A comparative study of seven co-ordinate Mo(II) and W(II) catalysts in the ring opening polymerization of norbornene

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Abstract

The ring-opening polymerization of norbornene was investigated in refluxing benzene solution with $[MI_2(CO)_3(L)(L')]$ (M = Mo, W; L = L' = NCCH_3, PPh_3, AsPh_3; L = NCMe, L' = PPh_3, AsPh_3) as catalysts. Turnover numbers (TNs) after 20 min ranged from 40 to 380 with the highest value recorded for $[WI_2(CO)_3(NCMe)_2]$. Under similar conditions Grubbs' catalyst, $[RuCl_2(PCy_3)_2(CHPh)]$, was at least 1000-fold more active. A first order relationship was obtained between the initial polymerization rate and $[WI_2(CO)_3(NCMe)_2]$ concentration. The catalytic activity of $[WI_2(CO)_3(NCMe)_2]$ showed exponential decay with $t_{1/2} = 600$ s.
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1. Introduction

Bencze and Kraut-Vass in 1985 showed that the seven co-ordinate Group 6 Mo(II) and W(II) complexes $[MX_2(CO)_3L_2]$ (X = Cl, Br; L = AsPh_3, PPh_3) were able to initiate ring-opening metathesis polymerization (ROMP) reactions of norbornene and norbornadiene [1]. Grubbs and co-workers [2] and Grubbs et al. [3], and many subsequent research groups [4,5] have since developed and refined alkylideneruthenium(II) complexes as highly active and robust polymerization catalysts. Recently, Baker and co-workers reported some preliminary studies on polymerization of norbornadiene, styrene, and phenylacetylene [6] using $[WI_2(CO)_3(NCMe)_2]$ and related organophosphine derivatives, and have investigated the reactions

of a possible intermediate, $[WI_2(CO)_2(nbd)]$ [7]. Herein, we report a comparative study of the catalytic polymerization of norbornene by seven coordinate Mo(II) or W(II) diiodotricarbonyl complexes.

2. Experimental

2.1. General

The Mo(II) and W(II) complexes used as catalysts ($[MI_2(CO)_3(PPh_3)_2]$ [8], $[MI_2(CO)_3(AsPh_3)_2]$ [8], $[MI_2(CO)_3(NCMe)_2]$ [9,10], $[MI_2(CO)_3(NCMe)(PPh_3)]$ [11], and $[MI_2(CO)_3(NCMe)(AsPh_3)]$ [11] (M = Mo, W)) were prepared by literature methods, and their purities were checked by satisfactory elemental analyses and spectroscopic (^{1}H NMR and IR) examination. $[RuCl_2(PCy_3)_2(CHPh)]$ was available commercially and used as supplied. The C_6H_6 solvent was dried by refluxing over CaH_2, and was

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distilled immediately before use. All reactions were performed under a dry nitrogen atmosphere using standard Schlenk line apparatus and procedures.

2.2. Polymerization reactions of norbornene

(a) *Comparison of catalysts*: Norbornene (0.61 g/ 6.5 mmol) was dissolved in dry degassed benzene ($25\,cm^3$) to give a 0.26 M solution. This solution was then brought to reflux (353 K) and to this was added an appropriate amount of metal complex (6.25×10^{-6} mol, e.g. 3.8 mg for $[WI_2(CO)_3(NCMe)_2]$) to form a 2.5×10^{-4} M solution. The solution was allowed to react for 20 min and cold MeOH ($100\,cm^3$) was added to quench the reaction. The solid polymer was filtered from the solution and then dried in vacuo before being weighed, results are given in Table 1. The molar ratio of norbornene to catalyst was maintained at 1000:1.

(b) *Yield against [WI₂(CO)₃(NCMe)₂] concentration data for the norbornene polymerization reaction*: Norbornene (0.61 g/6.5 mmol) was dissolved in dry degassed benzene ($25\,cm^3$) to form a 0.24×10^{-4} M solution. This was then brought to reflux (353 K) and an appropriate amount of the complex $[WI_2(CO)_3(NCMe)_2]$ was added to give a series

Table 1
Yield and turnover number for Mo(II) and W(II) initiated polymerization of norbornene

