The Detection of 'Living' Propagating Tungsten–Carbene Complexes in the Ring-opening Polymerization of Bicycloalkenes

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The tungsten–carbene complex $W(CHCMe_3)(OCH_2CMe_3)_2Br_2$, when mixed with $GaBr_3$, adds various bicyclo[2.2.1]hept-2-enes to form 'living' propagating carbene complexes which may be characterized by ^1H n.m.r. spectroscopy, and used to make block copolymers.

It has previously been shown that tungsten–carbene complexes, propagating the catalytic metathesis of acyclic alkenes, can be observed by ^1H n.m.r. spectroscopy.[1,2] Not only can the complexes be identified by the fine structure of their H_α signal, but their concentrations may also be determined. This method has now been applied to the ring-opening polymerization of bicycloalkenes (II)—(VIII), catalysed by (1)–GaBr$_3$ (2:1); see Scheme 1.
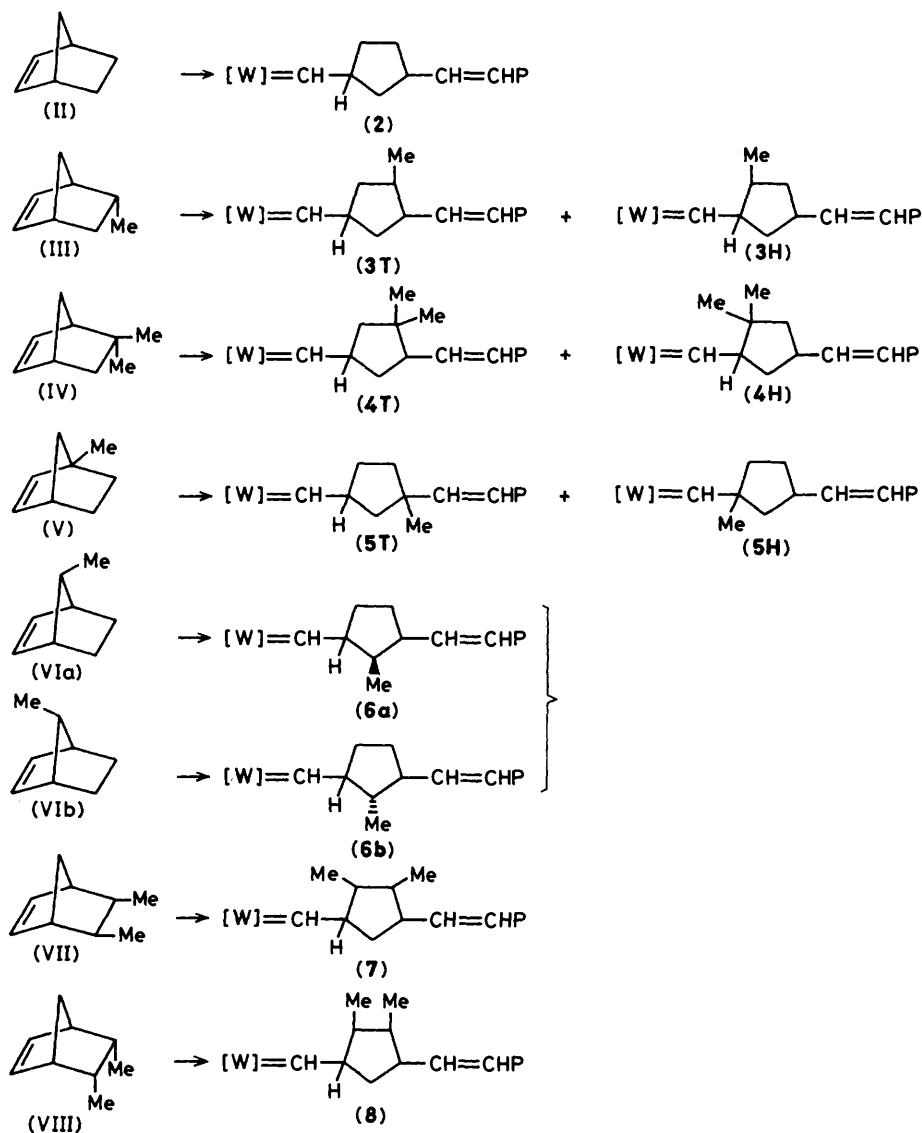
$$W(CHBu^t)(OCH_2Bu^t)_2Br_2$$
$$(1)$$
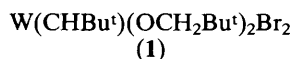
Compounds (II)—(VIII) (15 μl, 1.4×10^{-4} mol) were added to C_6D_5Br solutions of (1) (2.9×10^{-5} mol in 0.4 cm³)–GaBr$_3$ (2:1) at 240 K in an n.m.r. tube and the ^1H n.m.r. spectra run at 240 K (where reaction is very slow) after successive warmings to 20 °C. Some polymer was usually formed immediately on mixing owing to the momentary rise of temperature at the interface and in all cases the monomer ([M]/[W] = 5) was totally polymerized in less than 1 min at room temperature, while the initial complex (1) was *partially*

