Aryloxide ligand modification: new classical catalytic systems for olefin metathesis

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Abstract

The AM1-calculated partial oxygen charge of several phenoxide anions, potential ligands for tungsten-based classical catalytic systems for olefin metathesis, has been used as an indication of their electronwithdrawing ability. Based on the modeled set, a number of bis(aryloxide) derivatives of tungsten (VI) oxychloride have been synthesized by refluxing the parent phenol and $WOCl_4$ in toluene, and we have explored their ability to catalyze various metathesis applications. The studied complexes are precursors to active metathesis catalysts when heated in the presence of Bu_4Sn, and experimental conditions for the catalysis of ring opening metathesis polymerization (ROMP), acyclic diene metathesis (ADMET) polymerization, and ring closing metathesis (RCM) are reported. The catalytic ability of the studied complexes cannot be predicted based on a single structural or electronic parameter since ligand substitution also seems to affect other features such as solubility and chemical stability of the complex. Crystal data for bis(2,4,6-tribromophenoxy)tungsten (VI) oxychloride (**7**): Space group: P_1, triclinic. $a = 7.8459(5)$ Å, $\alpha = 94.100(1)°$, $b = 8.8504(5)$ Å, $\beta = 92.687(1)°$, $c = 14.2994(9)$ Å, $\gamma = 95.359(1)°$, $V = 984.64(10)$ Å^3, $R_1 = 0.0258$ and $wR_2 = 0.0628$. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Olefin metathesis continues to emerge as an exciting and useful tool for scientists in many disciplines. New applications and developments are parallel to the exploration and understanding of the properties of novel catalytic systems [1,2].

At the same time, several attractive applications in new fields such as asymmetric ring closing or the synthesis of biologically important molecules are a constant motivation for research on new catalysts structures, mainly concentrated on rational catalyst design of well-defined systems. A series of convenient synthetic procedures are available today, and catalyst modification can be achieved with ease through the choice of an appropriate ligand set [3–7].

Although most of the developments in acyclic diene metathesis (ADMET) polymerization have been accomplished using well-defined catalysts,

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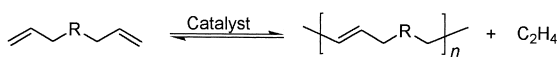 *E-mail address:* wagener@chem.ufl.edu (K.B. Wagener).

Fig. 1. General scheme for ADMET polymerization.

Fig. 3. Structures of three aryloxide tungsten precatalysts for ADMET polymerization.

we continue to investigate ill-defined (*classical*) catalytic systems in an effort to delineate effective relationships among the properties of the catalysts used, including catalytic activity. Such exploration should be the basis of the optimization of various synthetic methodologies involving olefin metathesis and especially the synthesis of unsaturated polymers using ADMET chemistry. In brief, ADMET polymerization can be described as a step-propagation condensation-type polymerization that produces an unsaturated polymer from terminal dienes. Ethylene is produced in every propagation step as the condensate, and its removal shifts forward the equilibrium shown in Fig. 1 ensuring the formation of a high molecular weight polymer [8,9].

ADMET polymerization is a virtually thermoneutral equilibrium process usually run under bulk conditions. Because of this, phase transitions from liquid monomer to solid polymer are common in ADMET chemistry. Only the most active and resistant (both chemically and thermally) metathesis catalysts can be employed in ADMET chemistry. Well-defined systems such as Schrock-type alkylidenes (e.g. **1**) or Grubbs-type ruthenium carbenes (**2**) have been used in most of the developments in ADMET chemistry because of the high activities displayed by both systems [9].
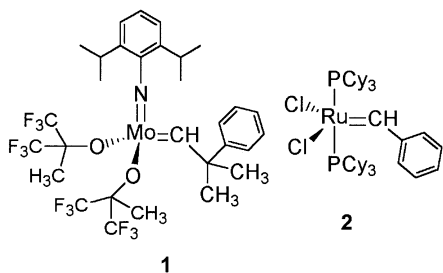
As an alternative to well-defined systems, we demonstrated that classical systems based on certain aryloxide complexes of tungsten (**3–5**) could also catalyze the synthesis of ADMET polymers when activated by some organotin compounds, and this methodology is now used in the synthesis of hydrocarbon and functionalized polymers via ADMET [10,11].

Some of the advantages exhibited by precatalysts **3–5** are their ease of synthesis and — in some cases — their remarkable thermal stability. These features as well as their high functionality tolerance have been shown in other metathesis applications. Some of these characteristics continue to attract our attention, and we have explored them and their implications on ADMET polymerization (Figs. 2 and 3).

