Progress toward new catalysts for acyclic diene metathesis (ADMET) polymerization reactions

Laura L. Blosch, A. Scott Gamble and James M. Boncella* Department of Chemistry and Center for Catalysis, University of Florida, Gainesville, FL 32611 (USA)

Abstract

The compounds Tp'W(CHR)(E)X (Tp' = hydridotris(3,5-dimethylpyrazolyl)borate; $R = CMe_3$, Ph; E = O, NPh; X = Cl, Br), 4a-c, have been synthesized by reaction of $Tp'W(CR)X_2$ ($R = CMe_3$, X = Cl; R = Ph, X = Br), 3a,b, with neutral alumina or aniline. Compounds 3a,b and 4a-c are air stable and thermally stable to >100 °C in the solid state. When combined with 1 equivalent of AlCl₃, Tp'W(CHPh)(NPh)Br, 4c, catalyzes the acyclic diene metathesis (ADMET) oligomerization of 1,9-decadiene, giving a mixture of 1,9,17-octadecatriene, 1,9,17,25-hexadodecatetraene and ethylene ($\approx 30\%$ conversion). The new alkylidene complex, 4a, is an efficient ring-opening metathesis polymerization (ROMP) catalyst in the presence of AlCl₃ as a co-catalyst.

Introduction

We have been interested in using the olefin metathesis reaction to synthesize polymers from acyclic dienes, as shown in eqn. (1), and have demonstrated the feasibility of this approach when an appropriate catalyst system is chosen [1]. The utility of catalysts for this reaction depends upon a number of factors, including their thermal stability, their reactivity with functional groups in the monomer, and their ability to ensure that olefin metathesis is the *only* reaction that consumes the monomer.



^{*}Author to whom correspondence should be addressed.

The reaction in eqn. (1) is a step-type condensation polymerization reaction [2] in which ethylene (or another low-molecular-weight olefin) is produced and removed to shift the equilibrium to produce polymeric species. Any polymerization reaction of this type must proceed to a high (>99%) conversion to produce high-molecular-weight polymers [4]. Thus an extremely efficient and selective catalyst is necessary to give highmolecular-weight products. Furthermore, the best experimental conditions for such a reaction employ as high a monomer concentration as possible (neat monomer).

The use of neat monomer as solvent gives rise to drastic changes in the reaction medium. As the monomer is converted to oligomers and polymers, the reaction mixture becomes more viscous and eventually solidifies. In order to achieve the maximum possible molecular weight, the reaction should be conducted at temperatures above the melting point of the polymer. Thus the best possible catalyst for a given reaction will remain active at temperatures above the melting point of the desired polymer. Finally, a catalyst that is tolerant of a variety of functionalized monomers would be most useful in the synthesis of a diverse range of polymers whose physical properties could be tailored by changing the functional group.

The well-defined alkylidene complexes $M(CHR)(NAr)(OR')_2$ (R = CMe₃, CMe₂Ph; R' = CMe(CF₃)₂; Ar = 2,6-C₆H₃-Pr¹₂; M = W, Mo) **1a**-d [5-7], act as efficient catalysts for the polymerization of acyclic dienes to give high-molecular-weight polymers [1-3]. Their utility for this reaction is ultimately limited by their thermal stability. Decomposition of these catalysts to inactive and largely unidentified products occurs rapidly above *ca*. 70 °C, thereby limiting the products to those that remain liquid at or near 70 °C. Thus we are interested in finding efficient metathesis catalysts that are also thermally stable.

Results and discussion

We have discovered that the complexes $Tp'W(CBu^{t})Cl_{2}$, **3a**, and $Tp'W(CHBu^{t})(O)Cl$ (Tp' = hydridotris(3,5-dimethylpyrazolyl)borate), **4a**, constitute a new class of tungsten alkylidyne and alkylidene complexes that are thermally stable in air to 270 °C and 150 °C, respectively [8]. We have begun a study of the use of the compounds Tp'W(CHR)(E)X ($R = Bu^{t}$, Ph; E = O, NPh; X = Cl, Br), **4a**-c, as precursors to active ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis (ADMET) polymerization catalysts. Complexes **3a**, **b** have been synthesized from W(CBu^t)Cl₃DME, **2a**, or W(CPh)Br₃DME, **2b**, as shown in Scheme 1. The yields in these reactions are 50% and 10% for **3a** and **3b**, respectively. It is not clear why there is such a poor yield in the synthesis of **3b**, and attempts at improving the yield of **3b** by changing the reaction conditions have proven unsuccessful. Complexes **3a** and **3b** can be con-



Scheme 2.

verted to $4\mathbf{a}-\mathbf{c}$ by reaction with alumina or aniline, as shown in Scheme 2; however, the best way to synthesize $4\mathbf{b}$ is by stirring a THF solution of $3\mathbf{b}$ for 24 h at room temperature, in air. All of these complexes have considerable thermal and air stability (solid samples of $3\mathbf{a},\mathbf{b}$ and $4\mathbf{a}-\mathbf{c}$ are stable to 100 °C and in air for several hours).