converted either into one new carbene species [with (II), (VII), and (VIII)] or into two new carbene species [with (III)—(VI)]. Complex (5H) gives a singlet, while all the other product carbenes give the expected doublet ($^3J_{HH}$ 10 Hz) for the H_α signal; see Figure 1.

The distinction between (3H), or (4H), and (3T), or (4T), is made on the basis that (3T), or (4T), is expected to give rise to the doublet closest in chemical shift to that for (2) or (5T). Complexes (6a) and (6b), which arise from reaction of a 1:1 mixture of (VIa) and (VIb), were assigned on the basis that the less reactive monomer[3] (VIb), will tend to react last and so give the higher carbene complex concentration.

Further addition of monomer (III) (15 μl, [M]/[W] = 5) to the solution containing (2) and residual (1), followed by warming to 20 °C, resulted in further conversion of (1) and total conversion of (2) into (3H) and (3T) (Figure 2, a → b). On addition of a further batch of (II) (10 μl, [M]/[W] = 3.3) to this solution, reconversion of *ca.* two thirds of (3H) and (3T) into (2) and a further decrease of (1) was observed (Figure 2, b → c).

The total concentration of carbene complexes remained constant during all these experiments, even after several hours

(II) → [W]=CH—⟨ring⟩—CH=CHP (2), with H

(III) → [W]=CH—⟨ring, Me⟩—CH=CHP (3T), with H + [W]=CH—⟨ring, Me⟩—CH=CHP (3H), with H

(IV) → [W]=CH—⟨ring, Me Me⟩—CH=CHP (4T), with H + [W]=CH—⟨ring, Me Me⟩—CH=CHP (4H), with H

(V) → [W]=CH—⟨ring⟩—CH=CHP (5T), with H and Me + [W]=CH—⟨ring⟩—CH=CHP (5H), with Me

(VIa) → [W]=CH—⟨ring⟩—CH=CHP (6a), with H and Me

(VIb) → [W]=CH—⟨ring⟩—CH=CHP (6b), with H and Me

(VII) → [W]=CH—⟨ring, Me Me⟩—CH=CHP (7), with H

(VIII) → [W]=CH—⟨ring, Me Me⟩—CH=CHP (8), with H and Me Me

Scheme 1. Products of reaction of bicycloalkenes (II)—(VIII) with (1)-GaBr$_3$. (P = Polymer chain; the main chain bonds to the rings are always *cis*.)

at room temperature. In one experiment where the concentrations of (1), (7), and (VII) were followed with time at 250 K there was an exact 1:1 relationship between the decrease of (1) and increase of (7), while the monomer disappeared at about seven times the rate of (1). Complexes (2)—(8) may thus clearly be described as 'living' polymers by analogy with living anionic,[4] cationic,[5] and co-ordination[6] polymerization systems. Figure 2 demonstrates that block copolymers can be made with these systems; in order to make them well defined it would be necessary to improve the mixing technique and to use a more efficient initiator. With the present technique the initial burst of reaction at the interface results in the production of a certain amount of quite high molecular weight polymer. From the ratio of product carbene and residual initiator carbene concentrations it may be estimated that the rate constant for propagation is at least 3 times that for initiation. We do not believe that back-biting to produce cyclic oligomers with the regeneration of initiator is of significance during the first few minutes of reaction under the present conditions.

