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Note

Radical anion forming activity of the Grubbs' catalyst and related organometallics: Michael acceptors as metathesis promoters

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Abstract

When several *p*-benzoquinones in methylene chloride solution are mixed at room temperature with $RuCl_2(PCy_3)_2(CHPh)$, $RuCl_2(PPh_3)_3$, $RhCl(PPh_3)_3$ and $CoBr_2(PPh_3)_2$, strong, well-resolved, persistent epr signals are observed, consistent with the formation of radical anions. In the case of the Grubbs' catalyst, $RuCl_2(PCy_3)_2(CHPh)$, evidence is presented that these signals arise from charge transfer. The Grubbs' catalyst, is also remarkable in that similar epr activity is observed using norbornadienes, and to a lesser extent during and after metathesis polymerisation of norbornene and cyclopentene. The dienes are also much more efficient promoters of initiation of these polymerisations than the monoenes, and evidence is presented that the presence of *p*-benzoquinone enhances the reactivity of the propagating metallacarbenes.

Keywords: Radical anions; *p*-Benzoquinones; Dienes and monoenes; Grubbs' catalyst; Ring-opening metathesis polymerisation; Basic organometallics

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1. Introduction

The Grubbs' catalyst, $RuCl_2(PCy_3)_2(CHPh)$ (**1**), has found widespread application in metathesis, including ring-opening and ring-closing reactions of synthetic application [1]. Investigation of the mechanism of these transformations is a subject of current interest [2]. A novel aspect of the Grubbs' catalyst, just revealed recently [3], is that it is sufficiently basic in solution to form persistent radical anions at room temperature from Michael acceptors such as tetracyanoethylene, *p*-benzoquinone, tetrafluoro-*p*-benzoquinone and its tetrachloro analogue.

2. Results and discussion

Epr spectroscopy of the reaction product of **1** with *p*-benzoquinone provides evidence for electron transfer generating radical anions. When equimolar solutions of *p*-benzoquinone and **1** (1×10^{-2} M) are mixed, the brick-coloured solution darkens over a period up to an hour to give an intense blue colour. At ambient temperature, the epr spectrum of this solution recorded in the $g = 2$ region consists of a complex signal of more than 20 lines, resolvable at low modulation [3]. This spectrum is not that of the free *p*-benzoquinone radical anion, but requires the intervention of nuclei not present in the benzoquinone. We conclude that this is due to hyperfine coupling with nuclei of the complexed Grubbs' catalyst. Rapid freezing of this solution gives a glass, whose spectrum in this region ($g = 2$) consists of a single broad (20 G) line. Scanned over a wider range, the epr spectrum of this glass shows the development of

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a new signal, attributable to Ru(III) with some indication of hyperfine splitting by Ru (Fig. 1a). In the absence of the quinone, weaker signals are observed in the epr spectrum of **1**, the major line being centred at $g = 4.3$ (Fig. 1b). Analysis of the Grubbs' catalyst by X-ray fluorescence spectroscopy shows it to contain about 0.1% iron, consistent with this observation of an epr signal typical of rhombic high-spin Fe(III). Similarly, the addition of tetrachlorobenzoquinone to a solution of **1** gives an epr spectrum with strong new features, also indicative of electron transfer from the Grubbs' catalyst (Fig. 1c). The relatively long-lifetime of the radical anion, generated from tetrachlorobenzoquinone with **1**, is reflected in the intensity of the $g = 2$ signal in Fig. 1c compared to that in Fig. 1a.

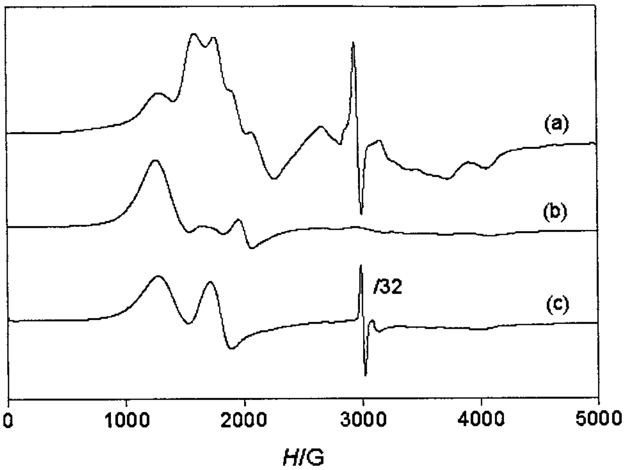
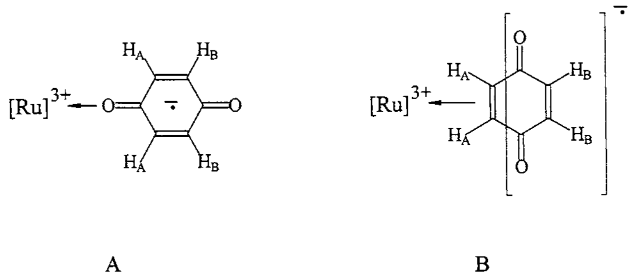