2. Experimental

2.1. Instrumentation and analysis

^{1}H (300 MHz) and ^{13}C NMR (75 MHz) spectra were run in either a Varian VXR-300 or a Varian Gemini-300 superconducting spectrometer system in CDCl$_3$ and are referenced to internal tetramethylsilane (0.05% v/v). ^{19}F NMR (282 MHz) spectra were run in a Varian VXR-300 superconducting spectrometer system in CDCl$_3$ and are referenced to internal CFCl$_3$ (0.05% v/v). Gel permeation chromatography analysis were performed in a Waters Associates model 590 chromatograph using either THF or

Fig. 2. Structures of two well-defined olefin metathesis catalysts.

chloroform as the eluent (1.0 ml/min). A UV–Vis (operating at 254 nm)/refractive index dual detector system was employed, and all molecular weight data are reported based on calibration with polystyrene standards. Gas chromatography analyses were performed in a Shimadzu GC-17A gas chromatograph, equipped with a 15-m, Hewlett-Packard HP5 (5% cross-linked phenylmethylsilicone) column.

2.2. Semi-empirical calculations

All calculations were performed using Hyperchem Pro release 5.1 for Windows [12]. Charge data were extracted from AM1 calculations on the phenoxide anion (singlet multiplicity declared in all cases) following an initial geometry optimization routine of the parent phenol using the MM + force field module.

2.3. Materials and techniques

All manipulations were performed under dry argon using standard Schlenk or drybox techniques unless specified. The purification of solvents was performed as described elsewhere [13]. 1,9-Decadiene (Aldrich Chemical) was distilled, dried over CaH_2, degassed by several freeze–pump–thaw cycles, stirred overnight on a potassium mirror and vacuum transferred to a flask containing 4 Å molecular sieves. Commercial grade dicyclopentadiene (DCPD) was purified by sublimation of the low boiling impurities under constant reduced pressure (9–10 cm Hg) for ca. 45 min, followed by addition of 4 Å molecular sieves under an argon atmosphere [14]. BHT (2,6-di-tert-butyl-4-methylphenol), α-ionone, tetrabutyltin, 2,6-dibromophenol, 2,4,6-tribromophenol, 2,6-dibromo-4-fluorophenol, 2,6-dibromo-4-nitrophenol, 3,5-dibromo-4-hydroxybenzonitrile, tungsten (VI) chloride, and tungsten (VI) oxychloride were purchased from Aldrich Chemical and used without further purification. The synthesis of complex **6** was performed as previously reported [20].

2.3.1. Synthesis of trans-bis(2,4,6-tribromophenoxy)tungsten (VI) oxychloride (7)

The synthesis of the title complex and analogues was performed by following slight modifications of the method published by Nugent et al. [15] for the synthesis of the parent complex **3**. A solution of 2,4,6-tribromophenol (3.82 g, 11.55 mmol, 1.96 equiv.) in 40 ml of anhydrous toluene was added to a solution of tungsten (VI) oxychloride (2.01 g, 5.88 mmol, 1.00 equiv.) in 40 ml of anhydrous toluene placed in a 250-ml Schlenk flask, and the resulting dark purple solution was refluxed under argon for 14 h. Removal of the solvent in vacuo yielded a dark purple/black solid. Dry CH_2Cl_2 (40 ml) was used to dissolve the solid, but only partial dissolution was observed after filtration. The filtered solid (3.89 g, 71%) was characterized as the expected product. Addition of a layer of n-pentane to the filtrate, and storage at $-30°C$ for 40 days afforded X-ray quality single crystals. ^{1}H NMR ($CDCl_3$) δ (ppm) = 7.60 (s). Anal. Calcd for $C_{12}H_4Br_6Cl_2O_3W$: C, 15.49; H, 0.43. Found: C, 15.24; H, 0.38.

Single crystal X-ray diffraction data were collected at 173 K on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å). Cell parameters were refined using 6813 reflections. A hemisphere of data (836 frames) was collected using the ω-scan method (0.3° frame width). The first 50 frames were re-measured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was $< 1\%$). Psi scan absorption corrections were applied based on the entire data set. The structure was solved by the Direct Methods in SHELX97, and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. A total of 218 parameters were refined in the final cycle of refinement using 3826 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 2.58% and

Table 1

Crystal data and structure refinement for complex **7**

Empirical formula	$C_{12}H_4Br_6Cl_2O_3W$
Formula weight	930.36
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P_1
Unit cell dimensions	$a = 7.8459(5)$ Å, $\alpha = 94.100(1)°$
	$b = 8.8504(5)$ Å, $\beta = 92.687(1)°$
	$c = 14.2994(9)$ Å, $\gamma = 95.359(1)°$
Volume	984.64(10) Å^3
Z	2
Density (calculated)	3.138 Mg/m^3
Absorption coefficient	18.320 mm^{-1}
$F(000)$	836
Crystal size	$0.16 \times 0.19 \times 0.23$ mm^3
Theta range for data collection	1.43° to 27.50°
Index ranges	$-10 \leq h \leq 9$, $-10 \leq k \leq 11$, $-17 \leq l \leq 18$
Reflections collected	6813
Independent reflections	4417 [$R_{int} = 0.0181$]
Completeness to $\theta = 27.50°$	97.5%
Absorption correction	Integration
Maximum and minimum transmission	0.129 and 0.039
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4417/0/218
Goodness-of-fit on F^2	0.996
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0258$, $wR_2 = 0.0628$ [3826]
R indices (all data)	$R_1 = 0.0323$, $wR_2 = 0.0647$
Extinction coefficient	0.00135(17)
Largest diff. peak and hole	1.537 and -1.000 e. Å

6.28%, respectively. Refinement was done using F^2 (Tables 1 and 2).

