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Hydrazide, diazenide and nitride complexes as olefin metathesis or ROMP procatalysts

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Abstract

The complexes $[MCl_4(NNR_2)]$ ($M=Mo,W$; $R_2=MePh, Ph_2$), $[MoCl(NNR_2)_2(PPh_3)_2]^+$, $[ReCl(NNAr)_2(PPh_3)_2]$ ($Ar=4$ -substituted phenyl), $[ReCl_3(NNR_2)_2py]$ ($R_2=Ph_2, PhMe$) and $[ReNCl_2(PMe_2Ph)_3]$ form efficient catalysts for metathesis and ring-opening metathesis polymerisation on activation with alkylating agents such as $EtAlCl_2$. These show activities comparable with other reported systems and stereochemical selectivity for the ROMP reaction of norbornene. Possible reaction mechanisms are discussed.

Keywords: Hydrazide complexes; Diazenide complexes; Nitride complexes; Stereochemical selectivity; Reaction mechanisms

1. Introduction

There has been intense recent interest in the development of catalysts for the metathesis of olefins using both intrinsically active alkylidene complexes, and catalysts generated in situ by the addition of Lewis acids to metal precursors [1,2]. Many of the systems involve a 'spectator ligand' such as oxo-, nitrosyl or imide and the role of these co-ligands in the catalysis process has been discussed at length. We have in the past prepared a wide range of Mo, W and Re complexes with hydrazido(2-) and diazenido-ligands which are formally isoelectronic with the imido-($M=NR$), and nitrosyl ligands respectively. However, the presence of the N–N system introduces additional electronic flexibility and we here report the first systematic investiga-

tion of the ability of a range of diazenide and hydrazide complexes to function as metathesis and/or ROMP procatalysts, comparing the results with those for the analogous imide species. There have been a few reports of nitride complexes being used as metathesis procatalysts [3,4], but we here report the first example of a rhenium nitride phosphine complex being used to generate an active ROMP or metathesis catalyst.

2. Results and discussion

2.1. Hydrazido-complex precursors

The complexes $[MCl_4(NNMePh)]$ $M=Mo$ (1), $M=W$ (2) [5], $[MoCl(NNMePh)_2(PPh_3)_2]^+$ (3), [6] $[ReCl_3(NNMePh)_2py]$ (4), [7] $[ReCl_3(PMe_2Ph)_3]$ (5) [8] and $[ReCl_3(NAr)_2py]$

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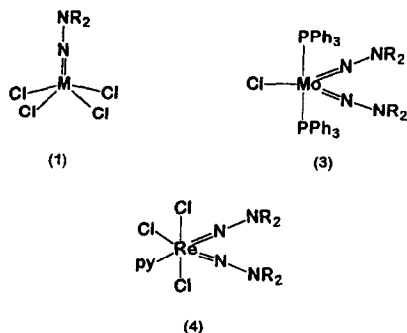


Fig. 1. The structures of hydrazide, diazenide and nitride complexes used in this study. Note: the hydrazide complexes (1) are possibly polymeric, linked via chloride bridges to give octahedral coordination.

(6) [9] were prepared by literature methods. The structures of (1), (3) and (4) are shown in Fig. 1.

On addition of EtAlCl_2 the Mo and W complexes [1,2] were active for the metathesis of pent-2-ene at room temperature with turnover rates comparable with WCl_6 . The other complexes have very low activities at room temperature, presumably due to the lower reactivity of the chloride ligands, but achieve good levels of metathesis at more elevated temperatures (90°C in chlorobenzene). It is interesting to note that

the bishydrazide Re complex (4) is active whereas the formally analogous bis(imido)-complex (9) is not, indicating a clear difference, presumably electronic in origin, between the two types of multiply bonded nitrogen ligand.

The activity of the complexes for Ring Opening Polymerisation Metathesis (ROMP) of strained ring olefins has also been investigated. The standard procedure adopted was to add 4 equivalents of a MeAlCl_2 activator (0.1 molar solution in hexane) to a solution of the complex in chlorobenzene at room temperature. The norbornene (1.2 g) was then added either all at once or dropwise over 3 min, the latter procedure giving noticeably higher yields (see Table 1). The yields are generally comparable with those obtained from other reported precursors such as $[\text{ReO}_3\text{Me}]$. The polymer was then isolated by quenching the reaction by pouring into an excess of cold methanol. Molecular weight determinations by permeation chromatography suggested molecular weights of the order of 8–10 000. However, the solid polymer became progressively more insoluble on standing, presumably as the result of oxidative cross-linking. Most of the precursors investigated gave ap-

