Detection of Diastereoisomers of Metallacyclobutane Intermediates in the Metathesis Polymerization of Norbornene and its Derivatives

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Addition of norbornene derivatives to racemic mixtures of chiral tungsten–carbene complexes is shown to lead to the formation of *transoid* diastereoisomeric tungstacyclobutanes that can be distinguished by ^{1}H n.m.r. spectroscopy; *cisoid* structures, though formed, are too unstable to be observed.

In situ studies using ^{1}H n.m.r. spectrometry have proved to be a valuable technique for the analysis of metallacyclobutane intermediates involved in the metathesis polymerization of norbornene derivatives catalysed by tungsten–carbene complexes of the type $W(=CR'R'')(OCH_2Bu^t)_2Br_2 \cdot GaBr_3$ ($\mathbf{1} \cdot GaBr_3$).[1—3] Various isomers can be distinguished for these metallacyclobutane intermediates, the structure of which correlates directly with the microstructure of the final polymer. Tungstacyclobutane precursors to living polymer chains, containing adjacent to the metal centre, *trans* carbon–carbon double bonds and head–head, head–tail, or tail–tail ring dyad structures, have already been described.[1—3] We now report (i) the observation of diastereoisomers which are the precursors to *iso*- or *syn*-diotactic ring dyad structures in the polynorbornene chains and (ii), the much lower stability of *cisoid* isomers compared with *transoid* isomers.

When norbornene (3 equiv.) is added to a solution of racemic $W(CHC^*HMeEt)(OCH_2Bu^t)_2Br_2 \cdot GaBr_3$ ($\mathbf{1a} \cdot GaBr_3$)[4,5] at 200 K, and the temperature is raised to 220 K, two main tungstacyclobutane species build up simultaneously in the ratio 3/4; these were identified† as isomers of the initial species $(\mathbf{2a})^+\ GaBr_4^-$ formed through the addition of one molecule of norbornene to the tungsten–carbon double bond of $(\mathbf{1a}) \cdot GaBr_3$. These two isomers are both *transoid* at bond C-8–C-3, according to difference nuclear Overhauser enhance-

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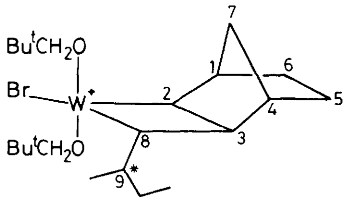
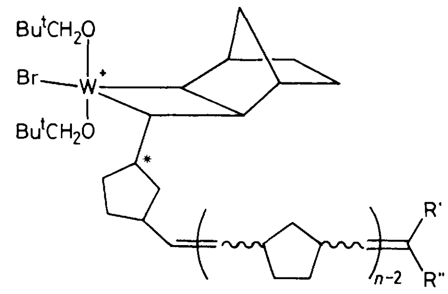
† ^{1}H n.m.r. (200 MHz, CD_2Cl_2, 220 K, δ) of $(\mathbf{2a})^+\ GaBr_4^-$ (partial assignment): *major isomer* (55—60%): δ 6.80 (d, 1H, H-2), 5.00 (d, 1H, $OC\mathit{H}_AH_B$), 4.75 or 4.90 (t, 1H, H-8), 4.84 (d, 1H, $OC\mathit{H}'_AH'_B$), 4.54 (d, 1H, $OCH_A\mathit{H}_B$), 4.23 (d, 1H, $OCH'_A\mathit{H}'_B$), 3.52 (s, 1H, H-4), 3.33 (s, 1H, H-1), 2.01 and 1.75 (m, 2H, H-5 and H-6), 1.58 (d, 3H, CH*Me*Et), 0.93 and 0.86 (s, 9H, $OCH_2\mathit{Bu}^t$), 0.69 (H-3). The H-3 signal position was found by determining the frequency at which irradiation caused H-2 and H-8 to become a singlet and a doublet respectively. Assignments of $OC\mathit{H}_2Bu^t$ signals was ascertained by selective decoupling experiments. *Minor isomer* (40—45%): H-2 at δ 7.06, H-8 at 4.90 or 4.75, $OCH_A\mathit{H}_B$ at 4.55 and H-4 at 3.49. The other signals were not resolved from those of the major isomer.



