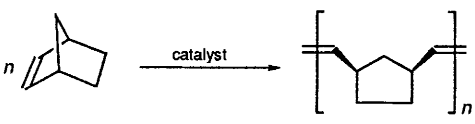
$[Mo_2(MeCN)_8][BF_4]_4$ Supported on Silica: an Efficient Heterogeneous Catalyst for the Ring-opening Metathesis Polymerization of Norbornene

Malachy McCann, Eoghan Mac Giolla Coda and Kenneth Maddock
Department of Chemistry, St. Patrick's College, Maynooth, Ireland

The dimolybdenum(II,II) complex salts $[Mo_2(MeCN)_8][BF_4]_4$ and $[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2$ have been supported on silica to give materials represented as $[Mo_2(MeCN)_8][BF_4]_4\text{–}SiO_2$ and $[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2\text{–}SiO_2$, respectively. Unsupported $[Mo_2(MeCN)_8][BF_4]_4$, $[Mo_2(MeCN)_8][BF_4]_4\text{–}SiO_2$, unsupported $[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2$ and $[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2\text{–}SiO_2$ were each tested as heterogeneous catalysts for the ring-opening metathesis polymerization of norbornene (bicyclo[2.2.1]hept-2-ene). In the absence of $AlEtCl_2$ cocatalyst $[Mo_2(MeCN)_8][BF_4]_4\text{–}SiO_2$ was the only species to polymerize norbornene, and at 90 °C and a reaction time of 48 h the polymerization was essentially quantitative. Species $[Mo_2(MeCN)_8][BF_4]_4$, $[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2$ and $[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2\text{–}SiO_2$ were found to be completely inactive without $AlEtCl_2$, even at elevated temperatures. In the presence of $AlEtCl_2$ cocatalyst $[Mo_2(MeCN)_8][BF_4]_4\text{–}SiO_2$ was the only material which failed to polymerize norbornene at room temperature.

The development of new and efficient homogeneous and heterogeneous catalysts for the ring-opening metathesis polymerization of norbornene-type monomers has attracted widespread interest over the past four decades.[1] In our laboratory we have been particularly interested in the synthesis and catalytic testing of bimetallic complexes containing multiple metal–metal bonds. The neutral and tetraanionic dimolybdenum(II,II) complexes $[Mo_2(\mu\text{-}O_2CMe)_4]$ and $K_4[Mo_2Cl_8]$ (Mo–Mo bond order = 4) have been shown[2] to polymerize 1-methylnorbornene (1-methylbicyclo[2.2.1]hept-2-ene) at 20 °C in the presence of added $AlEtCl_2$ cocatalyst. In addition, $[Mo_2(\mu\text{-}O_2CCF_3)_4]$ and the neutral diruthenium(II,III) complex $[Ru_2(\mu\text{-}O_2CMe)_4Cl]$ (Ru–Ru bond order = 2.5) polymerize the same monomer even in the absence of cocatalyst.[2] For the dimolybdenum(II,II) catalysts requiring the assistance of $AlEtCl_2$ cocatalyst it may be that the 'active' catalyst is a mixed Mo/Al species. For example, it is known that $[Mo_2(\mu\text{-}O_2CMe)_4]$ reacts with aluminium isopropoxide to give the *trans* diacetate $[Mo_2(\mu\text{-}O_2CMe)_2\{\mu\text{-}Al[OC(H)Me_2]_4\}_2]$.[3] Furthermore, Diefenbach[4] prepared and characterized Mo/Al complexes of the type $[Mo_2(O_2CR)_2\{Al(OC_6H_4Cl\text{-}p)_4\}_2]$ (R = Me, Bu^t or CF_3) and showed that they catalysed alkyne metathesis reactions.



