Contents lists available at ScienceDirect



Inorganic Chemistry Communications



journal homepage: www.elsevier.com/locate/inoche

Imidotungsten(VI) complexes with chelating phenols as ROMP catalysts $\stackrel{\leftrightarrow}{\sim}$

Juuso Hakala^a, Mikko M. Hänninen^b, Ari Lehtonen^{a,*}

^a Laboratory of Materials Chemistry and Chemical Analysis, Department of Chemistry, University of Turku, FI-20014, Turku, Finland
 ^b Laboratory of Inorganic Chemistry, Department of Chemistry, University of Jyväskylä, FI-40014 Jyväskylä, Finland

ARTICLE INFO

Article history: Received 10 February 2011 Accepted 20 May 2011 Available online 27 May 2011

Keywords: ROMP Phenolate ligands Tungsten Catalysis

ABSTRACT

Tungsten(VI) complexes of the type $[W(NPh)Cl_3(L)]$ (L= chelating phenolate) were studied as catalyst precursors for ROMP of 2-norbornene, dicyclopentadiene and 5-vinyl-2-norbornene. These compounds form active catalysts when treated by ethyl magnesium bromide. Moreover, polymerisations can be run under ambient atmosphere without complicated inert atmosphere techniques. Synthesis and crystal structure of a new precursor complex $[W(NPh)Cl_3(L^S)]$ (L^S=2,4-di-*tert*-butyl-6-(phenylthiomethyl)phenolate) are also described.

© 2011 Elsevier B.V. All rights reserved.

Ring-opening metathesis polymerization (ROMP) of norbornene derivatives generate polymers with diverse features, which can be tailored by the functional groups substituted at the backbone. The easiest way to run olefin metathesis is to use some well-defined catalysts, such as Mo-based Schrock catalysts or Ru-based Grubbs catalysts [1,2]. As these catalysts are expensive and highly sensitive to air and moisture, they are rarely used in the preparation of low-cost products, such as elastomers or other polymeric materials. For practical use, the isolation of active catalyst species is not necessary; for example, tungsten phenoxides [WCl_{6-x}(OAr)_x] and [WOCl_{4-v} $(OAr)_{v}$ are used on a regular basis as precursors for two-component catalyst systems, typically in the presence of an organometallic activator [3-6]. As typical for high-valent metal chlorides, these catalyst precursors are also rather sensitive towards water and other nucleophiles. Especially, if the coordination number of the metal centre is low, these compounds must be handled under an inert atmosphere using rather tedious practices. The hydrolytic stability of high-valent tungsten complexes can be improved by coordinative protection, i.e. by using chelating ligands, which carry a potentially coordinating neutral group within the molecule [7,8]. Such hemilabile ligands are important in catalysis because they stabilize inactive states while freeing up coordination sites when they are needed, thus adopting the role of a coordinating solvent [9].

E-mail address: Ari.Lehtonen@utu.fi (A. Lehtonen).

We have previously studied the phenoxide chemistry of imidotungsten(VI) and prepared compounds 1-3 with chelating phenoxides (see Fig. 1) using a simple two-step reaction [8,10]. The first step comprises a reaction of WOCl₄ with a stoichiometric amount of phenolic ligand precursor in CH₂Cl₂, whereas the second step involves a reaction of formed tungsten oxo compound with phenyl isocyanate in toluene, which reaction produces a final imido complex. These complexes are stable in air and they can be easily purified by crystallization or by column chromatography. Complex 4 was prepared similarly using 2,4-di-tert-butyl-6-(phenylthiomethyl)phenol [11] as a ligand precursor and it was isolated by crystallisation from dry acetonitrile in a moderate yield.¹ It is stable as a crystalline material under inert atmosphere but decomposes slowly in solutions. The molecular structure of **4** consists of neutral mononuclear units. in which the central W(VI) ion is surrounded by one terminal phenyl imido group, one bidentate phenolate and three chlorides (Fig. 2). As expected due to the strong structural trans-effect of the imido nitrogen, the neutral sulphur donor is situated trans to the imido group with the coordinative W-S bond length of 2.7221(11). The overall coordination geometry and bonding parameters around the

 $^{^{\}Rightarrow 2}$ Crystal data for **4**: C₂₇H₃₂Cl₃NOSW, space group P₁21/n₁, *a*=13.78090(20), *b*=14.04840(29), *c*=15.22950(29) Å, β=106.8858(11), V=2821.305(91), Z=4. The structure was refined on *F*² to R=0.0281, *w*R=0.0537 for all 5535 reflections. Singlecrystal data collections, data reduction and subsequent calculations were essentially as described in earlier papers from our group. [8,10].

