First evidence for radical anions in metathesis catalysis

Valia Amir-Ebrahimi, a James G. Hamilton, a Jane Nelson, a John J. Rooney, a Jillian M. Thompson, a Andrew J. Beaumont, b A. Denise Rooney c and Charles J. Harding a

a School of Chemistry, The Queen's University, Belfast, UK BT9 5AG
b Chemistry Department, National University of Ireland, Maynooth, Kildare, Ireland
c Chemistry Department, The Open University, Milton Keynes, UK MK7 6AA. E-mail: c.j.harding@open.ac.uk

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The Grubbs' catalyst, (PCy3)2RuCl2(-COPh), generates persistent radical anions on treatment with π-acceptors such as p-benzoquinones and a remarkably wide range of dienes and even simple alkenes.

In the course of an investigation of the metathesis polymerisation of several norbornadiene derivatives catalysed by (PCy3)2RuCl2(-COPh), we have noted that 2,3-bis(2,3-dicarbonyl)norbornadiene is slow to react even though it polymerises rapidly using RuCl3 /H2O as catalyst. Dass and Grubbs previously remarked on the reluctance of 2,3-bis(trifluoromethyl)norbornadiene to polymerise, so there is here a hint that those dienes which are also Michael acceptors may chelate to 1 in the di-end mode via a charge transfer interaction which retards normal initiation and/or propagation. Furthermore there is a very recent report that 1 is also a very good catalyst for methyl methacrylate polymerisation. This led us to conclude that 1 may be capable of reducing a variety of π-acceptors in solution to radical anions. We therefore decided to investigate, by EPR analysis, the presence of radical anions generated from strong π-acceptors such as tetrahydro- (2), tetrafluoro- (3), tetrachloro- (4) and dichloro[1,2]-p-benzoquinone (5).

When 0.5 cm3 of a (1-5) x 10^-3 M solution of 1 in CH2Cl2 is mixed with 0.5 cm3 of a solution of the of π-acceptor [(5-10) x 10^-2 M] in the same solvent under argon at room temperature, EPR spectra are observed which persist for many hours. Each diene generates a different EPR spectrum centred close to the free spin value, (g ~ 2.005, typical of radical anions) and bearing no resemblance to RuII-centred EPR signals in general or to RuII-bound alkenes in particular.

Using 2 we observed immediate strong well-resolved EPR signals (Fig. 1) that decay over a period of hours. The spectrum consists of a triplet of triplet of triplets, arising from coupling to three pairs of spin ½ nuclei, presumably the protons H₄ and H₅ (see 1) together with the 31P nuclei of the catalyst.

The EPR spectrum from 3 under these conditions is complex; on preliminary analysis, two distinct overlapping patterns of six and eight lines suggesting the existence of more than one radical species. When 1 is replaced by (phu)Ru(CO)₂Cl₂ (6) as donor, however, addition of 3 gave a weak simple 1:2:1 triplet which was stable over several hours (Fig. 2). By way of contrast, the addition of Grubbs' catalyst 1 to 4 generated a very strong doublet, while with 6, 4 generated only a very intense singlet. The behaviour of 6 with benzoquinone is different in nature from anything so far observed in this work. The initial weak complex signal evolves into a relatively intense five-line metal-centred signal due to coupling to two equivalent N atoms from the phen ligand, similar to those found previously for electrochemically generated Ru-centred radical anions.

The most striking result occurred on addition of norbornadiene 7 to 1. An intense sharp triplet (Fig. 3) is observed, which decays only by some 50% over 24 h. We believe this signal can be explained by delocalisation of unpaired spin over one alkene moiety, as represented by 1.

On treatment with 1, norbornene and cyclopentene afford similar but much weaker triplets, while benzonorbornadiene gives a similar triplet following on the disappearance of an initial short-lived doublet of around the same g value. We are, as yet, unable to assign these spectra.