The first studies using dimolybdenum(II,II) tetracarboxylates as heterogeneous catalysts were carried out by Smith *et al.*[5] in 1974. These workers used a dry-mix impregnation of $[Mo_2(\mu\text{-}O_2CR)_4]$ (R = Me or CF_3) on silica and alumina, and after activation to 300 °C the supported complexes showed high catalytic activity for the disproportionation of propene. From ESR studies of the $[Mo_2(\mu\text{-}O_2CMe)_4]\text{–}SiO_2$ system Howe[6] showed that during the thermal activation process oxidation of the molybdenum occurred ($Mo^{2+} \longrightarrow Mo^{3+} \longrightarrow Mo^{5+}$) and that a Mo^{5+} species was the active catalyst. Using a combination of ESR and extended X-ray absorption fine structure (EXAFS) spectroscopy Ichikawa and co-workers[7] recently reinvestigated this $[Mo_2(\mu\text{-}O_2CMe)_4]\text{–}SiO_2$–propene system. They found that a SiO_2-grafted $Mo_2{}^{5+}$ dinuclear species (Mo–Mo bond order = 3.5) is formed by thermal activation of $[Mo_2(\mu\text{-}O_2CMe)_4]\text{–}SiO_2$ at below 350 °C, and that it is this $Mo_2{}^{5+}$ moiety that is specifically active for propene metathesis. Furthermore, they also demonstrated that at an activation temperature of 450 °C the activity of the catalyst for propene metathesis markedly decreased. In addition, the EXAFS data showed that the catalyst activated at 450 °C had r(Mo–Mo) = 2.80 Å which indicated cleavage of the Mo–Mo multiple bond.

Recently, we have used the dianionic dimolybdenum(II,II) salt $[NEt_4]_2[Mo_2(\mu\text{-}O_2CMe)_2Br_4]$ and the dicationic dimolybdenum(II,II) salts $[Mo_2(\mu\text{-}O_2CR)_2(MeCN)_n][BF_4]_2$ (R = Me, n = 6; R = $CH_2{=}CMe_2$, n = 4) to catalyse the room temperature polymerization of norbornene (bicyclo[2.2.1]hept-2-ene) in the presence of $AlEtCl_2$.[8] It is thought that the lability of the MeCN ligands in the latter salts[9,10] is a contributory factor in the polymerization process. The synthesis of the air-sensitive octakis(acetonitrile)dimolybdenum(II,II) complexes $[Mo_2(MeCN)_8][CF_3SO_3]_4$[11] and $[Mo_2(MeCN)_8][BF_4]_4\cdot 2MeCN$[12] (containing only labile MeCN ligands) fuelled speculation that such complexes may have potential catalytic activity.[12] Herein we report on the use of $[Mo_2(MeCN)_8][BF_4]_4$ as a catalyst for the ring-opening metathesis polymerization of norbornene. In addition, $[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2$ and $[Mo_2(MeCN)_8][BF_4]_4$ have each been anchored on SiO_2 and tested as heterogeneous catalysts for the same reaction.

Experimental

The synthesis and reactions of the catalysts were carried out under N_2, and dry solvents were used throughout. Ace pressure tubes, purchased from Aldrich, were used for polymerization reactions conducted in the absence of cocatalyst. Ethylaluminium dichloride (25% by weight, 1.8 mol dm^{-3}) solution in toluene was obtained from Aldrich, and $[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2$ was prepared by the literature method.[10] The ^{13}C NMR spectra of the polymers, as solutions in $CDCl_3$, were run on a Bruker AC 80 spectrometer. The elemental analysis of $[Mo_2(MeCN)_8][BF_4]_4$ was carried out by the Microanalytical Laboratory, University College Cork, Ireland.

Preparation of $[Mo_2(MeCN)_8][BF_4]_4$.—A high-yield synthesis of $[Mo_2(MeCN)_8][BF_4]_4$ was accomplished using a method that had major advantages over the literature procedure used for the preparation of $[Mo_2(MeCN)_8][BF_4]_4 \cdot 2MeCN$.[12] Instead of requiring triethyloxonium tetrafluoroborate and a reflux period of 10 d the present method employs tetrafluoroboric acid–diethyl ether and a reaction time of 1 h at room temperature. In addition, the new method gives an increased yield of product. Thus to a suspension of $[Mo_2(\mu\text{-}O_2CMe)_4]$ (0.9 g, 2.1 mmol) in MeCN (80 cm^3) was added an 85% ether solution of $HBF_4 \cdot Et_2O$ (8 cm^3, 55 mmol). The mixture rapidly changed from red to dark blue. After stirring for 1 h the blue product was filtered off, washed with CH_2Cl_2 and then dried *in vacuo*. Yield 1.17 g (80%) (Found: C, 21.8; H, 3.0; N, 12.4. Calc.: C, 22.1; H, 2.8; N, 12.9%).