(2a)$^+$

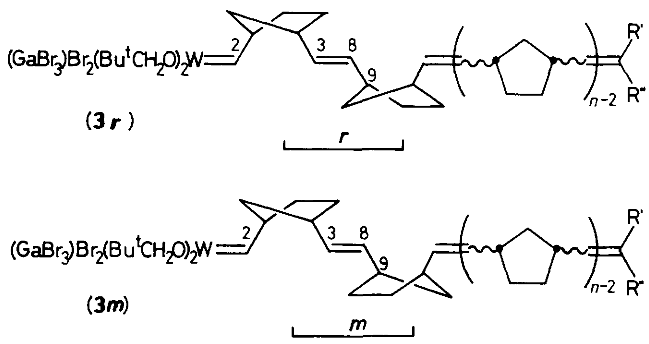


(4a)$^+$ R′ = H, R″ = CHMeEt
(4b)$^+$ R′ = H, R″ = Bu^t
(4c)$^+$ CR′R″ = C(CH$_2$)$_3$CH$_2$
(4d)$^+$ R′ = Me, R″ = CHMeEt

Scheme 1. *Transoid* metallacyclobutane intermediates in the polymerization of norbornene ($n \geqslant 2$).

ment (n.O.e.) measurements,‡ and are best distinguished by their H-2 doublets at δ 7.06 and 6.80 respectively ($^3J_{\text{H-2-H-3}}$ 9 Hz). Since the many other analogous species of type **(2)**$^+$ GaBr$_4^-$ that have previously been detected[1—3] only show a single *transoid* isomer (provided the norbornene derivative is symmetrically substituted), we attribute this observation of two isomers to the unique presence in **(2a)**$^+$ of a chiral centre at C-9 and conclude that the two species observed in this case are the resulting diastereoisomers. Diastereoisomers were similarly distinguished for the carbene complex W*(CHC*HMeEt)(OCH$_2$Bu^t)$_3$Br.[5]

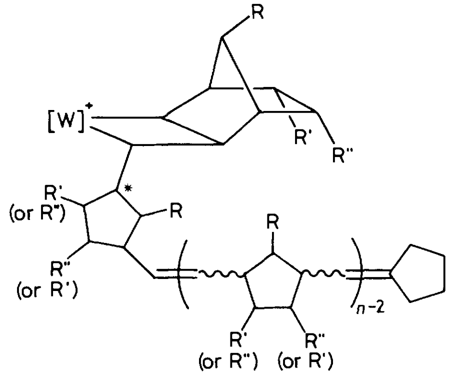
Two further weak doublets are moreover detected at δ 6.92 and 6.87 (ratio 5/3), which become stronger at 235 K as the result of further reaction of monomer, and correspond to the H-2 signals of two propagating tungstacyclobutane species **(4a)**$^+$GaBr$_4^-$ (Scheme 1). These are analogues of the two species previously described[1,2] for **(4b)**$^+$ and **(4c)**$^+$ (Scheme 1) and of those now also seen for **(4d)**$^+$ resulting from the reaction of norbornene with the carbene complex W[C(Me)CHMeEt](OCH$_2$Bu^t)$_2$Br$_2$·GaBr$_3$ (**1d**·GaBr$_3$).[4,5] The ^{1}H n.m.r. spectra (except the chain end signals) and relative ratios of the two isomers of these four **(4)**$^+$ derivatives, differing only in the nature of the polymer chain end, are identical.[1,2] Earlier, the two **(4)**$^+$ species observed in each case were incorrectly assigned[1,2] to *cisoid*/*transoid* isomers differing in the attachment (*cisoid* or *transoid*) of the polymer chain substituent at C-8 (Scheme 1). They may now be identified as the two *transoid* diastereoisomers analogous to those observed for **(2a)**$^+$: a chiral centre exists similarly at C-9 and difference n.O.e. experiments run on **(4c)**$^+$ confirmed that both isomers were *transoid.*§



(3r)

(3m)

Scheme 2



(4e)$^+$ R = H, R′ = R″ = Me
(4f)$^+$ R = Me, R′ = R″ = H
(4g)+ R = R′ = H, R″ = Me
(4h)$^+$ R = R″ = H, R′ = Me

Scheme 3. *Transoid* metallacyclobutane intermediates in the polymerization of substituted norbornenes ($n \geqslant 2$).

