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Dialkyl(2,2'-bipyridyl) dioxomolybdenum(VI) complexes: a new family of compounds for the ring-opening metathesis polymerization (ROMP) of norbornene

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Abstract

The 2,2'-bipyridyldioxomolybdenum(VI) complexes $[\text{Mo}(\text{bipy})\text{R}_2\text{O}_2]$ ($\text{R} = \text{Br}, \text{Me}, \text{Et}$), in combination with the Grignard reagent MeMgBr as cocatalyst, catalyse the ring-opening metathesis polymerization (ROMP) of norbornene at room temperature. The complex $[\text{Mo}(\text{bipy})\text{Me}_2\text{O}_2]$, when supported on Montmorillonite K10, catalyses the ROMP of norbornene in the absence of cocatalyst. The polymer produced by the $[\text{Mo}(\text{bipy})\text{Me}_2\text{O}_2]/\text{Montmorillonite K10}$ system has a significantly higher *cis* content and a more blocky distribution of *cis* and *trans* double bonds than the polymer produced by the unsupported catalyst/cocatalyst system.

Keywords: Metathesis; Polymerization; Ring-opening; Norbornene; Molybdenum; Supported reagent

1. Introduction

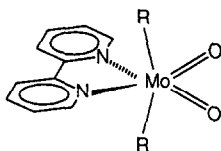
There is continued interest in the ring-opening polymerization (ROMP) of norbornene (bicyclo[2,2,1]hept-2-ene) due to the information which may be obtained, from the structure of the polymer, on the mechanism of the important alkene metathesis reaction [1]. Many catalyst systems for this reaction require the use of a reactive non-transition metal alkyl compound as a cocatalyst. However, such cocatalysts may be unnecessary if alkyl groups are present on the transition metal catalyst itself. The complex

methyltrioxorhenium(VII) has been reported to be an effective homogeneous catalyst for the ROMP of norbornene in the presence of EtAlCl_2 as cocatalyst. Furthermore, the same rhenium complex, when supported on alumina, functions as a heterogeneous catalyst for the metathesis of acyclic alkenes [2]. These latter reactions occur in the absence of a cocatalyst. It was therefore of interest to synthesise analogous organomolybdenum oxo complexes in order to attempt to carry out the ROMP of norbornene without the need for an added alkyl-containing cocatalyst.

Distorted octahedral complexes of the general formula $[\text{Mo}(\text{bipy})\text{R}_2\text{O}_2]$ (**1**), where $\text{R} = \text{Br}$ [3], Me [4] and Et [5], have been reported in the

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literature, and it was decided to test this class of complex as ROMP catalysts for norbornene.



- 1 a; R=Br
 b; R=Me
 c; R=Et

2. Experimental

2.1. Instrumentation

^{13}C NMR spectra were recorded on a Bruker AC 80 spectrometer. Samples were dissolved in CDCl_3 and TMS was used as a standard.

Molecular weights were obtained by gel permeation chromatography. Samples were dissolved in chlorobenzene (15 mg in 2 cm^3) and filtered through a $0.45\ \mu\text{m}$ Teflon syringe filter prior to injection. Molecular weights are given relative to polystyrene.

2.2. Preparation of dialkyl(2,2'-bipyridyl)di-oxomolybdenum(VI) complexes

Complexes $[\text{Mo}(\text{bipy})\text{R}_2\text{O}_2]$ (**1a–c**) were synthesised by literature methods [3,5]. To prepare the supported catalysts $[\text{Mo}(\text{bipy})\text{Me}_2\text{O}_2]$ (0.1 g) was dissolved in dichloromethane (10 cm^3) and added to a stirred slurry of the support material (alumina, silica or Montmorillonite K10; 10 g, which had been pre-dried in a vacuum oven at 180°C for 7 h) in dichloromethane (50 cm^3) to give a loading of 0.03 mmol of complex per g of support material. The solvent was evaporated in vacuo and the supported material was stored under nitrogen.

2.3. Typical procedure for polymerization of norbornene by $[\text{Mo}(\text{bipy})\text{R}_2\text{O}_2]$ in the presence of Grignard reagent as cocatalyst

All manipulations were carried out in air. The pale yellow molybdenum complex (15 mg) was placed in a test tube and 2 drops of a solution of MeMgBr cocatalyst (3 mol dm^{-3} in Et_2O) was added by syringe. The molybdenum compound immediately changed colour from pale yellow to purple. After ca. 30 s a solution of norbornene (0.5 g) in dichloromethane (1 cm^3) was added. Polymerization was immediate and exothermic. Ethanol was added and the gel-like polymer was then removed from the tube. Most of the catalyst was undissolved in the reaction mixture and remained in the tube when the polymer was removed. The polymer was then shaken with chloroform (10 cm^3) for 2 h, the solution was separated from any chloroform-insoluble cross-linked polymer present and the soluble polynorbornene was re-precipitated by addition to a solution of ethanol (100 cm^3) acidified with concentrated hydrochloric acid (0.5 cm^3).

