

Investigations on fluorinated aryloxy tungsten-based catalytic systems for acyclic diene metathesis polymerization¹

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Abstract

The synthesis of two new WOCl_4 derivatives that contain fluorinated aryloxy ligands are reported, along with a description of their behavior as precatalysts in the metathesis polymerization of hydrocarbon dienes and cycloolefins. Crystal data for *trans*-bis(2,6-dibromo-4-fluorophenoxy)tungsten (VI) oxychloride (**4**): Space group $P2_1/c$, monoclinic, $a = 15.1172$ (2) Å, $b = 7.9837$ (1) Å, $c = 16.6186$ (1) Å, $\beta = 112.7430$ (10)°, $V = 1849.77$ (4) Å³. $R_1 = 0.0240$ and $wR_2 = 0.0598$. Complex **4** catalyzes olefin metathesis when activated by Bu_4Sn or Bu_3SnH at 85 and 65°C respectively. Bis(pentafluorophenoxy)tungsten (VI) oxychloride (**5**) decomposes when exposed to the same experimental conditions. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

In recent years we have demonstrated that acyclic diene metathesis (ADMET) can provide access to polymeric materials bearing a wide variety of functionalities, and most of these developments have been achieved using molybdenum [1–5] or ruthenium [6,7] well-defined alkylidenes as catalysts. More recently, we have found that aryloxy tungsten complexes **1–3** can also cleanly catalyze the bulk ADMET polymerization of hydrocarbon and functional-

ized α, ω -dienes when an appropriate activator is chosen [8,9], overcoming the difficulties associated with the high Lewis acidity of the initially explored classical systems [10,11]. These complexes, widely used in other metathesis applications [12–18], provide an alternative to the well-defined catalysts and offer advantages based on their low cost, relative ease of preparation, and in some cases, high air and temperature resistance (Fig. 1).

The most significant advantage exhibited by tungsten aryloxides is found in their availability. Essentially quantitative yields of the desired aryloxy complex are obtained when the stoichiometry of its synthesis is appropriately controlled. Because of the high-yielding synthesis we, as well as others [15], have found that

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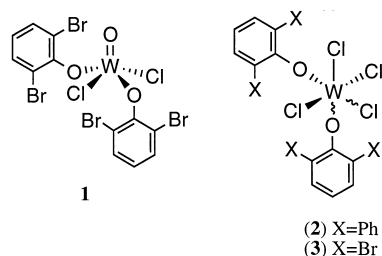


Fig. 1. Structures of complexes 1–3, previously reported as ADMET active catalysts [8].

further purification of the crude reaction mixtures is not a requirement in some cases. The elimination of tedious purification steps makes of these complexes the catalytic system of choice in a number of applications.

These features have prompted us to explore further the behavior of other aryloxy tungsten-based systems, especially those derived from fluorinated phenols, and to study the effect of fluorination on the catalytic activity and other physicochemical properties of the catalysts generated therefrom. The preliminary results of this study are described herein.

2. Experimental

2.1. General procedures and materials

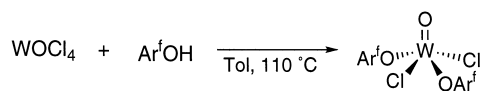
All manipulations were performed employing typical Schlenk techniques. Toluene and pentane were purified by distillation from Na/K alloy, while CaCl_2 was used in the case of chlorinated solvents. Diethyl ether and 1,2-dimethoxyethane were distilled from benzophenone sodium ketyl solutions. Hydrocarbon olefins were purified (> 99.9% purity) by fractional distillation from CaH_2 , stirring over a potassium mirror, and several freeze-pump-thaw cycles followed by a final vacuum transfer to a Rotaflo flask. WCl_6 , WOCl_4 , 2,6-dibromo-4-fluorophenol, and pentafluorophenol were purchased from Aldrich Chemical and used as received (Scheme 1).