Fig. 1. Epr spectra recorded as frozen glass in CH_2Cl_2 at − 120°C of (a) *p*-benzoquinone with **1**; (b) **1** and (c) *p*-tetrachlorobenzoquinone with **1**. In spectrum c, the intense line at $g = 2$ is shown reduced by a factor of 32.



Scheme 1.

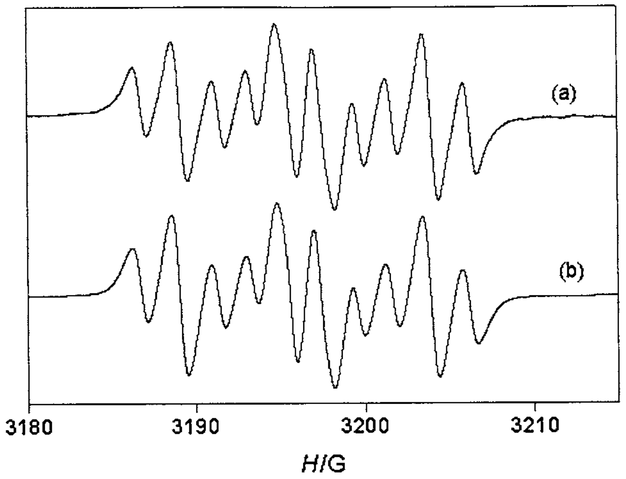


Fig. 2. (a) Epr spectrum recorded in CH_2Cl_2 at 20°C of *p*-benzoquinone with $RhCl(PPh_3)_3$; (b) simulation of this spectrum as a doublet ($A = 5.41$ G) of doublets ($A = 4.31$ G) of triplets ($A = 1.43$ G).

We do not know whether the quinone is bonded end-on or side-on to the Ru ion (Scheme 1), but clearly a donation of an electron pair to the metal is accompanied by strong and complete back donation of one electron to the organic moiety. However, infra red and laser Raman spectroscopic analyses of the [Ru]-quinone species suggest that the end-on formulation, **A** is correct, but this remains to be confirmed [4].

We also note that whereas radical anion formation is observed with benzoquinone and its halogen-substituted derivatives, addition of a solution of **1** to a range of alkyl-substituted benzoquinones fails to generate epr activity. Evidently electron-donating substituents raise the reduction potential of these latter acceptors so as to artmake electron transfer unfavourable.

Analogous strong epr signals have also been observed when methylene chloride solutions of the quinones are added to $RhCl(PPh_3)_3$ (Wilkinson's catalyst), $RuCl_2(PPh_3)_3$, and $CoBr_2(PPh_3)_2$. The spectrum of the complex of *p*-benzoquinone with $RhCl(PPh_3)_3$ is shown in Fig. 2; that for $CoBr_2(PPh_3)_2$ with the same quinone is very similar but much weaker and develops more slowly.

Simulation of the spectrum of *p*-benzoquinone with $RhCl(PPh_3)_3$ shows it to be a doublet of doublets of triplets ($A_1 = 5.41$ G, $A_2 = 4.31$ G, $A_3 = 1.43$ G) with the lines of the central region overlapping. No further hyperfine splitting is resolved at lower modulation amplitude (0.1 G). Although the spectrum has not been fully assigned, the dominant doublet splittings demand inequivalence of two spin-1/2 nuclei, probably the quinone protons, arising from lack of symmetry in the electron transfer adduct, although strong coupling to the phosphine groups of the rhodium complex cannot be ruled out. The behaviour of $RuCl_2(PPh_3)_3$ with *p*-benzoquinone clearly resembles that of **1**, with the immediate development of intense spectra showing very similar hyperfine splitting.