2.3.2. Synthesis of trans-bis(2,6-dibromo-4-(trifluoromethyl)phenoxy)tungsten (VI) oxychloride (8)

In an argon-purged drybox, tungsten (VI) oxychloride (1.02 g, 2.98 mmol, 1.0 equiv.) was charged to a 150-ml Schlenk flask, and dissolved in 10 ml of anhydrous toluene. The flask was sealed and taken to a Schlenk line, where a condenser was attached. A solution of 2,6-dibromo-4-(trifluoromethyl)phenol (1.90 g, 5.94 mmol, 1.99 equiv.) in 15 ml anhydrous toluene was then added via cannula, and the resulting mixture was refluxed for 48 h under argon. Removal of the solvent in vacuo afforded a dark red solid. Recrystallization of the title complex

was performed using *n*-pentane at $-30°$C. The combined yield after three attempted recrystallizations was 1.46 g (54%). X-ray quality single crystals were grown from concentrated CH_2Cl_2/toluene solutions in a drybox at $-30°$C. ^{1}H NMR (CDCl$_3$) δ (ppm) = 7.89 (s). ^{19}F NMR (CDCl$_3$) δ (ppm) = -62.9 (s). Anal.

Table 2

Selected bond lengths (Å) and angles (°) for complex **7**

Bond lengths (Å)		Bond angles (°)	
W−O1	1.684(4)	C1−O2−W	140.5(3)
W−O2	1.888(3)	C7−O3−W	159.2(3)
W−O3	1.859(3)	O1−W−O3	102.9(3)
W−Cl1	2.3104(13)	O1−W−O2	99.4(8)
W−Cl2	2.3302(13)	O2−W−O3	157.3(6)
W−Br1	3.149(3)	O1−W−Cl1	101.5(0)
O2−C1	1.349(6)	Cl1−W−Cl2	157.2(6)
O3−C7	1.345(6)	O2−W−Br1	75.3(3)

Calcd for $C_{14}H_4Br_4Cl_2F_6O_3W$: C, 18.51; H, 0.44. Found: C, 18.99; H, 0.58.

2.3.3. Synthesis of trans-bis(2,6-dibromo-4-cyanophenoxy)tungsten (VI) oxychloride (**9**)

In an argon-purged drybox, tungsten (VI) oxychloride (2.00 g, 5.85 mmol, 1.0 equiv.) was charged to a 250-ml Schlenk flask, and dissolved in 40 ml of anhydrous toluene. The flask was sealed and taken to a Schlenk line, where a condenser was attached. A solution of 3,5-dibromo-4-hydroxybenzonitrile (3.41 g, 12.31 mmol, 2.10 equiv.) in 100 ml of a 1:2 mixture of anhydrous toluene/ether was then added via cannula, and the resulting mixture was heated to 60°C for 4 h under an argon stream to ensure slow evaporation of the diethyl ether. The solution was then refluxed for an additional 48 h. Removal of the toluene in vacuo afforded a red solid. A series of two recrystallizations of the title complex in CH_2Cl_2/n-pentane at $-30°C$ afforded 3.19 g (66%) of a red microcrystalline solid. Attempts to obtain X-ray quality crystals turned futile. ^{1}H NMR δ (ppm) = 7.92 (s). Anal. Calcd for $C_{14}H_4Br_4Cl_2N_2O_3W$: C, 20.44; H, 0.49; N, 3.41. Found: C, 18.92; H, 0.69, N, 3.02.

2.3.4. Synthesis of trans-bis(2,6-dibromo-4-nitrophenoxy)tungsten (VI) oxychloride (**10**)

In an argon-purged drybox, tungsten (VI) oxychloride (2.01 g, 5.86 mmol, 1.0 equiv.) was charged to a 250-ml Schlenk flask, and dissolved in ca. 50 ml of anhydrous toluene. The flask was sealed and taken to a Schlenk line, where a condenser was attached. A solution of 2,6-dibromo-4-nitrophenol (3.41 g, 11.49 mmol, 1.96 equiv.) in 30 ml anhydrous toluene was then added via cannula, and the resulting mixture was refluxed for 48 h under argon. During this time, precipitation of a black microcrystalline solid occurred along with a slight decoloration of the solution. The solid was isolated by cannula filtration and washed twice with anhydrous pentane (2×25 ml). The resulting solid was virtually insoluble in halogenated and aromatic solvents at room temperature. Anal. Calcd for $C_{12}H_4Br_4Cl_2N_2O_7W$: C, 16.71; H, 0.47; N, 3.25. Found: C, 18.33; H, 0.99, N, 2.34.