Supporting $[Mo_2(MeCN)_8][BF_4]_4$ *and* $[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2$ *on Silica*.—Silica (3 g) was activated by heating at 140 °C for 16 h and then allowed to cool to room temperature. Under an atmosphere of N_2 the dimolybdenum(II,II) complex (0.3 g) was dissolved in MeCN (40 cm^3) and added to the silica. The resulting slurry was stirred for 170–240 h under N_2. Upon treating $[Mo_2(MeCN)_8][BF_4]_4$ with the silica the mixture slowly changed from deep blue to purple. The purple $[Mo_2(MeCN)_8][BF_4]_4\text{–}SiO_2$ powder was filtered off, washed with MeCN (50 cm^3) and then dried at room temperature *in vacuo*. When $[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2$ was treated with the silica the mixture gradually turned from red to light brown. The light brown $[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2\text{–}SiO_2$ powder was filtered off, washed with MeCN (50 cm^3) and then dried at room temperature *in vacuo*. It should be noted that the reaction filtrates from each of the above reactions with silica were coloured, suggesting that a loading of $< 9\%$ (by weight) of the molybdenum complexes was obtained.

Polymerization Reactions.—(a) *Without added cocatalyst*. These reactions were carried out in a glass pressure tube and under N_2. To a sample of unsupported catalyst (0.1 g) or supported catalyst (1.0 g) was added a solution of norbornene (0.5 g, 5.3 mmol) in chlorobenzene (5 cm^3). The resulting suspension was then stirred at a specified temperature for a given period of time. As polymerization proceeded the viscosity of the liquid phase increased noticeably. Ethanol (10 cm^3) was then added to induce polymer precipitation, and the combined solids (polynorbornene plus catalyst) were filtered off. Chloroform (40 cm^3) was added to dissolve the polymer and this was separated from the solid catalyst by decantation. The catalyst was washed with further portions of chloroform (3 × 3 cm^3). The combined chloroform extracts were added to ethanol (200 cm^3) containing concentrated HCl (1 cm^3). The precipitated white polynorbornene was filtered off, washed with ethanol, and then dried *in vacuo*. In reactions where chloroform-insoluble polynorbornene formed along with chloroform-soluble polynorbornene these polymers were readily separated from each other by the addition of chloroform following the initial precipitation of the polymer mixture with ethanol.

(b) *With added cocatalyst*. These reactions were carried out under N_2. Ethylaluminium dichloride solution (0.3 cm^3, 0.54 mmol) was added directly to the unsupported catalyst (0.1 g) or the supported catalyst (1.0 g). In each case the catalyst turned black, and after a contact time of 5 min a solution of nobornene (0.5 g, 5.3 mmol) in chlorobenzene (5 cm^3) was added. The mixture was stirred for 0.5 h, and then ethanol (10 cm^3) was added to precipitate the polymer. The polynorbornene was recovered as outlined above.

Results and Discussion

The four catalysts used in this study were unsupported $[Mo_2(MeCN)_8][BF_4]_4$, $[Mo_2(MeCN)_8][BF_4]_4\text{–}SiO_2$, unsupported $[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2$ and $[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2\text{–}SiO_2$. The binding of the Mo–Mo bonded complexes $[Mo_2(MeCN)_8][BF_4]_4$ and $[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2$ to SiO_2 is thought to occur at the surface OH groups upon removal of labile MeCN ligands from the complexes (Scheme 1). Although we do not have any direct physical evidence as to the exact structure of the silica-bound molybdenum complexes it is possible that either the Mo–Mo bond is retained on the silica surface {as observed for $[Mo_2(\mu\text{-}O_2CMe)_4]\text{–}SiO_2$[7]} or that it ruptures to give mononuclear species {as reported for $[Mo_2(\eta^3\text{-}C_3H_5)_4]\text{–}SiO_2$[13]}.