2.2. Synthesis of $\text{WOCl}_2(\text{OAr}^f)_2$

Bis(2,6-dibromo-4-fluorophenoxy)tungsten(VI) oxychloride (**4**) and bis(pentafluorophenoxy)tungsten(VI) oxychloride (**5**) were synthesized following the procedure previously published by Nugent et al. [16]. A mixture of WOCl_4 and the corresponding phenol in dry toluene, was heated to reflux for a given period of time (see below). Evaporation of the toluene afforded crude material, which was in some cases of appropriate purity for the studied reactions. Recrystallization from CH_2Cl_2 layered with *n*-pentane at -15°C afforded analytically pure **4**, while a second recrystallization from CH_2Cl_2 : toluene (1:4) was attempted for complex **5**. $\text{WOCl}_2(\text{O}-2,6\text{-Br}_2\text{-4-F-C}_6\text{H}_2)_2$ (**4**): Refluxed for 6 h. Yield: 66%. $^{19}\text{F-NMR}$ δ (ppm): -110.2 (t, $J = 9.2$ Hz). $\text{WOCl}_2(\text{O-C}_6\text{F}_5)_2$ (**5**): Refluxed for 72 h. Yield: 42%. $^{19}\text{F-NMR}$ δ (ppm): -151.74 (d, $J = 14.7$ Hz, 2 F, *o*); -155.29 (t, $J = 19.2$ Hz, 1 F, *p*); -161.27 (m, 2 F, *m*).

2.3. ADMET polymerization of 1,9-decadiene with complexes **4** and **5**

All ADMET polymerizations were performed following the previously reported procedure for aryloxy-tungsten based systems [8]. A rotaflo flask equipped with a magnetic stirrer is charged with 1,9-decadiene (250–400 equiv.), the tungsten complex (1 equiv.) and Bu_4Sn or Bu_3SnH (2 equiv.). This mixture is heated to 85°C under a steady argon flow until viscosity increase becomes evident. After this point, exposure to vacuum (for ethylene removal) is provided to achieve high molecular weights, and the polymerization is run until no further ethylene evolution is observed or until agitation becomes impossible. The polymers are purified by disso-



Scheme 1.

lution in CHCl_3 or toluene, precipitation into methanol and drying under vacuum at 50°C for at least 24 h.

2.4. ROMP of DCPD with complexes **4** and **5**

All ROMP polymerizations were conducted as based on the independent studies performed by Bell [12] and Kelsey et al. [13]. A solution of complexes **4** or **5** and DCPD in toluene was combined with a second solution of Bu_3SnH and monomer. This mixture was heated to 60°C for 2 h and poured directly into cold, stirring methanol.

2.5. X-ray analysis

Intensity data for **4** were collected at 173 K on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$). Cell parameters were refined using 8192 reflections. A hemisphere of data (1381 frames) was collected using the ω -scan method (0.3° frame width). The first 50 frames were remeasured 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 [19], 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 3878 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 2.40% and 5.98%, respectively. Refinement was done using F^2 .

2.6. Semi-empirical calculations

All calculations were performed using the CAChe WorkSystem, Release 3.8 [20]. An ini-

tial geometry optimization procedure was carried out using the MM2 force field module. Charge densities on the phenoxide anion atoms were extracted from AM1 calculations

3. Results and discussion

3.1. Aryloxy tungsten complexes and ADMET polymerization

In the last decade, aryloxy derivatives of tungsten (VI) chloride and oxychloride have been used extensively in the synthesis of unsaturated polymers using ROMP chemistry, [12,13] the metathesis polymerization of acetylenes, [17,18] and in the synthesis of carbo- and heterocyclic structures via ring-closing metathesis processes [14–16]. More recently, we have been able to demonstrate that the acyclic diene metathesis (ADMET) polymerization of terminal dienes can also be catalyzed by alkylidenes generated from compounds **1–3** [8]. We not only have found the experimental conditions for the polymerization of hydrocarbon and ester containing dienes, but also several organotin reagents (i.e., Bu_4Sn) that can be used as activators of these complexes in ADMET polymerization. The feasibility of ADMET polymerization catalysis using tungsten aryloxides was expanded to include polycarbostannanes; further, the polymerization of bis(alkenyl)tin dialkyls can be performed without any external activator, making of this process the first metathesis polymerization in which the monomer acts as the activator of the precatalytic system [9].

In light of the possibilities open in terms in ADMET polymerizable functionalities, and based on the significant mechanistic differences between ADMET and ROMP chemistry, [21] higher activities and longer lifetimes of the catalytic species with respect to the classical systems explored to date is highly desirable. With this in mind, we have begun to explore and identify possible active and stable ADMET classical catalysts.