All 'head' carbenes [(3H), (4H), (5H)] dominate over their 'tail' counterparts [(3T), (4T), (5T)], indicating that they are less reactive (Figure 1). Polymers of racemic (V) made with other catalysts frequently show strong head–tail bias,[7,8] consistent with propagation mainly by the head carbene (5H). On the other hand polymers of racemic (III) and (IV) do not normally show any head–tail bias.[9,10] However, this fact is not at variance with the observed imbalance in the head and tail carbene concentrations since (a) their relative concentration will be governed by the relative rate constants of the reactions (3T) + M → (3H) and (3H) + M → (3T), and (b) the head : tail carbene ratio observed under the present conditions will be that obtaining as [M] → 0, when the metal–carbene complex will be in its most relaxed and most stable geometric form and therefore also in its kinetically most discriminating form.[11] Under these circumstances the rate constant ratio for the above two reactions may be greater than that obtaining at higher [M].

A slow decrease in head : tail carbene ratio was observed when the solutions were left at 20 °C for longer periods [*e.g.*
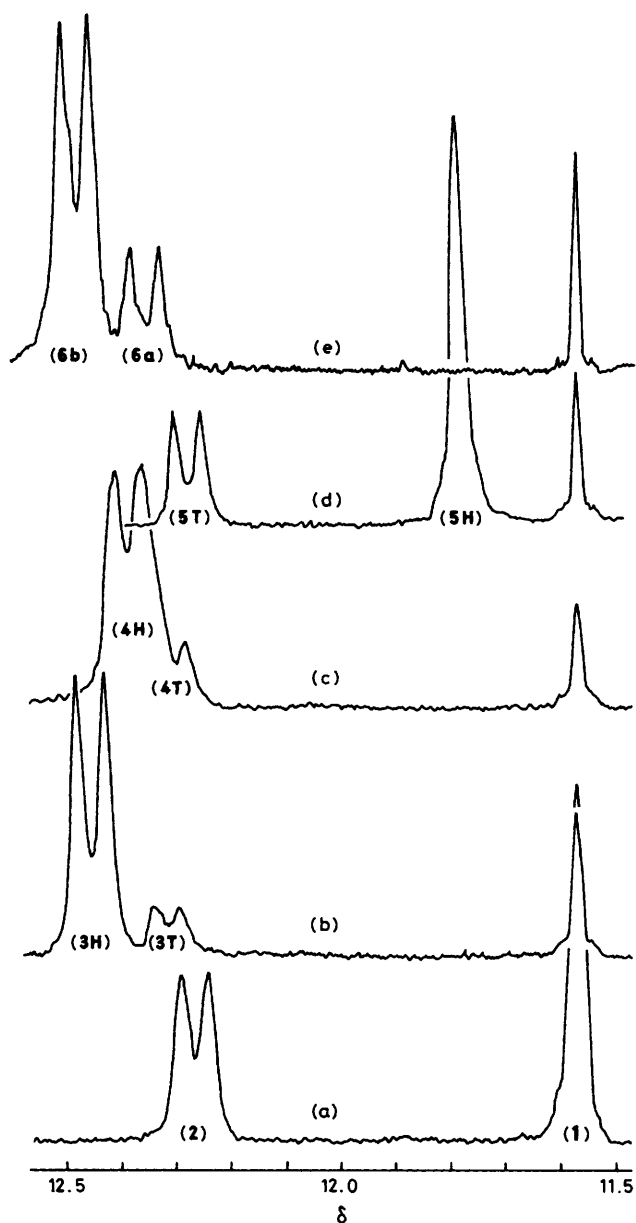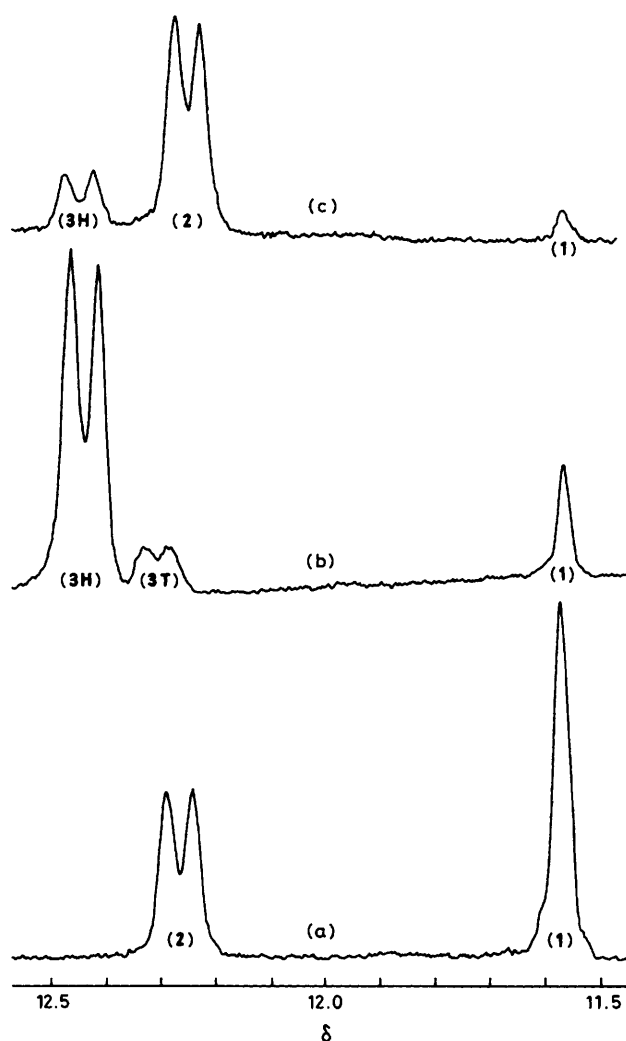
Figure 1. 200 MHz ^{1}H N.m.r. spectra of the carbene proton region after addition of (a) (II), (b) (III), (c) (IV), (d) (V), and (e) (VIa)–(VIb) (1:1) to (1)–GaBr$_3$ (2:1) followed by 3 min reaction at 293 K and cooling to 240 K. Numbers under the peaks indicate the assignments to the structures in Scheme 1. All spectra have been aligned on the singlet (δ 11.57) for (1) to correct for small variations of δ with W:Ga ratio.[2] The products from (VII) and (VIII) gave doublets centred on 12.36 and 12.50 respectively.