At higher temperatures (250 K), ring-opening rearrangement of the metallacycles occurs and the complexes **(4)**$^+$ GaBr$_4^-$ are converted into carbene complexes of the type **(3)**·GaBr$_3$ represented in Scheme 2.[1—3] One of the two detected diastereoisomers of **(4)**$^+$ will lead to **(3m)** and the other to **(3r)**.[6] An absolute assignment is, however, not possible.

These observations have been extended to symmetrically and unsymmetrically substituted norbornenes. For example, for each of the symmetrical monomers *endo,endo*-5,6-dimethylnorbornene[7] and *anti*-7-methylnorbornene,[8] two diastereoisomeric propagating metallacyclobutane species are observed similarly at 220—235 K after addition to W[$\overline{\text{C(CH}_2\text{)}_3\text{C}}H_2$](OCH$_2$Bu^t)$_2Br_2$·GaBr$_3$. Thus, compound **(4e)**$^+$ (Scheme 3) gives rise to two H-2 doublets at δ 7.39 and 6.91 (ratio 2/5) and compound **(4f)**$^+$ to two others at δ 6.84 and 6.60 (ratio 1/5). Under similar conditions, *endo*-5-methylnorbornene[9] has already been reported[2] to give rise to at least six observable propagating metallacyclobutanes. Four of them, differing in the head or tail position of the methyl substituent of the C$_5$H$_8$ rings, are represented in Scheme 3 [two **(4g)**$^+$ and two **(4h)**$^+$]. These and their four diastereoisomers account for the observed signals, but with some overlap of the doublets.

Similar observations were made for other monomers such as 1-methylnorbornene, 5,5-dimethylnorbornene, and *endo*-dicyclopentadiene. For the last, the four sets of diastereoisomeric pairs expected for **(4)**$^+$ are revealed at 235 K as eight H-2 doublets of comparable intensity at δ 7.35, 7.23, 7.19, 7.09 (double intensity), 6.98, 6.95, and 6.81.

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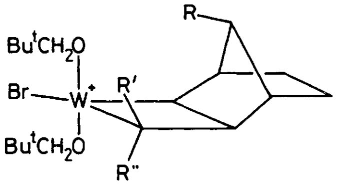
‡ Irradiation of the signal at δ 0.69 (H-3) enhances the signals at δ 7.06 and 6.80 (H-2); also the signals at δ 4.90 and 4.75 (H-8) to a similar extent, but less so than for the former (H-2) signals.[1]

§ Irradiation of the signal at δ 0.73 (H-3)[1,2] enhances both doublets at δ 6.92 and 6.87 (H-2) to a similar extent, the triplet at δ 4.93 (H-8)[1,2] being much less enhanced. Irradiation of the signal at δ 4.93 (H-8) enhances both singlets at δ 3.52 and 3.49 (H-4)[1,2] to a similar extent.



(2c)$^+$ $R = H, CR'R'' = \overline{C(CH_2)_3C}H_2$
(2d)$^+$ $R = H, R' = Me, R'' = CHMeEt$
(4i)$^+$ R = Me, R′ = H, R″ = polymer chain similar to that of (4f)$^+$ (Scheme 3)

Scheme 4. Undetected metallacyclobutane intermediates.

