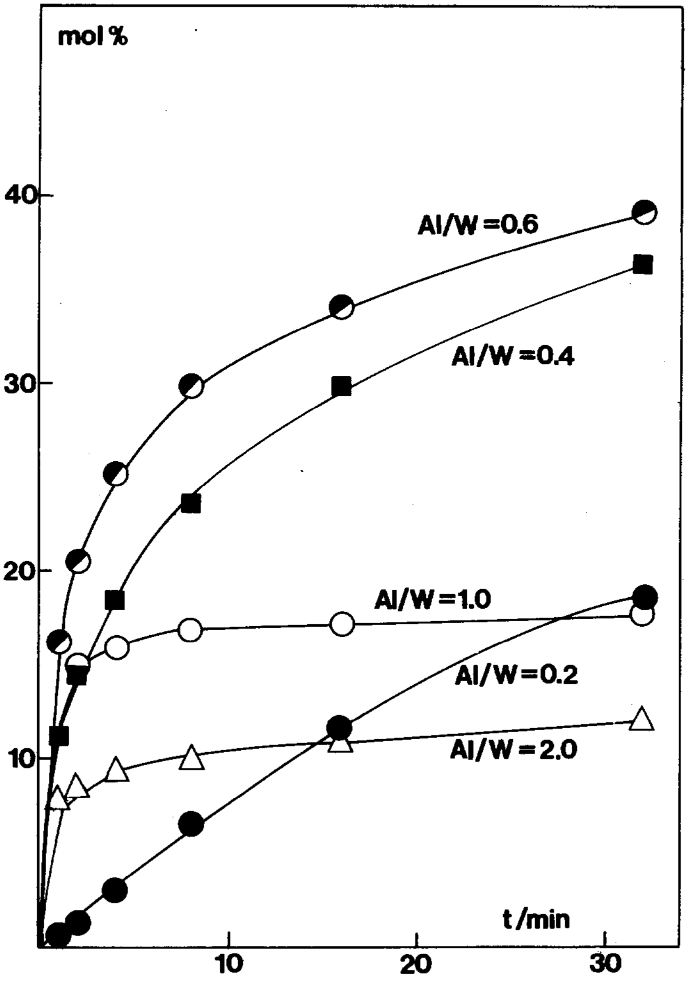


Fig. 3. Effect of $AlCl_3$ addition. The yield of cross-products in the cross-metathesis of allyltrimethylsilane and (*Z*)-2-pentene vs. *t* at various $AlCl_3/WCl_6$ molar ratios.

TABLE 1

EFFECT OF VARYING THE $AlBr_3/WCl_6$ RATIOS ON THE CROSS-METATHESIS OF ALLYLTRIMETHYLSILANE AND (*Z*)-2-PENTENE

Al/W [a]	$ClSiMe_3$/W [a]	*E*/*Z* [b]	Yield of cross-products after 1 min (%)	Selectivity [c] after 16 min (%)
0	2.1	0.2	0	96
0.2	2.9	0.4	1.5	94
0.4	3.4	0.5	14.0	94
0.6	3.4	0.5	14.4	94
1.0	3.2	0.5	15.0	91

[a] Molar ratio. [b] See Fig. 4. [c] Selectivity = [ATMS] + [metathesis products]/*C*(ATMS).

lyst and subsequent reductive elimination of the organic groups as demonstrated for PhC≡CNa [29], BuLi [28,31] or $EtAlCl_2$ [30]; in this process chloride ions are released from WCl_6 to form, in the above examples, NaCl, LiCl or $AlCl_3$. Hence in the case of ATMS as an activator two equivalents of $ClSiMe_3$ should be formed in the reduction of W^{VI} to W^{IV}, together with products such as propene and 1,5-hexadiene.

A comparison of the initial activity (Figs. 1 and 3) with the amount of $ClSiMe_3$ formed (Table 1) reveals that there is a close parallel. As the amount of $ClSiMe_3$ increases, indicating an increased allyl-group transfer, the initial activity increases. This demonstrates that allyl-group transfer beyond the two equivalents needed to reduce W^{VI} to W^{IV} is necessary to generate the active catalyst. In a calorimetric study of the system $WCl_6/EtAlCl_2$ [30], an Al/W ratio of 4 was found to give a tungsten species which interacts strongly with the added olefin, e.g. cyclohexene, but the question as to the optimum level of the tungsten/co-catalyst ratio is still a matter of controversy [30]. It is probable that the conversion of WCl_6 into active carbene is not stoichiometric; competing side reactions in the carbene generating step probably reduce the amount of tungsten that is converted into active carbene [21]. The relative amount of $ClSiMe_3$ (3.4 eq/WCl_6) formed at maximum rate can therefore not be interpreted as the actual amount of ATMS needed to generate an active carbene from WCl_6. Such a statement can only be justified if the total amount of active carbene is known.