2.4. Typical procedure for the polymerization of norbornene by $[\text{Mo}(\text{bipy})\text{Me}_2\text{O}_2]$ supported on Montmorillonite K10

All manipulations were carried out in air. The supported catalyst (1 g) was placed in a screw topped tube and to this was added a solution of norbornene (0.5 g) in dichloromethane (1 cm^3). The tube was sealed and shaken vigorously at room temperature. After the reaction was deemed complete (no further increase in the viscosity of the solution, ca. 2 h) the reaction mixture was poured into chloroform (50 cm^3) and stirred for several hours. The solution was then filtered to remove the supported catalyst and evaporated in vacuo to a small volume (ca. 5 cm^3). The polymer was then re-precipitated from ethanol/HCl as outlined above.

3. Results and discussion

3.1. Polymerization of norbornene by [Mo(bipy)Br₂O₂] (**1a**), [Mo(bipy)Me₂O₂] (**1b**) and [Mo(bipy)Et₂O₂] (**1c**) in the presence of various cocatalysts

The complexes [Mo(bipy)Br₂O₂] (**1a**), [Mo(bipy)Me₂O₂] (**1b**) and [Mo(bipy)Et₂O₂] (**1c**), in the presence of the Grignard reagent MeMgBr as cocatalyst, all polymerized norbornene efficiently, producing polymer containing mainly chloroform-insoluble cross-linked material (Table 1). [Mo(bipy)Me₂O₂] (**1b**) was the most effective, giving an overall yield of 88% of polynorbornene of which 24% was soluble in chloroform. Surprisingly, when similar polymerization reactions were attempted with the commonly used metathesis cocatalyst EtAlCl₂, all three molybdenum compounds produced only a small trace of insoluble polymer. The dialkyl compounds [Mo(bipy)Me₂O₂] (**1b**) and [Mo(bipy)Et₂O₂] (**1c**) are known to be unstable in acidic conditions [4], so it is possible that the strong Lewis acid EtAlCl₂ causes decomposition of the catalysts before polymerization can occur. EtAlCl₂ on its own is known to catalyse the ROMP of norbornene to a very small extent [6], and it is likely that the trace of polymer produced in these reactions comes from EtAlCl₂ alone.

Table 1
Polymerization of norbornene by dialkyl(2,2'-bipyridyl)dioxomolybdenum(VI) complexes with various cocatalysts

Catalyst	Cocatalyst	Yield of soluble ^a polymer (%)	Yield of insoluble ^a polymer (%)
[Mo(bipy)Br ₂ O ₂] (1a)	MeMgBr	10	30
[Mo(bipy)Br ₂ O ₂] (1a)	EtAlCl ₂	0	trace
[Mo(bipy)Me ₂ O ₂] (1b)	MeMgBr	24	64
[Mo(bipy)Me ₂ O ₂] (1b)	EtAlCl ₂	0	trace
[Mo(bipy)Me ₂ O ₂] (1b)	AlCl ₃	0	trace
[Mo(bipy)Me ₂ O ₂] (1b)	ZnCl ₂	0	0
[Mo(bipy)Me ₂ O ₂] (1b)	none	0	0
[Mo(bipy)Et ₂ O ₂] (1c)	MeMgBr	20	40
[Mo(bipy)Et ₂ O ₂] (1c)	EtAlCl ₂	0	trace
[Mo(bipy)Et ₂ O ₂] (1c)	none	0	0

^a In chloroform.

Polymerization reactions were also attempted with the molybdenum compounds **1b** and **1c** in the presence of the non-alkylated Lewis acids AlCl₃ and ZnCl₂ as cocatalysts. With AlCl₃ a small trace of insoluble polymer was formed, whereas with ZnCl₂ no polymerization was observed.

From the hydrocarbon products of thermolysis of [Mo(bipy)Et₂O₂] (**1c**) it has been suggested that metal carbenes may be involved in the thermal decomposition of these molybdenum alkyl compounds [5]. Therefore, polymerization of norbornene by **1b** and **1c** was attempted in the absence of cocatalyst. However, when the reaction mixture was warmed decomposition of the molybdenum compounds occurred and no polymerization was observed.

The chloroform-soluble polynorbornenes formed in reactions where MeMgBr was used as a cocatalyst were analysed by ¹³C NMR spectroscopy. The *cis* content of the polymers formed by the different catalysts was found to show little variation ($0.35 \leq \sigma_c \leq 0.40$), and all the polymers showed random distribution of *cis* and *trans* double bonds ($r_1 r_c = 1.05-1.10$).

