Synthesis of Molybdenum and Tungsten Alkylidene Complexes That Contain Sterically Demanding Arenethiolate Ligands

Erik M. Townsend,† Jakub Hyvl,† William P. Forrest,† Richard R. Schrock,*† Peter Müller,† and Amir H. Hoveyda‡

†Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States
‡Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467, United States

Supporting Information

ABSTRACT: Imido alkylidene complexes of Mo and W and oxo alkylidene complexes of W that contain thiophenoxide ligands of the type S-2,3,5,6-Ph4C6H (STPP) and S-2,6-(mesityl)2C6H3 (SHMT = S-hexamethylterphenyl) have been prepared in order to compare their metathesis activity with that of the analogous phenoxide complexes. All thiolate complexes were significantly slower (up to ∼10× slower) for the metathesis homocoupling of 1-octene or polymerization of 2,3-dicarbomethoxynorbornene, and none of them was Z-selective. The slower rates could be attributed to the greater σ-donating ability of a thiophenoxide versus the analogous phenoxide and consequently a higher electron density at the metal in the thiophenoxide complexes.

Mo(VI) and W(VI) imido alkylidene complexes are versatile catalysts for a variety of olefin metathesis reactions.1 The chemistry of four-coordinate catalysts with the formula M(NR)(CHR′)(X)(Y) has been dominated by compounds in which X and Y are oxygen-based ligands (alkoxides, arylloxides, biphenolates, and binaphtholates) or catalysts in which X is oxygen-based and Y is a pyrrolide: so-called monoalkoxide (or monoaryloxide) pyrrolide (MAP) catalysts. MAP catalysts have been responsible for a variety of Z-selective metathesis reactions in the last several years,1d,e,2 as well as the polymerization of norbornenes and norbornadienes to give cis,syndiotactic polymers.3 Missing in the list of X and Y ligands that have been explored in M(NR)(CHR′)(X)(Y) complexes are thiolates. In view of the recent success in the synthesis and Z-selectivity of thiolato ruthenium catalysts,4 we decided to explore some arylthiolate analogues of terphenoxide molybdenum imido and tungsten oxo complexes. A second reason to explore thiophenoxide complexes is that density functional theory (DFT) calculations carried out by Eisenstein and co-workers5 have led to the conclusion that an asymmetric ligand environment in which X and Y are a “donor” and an “acceptor” ligand leads to more rapid turnover as a consequence of the donor ligand being in the equatorial position of a TBP metallacyclobutane intermediate and thereby effectively leading to a more facile loss of olefin from the metallacyclobutane trans to it in the equatorial position.

A couple of imido alkylidene thiolate complexes have been prepared previously,6 but their metathesis reactivity was not explored in depth. Moreover, none of the thiolates in those compounds was an analogue of bulky 2,6-terphenoxide ligands such as 2,6-dimesitylphenoxy (hexamethy1terphenoxide or OHMT). In this paper we systematically compare a set of complexes that contain bulky thioterphenoxides with their terphenoxide analogues.

RESULTS AND DISCUSSION

The four imido alkylidene aryloxide complexes that we chose to compare and their arenethiolate analogues are shown in Figure 1. The two chosen arenethiols, HMTSH8 and TPPSH, are analogues of HMTOH and TPPOH,7 respectively. TPPOH was employed to synthesize the previously unreported TPPSH. TPPSH was synthesized from TPPOH, as shown in Scheme 1.

Figure 1. Imido complexes compared in this work (Ar = 2,6-i-Pr2C6H3; R = CMε2Ph; Pyr = pyrrolide; Me2Pyr = 2,5-dimethylpyrrolide).

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and described in the Experimental Section. The synthesis of HMTSH was first reported by Power.8

Three MAP complexes shown in Figure 1 (1-O,9 3-O10 and 4-O11) have been prepared previously. Compound 2-O was prepared straightforwardly in 78% isolated yield from Mo(NAr)(CHCMe2Ph)(OTf)2(dme) and 2 equiv of LiOTPP in toluene (eq 1).