2.3.5. ADMET polymerization of 1,9-decadiene

Hydrocarbon dienes such as 1,9-decadiene were polymerized following the general methodology described in our previous work [10]. In an argon-purged drybox, a mixture of the monomer (500 equiv. unless specified), precatalyst (1 equiv.) and activator (2.5 equiv.) were charged to a round bottom flask equipped with a high vacuum Kontes™ valve and a magnetic stirbar. The flask was sealed, taken to a Schlenk line, and heated to 90°C under a slow argon stream. After a significant increase in the mixture viscosity and during the first 2–3 h, short exposures to vacuum were performed until continuous vacuum was ensured for the remaining of the reaction, which was stopped when ethylene evolution ceased. The polymer was purified by dissolution of the crude mixture in $CHCl_3$, passage through a short pad of celite, precipitation of the $CHCl_3$ solution into cold, stirring methanol. All polymer samples were dried under vacuum at room temperature for ca. 48 h, and high yields (75–91%) of polymer were obtained in all cases. The polyoctenylene samples were characterized by conven-

Table 3
Acyclic diene metathesis polymerization of 1,9-decadiene

Complex	[W] mol.%[a]	M_n (NMR)[b,c]	M_n (GPC)[c,d]	PDI[d]
7	0.2	2300	6400	2.71
8	0.2	*neg*	11,300	2.11
9	0.4	1500	–	–

[a]Concentration with respect to monomer. Bulk polymerization at 85°C, $[Bu_4Sn] = 2.5 \times [W]$.

[b]Calculated via end-group analysis from ^{1}H NMR data, by integrating the signals corresponding to the terminal vinyl groups vs. internal olefin.

[c]Differences between number average molecular weight data calculated from NMR and GPC arise from the use of polystyrene standards in the calibration procedure.

[d]Determined by gel permeation chromatography in chloroform (see Experimental) using polystyrene standards.

tional methods and the results are summarized in Table 3.

2.3.6. Ring opening metathesis polymerization (ROMP) of DCPD

Solution polymerization of DCPD experiments were conducted as follows: A solution of the tungsten precatalyst and the organotin activator in anhydrous toluene was heated to 85°C. After 5–10 min, a 2-M solution of DCPD was added via syringe. Immediate gelation was observed in all cases, and the polymer was purified by addition of methanol to the swollen polymer in hot toluene. The polymer was dried in a vacuum oven (50°C) for 48 h until constant weight was obtained. Yields were almost quantitative in all cases although gas chromatography revealed the presence of small amounts (not determined) of DCPD in the combined extracts.

Bulk polymerization of DCPD was conducted by warming up DCPD (35–40°C) in glass vials, and adding the corresponding amount of precatalyst and cocatalyst directly to the liquid monomer. Heating of the resulting mixture for 6–24 h to ca. 90°C afforded solid, cross-linked polydicyclopentadiene which was not characterized.

2.3.7. ROMP of norbornene

A solution of precatalyst (1.0 equiv.) and activator (2.5 equiv.) in anhydrous toluene was heated to 85°C in a Schlenk flask equipped with a rubber septum and a magnetic stirbar under an argon atmosphere. After 5–10 min, a 2-M solution of norbornene (100 equiv. monomer) was added to the original mixture via syringe and an immediate color change could be observed along with an increase in the mixture viscosity. The polymerizations were stopped after 15 min for comparison of molecular weights at less than 100% conversion by the addition of methanol containing a small amount of BHT to the reaction mixtures. The solid polymers were decanted, re-dissolved in $CHCl_3$, filtered through a pad of celite, precipitated into methanol-BHT and dried under vacuum at room temperature.

Spectral data for all polynorbornene samples obtained in our study matched the reported literature values [1]. Molecular weight data obtained from gel permeation chromatography are shown in Fig. 9.

2.3.8. Ring closing metathesis (RCM) of diethyl diallylmalonate

A solution of precatalyst (1.0 equiv.) and activator (2.5 equiv.) in anhydrous toluene was heated to 85°C in a Schlenk flask equipped with a rubber septum and a magnetic stirbar under an argon atmosphere. After 5–10 min, neat diethyl diallylmalonate (25 equiv. unless specified) was added via syringe and the resulting mixture (1 M in diene) was stirred for and additional 4 h or until gas chromatography suggested a constant substrate to product ratio. The mixture was then cooled to room temperature and passed through a pad of celite. Removal of the solvent in vacuo afforded crude product, and no further purification was performed. Substrate to product ratios were found by cross-correlation of gas chromatography (using α-ionone as internal standard) and ^{1}H NMR data (through the integration of allylic methylene groups in both product and starting material).