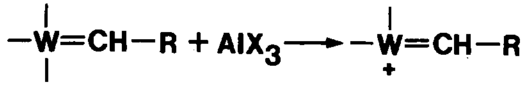
Catalytic activity

Lewis acidity or basicity have also a great influence on the catalytic activity (Figs. 1–3) whether this is expressed as the initial rate or as the total yield. The initial activity measured as the initial slope of the activity curves is increased slightly at an Al/W ratio of 0.2 compared to that in the absence of Al (Fig. 1). At an Al/W ratio of 0.4 there is a large increase in the initial activity, and for Al/W ratios in the range 0.4–2.0 it remains essentially the same; this holds for $AlBr_3$ (Fig. 1) and $AlCl_3$ (Fig. 3). Addition of diethyl ether on the other hand (Fig. 2) results in a lower initial activity, the effect being greater the higher the concentration of ether.

From the results presented in Figs. 1 and 3 we conclude that a minimum amount of AlX_3, in the range of 0.4 equiv. with respect to W, is needed in order to reach what seems to be the limiting value of the initial rate of our system. Furthermore the total yield is also substantially affected by the addition of AlX_3. If the Lewis acidity of the system is increased beyond a certain level, either by increasing the concentration of AlX_3 or by changing from $AlBr_3$ to $AlCl_3$, this results in a lowering of the total yield; e.g. compare Al/W = 0.6 to Al/W = 1.0 of Fig. 1 or the curves of Figs. 1 and 3 at similiar Al/W ratios.

The lower yield of metathesis products at high Lewis acidity can have various causes. Competing side reactions, such as e.g. allylation of the chlorobenzene solvent, consume ATMS and hence lower the yield of cross products. In our system we have observed that the selectivity to metathesis products decreases at high Al/W ratios (Table 1). The amount of Friedel–Crafts products found, however, is not large enough to explain the very drastic fall in the yield from 50% at Al/W = 0.60 to 20% at Al/W = 1.0. We therefore suggest that the lowering of the yield is caused by a reduced lifetime of the catalytic system at high Lewis acidity, the beneficial effect of the Lewis acid on the initial rate being offset by its long-term poisoning effect.

The increase in the initial reaction rate that we have observed on addition of AlX_3 to the system can have two causes which may operate separately or consecutively. Firstly, as indicated by the formation of increased amounts of $ClSiMe_3$, the total amount of active carbenes is probably increased on addition of AlX_3 to the system. Secondly, halide ion abstraction from the carbene complex AlX_3 can create a vacant coordination site at the carbene complex (eq. 5). In this way the ease of olefin coordination is increased. If olefin coordination is the rate-determining step, the reaction rate should increase on addition of AlX_3 to the system, as observed. Kress and Osborn [32], have found that a cationic carbene can indeed be the propagating carbene in the metathesis of (*Z*)-2-pentene. This carbene was formed by the reaction of a Lewis acid, e.g. $GaBr_3$ with $W(CHR)(OCH_2R)_2Cl_2$.



$$-\overset{|}{\underset{|}{W}}=CH-R + AlX_3 \longrightarrow -\overset{|}{\underset{+}{W}}=CH-R \qquad (5)$$

E / Z-Stereoselectivity

Besides the catalytic activity, another important aspect of a metathesis catalyst is the *E*/*Z*-stereoselectivity, and our system is very sensitive in this respect to addition of Lewis acid. This is shown for one of the cross-products, viz. 2-butenyltrimethylsilane in Fig. 4. Since the *E*/*Z* ratio at zero conversion is much larger with $AlBr_3$ or $AlCl_3$ present, the Lewis acid must be involved in propagating

