

Ring-opening Metathesis Polymerisation of Norbornene by OsO₄: Evidence for a Transient Oxametallacyclobutane

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When norbornene is treated with a catalytic amount of OsO₄ at 60 °C, a substantial yield of ring-opened metathesis polymer is obtained among the products; this result provides strong evidence that transient oxometallacyclobutane species are formed using this alkene oxidation reagent.

The mechanism of the reaction of OsO₄ with alkenes^{1,2} is now a classic problem in the field of oxidation reactions and catalysis. The textbook mechanism is a direct [3 + 2] cycloaddition leading to monomeric Os^{VI} glycolate which then dimerises to give the observed product (Scheme 1, path a,d). However, Sharpless³ has suggested that there could be an initial [2 + 2] cycloaddition to give an oxametallacyclobutane followed by its rapid expansion to the Os^{VI} glycolate (Scheme 1, path b,c). This has sparked off a lively and continuing debate with significant issues being, among others, whether the reaction is charge or orbital controlled^{3a,4} and the origin of the stereoselectivity in the asymmetric variant of the reaction.^{3b,5}

The intervention here of a transient oxametallacyclobutane species is difficult to prove especially if step c (Scheme 1) is very fast relative to step b. Although rare, such species are not unknown, for example an oxairidacyclobutane formed by oxygen atom transfer from O₂ to a coordinated alkene has recently been clearly identified⁶ and there is strong inferential evidence that such species initiate alkene metathesis reactions.^{7,8} Furthermore, oxametallacyclobutanes must be involved in the general Wittig-type reaction known in the field of alkene metathesis where living polymers have been end-capped by the addition of aldehydes and ketones.^{9,10} However, to date, no such species have been detected, either directly or indirectly, in Os-based systems.¹¹

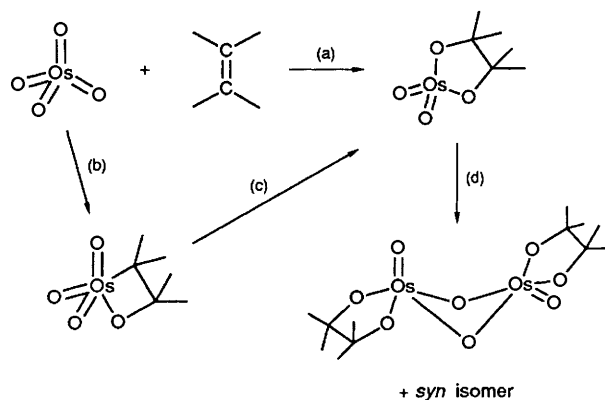
If an oxametallacyclobutane is indeed a transient in OsO₄ oxidations of alkenes, under the right conditions and with a favourable substrate, it might undergo, if only to a small extent, a retro [2 + 2] cycloaddition. Even a very small concentration of the resulting metallacarbene should be detectable by its propensity to initiate the formation of high molecular weight polymer from a suitable cyclic alkene. Indeed, we have have previously used just such an argument in a Ru-based polymerisation of norbornene⁷ (Scheme 2, M =

Ru). Thus, for example, when norbornene is treated, under molecular oxygen, with a series of compounds of the type RuCl₂(PPh₃)₄, norbornanone, norbornene epoxide and the corresponding polyethers are formed simultaneously with ring-opened metathesis polymer.⁷ Significantly, the rate of formation of the latter is diminished in the absence of molecular oxygen and we suggested that oxametallacyclobutane intermediates were responsible for both the oxidation and metathesis reactions.⁷ Norbornene is an ideal substrate for studies of this kind because release of strain energy should not only facilitate formation of the initiating species but also promote rapid propagation of the ring-opening metathesis reaction. Furthermore, high molecular weight polymers of norbornene have been obtained with many catalyst systems and their microstructures have been thoroughly examined and they are now well characterised.¹²

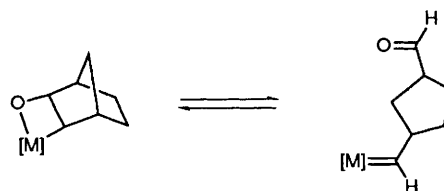
We now report that when norbornene (2.0 g), dissolved in chlorobenzene (2.0 cm³) was mixed with OsO₄ (30 mg) in chlorobenzene (0.5 cm³) and kept, sealed, at 60 °C for 3 days, 100 mg of ring-opened polymer was isolated. When the system was kept instead at room temperature for three weeks only 10 mg of polymer was obtained, so heating is undoubtedly beneficial. In a separate experiment, norbornene and OsO₄ (1:1) were allowed to react at room temperature and, as expected a mixture of the *syn* and *anti* isomers of the dimeric Os^{VI} glycolate (Scheme 1) was formed almost instantaneously (as followed by ¹H NMR spectroscopy). A portion of this mixture also polymerised norbornene in a similar manner, strongly suggesting that metallacarbenes are formed in the system according to Scheme 2 (M = Os).

The reaction of OsO₄ with alkene is greatly accelerated by the presence of nitrogenous bases^{1,2} and it is this which is the basis for the asymmetric variant of the reaction.^{3b} We found that the addition of an excess of pyridine (0.25 cm³) to the above system suppresses polymerisation even at 60 °C. This is consistent both with the fact that Os^{VI} glycolate complexes are more stable with amine ligands than without,² and with the detailed description^{3b} of the OsO₄-alkene reaction wherein the rate acceleration by bases is ascribed to an increase in the rate of rearrangement of the oxametallacyclobutane (Scheme 1, step c).