In the absence of added $AlEtCl_2$ cocatalyst $[Mo_2(MeCN)_8][BF_4]_4\text{–}SiO_2$ was the only species to polymerize norbornene. Species $[Mo_2(MeCN)_8][BF_4]_4$, $[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2$ and $[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2\text{–}SiO_2$ were found to be completely inactive without $AlEtCl_2$, even at elevated temperatures. In contrast, in the presence of $AlEtCl_2$ cocatalyst $[Mo_2(MeCN)_8][BF_4]_4\text{–}SiO_2$ was the only material which failed to polymerize norbornene at room temperature. Under these conditions $[Mo_2(MeCN)_8][BF_4]_4$ and $[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2$ produced polynorbornene in moderate yield, whilst the $[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2\text{–}SiO_2$ catalyst gave a low yield of polymer (Table 1). In those cases where polymer formation did occur in the presence of cocatalyst the polymerization reaction was instantaneous.

The non-cocatalysed polymerization of norbornene using $[Mo_2(MeCN)_8][BF_4]_4\text{–}SiO_2$ appeared to be the most promising and was therefore studied in detail. The yield of chloroform-soluble, ring-opened polynorbornene as a function of reaction temperature using this catalyst is summarized in Table 2. At room temperature the yield of polymer was extremely small, and this increased significantly as the reaction temperature was increased. Although the yield of soluble polymer rose to 48% upon raising the reaction temperature to 120 °C a large amount (30–50%) of chloroform-insoluble polynorbornene was also recovered. This insoluble polymer is thought to arise from either the addition polymerization of norbornene or by the internal cross-linking of the ring-opened polymer. At 90 °C the yield of chloroform-soluble polynorbornene was 32% with no insoluble polymer formation.

The data in Table 3 show the effect of reaction time on the $[Mo_2(MeCN)_8][BF_4]_4\text{–}SiO_2$ catalysed polymerization at

Table 1 Room temperature polymerization of norbornene in the presence of added $AlEtCl_2$ cocatalyst[a]

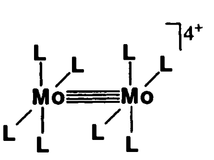
Catalyst	Polymer yield (%)[b]
$[Mo_2(MeCN)_8][BF_4]_4$	15
$[Mo_2(MeCN)_8][BF_4]_4\text{–}SiO_2$	0
$[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2$	17
$[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2\text{–}SiO_2$	3

[a] Solvent = chlorobenzene (5 cm^3); mass of norbornene = 0.5 g; mass of unsupported catalyst = 0.1 g; mass of supported catalyst = 1.0 g. [b] Chloroform-soluble polymer.

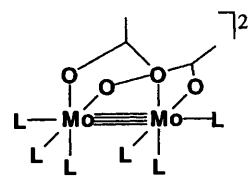
Table 2 Yield of polynorbornene as a function of reaction temperature using $[Mo_2(MeCN)_8][BF_4]_4\text{–}SiO_2$[a]

T/°C	Polymer yield (%)[b]
20[c]	1
45	4
60	8
90	32
120	48[d]

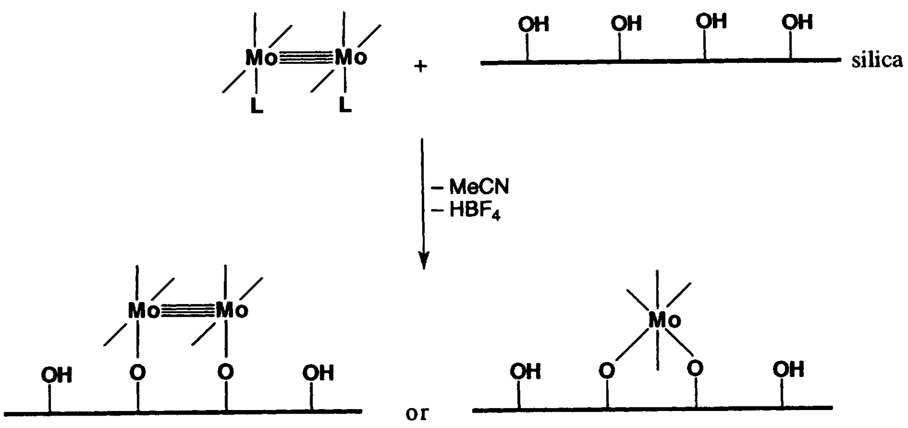
[a] Solvent = chlorobenzene (5 cm^3); mass of norbornene = 0.5 g; mass of $[Mo_2(MeCN)_8][BF_4]_4\text{–}SiO_2$ = 1.0 g; reaction time = 16 h. [b] Chloroform-soluble polymer. [c] Reaction time = 170 h. [d] A large amount (30–50%) of chloroform-insoluble polymer also formed.