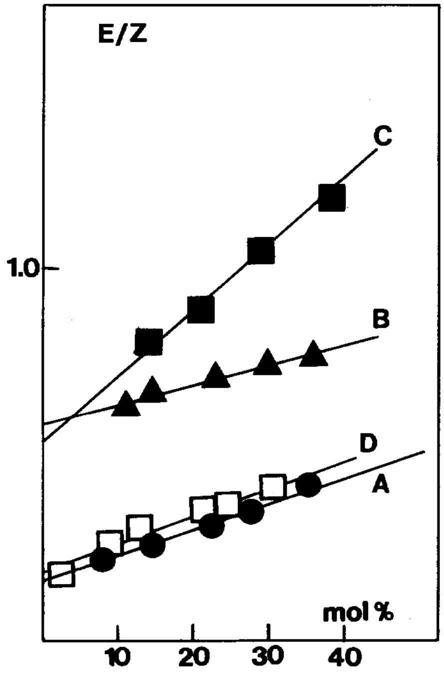


Fig. 4. *E*/*Z*-2-butenyltrimethylsilane ratio vs. yield of cross-products in the cross-metathesis of allyltrimethylsilane and (*Z*)-2-pentene. A: WCl_6, B: $WCl_6 + 0.6\ AlCl_3$, C: $WCl_6 + 0.6\ AlBr_3$, D: $WCl_6 + Et_2O$.

step (vide infra). Increase of the Lewis basicity of the system by the addition of diethyl ether, does not change the stereoselectivity (Fig. 4); This suggests that, in contrast to AlX_3, ether does not interfere in the propagating step [7].

For AlX_3 the *E*/*Z* ratio was found to reach a limiting value of 0.5 (Table 1) at a Al/W ratio of 0.4, no further change taking place on further AlX_3 addition. This parallels the sharp sudden increase in the initial reaction rate at the same Al/W ratio (vide supra).

Several explanations of the influence of the Lewis acid on the *E*/*Z*-stereoselectivity have been suggested [33–35]. Basset et al. [33] suggested that the Lewis acid induced "electronic changes in the coordination sphere of the tungsten atom". These changes would influence the relative stabilities of the various proposed metallacyclobutane intermediates. In contrast Katz [34] has suggested that the Lewis acid interact by cleaving the carbon–metal bond in the metallacycle, a metallapropyl cation, in which there is free rotation of the bonds being formed.

In view of the very close resemblance between the initial activity and the *E*/*Z* stereoselectivity apparent from Table 1, we conclude that the propagating carbene

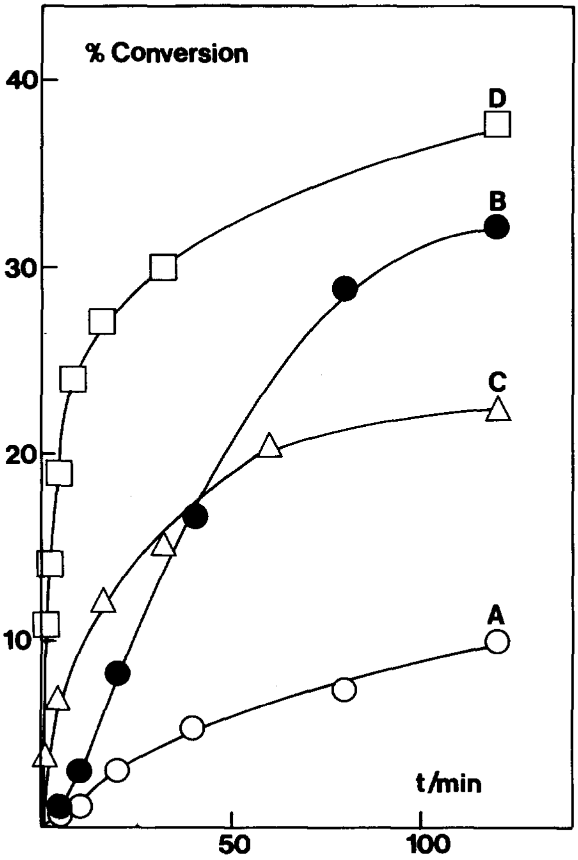


Fig. 5. Metathesis of (*Z*)-2-pentene with the catalyst system WCl_6/ATMS/$AlBr_3$. A: Al/W = 0, ATMS/W = 2; B: Al/W = 0, ATMS/W = 4; C: Al/W = 0.4, ATMS/W = 2 D: Al/W = 0.4, ATMS/W = 4.

complex is greatly modified by the Lewis acid, possibly in the extreme, to formation of a cationic tungsten carbene.