Table 1
Metathesis and ROMP activities

Complex	Metathesis ¹		ROMP ²	
	Time to reach equilibrium at room temperature ³	Turnovers at 90°C ⁴	Yield(%)	Stereochemistry of polymer ⁵ <i>cis/trans</i> ratio(%)
WCl_6	3–4 min	ND	83%	50:50
$[\text{WCl}_4(\text{NNMePh})]$	9–10 min	ND	90% ⁸ 83% ⁷	50:50
$[\text{ReCl}(\text{NNC}_6\text{H}_4\text{Cl-4})_2(\text{PPh}_3)_2]$	Inactive	45	90% ⁸	65:35
$[\text{ReCl}_3(\text{NNMePh})_2\text{py}]$	Inactive	25	33% ⁷	100:0
$[\text{ReCl}_3(\text{NPh})_2\text{py}]$	Inactive	Inactive	Inactive	Inactive
$[\text{ReNCl}_2(\text{PPh}_3)_2]$	Inactive	Inactive	Inactive	Inactive
$[\text{ReNCl}_2(\text{PMe}_2\text{Ph})_3]$ ⁶	Inactive	Active ⁶	92% ^a	53:47
$[\text{ReCl}_3(\text{PMe}_2\text{Ph})_3]$	Inactive	Inactive	Inactive	Inactive

¹ Metathesis of pent-2-ene to but-2-ene and hex-3-ene.

² ROMP of norbornene in chlorobenzene at room temperature.

³ Measured in sealed system at room temperature in 1,2-dichloroethane, time to give statistical mixture of the three olefins.

⁴ But-2-ene not retained at elevated temperature in chlorobenzene, so non-equilibrium system.

⁵ Determined by $^{13}\text{C-NMR}$ on CDCl_3 soluble component of polymer.

⁶ Inactive in chlorobenzene at 90°C for metathesis, but active in CH_2Cl_2 at 40°C .

⁷ Norbornene added at beginning of reaction.

⁸ Norbornene added slowly during reaction.

ND Not determined.

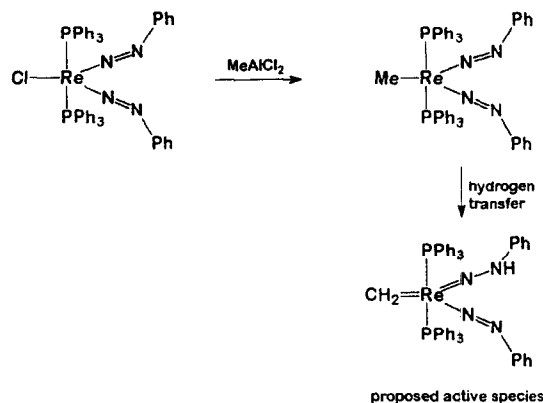
proximately equal amounts of the *cis* and *trans* isomers of the polymer as indicated by the ^{13}C -NMR. A notable exception was the complex $[\text{ReCl}_3(\text{NNMePh})_2\text{py}]$ (**4**) which gave exclusively the *cis* isomer, albeit in reduced yield using the single addition procedure. The *cis/trans* ratio of the polymer was estimated using ^{13}C -NMR of a solution of the polymer in CDCl_3 . Slow addition of the norbornene gave higher yields with a less stereospecific product distribution, and clearly the stereochemistry of polymerisation is dependent on the concentration of free olefin in the solution: GC analysis showed that the remainder of the norbornene remained unreacted in solution.

The mechanism of the metathesis reactions presumably involves the formation of an alkylidene hydrazido-complex, and we are currently investigating the reactions of the hydrazide precursors with appropriate alkyl lithiums in order to isolate stable alkylidene derivatives analogous to the imide species already reported by Schrock, Gibson and others.

2.2. Diazenido-complexes as precursors

The diazenido complexes $[\text{ReCl}(\text{NNAr})_2(\text{PPh}_3)_2]$ ($\text{Ar}=\text{C}_6\text{H}_5$, $\text{C}_6\text{H}_4\text{CH}_3$ -4, $\text{C}_6\text{H}_4\text{Cl}$ -4) (**7**) were prepared by the literature methods [10]. These were not active at room temperature on treatment with MeAlCl_2 or EtAlCl_2 , but showed good levels of activity on heating to ca 90°C in chlorobenzene as solvent (see Table 1). There is some dependence of the geometry of polynorbornene with the nature of the 4-substituent on the diazenide phenyl, which suggests the possibility of product control vis the nature of the substituents of the multiply bonded hydrazide or diazenide ligands. ROMP activity was also observed using Me_4Sn as the activator at elevated temperatures in chlorobenzene as solvent.

Again the mechanism presumably involves the initial formation of an alkyl $\text{Re}(\text{III})$ diazenide complex (Scheme 1). Formation of the



Scheme 1. A proposed mechanism for the formation of the active alkylidene catalyst from a $\text{Re}(\text{III})$ diazenide precursor.

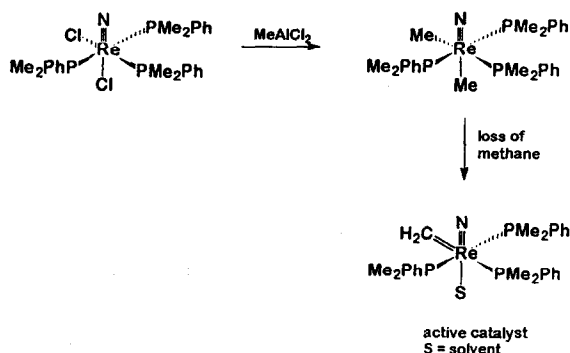
alkylidene required for metathesis activity may involve *intermolecular* elimination of alkane, but an alternative possibility is the transfer of hydrogen to ligated diazenide to give an alkylidene hydrazide(2-)-diazenide complex. The protonation of one of the diazenide ligands to hydrazide in the complex $[\text{ReCl}_2(\text{NNAr})(\text{NNHAr})(\text{PPh}_3)_2]$ has been well established. This raises the formal oxidation state of the rhenium to (V), more in line with the higher formal oxidation states usually found for metathesis catalysts. The reactions of the parent diazenide complexes with a range of alkyl lithium derivatives are currently under investigation.