3. Results and discussion

One of the most attractive properties of tungsten aryloxide complexes is the possibility of correlating the properties of the resultant catalyst through the modification of the aryloxide (or alcoxide) ligand present in the precatalyst. This is a feature previously addressed for both classical [16–18] and well-defined systems [19] and to a certain extent, the influence of these modifications on activity has been established.

Quignard et al. [17] established a correlation between the identity (size and electronwithdrawing ability) of the phenol substituent and the catalyst activity in acyclic olefin metathesis for a series of $WCl_4(OAr)_2$-based systems. Along
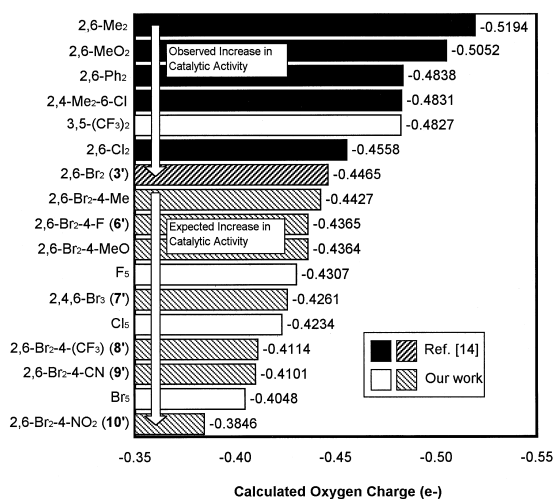
Fig. 4. AM1-Calculated oxygen charge for a series of phenoxide anions.

the same lines, Bell [16] established a correlation between the AM1-calculated charge on the ligand oxygen, and the experimental reduction potential for a series of $WOCl_2(OAr)_2$ systems. This correlation could be extrapolated to include the activity of the catalytic systems made upon activation and suggests an increase on catalytic activity as the result of an increase in the electronwithdrawing ability of the ligand.

During our initial experiments with classical systems as catalysts for ADMET polymerization, we explored aryloxide derivatives of tungsten (VI) oxychloride and tungsten (VI) chloride 3–5. Based on our early observations and following the pioneering approaches of Basset and Bell, we started a study on the former group through the modeling of a complementary series of phenoxides which can be used in the synthesis of systems of the type $WOCl_2(OAr)_2$. The appended results are shown in Fig. 4, and complement the preliminary results of our study [20].

Within the modeled set, the derivatives of 2,6-dibromophenoxide bearing a substituent on the *para* position are represented by the patterned columns. These potential ligands were chosen in light of the possibility of further

correlation of the complexes properties with the substituent Hammet constant, σ.

3.1. Synthesis of complexes 7–10

Complexes **7**–**10** were synthesized in a straightforward manner following the general procedure reported by Nugent et al. [15], which consists of refluxing $WOCl_4$ with the corresponding phenol in toluene (see Experimental). Essentially quantitative yields of crude material can be isolated following the removal of the solvent in vacuo, and the crude complex is usually of adequate purity to be used in metathesis chemistry. Complexes **7**–**9** can be purified through recrystallization, whereas complex **10** cannot. It is a black, insoluble powder which has not been included in our comparative experiments (Fig. 5).

3.2. Structural characterization

A detailed structural analysis of the parent 2,6-dibromophenoxide complex by Nugent et al. [15] revealed the asymmetry of complex (**3**). A non-bonding interaction between one of the bromine atoms and the metal renders the two aryloxide ligands inequivalent. We observed the same type of interaction in complexes **6** [20] and **7**, and envisioned the possibility of exploring its extent (through comparison of interatomic lengths and angles) as a quantitative parameter for predicting activity in the series (Fig. 5).
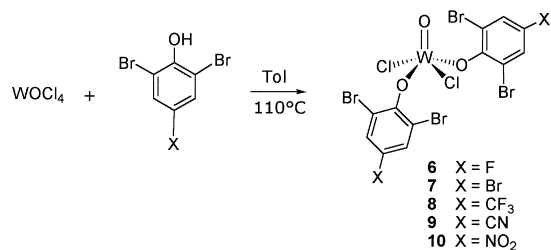

Fig. 5. General synthesis scheme for complexes **6**–**10**.
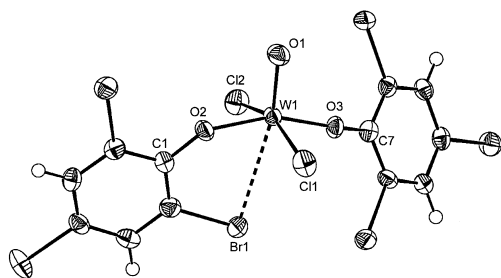
Fig. 6. Molecular structure of **7**, with 50% probability ellipsoids, showing a partial atom numbering scheme.

The structure generated by PLATON [21] from single crystal X-ray diffraction data of complex **7** is illustrated in Fig. 6, showing the inequivalent aryloxide ligands (Fig. 7).

