Metathesis Polymerisation of Norbornene and its Derivatives. Relative Stability of Tungstacyclobutane Intermediates and Kinetics of their Ring Opening to form Tungsten–Carbene Complexes

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A family of tungstacyclobutane intermediates in the catalytic ring-opening polymerisation of norbornenes have been studied by [1]H n.m.r.; their rates of rearrangement into tungsten–carbene complexes are reported and compared.

We have shown that intermediate metallacyclobutane and metal–carbene complexes involved in the metathesis polymerisation of norbornene and its derivatives can be identified by n.m.r. when the adduct $(1)\cdot GaBr_3$ and related compounds are used as catalysts at low temperature.[1,2] The successive formation of these two types of species can be followed directly, confirming the mechanism of olefin metathesis first postulated in 1970.[3] We now report more details on one of the two essential steps of this polymerisation mechanism, namely the cleavage of the tungstacyclobutane to the tungsten–carbene complex (Scheme 1).

$$W(CHBu^t)(OCH_2Bu^t)_2Br_2\cdot GaBr_3$$
$$(1)\cdot GaBr_3$$

$(2)^+$ GaBr$_4^-$

(A)
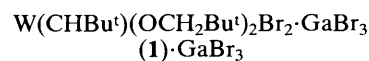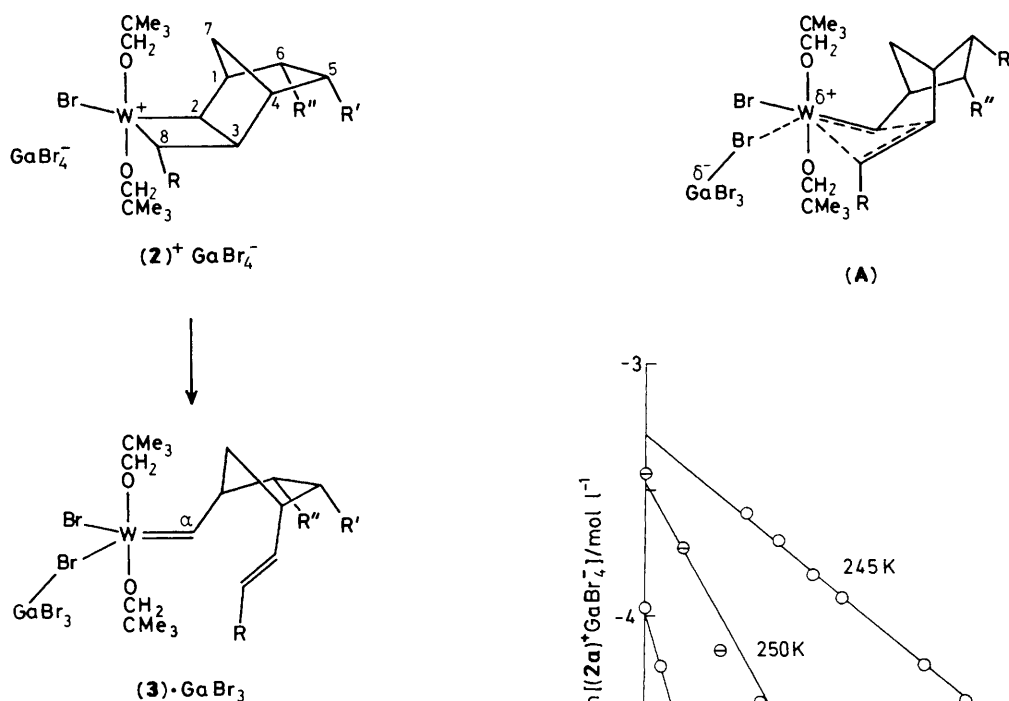
$(3) \cdot$ GaBr$_3$

a; R = Bu^t, R' = R'' = Me
b; R = Bu^t, R' = R'' = H
c; R = Bu^t, R' = Me, R'' = H
d; R = Bu^t, R' = H, R'' = Me
e; R = CH$_2$Bu^t, R' = R'' = H
f; R = CHEt$_2$, R' = R'' = H
g; R = C$_5$H$_8$CH=[CHC$_5$H$_8$CH]$_n$=CHBu^t ($n \geqslant 0$), R' = R'' = H

Scheme 1†

Figure 1. First-order plot of decay of $(2a)^+$GaBr$_4^-$ (Scheme 1) at three temperatures.