The mechanism for conversion of the alkylidyne complexes to the oxo-alkylidene complexes (Scheme 2) probably involves displacement of halide by OH^- or H_2O followed by proton transfer to the alkylidyne carbon in a fashion similar to the reactions used to synthesize W(CH-Bu^t)(O)Cl₂L₂ [4]. In the case of Tp'W(CHPh)(O)Br, **4b**, further reaction with water or hydroxide ion results in the formation of Tp'W(CH₂Ph)(O)₂, **5**, which has been independently synthesized from Tp'W(O)₂Cl, as shown in eqn. (2). We have not yet observed conversion of **3a** to the dioxo complex Tp'W(CH₂Bu^t)(O)₂ by reaction with water or alumina. This lack of reactivity may arise from the bulkiness of the neopentylidene group, or it may arise from a stronger interaction between W and Cl as compared to the W-Br interaction.



When **3b** and two equivalents of aniline in THF were heated to reflux for several days, conversion to the phenylimido benzylidene complex Tp'W(CHPh)(NPh)Br, **4c**, occurred in high yield (Scheme 2). Complex **4c** exhibits two resonances in the alkylidene region of the ¹H NMR spectrum, at 11.21 and 10.92 ppm, in a ratio of 4.8:1. We ascribe these peaks to two different rotational orientations of the benzylidene group. These two peaks show no signs of broadening or coalescence up to 110 °C. This behavior is consistent with the two rotameric forms of **4c** having a large activation barrier for their interconversion.

The compounds $4\mathbf{a}-\mathbf{c}$ do not catalyze the ring-opening metathesis polymerization of cyclooctene in the absence of co-catalyst, even up to 140 °C. However, addition of 1 equivalent of AlCl₃ to a solution of $4\mathbf{a}$ in cyclooctene results in an immediate and rapid polymerization reaction producing polyoctenamer in high (>90%) yield. Compound $4\mathbf{a}$ is an extremely efficient catalyst for this reaction, since it will polymerize 500 equiv. of cyclooctene to solid polyoctenamer in ca. 15 min in air at room temperature [8]. When ZnCl_2 was used as a co-catalyst with compound $4\mathbf{a}$, very slow ROMP of cyclooctene occurred over 2 months, producing low-molecular-weight oligomers rather than high-molecularweight polymers.

When 4c was dissolved in 1,9-decadiene and one equivalent of $AlCl_3$ was added, ¹H NMR spectroscopy showed that the 1,9-decadiene was converted into a mixture of ethylene, 1,9,17-octadecatriene, 1,9,17,25-hexadodecatetraene and unreacted 1,9-decadiene, as shown in eqn. (3).

Figure 1 shows the olefinic region of the ¹H NMR spectrum of the mixture of products from eqn. (3) after removal of 1,9-decadiene and ethylene. There was no evidence for the formation of any products arising from vinyl addition-type reactions of the internal olefinic bonds of the new product*. It is unclear whether the reaction shown in eqn. (3) proceeds slowly because of a lack of catalyst activity, or because of competing thermal deactivation processes. The observation that the

^{*}Vinyl addition crosslinking reactions have prevented the successful polymerization of acyclic dienes with well-known Lewis-acid-containing catalysts such as WCl₆/EtAlCl₂ [11].



Fig. 1. ¹H NMR (C_6D_6) of the metathesis product of 1,9-decadiene with the $3c/AlCl_3$ catalyst system.

 $4c/AlCl_3$ system is active for terminal olefin metathesis at elevated temperatures is encouraging, since 1a-d rapidly become inactive for acyclic diene metathesis chemistry above *ca*. 60 °C [12].

It is evident that the Tp' ligand imparts remarkable kinetic stability on normally very reactive W(VI) alkylidyne and alkylidene complexes. Despite their kinetic stability, complexes $4\mathbf{a}-\mathbf{c}$ can be used as metathesis catalysts as long as Lewis acids are present as co-catalysts. The apparent thermal stability of the $4\mathbf{c}/\text{AlCl}_3$ system suggests that the Tp' ligand may impart thermal stability to the catalytically active species as well. We are continuing to explore the use of polydentate ligands to increase the thermal stability of well-defined metathesis catalysts.