3.2. Prediction of electronic properties

The effect of ring substitution on the activity of the aryloxy complexes in olefin metathesis catalysis has been previously addressed [12,14,17,22]. The results of these investigations reveal an increase in catalytic activity as the aryloxy ligand is made more electron withdrawing (mainly through the incorporation of substituents with different electronic properties to the parent phenol). Bell, as part of his research in DCPD polymerization, modelled a series of phenoxide anions within the catalysts using semiempirical methods and correlated the calculated charge on the phenoxide oxygen with the experimental reduction potential of the metal complex synthesized therefrom. A linear correlation was observed among a series of the complexes grouped by their degree of halogen substitution from WOCl_4 [12]. Using a similar approach, we have explored a complementary series of phenoxides by calculating the electronic charge on the oxygen as a tool for activity prediction. The combined results of his and our work are presented in Fig. 2.

Note that the degree of substitution and the positional placement of fluorinated (and other halogen) substituents has a significant effect on the oxygen charge, and good correlation of this

calculated effect exists with the predicted from their Hammett δ constants. Thus, it is reasonable to state that complexes derived from more electron withdrawing phenoxides should exhibit high activity as metathesis catalysts as well. This observation encouraged us to synthesize complexes **4** and **5**.

3.3. Synthesis and polymerization studies of complexes **4** and **5**

The synthesis of complexes **4** and **5** is carried out in a straightforward manner, and moderate to good yields were obtained after recrystallization (see Section 2).

3.3.1. Bis(2,6-dibromo-4-fluorophenoxy)tungsten(VI) oxychloride (**4**).

The first system studied was complex **4**, obtained as dark red cubes after recrystallization. Upon contact with Bu_4Sn or Bu_3SnH at the appropriate activation temperature, complex **4** catalyzes the ADMET polymerization of 1,9-decadiene, and the reaction proceeds until no further evolution of ethylene is observed. (Yield = 67–81%, $M_n = 1300\text{--}1800$ g/mol). The $^1\text{H-NMR}$ of the polymer is shown in Fig. 3.

$^1\text{H-NMR}$ end-group analysis of the polymers reveal that low molecular weight was obtained,

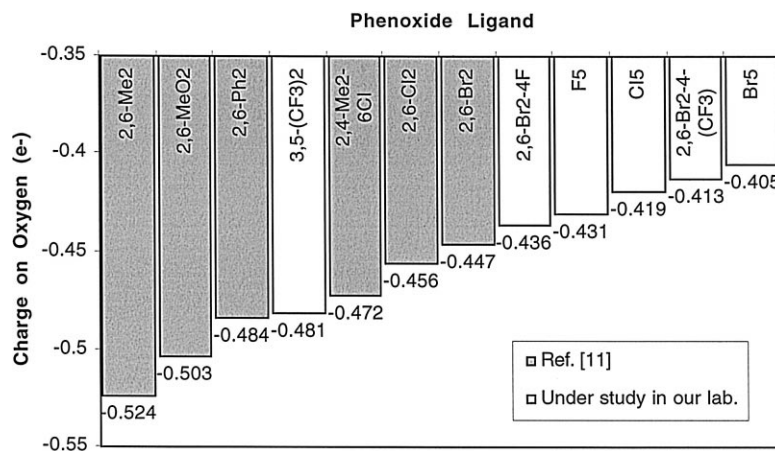


Fig. 2. Calculated oxygen charge for a series of phenoxide anions.

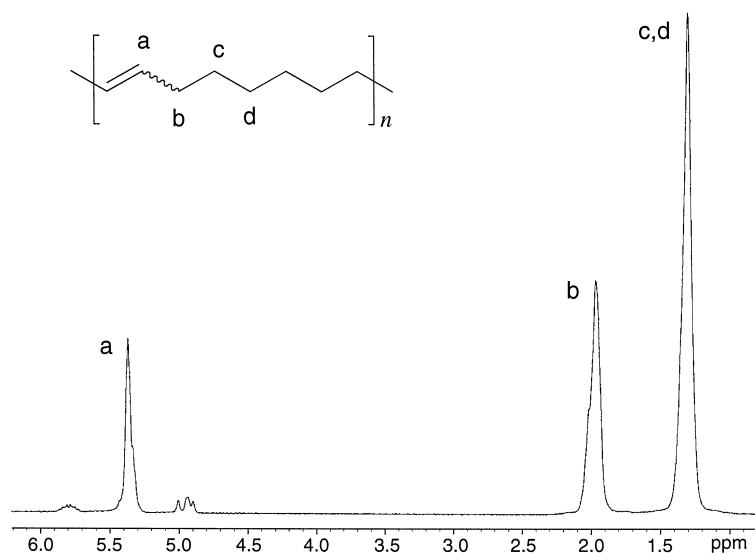


Fig. 3. $^1\text{H-NMR}$ of a polyoctenyene sample synthesized using complex **4** and Bu_3SnH .