A comparison of complex **7** to the previously reported complex **6** [20], suggests a tighter non-bonding W–Br interaction revealed in a shorter interatomic distance (3.149 vs. 3.206 Å). This feature as well as the angle about O2, (140.5° vs. 141.1° in **6**) implied a correlation between the electronics on the ligand and the solid state structure. A summary of structural data for complex **7** is shown in Table 2.

In contrast, crystallization of complex **8** turned out very difficult due to the high solubility of the complex in non-protic, non-coordinating solvents. A single crystal of low quality was grown from a mixture of CH_2Cl_2/toluene at $-30°C$, and although the amount of disorder found in the structure refinement was very high, X-ray diffraction data reveals interesting structural information. In contrast with complexes **3**, **6** and **7** and to our surprise, the ligand arrangement appears to be symmetrical in complex **8**, and no W–Br interaction can be observed. A view along a Cl–W bond shows the symmetrical arrangement of the ligand set, as well as the square-based pyramidal geometry. This observation suggest that the properties of the complex in the solid state (e.g. bond angles, lengths) cannot be used as an inference parameter for the catalytic activity of the alkylidenes generated therefrom, since the effect of the trifluoromethyl group on the complex electronics is not the only

significant variable influencing its conformation in the crystal.

3.3. ADMET chemistry

In order to explore the polymerizing ability of complexes **7**–**10** and in search of a useful probe for the comparison of their catalytic properties, we have studied the bulk polymerization of 1,9-decadiene. Following the behavior predicted from the study of complex **6** and complementing the range of classical catalysts for ADMET polymerization, we have observed that complexes **7** and **8** efficiently catalyze the condensation polymerization of this and other hydrocarbon dienes such as 1,8-nonadiene. Linear metathesis polymers can be obtained following the general methodology developed in our laboratory [10,20]. In concert with our previous experiments, Bu_4Sn proved again to be a better activator when compared to Bu_3SnH. Furthermore, the use of Bu_3SnH did not lead to an active catalyst when used with complexes **8** and **9**, which repetitively decomposed upon exposure to the standard polymerization conditions.

The ^1H and ^{13}C NMR spectra of a sample of polyoctenylene synthesized using complex **8** and Bu_4Sn are shown in Fig. 8. As demonstrated before for complexes **3**–**5** [10], a high molecular weight polymer is obtained from this polycondensation reaction, and this fact is evidenced in the absence of resonances attributed to vinyl end groups. Furthermore, analysis of the NMR data reveals that no isomerization of the olefin groups has taken place, a competing reaction
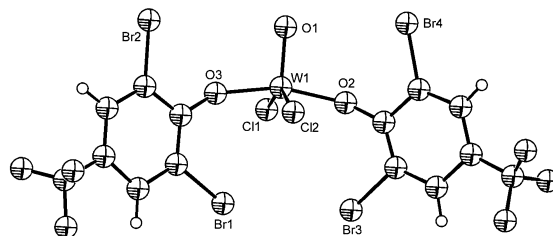

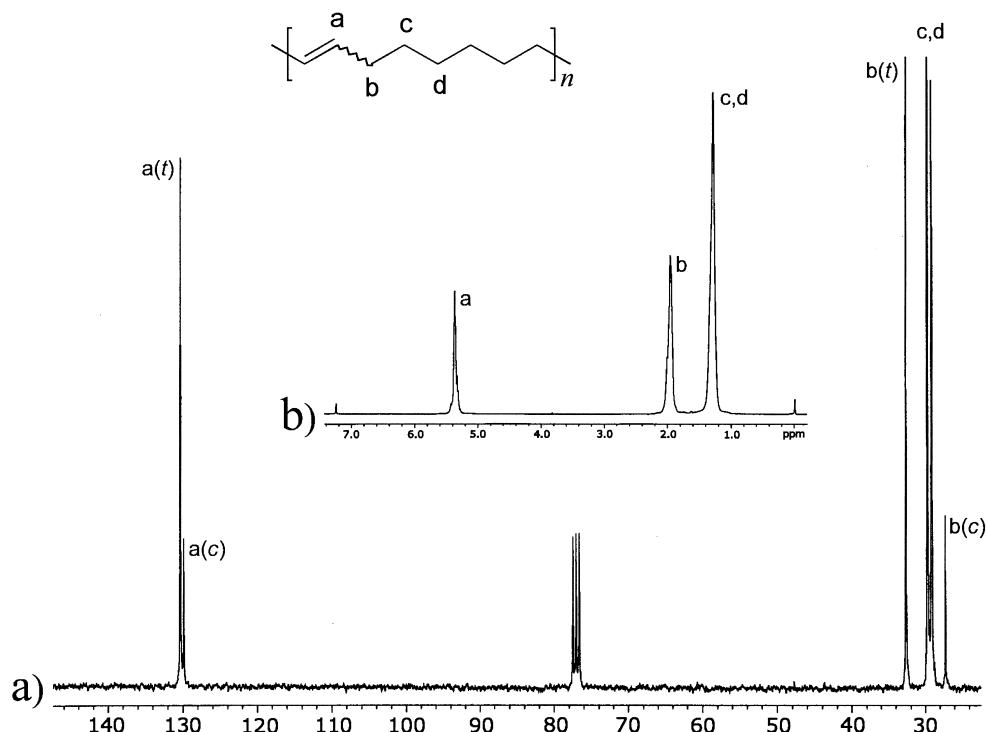Fig. 7. PLATON-generated structure of complex **8**.