Aside from its use as a test for the presence of metalla-



Scheme 1



Scheme 2

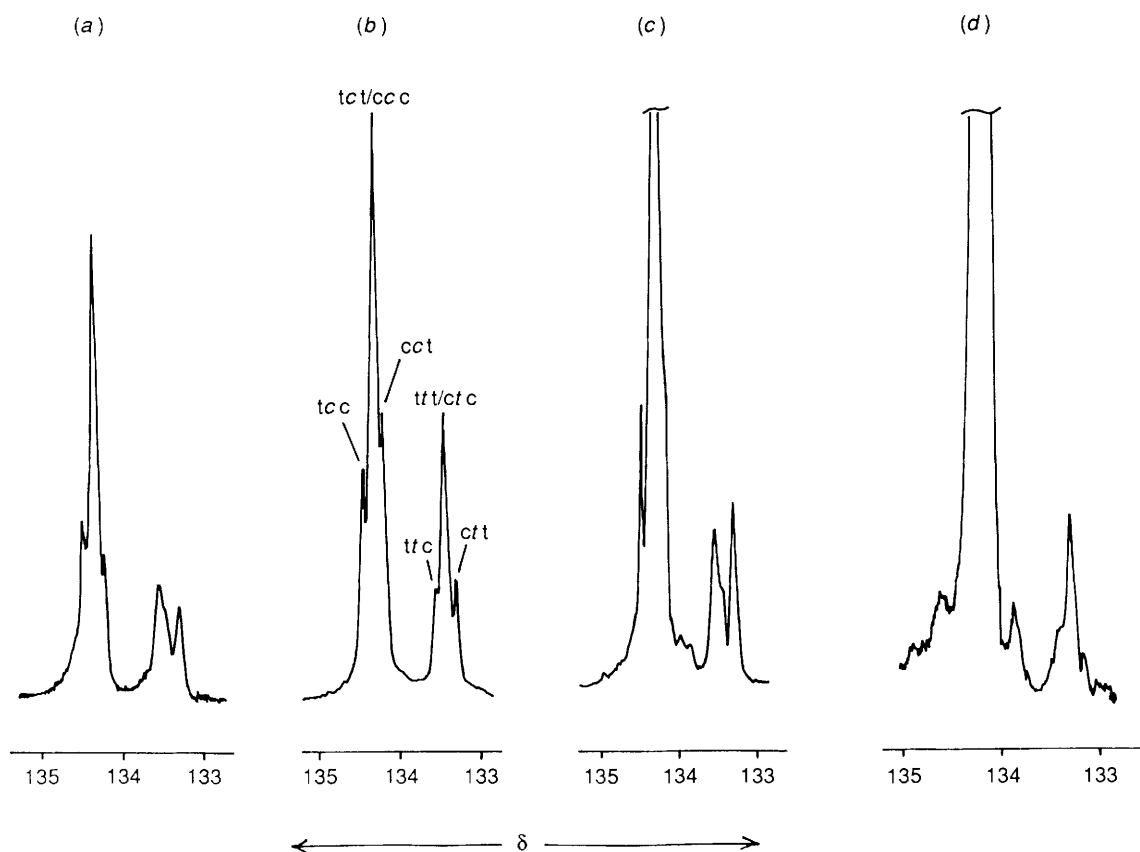


Fig. 1 ^{13}C NMR spectra (double bond region) of some polymers of norbornene. Catalysts are as follows; (a) OsO_4 , 60°C ; (b) OsCl_3 , 60°C in the presence of norbornadiene; (c) ReCl_5 , 20°C ; (d) RuCl_3 , 60°C , in the presence of dicyclopentadiene.

carbenes and hence oxametallacyclobutanes, the polymerisation reaction is of interest in its own right. Thus, in all cases, analyses by ^{13}C and ^1H NMR confirmed that the polymers contained 75–80% *cis* double bonds and were blocky ($r_t r_c = 3$).¹⁰ The *trans* junctions tend to occur in pairs as can be seen by the low intensity of the *ctc* and *tct* combined lines relative to the *tc* and *ctt* lines, Fig. 1(a), arising from the different possible triads in which a *trans* unit is central.¹² In this respect the behaviour of OsO_4 and its esters is very similar to that of ReCl_5 , Fig. 1(c), and in contrast to modified OsCl_3 and RuCl_3 Fig. 1(b) and (d) respectively, when the latter salts are induced to be high *cis* directing by the presence of bulky chelating dialkene ligands.¹² The polymers obtained show ^{13}C NMR features consistent with the idea that the *trans* units tend to occur in blocks, t_n , where $n > 2$.

Another interesting detail of the polymer structure, relevant to the oxidation reaction and which is again in common with the polymer made using ReCl_5 , is the prominent *ctt/ttc* features, Fig. 1(a) and (c). This has previously been commented upon and a mechanism for its formation suggested.¹² It has never been observed with a variety of noble metal trihalide catalysts in much lower oxidation states so it may be associated with high oxidation states in the propagating metallacarbene species.

Thus, both the production of ring-opened polymer and its microstructure provide strong evidence that osmium species in high oxidation states with oxo ligands can form oxametallacyclobutanes by [2 + 2] cycloaddition with alkenes. This in turn demonstrates the feasibility of such a mechanism in the reaction of OsO_4 with alkenes (Scheme 1, steps b and c).

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