With *endo,endo*-5,6-dimethylnorbornene (3 equiv.) and (1)·GaBr$_3$ at 235 K in CD$_2$Cl$_2$, the initial tungstacyclobutane (2a)$^+$GaBr$_4^-$ (Scheme 1) resulting from the addition of 1 equiv. of monomer to the W=CHBu^t double bond can be produced *in situ* in good yield (70%) and remains present after all the monomer is polymerised. This species is characterised most readily by the ^{1}H n.m.r. signals assigned to H-2, H-8, H-4, H-1, R (= Bu^t), and H-3, and by all the lines expected for the two non-equivalent OCH$_2$Bu^t ligands.‡ These can be distinguished from the spectra of residual (1)·GaBr$_3$ and polymer product.

The rate of conversion into the carbene complex (3a)·GaBr$_3$ (Scheme 1) was measured at three temperatures (245, 250, and 255 K) by integration of the H-2 signal and of

the H-α signals of the carbene product (Scheme 1). Good first-order plots were obtained (Figure 1) over two half-lives ($t_{1/2}$ = 43, 18, and 10.5 min, respectively) leading to the Arrhenius parameters A = 7 × 10^{11} s^{-1} ($\Delta S^{\ddagger}$ = −25 J K^{-1} mol^{-1}) and E_a = 72 kJ mol^{-1}. The addition of Bu$^n_4$N$^+$GaBr$_4^-$ [2 equiv./(1)] to the system was shown to have a negligible effect on the rate of ring opening.

These results are consistent with (2a)$^+$GaBr$_4^-$ behaving as a tight ion pair and rearranging in a concerted process *via* a specifically puckered transition state such as (A). Loss in rotational freedom of the GaBr$_4^-$ entity should contribute to the negative entropy of activation. A stepwise mechanism[4] cannot, however, be excluded.

Another important observation is that the rate of rearrangement is unaffected by the presence of excess of unpolymerised monomer. This precludes a mechanism in which metallacycle opening in (2)$^+$ GaBr$_4^+$ is stimulated by co-ordination of monomer.

With norbornene instead of *endo, endo*-5,6-dimethylnorbornene, the corresponding initial tungstacyclobutane (2b)$^+$-GaBr$_4^-$ (Scheme 1) is obtained similarly at 220 K.[1] Its first-order ring cleavage occurs at 235 K with a half-life of *ca.* 17 min, which shows that it is less stable than (2a)$^+$GaBr$_4^-$ (estimated half-life 150 min at 235 K). From *endo*-5-methyl-norbornene, two isomers (2c)$^+$GaBr$_4^-$ and (2d)$^+$GaBr$_4^-$ (1 : 1), are produced at 220 K;[2] these differ in the location of the *endo*-methyl group (position 5 or 6, respectively; Scheme 1). The two species show different stabilities, that of (2c)$^+$-GaBr$_4^-$ at 250 K being close to that of (2a)$^+$GaBr$_4^-$ at 250 K,

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† Dissociation of GaBr$_4^-$ in the tungstacyclobutane compounds and its co-ordination to tungsten in the carbene complexes, as well as the transoid structure at the 3,8-bond, have been discussed before[1]. Elsewhere[2] we have used X$_1$ to denote (2)$^+$ GaBr$_4^-$ and P$_1$ to denote (3)·GaBr$_3$; also 4_n^+ to denote (2g)$^+$.[1]