Compounds 1-S−3-S were prepared through addition of TPPSH or HMTSH to a bis-pyrrolide complex. Addition of 2 equiv of TPPSH to Mo(NAr)(CHCMe2Ph)(Me2Pyr)2 in diethyl ether led to 2-S, which was isolated as a bright orange solid in 65% yield (eq 2). Attempts to add only 1 equiv of TPPSH to Mo(NAr)(CHCMe2Ph)(Me2Pyr)2 to give 1-S were complicated by the formation of 2-S. Conditions were found that allowed a mixture that contains 78% 1-S to be formed (according to NMR spectra). Compound 1-S was isolated in 20% yield upon recrystallization of the mixture from a mixture of benzene and pentane. Like all thiolate compounds reported here, a single, sharp alkylidene resonance was observed for 1-S and 2-S in the 1H NMR spectrum with \( \text{J}_{\text{CH}} = 100-110 \text{ Hz} \), a value that is characteristic of an alkylidene in the syn conformation.

An X-ray structure of 1-S shows it to be a slightly distorted tetrahedron with all angles at the metal between 100 and 110° with the exception of S1−Mo1−N2 (126.91(6)°; Figure 2). The Mo−N bond lengths in 1-S are slightly longer than those found in the previously reported structure of 1-O (Mo−imido = 1.719(4) Å; Mo−pyrrolide = 2.048(4) Å),8 which can be interpreted as a sign of a greater \( \sigma \)-donor ability of TPPS in comparison to TPPO. The Mo−S−C angle is 112.66(7)°, as expected, consistent with relatively little sp hybridization and \( \pi \) donation from sulfur to the metal. In contrast, the Mo−O−C angle in 1-O is 157.2°,9 consistent with a greater degree of \( \pi \) donation from the phenoxide along with possibly a greater degree of steric hindrance as a consequence of the smaller size of O versus that of S. The long M−S bond relative to a M−O bond and acute M−S−C angle relative to a M−O−C angle are two significant and systematic differences between thiolate and phenoxide ligands that are recognizable in all of the complexes reported here.

An X-ray structure of 2-S shows the alkylidene to be in the syn configuration (Figure 3). Angles at the metal, Mo−ligand bond lengths, and M−S−C angles in 2-S are all similar to angles and metal−ligand distances found in 1-S.

Complex 3-S was synthesized through addition of 1 equiv of HMTSH to Mo(NAr)(CHCMe2Ph)(Pyr)2. Addition of 1 equiv of HMTSH led cleanly to 3-S as the sole alkylidene product, unlike in the case of 1-S, which is likely to be a...
consequence of the more sterically demanding nature of the HMTS ligand versus the TPPS ligand. Evaporation of the solvent led to pure 3-S in 65% yield.

Addition of 1.3 equiv of HMTSH to W(NAr)(CHCMe₂Ph)-(Pyr)₂(dmpe) led to essentially complete conversion to 4-S after 8 h. Two recrystallizations of the crude product yielded analytically pure 4-S in 70% yield. The purification procedure was similar to that required to obtain pure 4-O, as detailed elsewhere.¹¹

The three tungsten oxo arenethiolate complexes that were selected for comparison with phenoxide analogues are 5-S, 6-S, and 7-S (Figure 4). The three phenoxide-based catalysts (5-O,¹² 7-O,¹² and 6-O¹³) were prepared as described in the literature. The bis-thiolate complexes 5-S and 7-S were prepared in a manner analogous to that employed to prepare the bis-alkoxide compounds, namely addition of 2 equiv of the lithium salt of the phenoxide to W(O)(CH₅Bu)-Cl₂(PMe₂Ph)₂. However, the most convenient synthesis of 6-S was found to be addition of 2 equiv of HMTSH to the bis-pyrrolide precursor W(O)(CH₅Bu)(Me₂Pyr)(PMe₂Ph)₂; it, and its neophylidene analogue, have not been reported elsewhere. A single-crystal X-ray diffraction study showed the neophylidene derivative to be approximately halfway between a TBP and an SP structure (Figure 5; τ = 0.62¹⁴). The W=O distance (1.690(3) Å) is consistent with those in the previously reported W(O)(CH-t-Bu)(Me₂Pyr)(OHPT) (1.695(3) Å) and W(O)(CH-t-Bu)(Me₂Pyr)(OHMT)(PMe₂Ph) (1.694(2) Å).