from 5.5:1 to 2:1 after 120 min for (III)] and there was a reduction in the molecular weight of the high molecular weight fraction [for (II)] or even its total disappearance; the *cis* content of the recovered polymer also decreased. Thus secondary metathesis reactions continue long after the monomer has been consumed. These may be intermolecular or intramolecular such as have been observed with WCl$_6$–Me$_4$Sn as catalyst.[12]

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Figure 2. 200 MHz ^{1}H N.m.r. spectra of the carbene proton region after successive addition of (a) (II), (b) (III), and (c) (II) to (1)–GaBr$_3$ (2:1) followed by 3 min reaction at 293 K and cooling to 240 K.

References

1 R. R. Schrock, S. M. Rocklage, J. H. Wengrovius, G. A. Rupprecht, and J. D. Fellman, *J. Mol. Catal.*, 1980, **8**, 73.
2 J. Kress, M. Wesolek, and J. A. Osborn, *J. Chem. Soc., Chem. Commun.*, 1982, 514; J. Kress and J. A. Osborn, *J. Am. Chem. Soc.*, 1983, **105**, 6346.
3 J. G. Hamilton, K. J. Ivin, and J. J. Rooney, *J. Mol. Catal.*, 1985, **28**, 255.
4 M. Szwarc, 'Carbanions, Living Polymers and Electron Transfer Processes,' Wiley, New York, 1968; *Adv. Polym. Sci.*, 1983, **49**, 1.
5 T. Higashimura and M. Sawamoto, *Adv. Polym. Sci.*, 1984, **62**, 49; *Makromol. Chem. Suppl.*, in the press.
6 H. W. Turner, R. R. Schrock, J. D. Fellman, and S. J. Holmes, *J. Am. Chem. Soc.*, 1983, **105**, 4942.
7 J. G. Hamilton, K. J. Ivin, and J. J. Rooney, *Br. Polym. J.*, 1984, **16**, 21.
8 J. G. Hamilton, K. J. Ivin, G. M. McCann, and J. J. Rooney, *Makromol. Chem.*, in the press.
9 K. J. Ivin, L. M. Lam, and J. J. Rooney, *Makromol. Chem.*, 1981, **182**, 1847.
10 H. T. Ho, K. J. Ivin, and J. J. Rooney, *Makromol. Chem.*, 1982, **183**, 1629; *J. Mol. Catal.*, 1982, **15**, 245.
11 Ho Huu Thoi, B. S. R. Reddy, and J. J. Rooney, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 3307.
12 L. Reif and H. Höcker, *Makromol. Chem., Rapid Commun.*, 1981, **2**, 183; *Macromolecules*, 1984, **17**, 952.