Fig. 8. (a) ^{13}C NMR (75 MHz, CDCl$_3$) and (b) ^{1}H NMR (300 MHz, CDCl$_3$) of a polyoctenylene sample synthesized using complex **8** and Bu$_4$Sn.

observed in other metathesis applications of analogous complexes (e.g. **5**) [22,23].

Although no quantitative kinetic measurements have been made on the metathesis reactions catalyzed by systems based on complexes **6**–**9**, qualitative observations reveal two interesting features of the studied systems. The first characteristic is the apparent activity increase in agreement with the expected behavior for complexes (**3**–)**7**–**8** as ADMET catalysts, which seems to be especially evident for complex **8**. This is observed in a shorter induction period prior to ethylene release from the reaction mixture (attributed to the activation step as proposed by Quignard et al. [17]) In addition, the identity of the substituent X in the series affects not only the activity, but also seems to have a dramatic effect on the solubility properties of these complexes. While complex **8** is very soluble in conventional solvents, complex **10** is

virtually insoluble, limiting its usability in AD-MET polymerization and in other metathesis applications. Although limited solubility has also been observed for complex **9** at room temperature, the complex is useful at the experimental polymerization conditions. The solubility behavior of the complexes described may also account for a low percentage conversion in the case of complexes **7** and **9**, for which faster decomposition kinetics with respect to complex **8** prevents the formation of high molecular weight polymers.

Also noteworthy, especially while considering the application of this methodology to other metathesis processes, is the fact that along with an increased activity in olefin metathesis, a parallel effect on the reactivity towards polar functionalities is also apparent. This is evidenced in a poor air and moisture-resistance shown in all the complexes studied, a phe-

nomenon that is remarkably evident in complexes **9** and **10**.

3.4. ROMP chemistry

Complementary to the study of complexes **6**–**9** in ADMET polymerization, we have extended our explorations to include complexes **6**–**9** as precatalysts for ROMP. Processes as important as the industrial production of polydicyclopentadiene thermosets are grounded on the use of classical systems [18]. Heating bulk DCPD in the presence of complexes **6**–**9** and Bu_4Sn yields cross-linked PDCPD after a short induction time. Although no efforts have been made to determine the amount of residual monomer or the magnitude of the polymerization exotherm, we have begun to explore the effect of monomer to tungsten complex (M/W) molar ratio. Fast polymerizations have been observed at 5000:1 M/W both under solvent and bulk conditions.

At the same time, linear polynorbornene is obtained upon exposure of a 1-M toluene solution of freshly sublimed norbornene to a mixture of complexes **6**–**9** and Bu_4Sn in toluene at 85°C. The features of other aryloxide systems in the polymerization of norbornene have been previously reported [24,25].

Quantitative conversion of norbornene is required in order to use its ROMP as a probe for comparative catalytic activity among the systems studied. We have observed that in the case of solution polymerizations run for extended times (at W/M ratios of 100:1), catalyst decomposition occurs before the monomer is totally consumed and only lower yields of polymer can be obtained (71–84% purified polymer). Although it is safe to overlook this fact while studying ROMP chemistry, the difference in molecular weights (M_p) can be attributed to differences in either the propagation rates or the extent of activation, and we are still unable to determine which factor is more significant for the studied series. While stronger alkylating agents such as alkylaluminum or alkyllead compounds are needed for the conversion of analogous systems bearing less electronwithdrawing phenoxide ligands, milder cocatalysts (e.g. Bu_4Sn) can be used to activate systems in which the metal is made more electropositive [15,17,18]. We anticipate this (vide infra) to be the case for systems **6**–**9** which, having a similar affinity for norbornene differ in the amount of actual catalyst formed, not in their propagation kinetics. This would determine the number of growing chains and have a clear effect on the molecular weights observed among the series. In order to test this assumption, the formation of polynorbornene at short polymerization times should reveal features of the initiation (or activation in our case) and propagation. The GPC traces shown in Fig. 9 belong to the solution polymerization of norbornene stopped after 15 min, before catalyst decomposition becomes apparent and before any secondary processes take place. Monomodal molecular weight distributions were found in all cases and the polydispersities found ranged from 1.8 to 3.3. An increasing PDI value in the series **8**–**7**–**6** suggests that the availability (concentration and rate of formation) of initiating species varies based on the ligand substituent, affecting the properties of the polymers obtained. The largest PDI value was found in the case of complex **9**; this observation was attributed to an inefficient initiation step, in agreement with other metathesis processes. It is noteworthy that if a constant extent of activation
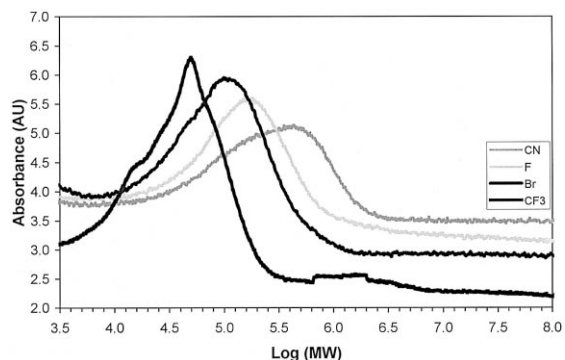