$[Mo_2(MeCN)_8]^{4+}$



$[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_8]^{2+}$



Scheme 1 L = MeCN

Table 3 Effect of reaction time on the $[Mo_2(MeCN)_8][BF_4]_4$–SiO_2 catalysed polymerization of norbornene[a]

T/°C	Reaction time/h	Polymer yield (%)[b]
90	2	3
90	16	32
90	48	97
120	2	5[c]
120	16	48[c]

[a] Solvent = chlorobenzene (5 cm^3); mass of norbornene = 0.5 g; mass of $[Mo_2(MeCN)_8][BF_4]_4$–SiO_2 = 1.0 g. [b] Chloroform-soluble polymer. [c] A large amount (30–50%) of chloroform-insoluble polymer also formed.

Table 4 Effect of $[Mo_2(MeCN)_8][BF_4]_4$–SiO_2 : monomer mass ratio on the yield of polynorbornene[a]

Mass of catalyst/g	Polymer yield (%)[b]
0.1	7
0.25	15
0.5	33
1.0	97

[a] Reaction temperature = 90 °C; reaction time = 48 h; solvent = chlorobenzene (5 cm^3); mass of norbornene = 0.5 g. [b] Chloroform-soluble polymer.

Table 5 Reuse of the $[Mo_2(MeCN)_8][BF_4]_4$–SiO_2 catalyst[a]

Monomer batch no.	Polymer yield (g per g of catalyst)[b]
1	0.49
2	0.32
3	0.14
4	0.03

[a] Reaction temperature = 90 °C; reaction time = 48 h; solvent = chlorobenzene (5 cm^3); mass of norbornene = 0.5 g; original mass of $[Mo_2(MeCN)_8][BF_4]_4$–SiO_2 = 1.0 g. [b] Chloroform-soluble polymer.

reaction temperatures of 90 and 120 °C. At 90 °C and a reaction time of 48 h the yield of soluble polymer was essentially quantitative. Although there was a significant increase in the yield of soluble polymer formation on increasing the reaction time at 120 °C there was still a large amount of insoluble polynorbornene formed. To optimize further the polymerization reaction using $[Mo_2(MeCN)_8][BF_4]_4$–SiO_2 the effect of catalyst : monomer mass ratio was examined at a reaction temperature of 90 °C and a reaction time of 48 h (Table 4). As expected, an approximately linear relationship was found between the mass of catalyst used and the yield of polynorbornene.

The ability of a single 1 g sample of the $[Mo_2(MeCN)_8][BF_4]_4$–SiO_2 catalyst to polymerize more than one 0.5 g batch of norbornene was also investigated. As the amount of catalyst available for reuse decreased after each catalytic run (due to handling losses) the yield of polymer was expressed in terms of grams of polymer obtained per gram of catalyst used. The results displayed in Table 5 reveal that the catalyst deactivates steadily after each batch of fresh monomer, and that after polymerizing the third 0.5 g batch of norbornene the catalyst becomes essentially inactive.

The shelf-life of the $[Mo_2(MeCN)_8][BF_4]_4$–SiO_2 catalyst was also studied. Under the same experimental conditions (90 °C; 16 h) a freshly prepared sample of the catalyst polymerized approximately seven times as much norbornene as did a catalyst sample which was 4 weeks old. The aged samples of catalyst had been stored under N_2 at 5 °C, and had been part of the same preparations from which the fresh catalyst samples were taken.