All three thiolate-based complexes (5-S—7-S) show lower stability than their alkoxide analogues; free thiol is slowly formed in solution, but the product or products of decomposition was/were not identified.

X-ray-quality crystals of 7-S were grown from benzene-d₆. The structure is displayed in Figure 6. The overall structure is similar to that of 2-S described earlier.

![Figure 4. Oxo complexes compared in this work (R¹ = CMe₂Ph; R² = CMe₃; Me₂Pyr = 2,5-dimethylpyrrolide).](https://example.com/figure4)

![Figure 5. Thermal ellipsoid plot (50% probability ellipsoids) of W(O)(CHCMe₂Ph)-(Me₂Pyr)(PMe₂Ph). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): W1–C1 = 1.901(5), W–O1 = 1.690(3), W1–N1 = 2.099(3), W1–N2 = 2.117(3), W1–P₁ = 2.5776(10); W1–C(1)–C2 = 140.3(4).](https://example.com/figure5)

![Figure 6. Thermal ellipsoid drawing of 7-S (50% probability ellipsoid). Selected distances (Å) and angles (deg): W(1)–C(1) = 1.938(2), W(1)–O(1) = 1.6871(16), W(1)–S(1) = 2.4306(5), W(1)–S(2) = 2.4228(5), W(1)–P(1) = 2.5488(6); W(1)–S(1)–C(21) = 116.08(6), W(1)–S(2)–C(51) = 106.14(6).](https://example.com/figure6)

We chose the homocoupling of 1-Octene and the polymerization of 2,3-dicarbomethoxynorbornadiene as the two metathesis test reactions. The experimental data for the homocoupling of 1-octene by imido alkylidene and oxo alkylidene complexes are shown in Table 1. The procedure (a capped 20 mL vial opened only for sampling) is described in the Experimental Section. The most dramatic comparison in terms of the Z-selectivity is 6-O and 6-S.

### Table 1. Homocoupling of 1-Octene

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<th>Z (%)</th>
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<tr>
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<td>0.25/1/6/24</td>
<td>56/60/67/68</td>
<td>19/19/18/18</td>
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<tr>
<td>1-S</td>
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<td>0/2/6/22</td>
<td>n.d./n.d./40/44</td>
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<td>0/0/13/46</td>
<td>n.d./n.d./21/19</td>
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<tr>
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<td>24</td>
<td>3</td>
<td>n.d.</td>
</tr>
<tr>
<td>3-O</td>
<td>0.25/1/6/24</td>
<td>64/62/67/77</td>
<td>19/21/23/24</td>
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<tr>
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<td>0/0/7/19</td>
<td>n.d./n.d./52/54</td>
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<td>34/52/66/72</td>
<td>86/75/46/43</td>
</tr>
<tr>
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<td>0/1/4/14</td>
<td>n.d./n.d./69/62</td>
</tr>
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<td>94/92/91/78</td>
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Catalyst 6-0 is known to be exceptionally Z-selective for the homocoupling of terminal olefins, although under the conditions employed the conversion was limited to 63% after 24 h. In comparison, catalyst 6-S produced only 6% coupled product after 24 h and that product was only 17% Z. It should be noted that the percentage of Z often degenerates with time, as with 4-O (86/75/46/43), 5-0 (94/92/91/78), or 7-0 (42/38/21/20). The percentage of Z does not appear to degenerate as extensively with the thiophenoxide catalysts (as a consequence of secondary metathesis) as with the phenoxide catalyst analogue. The major finding is that the turnover rate for thiophenoxide catalysts is only approximately one-third to as little as one-tenth (as with 6-0 vs 6-S) the turnover rate of the analogous phenoxide complex.