We have also found that when *p*-benzoquinone or norbornadiene is added in carbon tetrachloride to **1**, radical anions are not observed even though the diene again polymerises rapidly. It may be that this solvent quenches the free radicals as **1** has been found recently

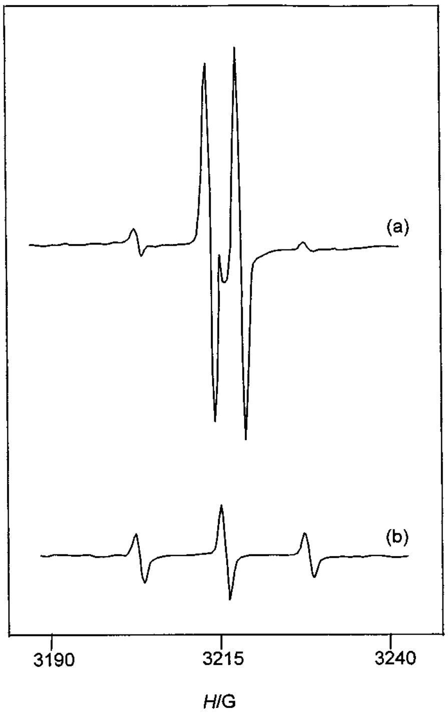


Fig. 3. Epr spectra recorded in CH_2Cl_2 at 20°C of benzonorbornadiene with $RuCl_2(PCy_3)_2(CHPh)$; (a) initial scan, after 5 min; (b) final scan, after 90 min; $g = 2.0046$, A(triplet) = 12.0 G; A(doublet) = 4.0 G.

to be an excellent catalyst for the Kharasch (free radical) addition of $CHCl_3$ across the double bonds in a variety of olefins [5].

The most surprising result however is that using **1**, strong epr signals are also obtained during the ring-opening metathesis polymerisation (ROMP) of norbornadiene, 5-methylenenorbornene and benzonorbornadiene[1]. The common feature for all these spectra is the appearance of a 1:2:1 long-lasting, sharp triplet as shown in Fig. 3b for benzonorbornadiene. This triplet is also observed but is much weaker using norbornene, cyclopentene and several other monoenes. An intense symmetrically positioned doublet initially appears in the case of benzonorbornadiene, Fig. 3a, which disappears quite suddenly, but reappears when fresh monomer is mixed into the solution. Obviously the doublet is associated with the polymerisation process as it disappears once the monomer has been consumed as ring-opened polymer. In an experiment where neat norbornadiene was added to an epr tube already containing a few drops of the methylene chloride solution of **1** (1×10^{-2} M), immediate very fast reaction occurred with almost completely colourless polymer forming from the norbornadiene above the coloured solution. Epr analysis of the solution at the bottom of the epr tube revealed the usual strong 1:2:1 triplet, but the polymer itself lying above this solution showed a much weaker, more transient well-resolved 1:3:3:1 quartet with each line further resolved as a 1:2:1 triplet ($g \approx 1.99$; A(quartet) = 11.0 G; A(triplet) = 1.5 G). Quite clearly free radical activity is propagating away from the Ru complex into the polymer itself and this may also be the source of the appearance and then sudden disappearance of the doublet observed during reaction of benzonorbornadiene (Fig. 3). Such free radical activity could be responsible for secondary reactions which often cause cross-linking, particularly following the ROMP of diene monomers when using Ru-based catalysts. Secondary metathesis is often postulated as the cause of these effects.

The free radical properties associated with **1** may also be involved in initiation because in separate experiments we have found that norbornadiene initiates ROMP about ten times more efficiently than norbornene; the monoene and diene however copolymerise at equal rates [6]. About the same ratio of the intensities of the epr signals due to diene and monoene is also obtained. This suggests that norbornadiene, in very small relative quantities, may be a very useful additive to ADMET systems involving **1** where it may enhance initiation and thus metathesis rates. We have also observed that addition of *p*-benzoquinone, even up to a 50-fold molar ratio with respect to **1** in methylene chloride, enhances the intrinsic reactivity of the metallacarbene propagating species, as shown by the significant increase in the incorporation of homodyads from cyclopentene into copolymers with norbornene at low conversion [6]. When hydrogen-bonding phenols and strongly acidic alcohols are added to **1**, similar effects on the copolymerisation are also noted [7] and attributed to a reduction in electron density at the Ru ion brought about by hydrogen bonding to the chloride ligands. The formation of radical anions by *p*-benzoquinone should also reduce the electron density at the central Ru ion in the propagating species. In addition, Grubbs et al. [1a,2a] have reported that beneficial effects on the rate of metathesis are achieved by adding Brönsted acids or by incorporating halogen bridges to relay charge to a second metal ion via binuclear complexes. However, our work now emphasises a third possibility of optimising catalytic activity through addition of Michael acceptors and even dienes.