3.2. Supported dimethyl(2,2'-bipyridyl)dioxomolybdenum(VI) catalysts

The results above demonstrate that bipyridyl-dioxomolybdenum(VI) complexes, especially [Mo(bipy)Me₂O₂] (**1b**), are highly efficient catalysts for the ROMP of norbornene in the presence of Grignard reagent as cocatalyst. The organometallic oxo complex [MeReO₃], when supported on alumina, was reported to catalyse the metathesis of alkenes in the absence of cocatalyst [2]. Therefore, catalyst materials were prepared containing **1b** supported on alumina, silica and the clay mineral Montmorillonite K10. The catalysts were initially prepared to give a loading of 0.03 mmol per g of the support material. When polymerization of norbornene was attempted using the above supported materials, only the [Mo(bipy)Me₂O₂]/Montmorillonite K10 mixture showed any activity, giving

Table 2
Polymerization of norbornene by $[\text{Mo}(\text{bipy})\text{Me}_2\text{O}_2]$ supported on Montmorillonite K10

Catalyst loading (mmol per g)	Mass of supported catalyst (g) ^a	Polymer yield (%)
0.03	1	12
0.3	0.1	4
0.2	0.15	5
0.12	0.25	20

^a As the catalyst loading was increased the mass of catalyst used was reduced in order to keep the $[\text{Mo}]:[\text{norbornene}]$ ratio roughly constant (ca. 1:200).

a yield of 12% of chloroform-soluble polynorbornene after 2 h (Table 2). This result clearly shows that polymerization of norbornene by an oxomolybdenum complex is possible without the need for a reactive metal alkyl compound as a cocatalyst. Previous examples of molybdenum complexes which can catalyse the ROMP of norbornene in the absence of a cocatalyst include $[\text{Mo}(\mu\text{-O}_2\text{CCH}_3)_2\text{Br}_4]$ [7] and $[\text{Mo}_2(\text{CH}_3\text{CN})_8][\text{BF}_4]_4/\text{SiO}_2$ [8]. $[\text{Mo}(\text{bipy})\text{Me}_2\text{O}_2]$ (**1b**) only showed activity when supported on the strongly acidic clay mineral Montmorillonite K10, and not on silica or alumina. This behaviour is consistent with the idea that Lewis acidity is an important property of the cocatalyst in a metathesis catalyst system. ¹³C NMR analysis of the polymers produced in these systems showed a higher *cis* content ($\sigma_c = 0.60$) with a blocky distribution ($r_1 r_c = 3.7$) [1]. This contrasts with the microstructure of the polymer prepared using the unsupported $[\text{Mo}(\text{bipy})\text{Me}_2\text{O}_2]/\text{MeMgBr}$ catalyst/cocatalyst system. A high surface area material like Montmorillonite K10 (ca. 220–270 m² g⁻¹) may be able to accommodate a higher loading than the 0.03 mmol of $[\text{Mo}(\text{bipy})\text{Me}_2\text{O}_2]$ per g of the support material as used in the above experiment. Therefore, supported catalysts were prepared with the loading of $[\text{Mo}(\text{bipy})\text{Me}_2\text{O}_2]/\text{Montmorillonite K10}$ varying from 0.03–0.3 mmol per g, and the polymerization of norbornene by these catalysts was

carried out as before (Table 2). When the catalyst loading was increased to 0.2 mmol per g or above the yield of polymer produced decreased to only 4%. This effect could be due to overloading of the supported material, whereby too much of the molybdenum complex is present to be accommodated in a mono-layer coverage of the clay, and the material starts to behave simply as finely divided $[\text{Mo}(\text{bipy})\text{Me}_2\text{O}_2]$ powder. When the catalyst loading was 0.12 mmol per g a yield of 20% of polynorbornene was observed, and when the mass of this supported catalyst used in the reaction was increased from 0.25 g to 0.75 g the yield of polynorbornene was increased to 35%. The polymer produced in this reaction had a similar microstructure to that produced from the supported catalyst with a loading of 0.03 mmol per g, with $\sigma_c = 0.60$ and $r_1 r_c = 4.0$. The polymer had \overline{M}_w of 358000 and \overline{M}_n of 192000 (polydispersity 1.86).

These results demonstrate that molybdenum oxo compounds $[\text{Mo}(\text{bipy})\text{R}_2\text{O}_2]$ (**1a–c**) are efficient catalysts for the ROMP of norbornene in the presence of a Grignard reagent cocatalyst. When the molybdenum complex $[\text{Mo}(\text{bipy})\text{Me}_2\text{O}_2]$ (**1b**) was supported on Montmorillonite K10, a strongly acidic solid material, polymerization occurred without the need for a reactive non-transition metal alkyl compound as a cocatalyst. The polymer produced by this supported catalyst differed markedly from that produced by the unsupported system, having a significantly higher *cis* content (ca. 60%) and a blocky distribution of *cis* and *trans* double bonds. The polymer also had a high molecular weight but was freely soluble in chloroform, indicating a very low degree of cross-linking.

Acknowledgements

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