The rates of polymerization of DCMNBD by phenoxide and thiophenoxide catalysts are given in Table 2. For catalysts of types 1 and 2 the thiophenoxide catalyst again is slower by a factor of 3–4. For complexes of the types 3–7 the actual difference in rates is not known because polymerization by the phenoxide catalysts was complete when first measured. Nevertheless, it is clear that the rate differences are significant in all examples. For example, polymerization with 4-O was complete in 15 min, while it had essentially not begun after 15 min for 4-S. Rates of initiation versus polymerization are potentially important issues that were not explored in these experiments. No thiophenoxide catalyst produced only cis polymer, as is found for the HMTO MAP initiators, 3-0, 4-O, and 6-O.

**CONCLUSIONS**

We conclude that the selection of thiophenoxide imido and oxo alkylidene analogues of phenoxide complexes explored here offers no advantages over phenoxide complexes, at least for the two generic metathesis test reactions. Because the metathesis activity of Mo and W high-oxidation-state alkylidene complexes of the type M(Z)(CHR')(X)(Y) has been observed to correlate with the electron-withdrawing ability of the X and Y ligands, the slower rates could be attributed simply to the greater σ-donating ability of a thiophenoxide. Consequently, the metallacyclobutane may be a much higher energy complex relative to the alkylidene when a thiophenoxide is present in place of a phenoxide.

The lower degree of Z selectivity is perhaps more difficult to correlate in a quantitative manner with any given property of thiophenoxides versus phenoxides. Compound 6-O was the most successful for both test reactions, and in each case the contrast between the results with 6-O and with 6-S were the most dramatic. Among the possible reasons for the loss of Z selectivity is that TBP metallacyclobutanes derived from MAP complexes analogous to 6-O, which have been shown to contain the sterically demanding phenoxide ligand in an axial position where their steric bulk enforces all substituents in the metallacyclobutane complex to face away from the phenoxide, simply do not contain the HMTS ligand in an axial position in an analogous TBP metallacyclobutane complex. In combination with all the other differences between phenoxides and thiophenoxides, most notably the steric consequences of a long M–S bond relative to a M–O bond and a relatively acute M–S–C angle, it is perhaps not surprising in retrospect that the sensitive balance that gives rise to Z-selective reactions is disrupted to a dramatic degree in thiophenoxide analogues of highly Z-selective phenoxide catalysts.

### EXPERIMENTAL SECTION

**General Procedures.** All manipulations of air- and moisture-sensitive materials were performed in oven-dried (175 °C) or flame-dried glassware on a dual-manifold Schlenk line or a Vacuum Atmospheres glovebox under a nitrogen atmosphere. NMR measurements of air- and moisture-sensitive materials were carried out in Teflon-valve-sealed J. Young type NMR tubes. Anhydrous ether, pentane, toluene, THF, benzene, and CHCl₃ were sparged with nitrogen and passed through activated alumina prior to use. Chloroform-d and CD₃OD were stored over molecular sieves.

The following chemicals were purchased from Aldrich and used as received: sulfur, LiAlH₄, n-butyllithium, sodium hydride, N,N-dimethylthiocarbamoyl chloride, N,N-dimethylacetamide, benzaldehyde, and sulfuric acid. I-Octene was purchased from Aldrich, dried over calcium hydride, and degassed by three freeze–pump–thaw cycles; the mixture containing calcium hydride was filtered in the glovebox before use. The following substances were prepared according to literature procedures: 1-O (Mo(NAr)(CHCMe₂Ph)(Me₂pyr)(OTPP)), 3-O (Mo(NAr)(CHCMe₂Ph)(Pyr)(OHMT)), 4-O (W(NAr)(CHCMe₂Ph)(Pyr)(OHMT)), 5-O (Mo(NAr)(CHCMe₂Ph)(O)₂(dme)), 6-O (Mo(NAr)(CHCMe₂Ph)(Me₂pyr)), 7-O (Mo(NAr)(CHCMe₂Ph)(Pyr)(NaOTPP)), 8-O (Mo(NAr)(CHCMe₂Ph)(Pyr)(NaOTPP)).