Entry	Complex	Yield[a]	TN[b]
1	$[MoI_2(CO)_3(PPh_3)_2]$	6 (4–8); 0.04	60
2	$[MoI_2(CO)_3(AsPh_3)_2]$	18 (17–21); 0.11	180
3	$[MoI_2(CO)_3(NCMe)_2]$	21 (20–22); 0.12	210
4	$[MoI_2(CO)_3(NCMe)(PPh_3)]$	15 (13–17); 0.09	150
5	$[MoI_2(CO)_3(NCMe)(AsPh_3)]$	19 (18–20); 0.11	190
6	$[WI_2(CO)_3(PPh_3)_2]$	9 (6–12); 0.05	90
7	$[WI_2(CO)_3(AsPh_3)_2]$	23 (19–27); 0.14	230
8	$[WI_2(CO)_3(NCMe)_2]$	25 (12–38); 0.15	250
9	$[WI_2(CO)_3(NCMe)(PPh_3)]$	20 (17–23); 0.12	200
10	$[WI_2(CO)_3(NCMe)(AsPh_3)]$	30 (22–35); 0.18	300
11	$[RuCl_2(PCy_3)_2(CHPh)]$	100; 0.61[c]	1000

[a] Obtained after 20 min reaction (353 K) followed by quenching the reaction with MeOH and weighing the mass of dried polymer. Yields (%) quoted are average with ranges obtained in parentheses; followed by average polymer mass (g).

[b] Moles of polymer/moles of catalyst based upon average yield after 20 min.
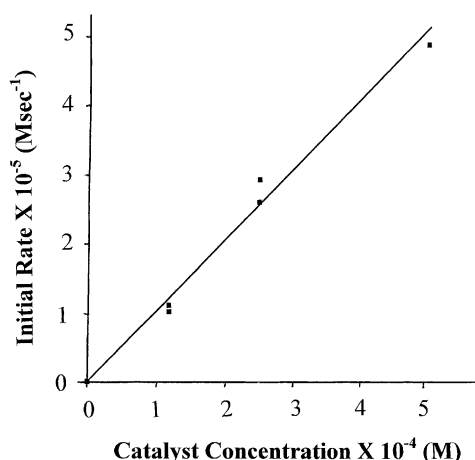
[c] Reaction complete in <1 s.

Fig. 1. Plot on initial rate of the $[WI_2(CO)_3(NCMe)_2]$ catalysed polymerization of norbornene in C_6H_6 solution at 353 K against catalyst concentration.

of 1.2×10^{-4}, 2.5×10^{-4} and 5.0×10^{-4} M solutions. After 20 min had elapsed the reaction mixture was quenched with cold MeOH. The solid polymer was filtered from the solutions and then dried in vacuo before being weighed, the results are plotted as shown in Fig. 1.

(c) *Yield against time data for [WI₂(CO)₃(NCMe)₂] catalysed norbornene polymerization reaction*: Norbornene (11.8 g/125 mmol) was dissolved in dry degassed benzene ($500\,cm^3$) to form a 0.26 M solution. This was then brought to reflux (353 K) and the complex $[WI_2(CO)_3(NCMe)_2]$ (0.08 g/0.125 mmol) was added to give a 2.5×10^{-4} M solution. After a given time period had elapsed a sample ($20\,cm^3$) was removed and quenched with cold MeOH. The amount of polymer in each aliquot was measured and data are recorded as shown in Fig. 2.

3. Results and discussion

The ring-opening polymerization of norbornene was investigated in refluxing benzene solution under an inert N_2 atmosphere with various seven co-ordinate Mo(II) and W(II) complexes as catalysts. ^{13}C NMR spectra ($CDCl_3$) of the norbornene polymers, showed four series of signals centered at δ +32, +38, +42 and +133 ppm consistent with the expected product,
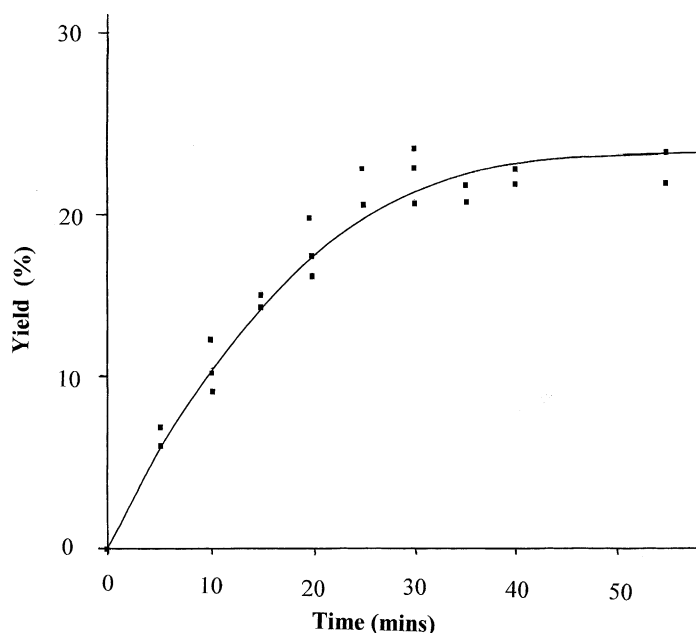
Fig. 2. Plot illustrating the time course of the reaction for the $[WI_2(CO)_3(NCMe)_2]$ catalysed polymerization of norbornene in C_6H_6 solution at 353 K. A maximal yield of 23% was obtained after ~40 min. The line as drawn is calculated from $t_{1/2} = 600\,s$.