Metathesis of (Z)-pentene initiated by ATMS

We also studied the metathesis of (Z)-2-pentene using WCl_6 as the catalyst precursor and ATMS acting as a co-catalyst. We have found that as in the case of the cross-metathesis experiments (Figs. 1 and 3), the addition of Lewis acid shortens the induction period and increases the initial rate; e.g. compare curves A and C or curves B and D of Fig. 5. We also noted that the self-metathesis activity depends on the ATMS/W ratio, as can be seen from curves A and B or curves C and D of Fig. 5. The maximum activity, in terms of either initial rate or conversion was found at a ATMS/W ratio of 4 (curve D in Fig. 5). At higher ratios the cross-metathesis becomes important and hence there is a lower yield of (Z)-2-pentene self-metathesis products.

Metathesis of alkenylsilanes other than ATMS

From the results presented to this point in this paper and those described

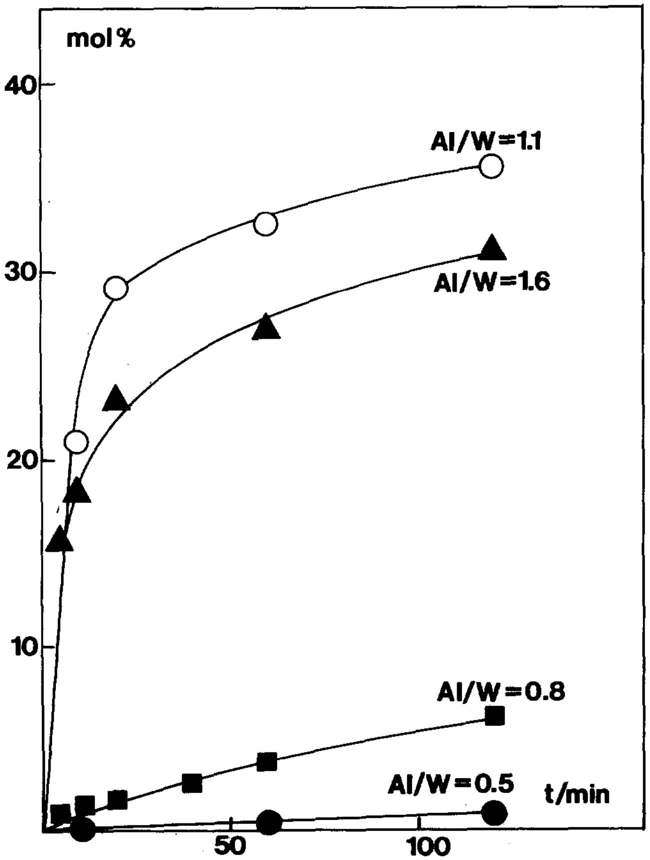


Fig. 6. The yield of cross-products in the cross-metathesis of 3-butenyltrimethylsilane and (Z)-2-pentene at various $AlBr_3/WCl_6$ molar ratios.

previously [11] it seems likely that the key requirement for the activation of WCl_6 with alkenylsilanes is that the olefinic bond is β to Si. It is known [36] that in a series of alkenylsilanes $R_3Si(CH_2)_nCH{=}CH_2$ the reactivity in ionic additions, e.g. of $(SCN)_2$, falls in the following order $n = 1 \gg 2 > 0$. The exceptionally high reactivity of allylsilanes in such reactions is usually attributed to the influence of the silicon atom on the β-carbon atom ("the β-effect" for which several factors are responsible; the effect can be related to the high electron donating power of the R_3SiCH_2 group [36]. Replacement of the alkyl groups on the silicon by electronegative substituents reduces the $+I$ effect, which leads to a lower reactivity in ionic additions [36]. In the light of such considerations and in order to throw light on the way in which the β-effect influence the activation of WCl_6 by alkenylsilanes we studied a case in