regardless of the precatalyst batch (crude mixtures or recrystallized products) or the activator (Bu_4Sn or Bu_3SnH) used. These results oppose to the high conversions and molecular weights previously obtained with complexes **1–3** under similar conditions [8]. This fact, although not a clear indication of the catalytic activity, contradicts the behavior predicted from our calculations. However, neither the subtle structural differences (see below) with respect to its non-flu-

orinated analog **1** nor the expected effect on the metal, are significant to suggest such difference in reactivity. We are currently optimizing the conditions for polymerization with complex **4**.

Single crystal X-ray analysis shows similar features between complexes **4** and its non-fluorinated analog **1** [15]. Inequivalent phenoxide ligands are present due to a presumably weak interaction between Br1 and the tungsten atom (see Fig. 4), and such geometry distortion is (in

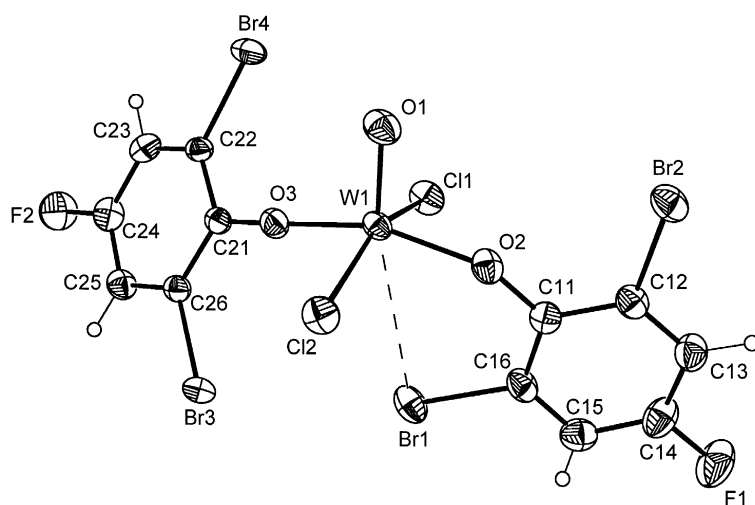


Fig. 4. Molecular structure of **4**, with 50% probability ellipsoids, showing the atom numbering scheme.

Table 1
Selected bond distances (Å) and angles (°) for structure **4**

Bond lengths (Å)		Bond angles (°)	
W–O1	1.679(3)	W–O2–C11	142.1(3)
W–O2	1.879(3)	W–O3–C21	162.5(3)
W–O3	1.856(3)	O2–W–O3	157.6(1)
W–C11	2.337(1)	O–W–Br1	166.9(1)
W–C12	2.309(1)	C11–W–Br1	77.08(3)
W–Br1	3.205(7)	C12–W–Br1	79.34(3)
O2–C11	11.337(5)	C11–W–C12	155.9(4)
O3–C21	1.352(5)	O3–C21	

both cases) also reflected in the inequivalent W–O–C bond angles (Table 1).

However, a detailed observation of the structure reveals that the incorporation of the fluorine substituent in the *para* position causes an increase of the W · · · Br1 distance (3.205 Å in **4** vs. 3.120 Å in **1**). This decreased interaction is also evidenced by the wider bond angle on O2 (139.2° in **1** to 142.1° in **4**). These observations can be justified by appealing to a larger extent of π donation from the oxygen orbitals of the aryloxy ligand to the empty metal orbitals, a phenomenon well documented elsewhere [22,23]. The effect of the modification of electronic properties of the aryloxy ligand on the structure of their complexes is currently under study in our laboratory.

3.3.2. Bis(pentafluorophenoxy)tungsten (VI) oxychloride (**5**)

Although pentafluorophenoxide derivatives of several transition and main group metals have been previously synthesized, [24] only one report of their use in the synthesis of a metathesis catalyst was found in the literature [25]. The pentafluorophenol acidity—and the implied electron withdrawing properties of its conjugated base—are highlighted therein. This fact along with the low calculated oxygen charge prompted us to synthesize complex **5**, which was obtained as a bright orange microcrystalline solid. To date we have not been able to obtain crystalline material suitable for X-ray analysis.