poly(cyclopentylene vinylene). Spectra were visually similar to those described by Bencze and Kraut-Vass [1] indicating a slight excess of the *cis* configuration of the double bond. Average polymer molecular weights were not determined. We kept reaction conditions identical to those reported by Bencze and Kraut-Vass [1] in order to enable suitable comparisons to be made: Temperature $= 353\,K$, [complex] $= 0.25\,mM$, [norbornene] $= 0.26\,M$. The yields of polymer produced after 20 min, and turnover numbers (TNs) are given in Table 1. The reactions were generally repeated 3–6 times and ranges of yields (average in parentheses) were obtained for each complex. The variations in yields for each individual catalysts might be explained by errors associated with weighing of the small quantities (~5 mg) required and/or a possible sensitivity of the polymerization reaction to trace impurities in the sample since different 'batches' of the same analytically pure catalyst gave different results. Despite these inconsistencies in yield, a general picture does emerge with yields and TNs generally comparable with those obtained by Bencze and Kraut-Vass for related catalysts, and we also note that the W(II) complexes are more active than their Mo(II)

analogues. Bencze and Kraut-Vass also found that the dibromo complexes were less active than analogous dichloro complexes, and this would lead us to expect that the diiodo complexes should be comparatively poor catalysts. However, we have found that the diiodo complexes were considerably more active than the other halide derivatives; compare entry 1 with $[WX_2(CO)_3(PPh_3)_2]$ (X = Cl, 0.5%, 20 min; X = Br, 0%, 20 min), and entry 6 with $[WCl_2(CO)_3(PPh_3)_2]$ (4%, 23 min). The rate determining step in the reaction has been shown [12] to be dissociation of L followed by alkene co-ordination to the metal centre. Reaction mechanisms at metal centers are usually accelerated by bulky spectator ligands; the increased rate for the diiodo species is consistent with this. It would also be expected that complexes with labile ligands would show greater activity. We found that complexes with acetonitrile ligands were considerably more active than analogous complexes with organophosphine ligands and of comparable activity to complexes with organoarsine ligands; compare entries 1 (and 4) with 3; 6 (and 9) with 8; 8 with 7, and 3 with 2. This enhanced activity of complexes with NCMe ligands may be attributable to the increased

lability of the NCMe ligand over PPh_3 [13]. The Group 6 metal complex which produced the highest recorded yield was $[WI_2(CO)_3(NCMe)_2]$ (entry 8) although $[WI_2(CO)_3(NCMe)(AsPh_3)]$ (entry 10) gave consistently high yields.

Yield and TN data for Grubbs' catalyst, $[RuCl_2-(PCy_3)_2(CHPh)]$, is also included in Table 1 (entry 11). This enabled a realistic assessment of these Group 6 metal complexes against this 'benchmark' catalyst. The Group 6 metal complexes gave yields of $\sim 20\%$ ($t = 20\,min$), which would indicate conversion rates of $\sim 0.15\,TN\,s^{-1}$. By comparison, $[RuCl_2(PCy_3)_2(CHPh)]$, showed complete instantaneous conversion of norbornene to polymer with a conversion rate of $>1000\,TN\,s^{-1}$, calculated for $t < 1\,s$. Thus, the Group 6 metal complexes were less active catalysts by a least 3 (and probably 4 or more) orders of magnitude. In order to further understand this comparatively poor catalytic activity, one of the more active Group 6 metal catalysts, $[WI_2(CO)_3(NCMe)_2]$, was studied in more detail.