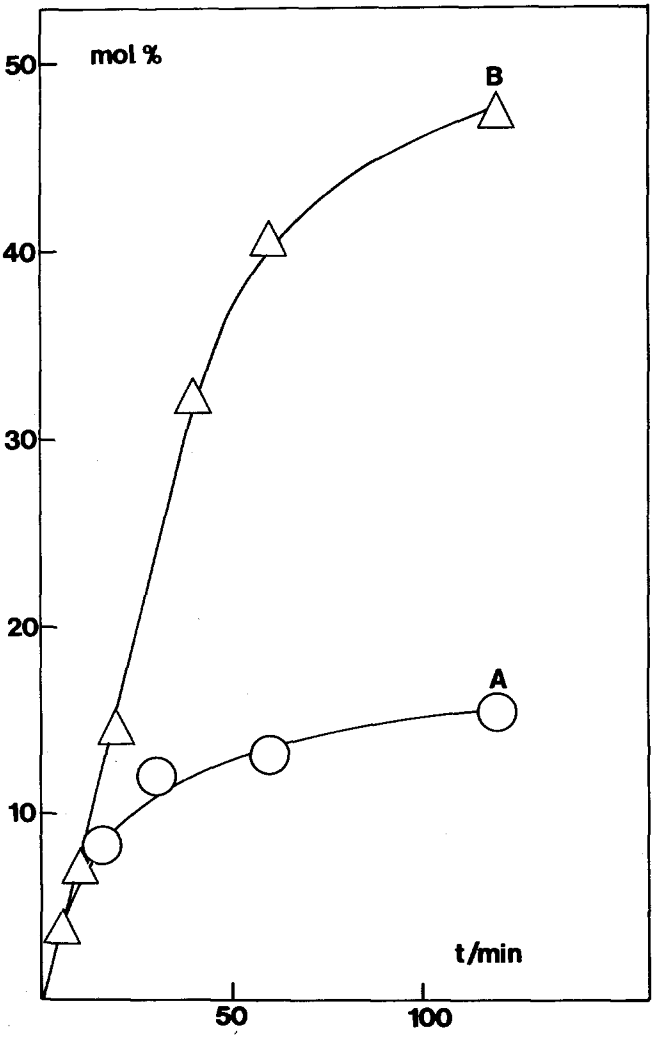


Fig. 7. The yield of cross-products in the cross-metathesis of (Z)-2-pentene and allyltrimethoxysilane (A) or allyltrichlorosilane (B) with the catalyst system $WCl_6 + 2\ SnMe_4$.

which the olefinic bond is γ to carbon, viz. 3-butenyltrimethylsilane (BTMS) and two cases involving allylsilanes with electronegative substituent at silicon, viz. allyltrichlorosilane and allyltrimethoxysilane.

We have previously found [11] that the yield obtained on cross-metathesis of BTMS and (*Z*)-2-pentene in the absence of AlX_3 reached only 5% in 20 h, which is substantially lower than the 40% yield after 300 min observed for ATMS (curve A, Fig. 2). However, as was the case for ATMS, the reactivity of BTMS is strongly affected by the addition of AlX_3 to the system, as shown in Fig. 6. The role of AlX_3 in the activation and in the propagating step is probably the same in both cases. It is significant that the amount of Lewis acid needed to increase the rate is markedly higher for BTMS than for ATMS. The lower reactivity of BTMS was expected from the arguments outlined above. BTMS, having the double bond in the γ-position, should have a lower tendency to transfer the butenyl group to tungsten. At high Al/W ratios the initial alkylation of W probably takes place via an intermediate Al-alkyl to give a substantially more active system.

The operation of the β-effect in the activation of WCl_6 with alkenylsilanes is also nicely demonstrated by the results for allyltrichlorosilane and allyltrimethoxysilane. Both of these alkenylsilanes were inactive in the cross-metathesis with (*Z*)-2-pentane, probably because the electron withdrawal by the substituents on silicon lowers the reactivity towards tungsten Alternatively the substrates with polar substituents might possibly act as catalyst poisons and so block the reaction. To examine this possibility we studied the metathesis of the two silanes with WCl_6 as the catalyst precursor and $SnMe_4$ as the co-catalyst; in such experiments the initiation is not by the silanes themselves, which are only substrates. We found that both substrates underwent metathetical conversion (Fig. 7), and allyltrichlorosilane gave an ca. 45% yield of cross-products within 120 min. A slow deactivation was observed in the case of allyltrimethoxysilane, and this resulted in a limiting yield of cross-products of around 15%. In our opinion the data in Fig. 7 demonstrate that a poisoning effect of the polar substituents could not fully account for the total lack of catalytic activity in the absence of added co-catalyst.

We therefore conclude that ATMS has a unique ability among alkenylsilanes to activate WCl_6 to give an active metathesis catalyst. This ability of ATMS is probably due to the β-effect. If this β-effect is offset either by changing the position of the olefinic bond or by electronegative substituents on silicon the activating power is reduced or completely lost.