Experimental

Unless otherwise noted, all procedures were carried out under argon atmosphere using Schlenk techniques or in a N_2 -filled dry-box. Solvents were distilled from sodium benzophenone ketyl (pentane, diethyl ether, toluene and tetrahydrofuran) or P_2O_5 (CH₂Cl₂) prior to use. NMR spectra were obtained using Varian VXR-300 or GE-QE300 spectrometers. Chemical shifts were referenced to the residual protons of the deuterated solvents and are reported relative to TMS. The elemental analyses and mass spectra were obtained from the service facility of our department. The compounds potassium hydridotris(3,5-dimethylpyrazolyl)borate [13], W(CBu^t)Cl₃DME [9], W(CPh)Br₃DME [10], Tp'W(CBu^t)Cl₂ and Tp'W(CHBu^t)(O)Cl [8] were synthesized using published procedures. The compound PhCH₂MgBr was used as a 2.0 M solution in THF (Aldrich).

Preparation of $Tp'W(CPh)Br_2$ (3b)

A THF solution of W(CPh)Br₃DME (1.00 g, 1.66 mmol) was cooled to -78 °C and a THF solution of KTp' (0.56 g, 1.7 mmol) was added with stirring, resulting in a gradual color change to dark green. The solution was warmed to 25 °C and allowed to stir for 24 h, after which time the solvent was removed under reduced pressure. The product was dissolved in toluene and passed through a Florisil[®] plug, giving a blue-green solution. Solvent removal and successive pentane washes gave the product as a blue solid in 10% yield; m.p. 218 °C in air (decomp.). ¹H NMR (CD₂Cl₂): δ (ppm) = 7.68 (2H, t, meta-Ph); 7.25 (2H, d, ortho-Ph); 6.78 (1H, t, para-Ph); 6.35, 5.97 (2:1H, s, Tp' ring H's); 2.58, 2.52, 2.45, 2.42 (3:3:6:6H, s, Tp' Me's). ¹³C NMR (CD₂Cl₂): δ (ppm) = 327.3 (=CPh); 154.8, 154.4, 147.8, 144.2 (Me-substituted ring C's of Tp'); 140.0, 138.1, 131.9, 126.2 (Ph); 108.3 (Tp' unsubstituted ring C's overlapping); 19.4, 15.0, 13.2, 12.5 (Tp' Me's). Elem. anal.: calc. for C₂₂H₂₇BBr₂N₆W: C, 36.20; H, 3.73; N, 11.52; found: C, 36.29; H, 3.91; N, 11.05.

Preparation of Tp'W(CHPh)(O)Br (4b)

A solution of **3b** and ≈ 1 ml H₂O in THF was stirred in air for 2 days or until the solution color had changed from blue to gold. Solvent removal and chromatography on Florisil[®] (Et₂O) gave the product as an orange-red solid ($\approx 75\%$ yield); m.p. 210 °C in air (decomp.). The product was recovered as a mixture of rotamers. *Major*: ¹H NMR (C₆D₆): δ (ppm) = 10.97 (1H, s, =CHPh); 7.60–6.60 (5H, m, Ph); 5.48, 5.21 (2:1H, s, Tp' ring H's); 3.00, 2.69, 2.08, 2.00, 1.95, 1.87 (3H each, s, Tp' Me's). ¹³C NMR (C₆D₆): δ (ppm) = 290.2 ($J_{W-C} = 151$ H; CHPh); 154.5, 154.3, 153.9, 145.8, 144.6, 144.2 (Me-substituted ring C's of Tp'); 141.7, 133.5, 132.1, 127.0 (Ph); 108.5, 108.2, 108.0 (Tp' unsubstituted ring C's); 17.2, 17.0, 16.3, 12.5, 12.4, 12.1 (Tp' Me's). *Minor*: ¹H NMR (C₆D₆): δ (ppm) = 11.40 (1H, s, =CHPh); 7.60–6.60 (5H, m, Ph); 5.48, 5.33, 5.36 (1H each, s, Tp' ring H's); 3.13, 2.20, 2.15, 2.02, 1.92, 1.90 (3H each, s, Tp' Me's). MS: M⁺ = 666.11. Elem. anal.: calc. for C₂₂H₂₈BBrN₆OW: C, 39.61, H, 4.23; N, 12.60; found: C, 38.67; H, 4.27; N, 11.83.