The initial reaction rate for the $[WI_2(CO)_3(NCMe)_2]$ catalysed polymerization of norbornene was estimated by quenching reactions 20 min after initiation of the reaction. A minimum monomer:catalyst ratio of 500:1 was used during these studies, and data were obtained in triplicate. These initial reaction rate data are plotted against catalyst concentration as shown in Fig. 1. Bencze and Kraut-Vass had previously reported a first order dependence for this type of data in their catalytic systems. This straight line plot as shown in Fig. 1 confirmed this first order dependence on catalyst (metal complex) concentration and, hence, a rate equation $W = k[cat]$ may be written, with k evaluated as $\sim 0.1\,s^{-1}$. This rate constant is comparable to that we calculate was observed by Bencze and Kraut-Vass of $0.024\,s^{-1}$ for $[WCl_2(CO)_3(AsPh_3)_2]$ ($W = 1.2 \times 10^{-4}\,M\,s^{-1}$ at $5 \times 10^{-3}\,M$ catalyst concentration).

The dependence of reaction yield against time for the $[WI_2(CO)_3(NCMe)_2]$ catalysed polymerization of norbornene was investigated next. A plot of reaction yield against time is as shown in Fig. 2, where it is clearly observed that the reaction effectively stops after $\sim 30\,min$. The maximal yield of $\sim 23\%$ was within the range observed for this complex in comparative studies (Table 1). Since the relationship between the rate of polymerization and catalyst concentration has
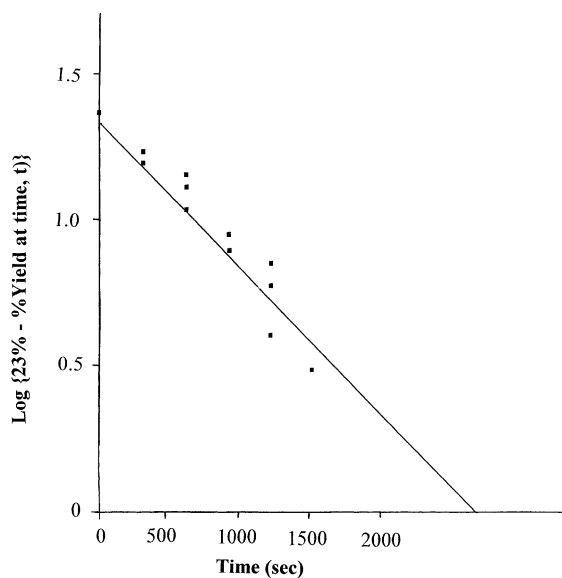

Fig. 3. First order lot of data as given in Fig. 2. The best straight line has a gradient of $5.0 \times 10^{-4}\,s^{-1}$ and, hence, a k of $1.15 \times 10^{-3}\,s^{-1}$.

been established as dependent on catalyst concentration the plot clearly shows that the catalyst is being poisoned or deactivated in some manner. The data in Fig. 2 were fitted by a first order log plot (Fig. 3) which gave a rate constant of deactivation of $1.15 \times 10^{-3}\,s^{-1}$. From this we calculated the half-life ($t_{1/2}$) of the catalytic complex to be $600\,s$. The curve drawn as shown in Fig. 2 is the theoretical line based upon this $t_{1/2}$ value. We have not been able to identify the reason why our complexes become deactivated and we can only assume it is due to their inherent thermal and moisture sensitivity. However, Bencze and Kraut-Vass reported that these type of catalysts with phosphorus and arsenic donor ligands were highly tolerant to poisoning effects of water and oxygen. It may be the labile acetonitrile ligands in our systems makes these complexes considerably more thermal- and air-sensitive.

4. Conclusion

Seven-coordinate Mo(II) and W(II) complexes are catalysts for the polymerization of norbornene and TNs of up to 380 were observed. However, these catalyst systems deactivate with time ($t_{1/2} =$

600 s for $[WI_2(CO)_3(NCMe)_2]$). Grubbs' catalyst, $[RuCl_2(PCy_3)_2(CHPh)]$, was found to be at least 3 orders of magnitude more active than these Group 6 metal complexes.

Acknowledgements

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