Finally, using ^{13}C NMR spectroscopy the *cis* content (σ_c) of the soluble unsaturated polynorbornene, obtained using $[Mo_2(MeCN)_8][BF_4]_4$–SiO_2 (90 °C), was found to be 0.72. The same value of σ_c was obtained for the soluble polymer formed at 120 °C. For $[Mo_2(\mu\text{-}O_2CMe)_4]$, $[Mo_2(\mu\text{-}O_2CCF_3)_4]$ and $K_4[Mo_2Cl_8]$ the values of σ_c for the unsaturated poly-1-methylnorbornenes were 0.47, 0.41 and 0.46, respectively.[2] It has been suggested[14] that if the catalytically active metal centre has a high co-ordination number, and thus providing a more crowded environment for the approach of monomer, the formation of *cis* double bonds is favoured. It is envisaged that the anchoring of $[Mo_2(MeCN)_8][BF_4]_4$ onto the silica surface may indeed create a lot of steric congestion about the molybdenum atoms and thus induce the formation of more *cis* junctions during the polymerization reaction. This conclusion is substantiated by the fact that unsupported $[Mo_2(MeCN)_8]$-$[BF_4]_4$ in the presence of $AlEtCl_2$ produces polynorbornene with $\sigma_c = 0.36$.

References

1 For example, A. W. Anderson and N. G. Merckling, *US Pat.*, 2 721 189, 1955 (to DuPont); N. Calderon, E. A. Ofstead and W. A. Judy, *J. Polym. Sci., Part A*, 1967, **5**, 2209; R. J. Minchak, *US Pat.*, 3 853 830, 1974 (to B. F. Goodrich); K. J. Ivin, *Olefin Metathesis*, Academic Press, London, 1983, ch. 13; L. R. Gilliom and R. H. Grubbs, *J. Am. Chem. Soc.*, 1986, **108**, 733; C. J. Schaverien, J. C. Dewan and R. R. Schrock, *J. Am. Chem. Soc.*, 1986, **108**, 2771; J. G. Hamilton, O. N. D. Mackey, J. J. Rooney and D. G. Gilheany, *J. Chem. Soc., Chem. Commun.*, 1990, 1600; W. A. Herrmann, W. Wagner, U. N. Flessner, U. Volkhardt and H. Komber, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1636; B. L. Goodall, W. J. Kroenke, R. J. Minchak and L. F. Rhodes, *J. Appl. Polym. Sci.*, 1993, **47**, 1993; M. McCann and D. McDonnell, *J. Chem. Soc., Chem. Commun.*, 1993, 1718.

2 J. G. Hamilton, K. J. Ivin, M. McCann and J. J. Rooney, *Makromol. Chem.*, 1985, **186**, 1477.

3 J. Lamotte, O. Oideberg, L. Dupont and P. Durbut, *Cryst. Struct. Commun.*, 1981, **10**, 59.

4 S. P. Diefenbach, *US Pat.*, 4 704 377, 1987.

5 J. Smith, W. Mowat, D. A. Whan and E. A. V. Ebsworth, *J. Chem. Soc., Dalton Trans.*, 1974, 1742.

6 R. F. Howe, *J. Chem. Soc., Faraday Trans. 1*, 1975, 1689.

7 Q. Zhuang, A. Fukuoka, T. Fujimoto, K. Tanaka and M. Ichikawa, *J. Chem. Soc., Chem. Commun.*, 1991, 745.

8 M. McCann and P. Guinan, *Polyhedron*, 1991, **10**, 2283.

9 W. Clegg, G. Pimblett and C. D. Garner, *Polyhedron*, 1986, **5**, 31; G. Pimblett, C. D. Garner and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 1986, 1257.

10 F. A. Cotton, A. H. Reid and W. Schwotzer, *Inorg. Chem.*, 1985, **24**, 3965.

11 J. M. Mayer and E. H. Abbott, *Inorg. Chem.*, 1983, **22**, 2774.

12 F. A. Cotton and K. J. Wiesinger, *Inorg. Chem.*, 1991, **30**, 871.

13 Y. Sato, Y. Iwasawa and H. Kuroda, *Chem. Lett.*, 1982, 1101.

14 K. J. Ivin, D. T. Laverty, J. H. O'Donnell, J. J. Rooney and C. D. Stewart, *Makromol. Chem.*, 1979, **180**, 1989.

Received 21*st December* 1993; *Paper* 3/07503F