^{*} Corresponding author at: University of Turku, Department of Chemistry, FIN-20014 TURKU, Finland. Tel.: + 358 2 3336733; fax: + 358 2 3336700.

^{1387-7003/\$ –} see front matter $\ensuremath{\mathbb{C}}$ 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.inoche.2011.05.021

 $^{^1}$ WOCl₄ (1.0 mmol, 340 mg) and 2,4-di-tert-butyl-6-(phenylthiomethyl)phenol (1.0 mmol, 330 mg) were heated in CH₂Cl₂ (20 ml) at reflux temperature for 2 h. The intense red solution was evaporated and the residue was dissolved in PhMe (10 ml) and refluxed with phenyl isocyanate (1.5 mmol, 0.16 ml) for 2 h. Filtered solution was evaporated and residue was crystallised from acetonitrile (2 ml) at refrigerator to obtain **4** in a 28% (180 mg) yield as deep purple crystals. NMR $\delta_{\rm H}$ (CDCl₃, standard SiMe₄): 7.57–7.64 (overlapping signals, 4H, ArH_{thioether} and ArH_{imido}), 7.48 (d, *J*=2.4 Hz, 1H, ArH_{phenolate}), 7.39 (overlapping signals, 5H, ArH_{thioether} and ArH_{imido}), 7.17 (d, *J*=2.4 Hz, 1H, ArH_{phenolate}), 7.09 (m, 1H, ArH_{imido}), 4.77 (2H, CH₂-S), 5.35 (m, 6H), 1.48 (9H, tBu), 1.34 (9H, tBu). Found: C, 46.3; H, 5.0. C₂₇H₃₂Cl₃NOSW requires C, 45.8; H, 4.6%.



Fig. 1. Catalyst precursors for ROMP of norbornene derivatives.

metal ion are comparable to those found for structurally corresponding aminophenolate and iminophenolate compounds [8,10].

We have earlier found that catalyst precursor 1 polymerises norbornene derivatives when activated by Et₂AlCl [8]. In the present study we have applied precursors 1-4 in two-component catalyst system using ROMP of 2-norbornene, dicyclopentadiene and 5-vinyl-2-norbornene (the mixture of endo and exo) as test reactions. 2-norbornene and dicyclopentadiene were polymerised in various reaction media (toluene, chlorobenzene, 1,2-dichlorobenzene) whereas 5-vinyl-2-norbornene was polymerised without any solvent. The overall conversion of monomer to methanol-insoluble polymers was used as a measure of activity. Imidotungsten(VI) complexes 1-4 were dissolved in solvent/cycloalkene mixtures and were activated by ethyl magnesium bromide in a 200:5:1 monomer:activator: tungsten ratio. The conceivable role of the organomagnesium activator is to replace two chloride ligands on tungsten with alkyl groups; the resultant organotungsten intermediate would then undergo an α -elimination reaction to afford the corresponding alkylidene derivative [1]. Moreover, the excess Grignard reagent can scavenge protic impurities from the reaction mixture. As a result, the solutions changed from a red to a yellow and viscosity of the solution increased with time. The polymeric materials that formed were precipitated by methanol, dried and weighed. In all experiments, poly(2-norbornene) and poly(cyclopentadiene) were formed in 85-95% yields as white solid materials whereas the polymers of 5-vinyl-2-norbornene were isolated in 40-50% yields as sticky solids. All catalyst precursors presented practically similar activity in studied reactions. Spectral



Fig. 2. A molecular structure of **4**. Thermal ellipsoids are drawn at 30% probability level. Selected bond distances (Å) and angles (°) N1–W1: 1.736(3), O1–W1: 1.866(2), S8–W1: 2.7221(11), C11–W1: 2.3712(11), C12–W1: 2.3209(10), Cl3–W1: 2.3619(11), N1–W1–S8: 171.20(9), O1–W1–S8: 76.12(7).

analyses of these polymers indicate that the polymerisation of dicyclopentadiene and 5-vinyl-2-norbornene occurs through norbornene rings while the additional C=C double bonds remain intact.