Alternative preparations of 4b

(a) The complex may be prepared directly from the crude product formed in the synthesis of **2b** in approximately the same overall yield.

(b) A THF solution of **3b** was stirred with 25 g alumina (Fisher) for 1 week until the solution turned orange. Filtration and solvent removal gave an oily solid, which was a mixture of **4b** and **5**. The alkylidene was purified by chromatography on alumina, and recovered in $\leq 25\%$ yield.

Preparation of Tp'W(CHPh)(NPh)Br (4c)

A THF solution of **3b** (0.27 g, 0.37 mmol) and aniline (0.082 g, 0.86 mmol) was heated to reflux for 3 days, resulting in a color change from blue to orange-brown. After solvent removal, the product was chromatographed on alumina, eluting one orange band with Et₂O. The product could be recrystallized from Et₂O. Yield 0.20 g (73%) as two rotational isomers. *Major*: ¹H NMR (toluene- d_8): δ (ppm) = 11.21 (1H, s, =CHPh); 7.57-6.60 (10H, m, Ph); 5.59, 5.47 (1:2H, s, Tp' ring H's); 2.87, 2.52, 2.11, 2.08, 2.04, 2.03 (3H each, s, Tp' Me's). *Minor*: ¹H NMR (toluene- d_8): δ (ppm) = 10.92 (1H, s, =CHPh); 7.57-6.60 (10H, m, Ph); 5.52, 5.26 (2:1H, s, Tp' ring H's); 2.98, 2.70, 4 peaks in the region 2.15-1.95 (3H each, s, Tp' Me's).

Preparation of $Tp'W(O)_2Cl$

A slurry of KTp' (9.84 g, 2.93 mmol) in 100 ml THF was added by cannula under argon to a rapidly stirred room-temperature slurry of $W(O)_2Cl_2$ (8.33 g, 2.93 mmol) in 150 ml THF. Undissolved KTp' was rinsed in with an additional portion of THF (50 ml). Since neither starting material nor product is very soluble in THF, the reaction mixture was allowed to stir for 48 h. The THF was filtered from the solid residue, which was washed with THF $(3 \times 50 \text{ ml})$. The remaining pale blue-green solid was Soxhlet extracted into 250 ml CHCl₃ for 36 h to remove the insoluble blue material. The extract was concentrated slightly and cooled to -20 °C, giving a white microcrystalline solid. Yield (2 crops) 12.01 g (75%), m.p. > 280 °C in air. ¹H NMR (CDCl₃): δ (ppm) = 5.89, 5.87 (1:2H, s, Tp' ring H's); 2.68, 2.66, 2.36, 2.34 (6:3:6:3H, s, Tp' Me's). ¹³C NMR (CDCl₃): $\delta(\text{ppm}) = 154.58, 154.40, 146.81, 144.74$ (Tp' Me substituted ring C's); 107.76 (Tp' unsubstituted ring C's overlapping); 15.58, 14.80, 12.83, 12.32 (Tp' Me C's). IR (Nujol): v (cm⁻¹) = 2551.2 (B–H, ws); 597.8, 916.3 (W=O, ms, ss). MS (C.I.): $M^+ = 549.12$. Elem. anal.: calc. for $C_{15}H_{22}ClO_2W$: C, 32.85; H, 4.04; N, 15.32; found: C, 33.41; H, 4.17; N, 15.30.

Preparation of $Tp'W(CH_2Ph)(O)_2$ (5)

To a room-temperature slurry of $Tp'W(O)_2Cl$ (10.50 g, 0.91 mmol) in 125 ml THF, 1 equivalent of PhCHMgBr (0.46 ml of 2 M THF solution) was added by cannula under argon. The slurry became progressively more green as the solids gradually dissolved. After 12 h, the solution was dark orange-brown with a flocculant white precipitate. The THF was removed under reduced pressure, and the product was extracted into toluene and filtered through Celite[®] filtering aid to remove magnesium salts. Removal of toluene under reduced pressure gave a pale tan solid, which was recrystallized from dichloromethane at -20 °C. Yield 0.38 g (69%), m.p. 180 °C in air (decomp.). ¹H NMR (CDCl₃): δ (ppm) = 7.48 (2H, d, ortho-benzyl H's); 7.33 (2H, t, meta-benzyl H's); 6.96 (1H, t, para-benzyl H); 5.97, 5.87 (2:1H, s, Tp' ring H's); 3.19 (2H, s, PhCH₂W); 2.92, 2.58, 2.43, 2.36 (6:3:6:3 H's, s, Tp' Me's). ¹³C NMR (CDCl₃): δ (ppm) = 153.65, 153.30, 148.82, 147.27 (Me substituted Tp' ring C's); 144.45 (*ipso*-benzyl C); 129.25, 127.88, 124.08 (benzyl C's); 108.01, 107.48 (Tp' unsubstituted ring C's); 60.10 (WCH₂Ph); 15.59, 15.32, 12.66, 12.55 (Tp' Me's). IR (Nujol): ν (cm⁻¹) = 2549 (B–H, ws); 957, 916 (W=O, ms, ss). MS (C.I.): M⁺ = 605.202. Elem. anal.: calc. for C₂₂H₂₉BN₆O₂W: C, 43.73; H, 4.84; N, 13.91; found: C, 43.34; H, 4.95; N, 13.50.