‡ ^{1}H N.m.r. of (2a)$^+$ GaBr$_4^-$ (200 MHz; CD$_2$Cl$_2$; 235 K): δ 7.14 (d, 1H, H-2), 5.07 (d, 1H, OCH$_A$H$_B$Bu^t), 5.06 (d, 1H, OCH$_A$H$_B$Bu^t), 4.89 (d, 1H, H-8), 4.53 (d, 1H, OCH$_A$H$_B$Bu^t), 4.38 (d, 1H, OCH$_A$H$_B$Bu^t), 3.47 (s, 1H, H-4), 3.17 (s, 1H, H-1), 1.25 (s, 9H, Bu^t), 0.94 and 0.91 (s, 9H, OCH$_2$Bu^t), and 0.82 (H-3). The resonances expected for H-5, H-6, H-7 and R' = R'' (= Me) could not be safely distinguished from the corresponding signals of the polymer product. The triplet expected for H-3 was not clearly visible, but was located by finding the frequency at which irradiation caused the two doublets assigned to H-2 and H-8 to become singlets; *cf.* assignments in closely related species.[1]
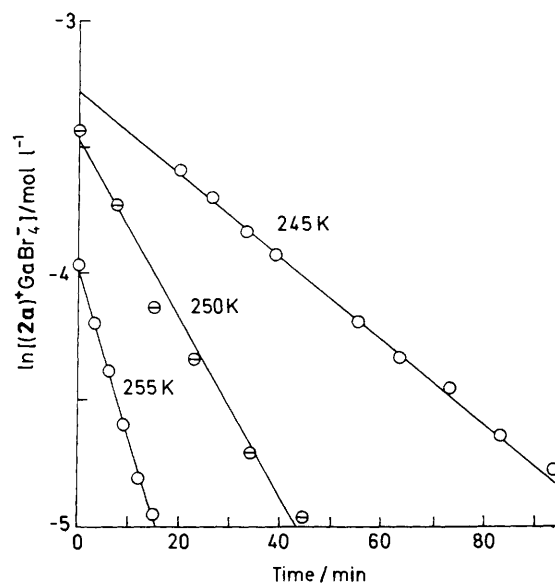
and that of (**2d**)$^+$GaBr$_4^-$ at 235 K being close to that of (**2b**)$^+$-GaBr$_4^-$ at 235 K. A significant degree of stability is thus conferred on the metallacycle by the presence of an *endo*-methyl group on C-5. This effect is specific and is not induced by methyl substituents in other positions (*endo*-6, *exo*-5, *exo*-6, 1, or 7). It may be interpreted in terms of a repulsion between the *endo*-methyl group at C-5 and either the developing p_π orbital at C-3 or the C–H bond at C-3, which would raise the level of the transition state (**A**) and hence the activation energy of the cleavage reaction.

Use of other carbene complexes such as W(CHCH$_2$Bu^t)-(OCH$_2$Bu^t)$_2$Br$_2$·GaBr$_3$ and W(CHCHEt$_2$)(OCH$_2$Bu^t)$_2$-Br$_2$·GaBr$_3$, with norbornene as monomer, leads respectively to compounds (**2e**)$^+$GaBr$_4^-$ and (**2f**)$^+$GaBr$_4^-$ bearing a different substituent (R) on C-8 (Scheme 1). The former, for which R is the primary alkyl group CH$_2$Bu^t, appears less stable ($t_{1/2}$ = 5 min at 235 K) than (**2b**)$^+$ GaBr$_4^-$ (R = Bu^t), whereas the latter, for which R is the secondary alkyl group CHEt$_2$, is more stable ($t_{1/2}$ = 3 min at 250 K). This unexpected reactivity order suggests that the opening rate of these metallacyclobutanes depends on both steric and electronic properties of the substituent on C-8.[5]

The chain-propagating metallacyclobutane (**2g**)$^+$GaBr$_4^-$ (Scheme 1), in which R (at C-8) is the polymer chain obtained after insertion of more than 1 equiv. of norbornene into the initial tungsten–carbene double bond, is produced by the further reactions of (**3b**)·GaBr$_3$ with norbornene.[1] This rearranges with a half-life of *ca.* 6 min at 250 K (or 60 min at 235 K). Its stability is thus greater than that of the initial (**2b**)$^+$-GaBr$_4^-$ (R = Bu^t) but similar to that of (**2f**)$^+$GaBr$_4^-$, in which the CHEt$_2$ group can be considered as a model of the polynorbornene chain of (**2g**)$^+$GaBr$_4^-$. The homologous propagating metallacyclobutanes derived from systems **e** and **f** (Scheme 1) behave similarly; those bearing an *endo*-methyl substituent at the 5-position are again more stable.

Finally, we note metal ligand effects on the stability of these compounds. Replacement in (**2b**)$^+$GaBr$_4^-$ of all bromine by chlorine atoms gives a derivative with half-life raised to 7 min at 250 K. Replacement of the two neopentyloxy groups of (**2b**)$^+$GaBr$_4^-$ by two isopropyloxy ligands also enhances the stability of the metallacyclobutane ($t_{1/2}$ = 50 min at 235 K). These observations may be explained by (a) the weaker co-ordinating power of GaCl$_4^-$ as compared with GaBr$_4^-$, and (b) the stronger π-donation of the ligands decreasing the Lewis acidity at tungsten.

Details of the preparation of the various compounds, of the n.m.r. spectra of the tungstacyclobutanes, and of the kinetics of rearrangement into tungsten–carbene complexes, along with a discussion of the relation between the relative stability of the metallacycles and the rate and stereoselectivity of ring-opening polymerisation and olefin metathesis reactions, will be given in a full paper.[6]

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