

First evidence for radical anions in metathesis catalysis

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The Grubbs' catalyst, $(\text{PCy}_3)_2\text{RuCl}_2(=\text{CHPh})$, 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 $(\text{PCy}_3)_2\text{RuCl}_2(=\text{CHPh})$ (**1**), we have noted¹ that 2,3-bis(ethoxycarbonyl)norbornadiene is slow to react even though it polymerises rapidly using $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ as catalyst. Dias and Grubbs² 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-*endo* mode via a charge transfer interaction which retards normal initiation and/or propagation. Furthermore there is a very recent report³ 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 dichlorodicyano-*p*-benzoquinone (**5**).

When 0.5 cm^3 of a $(1-5) \times 10^{-3} \text{ M}$ solution of **1** in CH_2Cl_2 is mixed with 0.5 cm^3 of a solution of the π -acceptor [$(5-10) \times 10^{-2} \text{ M}$] 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, ($g \sim 2.005$, typical of radical anions) and bearing no resemblance to Ru^{III} -centred EPR signals in general⁴ or to Ru^{III} -bound alkenes in particular.⁵

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 $\frac{1}{2}$ nuclei, presumably the protons H_A and H_B (see **I**) together with the ^{31}P nuclei of the catalyst.

The EPR spectrum from **3** under these conditions is complex; on preliminary analysis, two distinct overlapping patterns of six

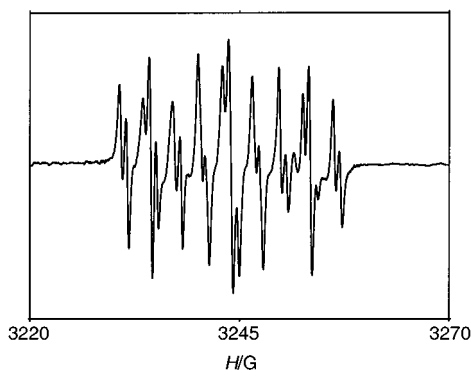


Fig. 1 EPR spectrum of Grubbs' catalyst **1** ($1 \times 10^{-3} \text{ M}$) with benzoquinone **2** ($1 \times 10^{-1} \text{ M}$), recorded in CH_2Cl_2 at 20°C , showing the 1:2:1:2:4:2:1:2:1 triplets. $g = 2.0048$; $A_1 = 4.8 \text{ G}$, $A_2 = 1.6 \text{ G}$, $A_3 = 0.4 \text{ G}$.

and eight lines suggesting the existence of more than one radical species. When **1** is replaced by $(\text{phen})\text{Ru}(\text{CO})_2\text{Cl}_2$ (**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 previously⁶ 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 **I**.

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.

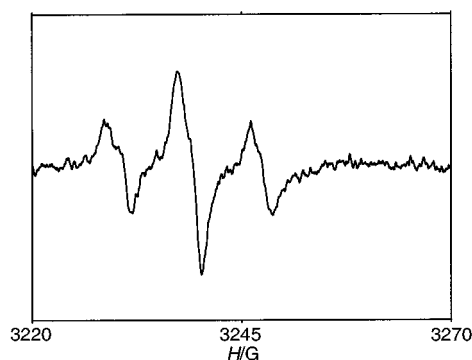


Fig. 2 EPR spectrum of **6** ($5 \times 10^{-3} \text{ M}$) with tetrafluorobenzoquinone **3** ($5 \times 10^{-2} \text{ M}$), recorded in CH_2Cl_2 at 20°C . $g = 2.0075$; $A = 8.6 \text{ G}$.

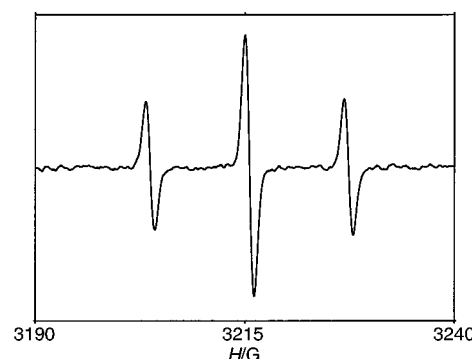
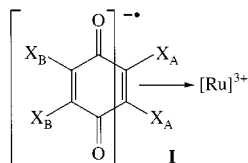


Fig. 3 EPR spectrum of **1** ($1 \times 10^{-3} \text{ M}$) with norbornadiene **7** ($2 \times 10^{-1} \text{ M}$), recorded in CH_2Cl_2 at 20°C . $g = 2.0064$; $A = 12.0 \text{ G}$.



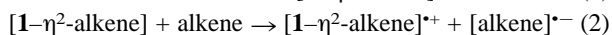
The presence of **2**, **3** or **4** enhances the activity of the Grubbs catalyst without changing the *cis* content of the polynorbornadiene (16%) as found using **1** alone. Similar results have also been obtained⁷ when **4** is used as a cocatalyst with mesityl-Mo(CO)₃ for phenylacetylene and norbornene 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 benzoquinone radical anion,⁸ a consequence of the η²-binding of **2** to the Ru^{II} centre as in **I**. 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 X_B and X_A sets in Fig. 1 and 2 is explained; in Fig. 2, indeed, the F_A 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 alkenes in accordance with eqns. (1) and (2). In support



of this we note that norbornadiene, which may act *in lieu* of two alkene molecules and chelate as in **I**, generates a more intense 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] cycloaddition 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.[‡]

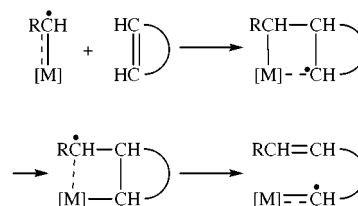
(iv) Not only is the EPR technique now seen as a valuable novel probe in metathesis reactions but it can also be employed for a wide variety of organometallic systems and other catalytic processes where the presence of suitable π-acceptors may also act as important promoters. With the objective of identifying, *via* detailed assignment of their spectra, the radical anions

observed in this work, we plan experiments to replace by 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.⁹ 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 metalla-radicals.



We believe that a metalla-carbenium ion mechanism is responsible when the most acidic metathesis catalysts are used, but the new metalla-radical scheme applies using **1** or when Mg-based catalysts (Grignard reagents) are active.

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