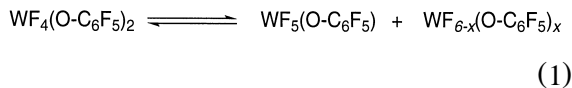
Contrary to our expectations, we have been unable to find appropriate experimental conditions for the catalysts of olefin metathesis with complex **5**. In the attempted ADMET polymerization of 1,9-decadiene, **5** decomposes to an insoluble black precipitate upon immediate contact with Bu₃SnH. In turn, addition of Bu₄Sn to a solution of **5** in 1,9-decadiene, continuous heating at 85°C causes decomposition of the tungsten species. Efforts to prolong the life of the activated complex (using either Bu₄Sn or Bu₃SnH as activator) by means of the addition of Lewis bases such as ethyl ether, DME and triphenylphosphine have also proved futile. This complex is shown to be inactive towards metathesis chemistry.

Preliminary analysis of these results suggests that a modification of the electronic properties of the metal center have indeed taken place. At the same time, the propensity to decomposition has also increased yielding a very unstable complex, unsuitable for metathesis catalysis. These results also lead us to believe that the open coordination site *trans* to the apical oxo ligand is involved in bimolecular decomposition pathways of this specific complex. This observation is based on the observed protection of this site by Br1 in the case of complexes **1** and **4**, which causes a geometry distortion from the expected symmetrical square-based pyramidal towards the observed pseudo-octahedral geometry. Such blocking should take active part in the stabilization of the complex. In the case of complex **5**, this extra stabilization is not present and decomposition takes place faster.

In order to establish the extent of decomposition (vs. conversion to active catalyst), we attempted the ring opening polymerization of dicyclopentadiene. Again, immediate decomposition upon contact with Bu₃SnH was observed, confirming the presence of a very susceptible product formed in this initial reaction. Studies of the behavior of complex **5** as a ROMP precatalyst in the presence of external Lewis bases are under progress within our research group.

3.3.3. Bis(pentafluorophenoxy)tungsten (VI) chloride

In consideration of the unsuccessful attempts to catalyze olefin metathesis using complex **5**, we attempted the synthesis of a pentafluorophenoxide derivative of WCl_6 , by refluxing pentafluorophenol and WCl_6 in CCl_4 [26]. ^{19}F -NMR analysis of the crude mixture after solvent removal suggested a mixture of complexes with various degrees of halide substitution, as well as geometric isomers of some of these components. Five sets of resonances were identified in the ^{19}F -NMR spectrum and several attempts to crystallize out a single component for analysis were also fruitless. The lack of selectivity observed can be easily understood in view of the pseudohalide character of the pentafluorophenoxide ion, a feature observed previously by Majid et al. [27] who suggested a redistribution equilibrium of the type



which would account for the existence of several pentafluorophenoxide WF_6 derivatives with different degrees of substitution.

No catalytic behavior was observed in the attempted ADMET polymerization of 1,9-decadiene under any of the experimental conditions described when the reaction crude was employed. However, some complementary experiments with this crude show its activity in the ROMP of DCPD. Crosslinked polydicyclopentadiene was obtained after the addition of Bu_3SnH to a solution of DCPD and the isomeric mixture described, at $65^\circ C$. We are currently concentrated on the isolation of a single isomer, and the results of these investigations will be reported in a following account.

4. Conclusions

Our studies on the synthesis of fluorinated aryloxy tungsten as olefin metathesis continue

as an extension of our search for novel ADMET active catalytic systems. The preliminary results described herein confirm several features of the electronic and steric properties of the two phenols studied. We have been able to demonstrate that the synthesis of complex **4** proceeds with relative ease, and that this complex catalyzes the ADMET polymerization of hydrocarbon dienes (e.g., 1,9-decadiene). Preliminary observations of the behavior of complex **5** as an olefin metathesis precatalyst reveal that very unstable species are formed when in contact with tin-based activators, and this can be due to the conjugated effect on the electronic properties on the tungsten center, while very small steric changes are introduced with respect to the parent $WOCl_4$. Studies on the relationship between structure and catalytic activity of novel ADMET catalysts remain active within our research group.

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