All manipulations of air- and moisture-sensitive materials were performed in oven-dried (175 °C) or flame-dried glassware on a dual-manifold Schlenk line or a Vacuum Atmospheres glovebox under a nitrogen atmosphere. NMR measurements of air- and moisture-sensitive materials were carried out in Teflon-valve-sealed J. Young type NMR tubes. Anhydrous ether, pentane, toluene, THF, benzene, and CHCl₃ were sparged with nitrogen and passed through activated alumina prior to use. Chloroform-d and CD₃OD were stored over molecular sieves. The following chemicals were purchased from Aldrich and used as received: sulfur, LiAlH₄, n-butyllithium, sodium hydride, N,N-dimethylthiocarbamoyl chloride, N,N-dimethylacetamide, benzaldehyde, and sulfuric acid. I-Octene was purchased from Aldrich, dried over calcium hydride, and degassed by three freeze–pump–thaw cycles; the mixture containing calcium hydride was filtered in the glovebox before use. The following substances were prepared according to literature procedures: 1-O (Mo(NAr)(CHCMe₂Ph)(Me₂pyr)(OTPP)), 3-O (Mo(NAr)(CHCMe₂Ph)(Pyr)(OHMT)), 4-O (W(NAr)(CHCMe₂Ph)(Pyr)(OHMT)), 5-O (Mo(NAr)(CHCMe₂Ph)(O)₂(dme)), 6-O (Mo(NAr)(CHCMe₂Ph)(Me₂pyr)), 7-O (Mo(NAr)(CHCMe₂Ph)(Pyr)(NaOTPP)), 8-O (Mo(NAr)(CHCMe₂Ph)(Pyr)(NaOTPP)).
resulting mixture was stirred for 30 min in the ice bath, after which time the N,N-dimethylthiocarbamoyl chloride solution was injected in dropwise via syringe. This mixture was stirred at room temperature overnight under N₂. At this time a sample showed the reaction to be ~65% complete. An additional 407 mg of NaH (60% mineral oil dispersion, 10.2 mmol, 0.81 equiv) was added in portions, followed by 1.45 g (9.6 mol) of N,N-dimethylthiocarbamoyl chloride (11.70 mmol, 0.93 equiv) in the same manner as before. After the reaction mixture was stirred for 18 h at room temperature, TLC analysis still showed incomplete conversion. Still more NaH dispersion (156 mg) and 1.45 g more of (Me₂NC(O)STPP). The THF was filtered to give 256 mg of an orange solid, which was washed with acetonitrile. A 1 H NMR spectrum of this solid showed it to be 86% product and 14% 2-S. The solid was triturated with diethyl ether, filtered, and recrystallized from benzene and pentane. Three crops were obtained for a total of 88 mg of pure product (20% yield): 1 H NMR (CD₂Cl₂, 20 °C, 500 MHz) δ 11.82 (s, 1H, CH(CMe₂Ph)), 7.52 (s, 1H, Hpara, on STPP), 7.39 (m, 2H, aryl), 7.35 (15H, aryl), 7.34 (m, 4H, ary), 7.20 (2H, Me₂), 7.10–6.98 (overlapping m, 12H, aryl), 2.29 (brs, 3H, NMe₂), 2.04 (brs, 3H, NMe₂). 13C{1H} NMR (CD₂Cl₂, 20 °C) δ 166.67, 146.76, 142.45, 141.95, 141.33, 134.02, 131.32, 130.25, 127.96, 127.45, 126.84, 126.73, 126.39 (one methyl signal because of interconversion); HRMS calc [M + H]+ 486.1886, found [M + H]+ 486.1886. Anal. Calc. for C₅₈H₅₈MoN₂S: C, 76.43; H, 6.74; N, 3.02. Found: C, 76.83; H, 6.37; N, 3.05.