Finally, it should be noted that diastereoisomers found for a given complex show not only different chemical shifts ($0.05 < \Delta\delta < 0.5$) and initial ratios ($0.2 < \rho < 1$), but also different stabilities, the least abundant diastereoisomer being generally also the least stable.¶

As a consequence of the identification of the above diastereoisomers, we conclude that *no* cisoid *metallacyclobutane intermediate is ever detected* in any of the polymerization reactions, even at 220 K. However, such species must be formed as the precursors to the *cis* double bonds actually found by ^{1}H n.m.r. in the final polymers, so that it may be concluded that a *cis* substituent at C-8 reduces the stability of *cisoid* complexes [isomers of (**2**)$^+$ and (**4**)$^+$] through its interaction with the other synclinal atoms of the substituted metallacycles. Rearrangement of these isomers into tungsten–carbene complexes thus occurs very rapidly after *cis* addition of monomer to the metal–carbon double bond, which implies that the rate of formation of the *cis* carbon–carbon double bonds should decrease with decreasing monomer concentration at 220 K, whereas *trans* double bond formation should be concentration independent. This prediction has yet to be verified experimentally. Further, we find for all polymers a low *cis* double bond content (5—40%) which indicates that *trans* addition of monomer to these living carbene complexes must be faster than *cis* addition. Note also that no initial intermediate (**2**)$^+$ $GaBr_4^-$ can be detected if the initial carbene ligand of complexes (**1**).$GaBr_3$, and consequently the expected C-8 carbon of (**2**)$^+$, is disubstituted (R′, R″ ≠ H, Scheme 4). This was already reported[3] for (**2c**)$^+$ expected from $[W(\overline{C(CH_2)_3C}H_2](OCH_2Bu^t)_2Br_2{\cdot}GaBr_3$ (**1c**·$GaBr_3$) and norbornene,[2] and has now been confirmed for (**2d**)$^+$ expected from $W[C(Me)\ (CHMeEt)](OCH_2Bu^t)_2Br_2{\cdot}GaBr_3$ (**1d**·$GaBr_3$) and norbornene (Scheme 4). Similarly, no propagating intermediate (**4i**)$^+$ $GaBr_4^-$ (Scheme 4), even *transoid*, can be detected when *syn*-7-methylnorbornene[8,10] is added to $W[\overline{C(CH_2)_3C}H_2](OCH_2Bu^t)_2Br_2{\cdot}GaBr_3$. In this case, the instability results probably from the reverse interaction between the *syn* methyl substituent at C-7 and the atoms or ligands surrounding the metal.

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¶ Half-lives at 250 K: (**2a**)$^+$: 4 and 7 min. (**4e**)$^+$: 20 and 60 min.
at 235 K: (**4a—d**)$^+$: 20 and 40 min.

References

1 J. Kress, J. A. Osborn, R. M. E. Greene, K. J. Ivin, and J. J. Rooney, *J. Am. Chem. Soc.*, 1987, **109**, 899.
2 J. Kress, J. A. Osborn, K. J. Ivin, and J. J. Rooney, in 'Recent Advances in Mechanistic and Synthetic Aspects of Polymerization, ed. A. Guyot and M. Fontanille, Reidel, Dordrecht, p. 363, 1987.
3 J. Kress, J. A. Osborn, V. Amir-Ebrahimi, K. J. Ivin, and J. J. Rooney, *J. Chem. Soc., Chem. Commun.*, 1988, 1164.
4 J. Kress, M. Wesolek, and J. A. Osborn, *J. Chem. Soc., Chem. Commun.*, 1982, 514.
5 J. Kress and J. A. Osborn, *J. Am. Chem. Soc.*, 1987, **109**, 3953.
6 K. J. Ivin, G. Lapienis, and J. J. Rooney, *Polymer*, 1986, **21**, 436; *J. Chem. Soc., Chem. Commun.*, 1979, 1068.
7 R. M. E. Greene, K. J. Ivin, G. M. McCann, and J. J. Rooney, *Makromol. Chem.*, 1987, **188**, 1963.
8 J. G. Hamilton, K. J. Ivin, and J. J. Rooney, *J. Mol. Catal.*, 1985, **28**, 255.
9 K. J. Ivin, L. M. Lam, and J. J. Rooney, *Makromol. Chem.*, 1981, **182**, 1847.
10 J. Kress, J. A. Osborn, and K. J. Ivin, *Makromol. Chem.*, to be published.