Fig. 1 EPR spectrum of Grubbs' catalyst 1 (1 x 10^-3 M) with benzoquinone 2 (1 x 10^-3 M), recorded in CH2Cl2 at 20 °C, showing the 1:2:1:2:4:2:1:2:1 triplets, g = 2.0048, A₄ = 4.8 G, A₅ = 1.8 G, A₁ = 0.4 G.

Fig. 2 EPR spectrum of 6 (5 x 10^-3 M) with tetrachlorobenzquinone 3 (5 x 10^-2 M), recorded in CH2Cl2 at 20 °C, g = 2.0075, A = 8.6 G.

Fig. 3 EPR spectrum of 1 (1 x 10^-3 M) with norbornadiene 7 (2 x 10^-3 M) recorded in CH2Cl2 at 20 °C, g = 2.0064, A = 12.9 G.

The presence of 2, 3 or 4 enhances the activity of the Grubbs catalyst without changing the cty content of the polybenzobuta diene (10%) as found using 1 alone. Similar results have also been obtained when 4 is used as a cocatalyst with mesityl-Mo(CO)₅ for phenylacetylene and norbornene polymerisations.

Several major points arise from this work.

(i) Species 1 is remarkably effective at forming radical anions even from simple olefins.

(ii) The spectrum generated by treatment of 2 with 1 indicates the loss of equivalence of the four protons in the benzopropion radical anion, a consequence of the π-binding of the Ru⁶⁺ centre as in 1. Following π-donation from the coordinated C=C moiety, electron transfer takes place from the ruthenium cation to the uncoordinated C=C group. In this way the inequivalence of the X₈ and X₉ sets in Fig. 1 and 2 is explained; in Fig. 2, indeed, the F₈ set is seen to be EPR silent.

(iii) The mechanism of initiation and perhaps even propagation of the metathesis reaction involves radical anions even for simple alkynes in accordance with eqns. (1) and (2). In support of this we note that norbornadiene, which may act in lieu of two alkynes, generalises a more intimate signal than norbornene and also initiates polymerisation far more efficiently. This suggests that in metathesis the substrate itself may act as a cocatalyst by virtue of radical anion formation, as supported by the cocatalytic effect noted above for quinones 2, 3 and 4. While there is evidence for involvement of anion radicals in the initiation step, we do not know whether this extends to the [2 + 2] cycladdition propagation step. Should this prove to be so, it raises very fundamental questions about the exact theoretical nature (concerted or otherwise) of the key step.

(iv) Not only is the EPR technique now seen as a valuable novel probe in metathesis reactions but it can also be employed for a wide variety of organometallic systems and other catalytic processes where the presence of suitable π-acceptors may also act as important promoters. With the objective of identifying, via a detailed assignment of their spectra, the radical anions observed in this work, we plan experiments to replace the ²H both olefinic H atoms and the α-H atom of the carbene ligand. We also intend to examine the behaviour of more recent analogues of 1, which lack the phosphine ligands. The elucidation of the nature and reactivity of the radical anions involved should assist in the design of improved catalysts for metathesis.

Notes and references

† EPR spectra were recorded at X-band frequencies in liquid CH₂Cl₂ at room temperature. No signals were observed from solutions of 1 in the absence of added substrates.
‡ We have now found that 1 polymerises α-methylstyrene and simultaneously generates EPR-active species. This information, together with the knowledge that Grignard reagents also catalyse free radical addition polymerisation (ref. 10) and metathesis polymerisation of norbornene (ref. 11), suggests a novel mechanism based on metallo-radicals.

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\begin{align*}
\text{RCH-CH} & \to [\text{M}][\text{RCH-CH}]^{-} \\
\text{RCH-CH} & \to [\text{M}][\text{RCH-CH}]^{-}
\end{align*}
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We believe that a metallo-carbene ion mechanism is responsible when the most acidic metathesis catalysts are used, but the new metallo-radical scheme applies under or when Mg-based catalysts (Grignard reagents) are active.


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