Infra red and laser Raman spectra indicate that phenols mixed with **1** hydrogen bond via the chloride ligands. In accord with this, we have observed that on adding phenols to solutions of **1** with *p*-benzoquinone in methylene chloride, the intensities of the epr signals remain about the same, but the coupling constants for the manifold of lines are substantially changed.

Another very recent report [8] shows that **1** is also very efficient in the promotion of controlled free radical polymerisation of vinyl monomers such as methyl

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[1] Experimental details and procedures are given in [3].

methacrylate. We have also found that **1** is a very good catalyst for the polymerisation of α-methylstyrene in methylene chloride at room temperature, with this system also showing weak epr signals due to organic radicals.

3. Experimental

Solutions of metal complex (2×10^{-3} M) and acceptor (2×10^{-2} M) for the spectra of radicals were prepared in dried, helium-degassed before mixing equal volumes (0.25 ml) of these two solutions to give concentrations of half these values. Solutions for the wider scan frozen glass spectra were prepared similarly but at equimolar concentrations of 10^{-2} M after mixing. The spectra of radical anions were recorded at a modulation amplitude of 0.1 and 1 G and microwave power of 1 mW, which was confirmed to be below saturation level for the radical anions. For the frozen glasses, a modulation amplitude of 20 G and microwave power of 5 mW were used. X-band spectra were recorded on a Varian E109 spectrometer operating at 9 GHz and using a Hewlett Packard 5324A frequency counter. Field calibration was made with dpph. Spectral simulation was made with the program WINSIM.

4. Conclusions

This preliminary report draws attention to an exciting new area of radical anion formation and reactions using a variety of Michael acceptors and basic organometallic complexes including the Grubbs' catalyst and the Wilkinson's catalyst. There are also strong indications that the presence of Michael acceptors can moderate and promote ROMP using **1**. However most of the epr signals remain to be assigned fully and the structures of these novel charge-transfer complexes elucidated completely. Of particular interest for the metathesis field is the source of the long-lived triplet (Fig. 3b) arising from interaction of **1** with many dienes and monoenes. We are currently carrying out experiments with labelled quinones and with ENDOR spectroscopy on several of these systems, which will enable us to unequivocally assign the spectra.

References

[1] (a) E.L. Dias, R.H. Grubbs, Organometallics 17 (1998) 2758. (b) R.H. Grubbs, S.J. Miller, G.C. Fu, Acc. Chem. Res. 28 (1995) 446.

[2] (a) E.L. Dias, S.T. Nguyen, R.H. Grubbs, J. Am. Chem. Soc. 119 (1997) 3887. (b) M. Ulman, R.H. Grubbs, J. Org. Chem. 64 (1999) 7202.

[3] V. Amir-Ebrahimi, A.J. Beaumont, J.G. Hamilton, C.J. Harding, J. Nelson, D. Rooney, J.J. Rooney, J.M. Thompson, J. Chem. Soc. Chem. Commun. (1999) 1621.

[4] D. Rooney, J.J. Rooney (unpublished results).

[5] J.A. Tallarico, L.M. Malnick, M.L. Snapper, J. Org. Chem. 64 (1999) 344.

[6] V. Amir-Ebrahimi, D.G. Corry, J.G. Hamilton, J.J. Rooney, J.M. Thompson, Macromolecules 33 (2000) 717.

[7] B. Al Samak, V. Amir-Ebrahimi, D.G. Corry, J.G. Hamilton, S. Rigby. J.J. Rooney, J.M. Thompson, J. Mol. Catal. (2000) in press.

[8] F. Simal, A. Demonceau, A. Noels, Angew. Chem. Int. Ed. Engl. 38 (1999) 538.