Metathesis studies of Tp'W(CHPh)(NPh)Br (4c)

(a) 4c and 1,9-decadiene (1:10) were combined in an NMR tube with toluene- d_8 . No change in the ¹H NMR spectrum was observed after heating the sample for 12 h at 90 °C. 30 min after the addition of 1 equivalent AlCl₃, a peak at 5.27 ppm was observed in the ¹H NMR spectrum, corresponding to ethylene. After 18 h, the amount of ethylene had increased and a peak had appeared at 5.42 ppm, corresponding to internal olefinic protons. The sample was cooled to -78 °C, the pressure in the tube was reduced and the sample was warmed to 25 °C (¹H NMR indicated removal of ethylene). This evacuation procedure was repeated periodically over a period of 68 h, after which time the ratio of terminal to internal olefins was about 4:1. Warming the sample to 90 °C for 2 h resulted in conversion to a 2:1 ratio of terminal to internal olefins. Heating for a further 10 h gave a ratio approaching 1:1.

(b) 4 ml (3 g, 22 mmol) 1,9-decadiene, 4c (0.04 g, 0.054 mmol; 400:1) and AlCl₃ (0.01 g, 0.07 mmol) were combined in a Schlenk tube with a stir bar. The pressure in the tube was reduced and the mixture was warmed to 85 °C. The temperature was maintained between 80 and 90 °C for 3 days, with the vacuum being refreshed periodically. ¹H NMR analysis of the product mixture indicated about 30% conversion to oligomers. Removal of the 1,9-decadiene under reduced pressure left a mixture of dimer and trimer in a 7:4 ratio. The presence of internal olefins and absence of vinyl addition products was confirmed by ¹³C NMR.

Acknowledgement

We acknowledge the National Science Foundation (DMR-8912026) and the Shell Development Company for their financial support of this research.

References

1 K. B. Wagener, J. M. Boncella, J. G. Nel, R. P. Duttweiler and M. A. Hillmyer, Makromol. Chem., 191 (1990) 365.

- 2 K. B. Wagener, J. G. Nel, J. Konzelman and J. M. Boncella, Macromolecules, 23 (1990) 5155.
- 3 K. B. Wagener, J. M. Boncella and J. G. Nel, Macromolecules, 24 (1991) 2649.
- 4 G. Odian, Principles of Polymerization, Wiley, New York, 1981, pp. 40-179.
- 5 R. R. Schrock, R. T. DePue, J. Feldman, C. J. Schaverien, J. C. Dewan and A. H. Liu, J. Am. Chem. Soc., 110 (1988) 1423.
- 6 R. R. Schrock, R. T. DePue, J. Feldman, K. B. Yap, D. C. Yang, W. M. Davis, L. Park, M. DiMare, M. Schofield, J. Anhaus, E. Walborsky, C. Krüger and P. Betz, Organometallics, 9 (1990) 2262.
- 7 R. R. Schrock, J. S. Murdzek, G. C. Bazar, J. Robbins, M. DiMare and M. O'Regan, J. Am. Chem. Soc., 112 (1990) 3875.
- 8 L. L. Blosch, K. Abboud and J. M. Boncella, J. Am. Chem. Soc., 113 (1991) 7066.
- 9 R. R. Schrock, J. Sancho and S. F. Pedersen, Inorg. Synth., 26 (1990) 50.
- 10 A. Mayr and G. A. McDermott, J. Am. Chem. Soc., 108 (1986) 548.
- 11 K. B. Wagener and M. L. Hamberg, Macromolecules, 20 (1987) 2949.
- 12 J. M. Boncella and K. B. Wagener, unpublished results.
- 13 S. Trofimenko, J. Am. Chem. Soc., 89 (1967) 3170.