References

1 P.B. van Dam, M.C. Mittelmeijer and C. Boelhouwer, J. Chem. Soc., Chem. Commun., (1972) 1221.
2 C. Boelhouwer and J.C. Mol, J. Am. Oil. Soc., 61 (1984) 425.
3 J.C. Mol, J. Mol. Catal., 15 (1982) 35.
4 R.H. Bosma, A.P. Kouwenhoven and J.C. Mol, J. Chem. Soc., Chem. Commun., (1981) 1081.
5 R.H.A. Bosma, G.C.N. van den Aardweg and J.C. Mol, J. Organomet. Chem., 255 (1983) 159.
6 R.H.A. Bosma, G.C.N. van den Aardweg and J.C. Mol, J. Organomet. Chem., 280 (1985) 115.
7 F. Quignard, M. Leconte and J.M. Basset, J. Chem. Soc., Chem. Commun., (1985) 1816.
8 R. Streck, J. Mol. Catal., 15 (1982) 3.
9 R.A. Friedman, S.M. Nosakova, Yu. B. Kruykov, A.N. Bashkirov, N.S. Nametkin and V.M. Vdovin, Izv. Akad. Nouk. SSSR Ser. Khim., 20 (1971) 2100.
10 T. Chan and I. Fleming, Synthesis, (1979) 761.
11 M. Berglund, C. Andersson and R. Larsson, J. Organomet. Chem., 292 (1985) C15.

12 I.A. Oreshkin, L.I. Red Kina, I.L. Kershenbaum, G.M. Chernenko, K.L. Makovetsky, I.L. Tinyakova and B.A. Dolgoplask, Europ. Polym. J., 13 (1977) 447.

13 K.J. Ivin, Olefin Metathesis, Academic Press, London, 1982, Chapter 2.

14 S.A. Matlin and P.G. Sammes, J. Chem. Soc., Perkin Trans. 1, (1978) 624.

15 M. Gilet, A. Mortreux, J. Folest and F. Petit, J. Am. Chem. Soc., 105 (1983) 3876.

16 J. Scanlon and D.E. Willis, J. Chrom Sci., 23 (1985) 333.

17 N. Furuya and T. Sukawa, J. Organomet. Chem., 96 (1975) C1.

18 J. Pola, M. Jakoubkova and V. Chvalovsky, Collct. Czech. Chem. Commun., 43 (1978) 3391.

19 C.R. Hauser and C.R. Hance, J. Am. Chem. Soc., 74 (1952) 5092.

20 M. Berglund and C. Andersson, J. Mol. Catal., in press.

21 R.H. Grubbs in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, 1982, Chapter 54.

22 I.S.A. Khrem, D.V. Auetisyan, R.S. Vartanyan, K.G. Shakhatuni and M.E. Volpin, Izv. Akad. Nauk. SSSR, Ser. Khim., 24 (1975) 2327.

23 J. Levisalles, H. Rudler, D. Cuzin and T. Rull, J. Mol. Catal., 26 (1984) 231.

24 I. Ya. Ostrovskaya, L.I. Redkina and K.L. Makovetsky, Izv. Akad. Nauk. SSSR, Ser. Khim., 29 (1980) 2650.

25 I. Haiduc and V. Popa, Adv. Organomet. Chem., 15 (1977) 113.

26 D.H. O'Brien and T.J. Hairstone, Organomet. Chem. Rev., A7 (1971) 95.

27 V. Dragutan, A.T. Balaban and M. Dimonie, Olefin metathesis and ring-opening polymerisation, Wiley, New York, 1985, Chapter 6.

28 K. Ichikawa, T. Takagi and K. Fukuzumi, Trans. Met. Chem., 1 (1976) 54.

29 K. Ichikawa, T. Takagi and K. Fukuzumi, Bull. Chem. Soc. Jpn, 49 (1976) 750.

30 D.H. Singleton and D.J. Eatough, J. Mol. Catal., 8 (1980) 175.

31 I.-L. Wang, M.R. Merapace and M. Brown, J. Catal. 26 (1972) 455.

32 J. Kress and J.A. Osborn, J. Am. Chem. Soc., 105 (1983) 6346.

33 N. Taghizadeh, F. Quignard, M. Leconte, J.M. Basset, J.P. Laval and A. Lattes, J. Mol. Catal., 15 (1982) 219.

34 T.J. Katz and W.H. Hersh, Tetrahedron Lett., (1977) 585.

35 K.C. Ott, J.B. Lee and R.H. Grubbs, J. Am. Chem. Soc., 104 (1982) 2942.

36 A.W.P. Jarvie, Organomet. Chem. Rev., A 6 (1970) 153.