Fig. 9. GPC traces of four polynorbornene samples synthesized using complexes **6**–**9**.

and similar initiation kinetics were to be assumed for all four complexes, then the overall propagation constants extrapolated from differences in the molecular weights would still fall within the same order of magnitude. The effect of substitution on the conversion kinetics has been subject to further exploration using a more sensitive probe based on RCM chemistry.

3.5. Ring closing metathesis

The behavior and applicability of the complexes reported herein as precatalysts for RCM was also explored. Our findings suggest that while complexes **6**–**8** effectively catalyze the RCM of diethyl diallylmalonate, complex **9** decomposes before any significant conversion of the starting material occurs (Table 4). Our experimental methodology consists in the introduction of the olefin after 5 min of interaction of the W complex with Bu_4Sn at the activation temperature (90°C), and monitoring the reaction by GC and NMR spectroscopy.

The results shown in Table 4 are in concert with the observed behavior of complexes **6**–**9** in both ADMET and ROMP chemistry, for they suggest that the identity of substituent X seems to affect not only the electronics of the complex (both in activity and chemical stability) but also its solubility. At the same time, the increased chemical sensitivity of complexes **6**–**9** with respect to their parent, non-substituted complex **3**, can be observed in the substrate to precatalyst

ratio (S/W) required to drive the reaction to excellent yields. While complex **3** has been reported to yield the cyclic diester in 86% after 1 h at 90°C, the use of complex **8** only afforded the product in similar yields (89%) when for longer periods of time (ca. 4 h). Carrying out the reaction at lower S/W ratio and lower concentration (0.25 M) resulted in very high percent conversion (Table 4, entry 4). Attempts to carry out the reaction using the same conditions reported for **3** and Et_4Pb [15], derived in a 47% conversion (NMR) after 60 min, and 50% (NMR) after 90 min. Although this decreased conversion could be attributed to a faster decomposition of the alkylidene formed upon activation, we believe it reflects the lower extent of activation achieved with Bu_4Sn when compared to Et_4Pb. A systematic exploration of activation time, Lewis bases as catalyst stabilizers, and very especially the effect of the solvent in both RCM and acyclic olefin metathesis catalyzed by complexes **6**–**9** is the subject of our current investigations, and will be reported in a following account.

4. Conclusions

We have designed, synthesized, and investigated the properties of a series of tungsten complexes in the catalysis of various olefin metathesis processes. Complexes **7**–**9** catalyze the ADMET polymerization of hydrocarbon dienes, the ring opening polymerization of norbornene and DCPD, and — to some extent — the RCM of diethyl diallylmalonate. An exploration of catalysis conditions in the above mentioned processes reveals that substitution of the aryloxide ligand causes a modification of the electronics of the complexes, evidenced not only in qualitative differences in catalytic activity, but also in the chemical stability and the solubility behavior exhibited by the studied complexes. Although initially considered as a possible tool in the prediction of the physicochemical behav-

Table 4
RCM of diethyl diallylmalonate

Complex	Conditions[a]	%C 90 min[b]	%C Final[b]
6	[S] = 1 M, [S]/[W] = 25	51 (46)	86 (88)
7	[S] = 1 M, [S]/[W] = 25	37 (–)	54 (49)
8	[S] = 1 M, [S]/[W] = 25	57 (50)	89 (90)
8	[S] = 0.25 M, [S]/[W] = 12.5	74 (71)	94 (92)
9	[S] = 1 M, S/W = 25	< 10 (–)	29 (19)

[a] Toluene, 85°C, $[Bu_4Sn] = 2.5 \times [W]$, 5-min activation time.
[b] Determined by gas chromatography (see Experimental) using α-ionone as internal standard. Values in parenthesis were extracted from ^1H NMR data by integrating the signals corresponding to the allylic methylene group of product and diene.

ior of complexes **3,6–10**, structural analysis show that the observation of properties in the solid state cannot be associated with features such as catalytic activity. We encourage our colleagues in the field of olefin metathesis to explore complexes **7–9** in other metathesis applications.

Acknowledgements

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