2.3. Nitride complexes as precursors

The five coordinate and six coordinate nitride complexes $[\text{ReNCl}_2(\text{PPh}_3)_2]$ (**8**) and $[\text{ReNCl}_2(\text{PMe}_2\text{Ph})_3]$ (**9**) were prepared by the literature routes [11]. The five coordinate complex (**8**) was completely inactive for both metathesis and ROMP even at 90°C in chlorobenzene. Indeed the synthesis and characterisation of the stable dimethyl complex $[\text{ReNMe}_2(\text{PPh}_3)_2]$ was reported comparatively recently [12], and the corresponding diphenyl derivative has been known since the mid-1960s [13]. However, the six coordinate nitride is very

active for ROMP metathesis in chlorobenzene at room temperature, giving virtually equal amounts of the *cis* and *trans* isomers. Significantly the complex $[\text{ReCl}_3(\text{PMe}_2\text{Ph})_3]$ is completely inactive for ROMP even at 90°C in chlorobenzene, indicating the importance of the nitride ligand in conferring activity. The ^{31}P -NMR of the nitride complex (9) in chlorobenzene prior to the addition of norbornene showed a doublet and triplet slightly shifted to lower field from the parent nitride with slight changes in P–H and P–P coupling constants. This suggests that the alkylidene complex presumed to be the intermediate must have an analogous structure to the nitride, and we propose the solvated six coordinate species shown in Scheme 2. Interestingly the six-coordinate nitride is not active at all for metathesis of pent-2-ene in chlorobenzene, but achieves good conversion to hex-3-ene in dichloromethane at room temperature. This is consistent with the type of solvent involvement discussed above.

The inactivity of the five coordinate nitride is explicable if the elimination of alkane to form the alkylidene is an *intra* molecular process, as here the two methyl groups are in pseudo *trans* locations in the base of the square plane. In the six coordinate species these are forced into *cis* positions in the octahedral coordination sphere and methane elimination occurs readily. This



Scheme 2. A proposed mechanism for the formation of the alkylidene intermediate from the six coordinate Re(V) nitride precursor.

offers the interesting possibility of activation of the five coordinate dialkyl species via the addition of a neutral ligand, and we are currently investigating this reaction as well as the effects of varying the steric effects of the phosphine groups by substituting methyl for ethyl etc.

3. Conclusions

We have shown for the first time that hydrazide (Mo, W, Re) diazenide (Re) and nitride (Re) complexes can act as precursors for efficient metathesis and ROMP catalysis. These precursors are very simple to prepare, and are air and water stable, and variation of the phosphine ligands potentially provides a convenient route to control the stereochemistry of catalysis and of generation of the active species under conditions suitable for olefins with reactive functional groups.

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References

- [1] A. Keller, J.M. Sobzac and J.J. Ziolkowski, in Molybdenum, an Outline of its Chemistry and uses, J. Braithwaite and J. Haber (Eds.), Elsevier, Amsterdam, 1995, p. 618.
- [2] J. Feldman and R.R. Schrock, *Prog. Inorg. Chem.*, 39 (1991) 1.
- [3] K. Seyferth and R. Taube, *J. Mol. Catal.*, 28 (1985) 52.
- [4] K. Seyferth and R. Taube, *J. Organomet. Chem.*, 229 (1982) C19.
- [5] J.R. Dilworth and S. Morton, *Transition Metal Chem.*, 12 (1987) 41.
- [6] J. Chatt, B.A.L. Crichton, J.R. Dilworth, P. Dahlstrom and J. Zubieta, *Inorg. Chem.*, 21 (1982) 2383.
- [7] J.R. Dilworth and B. Coutinho, unpublished results.
- [8] G.W. Parshall, *Inorg. Syn.*, 7 (1977) 110.
- [9] A.D. Horton, R.R. Schrock and J.H. Freudenburger, *Organometallics*, 6 (1987) 893.

- [10] J.R. Dilworth, S.A. Harrison, D.R.M. Walton and E. Schweda, *Inorg. Chem.*, 24 (1975) 2594.
- [11] J. Chatt, C.D. Falk, G.J. Leigh and R.J. Paske, *J. Chem. Soc. A* (1969) 2288.
- [12] V. Wing-Wah Yam, Kwok-Kwong Tam and Tung-Fong Lai, *J. Chem. Soc. Dalton Trans* (1993) 651.
- [13] J. Chatt, J.D. Garforth and G.A. Rowe, *J. Chem. Soc. A* (1966) 1834.