Microstructures of the norbornene polymers were analysed by ¹H NMR, ¹³C NMR and IR spectroscopy to estimate the contents of *cis* and trans (-HC=CH-) units in a polymer backbone. The proton spectra peaks from 5.2 to 5.4 ppm indicate the presence of unsaturated structures, which arise from ring-opening polymerization chains. More precisely, in a CDCl₃ solution, the *cis* and *trans* ethylenic protons give peaks at 5.24 and 5.38, respectively. Corresponding α -protons show resonances at 2.8 and 2.45 ppm [12,13]. For ethylenic carbon atoms, two sets of resonances are seen: one for carbon atoms positioned in trans RHC=CHR groups (around 133 ppm) and another for carbon atoms positioned in cis RHC=CHR groups (around 134 ppm) [12,13]. The IR spectra of studied polymers show absorption bands at ca. 730 and 970 cm⁻¹ for bending modes due to *cis* and *trans* substituted C=C double bonds [14]. The microstructures of polydicyclopentadiene and poly(5-vinyl-2-norbornene) were also studied by abovementioned spectroscopy although the analysis of NMR spectra is more complicated due to the additional C=C double bond in the monomeric units. Nevertheless, IR absorption intensities can be used to assess the stereochemistry of the polymers. Though it is difficult to estimate the exact intensity ratio of these IR-bands, in all spectra their intensity is consistent with the results obtained by NMR. Accordingly, it was found that in all polymers, the cis-content is clearly over 80%. The high cis-content can be explained by the steric hindrance of the catalytically active species. It is known, that the low coordination number of the metal site favours the *trans* products, whereas more crowded metal centre yields predominantly cis double bonds [Ref 1, p. 241]. In the studied catalyst systems, the supposed activation process, *i.e.* dialkylation and α -elimination, leads to the formation of pentacoordinated carbene species. As studied catalyst precursors have closely similar structures, they performed essentially similarly under identical conditions.

In conclusion, imidotungsten(VI) complexes with chelating phenolates can be activated by EtMgBr to catalyse ROMP of norbornene derivatives. Polymerisations can be run simply under ambient conditions without inert atmosphere techniques. All solid polymers have a high *cis*-content.

Acknowledgement

Turku University Foundation and University of Jyväskylä are acknowledged for financial support.

Appendix A. Supplementary material

CCDC 812274 contains the supplementary crystallographic data for compound **4**. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

- [1] K.J. Ivin, J.C. Mol, Olefin Metathesis and Metathesis Polymerization, Academic Press, London, 1997.
- [2] R.H. Grubbs (Ed.), Handbook of Metathesis, Vol. 3, Wiley-VCH, Weinheim, Germany, 2003.
- [3] F. Lefebvre, M. Leconte, S. Pagano, A. Mutch, J.M. Basset, Polyhedron 14 (1995) 3209
- [4] (a) FJ. Gómez, K.A. Abboud, K.B. Wagener, J. Mol. Catal. A: Chem. 133 (1998) 159;
 (b) FJ. Gómez, M.S. Manak, K.A. Abboud, K.B. Wagener, J. Mol. Catal. A: Chem. 160 (2000) 145.
- [5] D.R. Kelsey, D.L. Handlin, M. Narayana, B.M. Scardino, J. Polym. Sci. A: Polym. Chem. 35 (1997) 3027.
- [6] F. Quignard, M. Leconte, J.-M. Basset, L.-Y. Hsu, J.J. Alexander, S.G. Shore, Inorg. Chem. 26 (1987) 4272.
- [7] (a) P.A. van der Schaaf, J. Boersma, W.J.J. Smeets, A.L. Spek, G. van Koten, Inorg. Chem. 32 (1993) 5108;

- (b) P.A. van der Schaaf, D.M. Grove, W.J.J. Smeets, A.L. Spek, G. van Koten, Organometallics 12 (1993) 3955;
- (c) P.A. van der Schaaf, R.A.T.M. Abbenhuis, W.P.A. van der Noorth, R. de Graaf, D. M. Grove, W.J.J. Smeets, A.L. Spek, G. van Koten, Organometallics 13 (1994) 1433.
- [8] A. Lehtonen, H. Balcar, J. Sedláček, R. Sillanpää, J. Organomet. Chem. 693 (2008) 1171
- [9] H. Grützmacher, Angew. Chem. Int. Ed. 47 (2008) 1814.
 [10] M.M. Hänninen, R. Sillanpää, H. Kivelä, A. Lehtonen, Dalton Trans. (2011) 2868.
- [11] B. Lian, K. Beckerle, T.P. Spaniol, J. Okuda, Eur. J. Inorg. Chem. (2009) 311.
- [12] C. Larroche, J.P. Laval, A. Lattes, M. Leconte, F. Quignard, J.M. Basset, J. Org. Chem. 47 (1982) 2019.
- [13] J.L. Brumaghim, G.S. Girolami, Organometallics 18 (1999) 1923.
- [14] N. Cobo, M.A. Esteruelas, F. González, J. Herrero, A.M. López, P. Lucio, M. Oliván, J. Catal. 223 (2004) 319.