**Mo(NAR)(CH(CMe₂Ph))(Pyr)(TPSSH) (2-S).** In the glovebox, a 50 mL round-bottom flask was charged with a stir bar, 275 mg of Mo(NAR)(CH(CMe₂Ph))(Me₄Pyr) (0.465 mmol, 1.0 equiv), 20 mL of acetonitrile, and 5 mL of benzene. This mixture was stirred at room temperature, and to it was added 183 mg of TPSSH (0.442 mmol, 0.95 equiv) in four portions (one every 75 min). After the additions, the flask was capped and the mixture stirred for 18 h at room temperature. The resulting mixture was filtered to give 256 mg of an orange solid, which was washed with acetonitrile. A 1 H NMR spectrum of this solid showed it to be 86% product and 14% 2-S. The solid was triturated with diethyl ether, filtered, and recrystallized from benzene and pentane. Three crops were obtained for a total of 88 mg of pure product (20% yield): 1 H NMR (CD₂Cl₂, 20 °C, 500 MHz) δ 11.82 (s, 1H, CH(CMe₂Ph)), 7.52 (s, 1H, Hpara, on STPP), 7.39 (m, 2H, aryl), 7.30–6.85 (15H, aryl), 6.81 (m, 2H, ary), 5.71 (s, 2H, NC₄H₂Me₂), 3.25 (br d, 2H, CHMe₂), 2.04 (br s, 6H, NC₄H₂Me₂), 1.51 (s, 6H, CH(CMe₂Ph)), 1.20–0.65 (br d and sharp d, 12H, CH₂Me₂); 13C{1H} NMR (CD₂Cl₂, 20 °C) δ 290.64, 153.60, 148.47, 145.67, 142.98, 142.61, 142.22, 140.82, 137.89, 132.31, 131.11, 131.94, 130.04, 129.33, 128.78, 128.57, 128.03, 127.81, 127.78, 127.13, 126.64, 126.60, 125.76, 125.70, 125.03, 108.76, 55.05, 32.40, 30.21, 28.52, 26–21 (broad signals). Anal. Calc. for C₂₃H₂₆MoNS: C, 76.43; H, 7.64; N, 3.02. Found: C, 76.83; H, 6.37; N, 3.05.

**Mo(NAR)(CH(CMe₂Ph))(Pyr)(SHMT) (3-S).** In the glovebox, a 50 mL round-bottom flask was charged with 275 mg of Mo(NAR)(CH(CMe₂Ph))(Me₄Pyr) (0.465 mmol, 1.0 equiv), 193 mg of TPSSH (0.465 mmol, 1.0 equiv), 15 mL of diethyl ether, and a stir bar. This flask was capped and the mixture stirred at room temperature for 20 h. The solvent was removed in vacuo (1 H NMR showed mixture of starting material, 1-S, and product). Toluene (10 mL) was added to the residue, along with another 1 equiv of TPSSH (193 mg). This mixture was capped and stirred at room temperature for 18 h, after which time the solvent was removed and the residue triturated with ether. Filtration gave 370 mg of pure orange solid product (65% yield). Addition of 2 equiv of TPSSH at the beginning of the reaction, rather than the portionwise addition described elsewhere, is a logical alternative that was not tried: 1 H NMR (CD₂Cl₂, 20 °C, 500 MHz) δ 12.72 (s, 1H, CH(CMe₂Ph)), 7.35–6.90 (50H, ary, many overlapping signals), 3.48 (sept, 2H, CH₂Me₂₂, JHH = 7 Hz), 1.25 (br s, 6H, CH₂Me₂), 0.96 (d, 6H, CH₃₂, JHH = 7 Hz); 13C{1H} NMR (CD₂Cl₂, 20 °C) δ 153.78, 149.23, 146.51, 142.77, 141.91 (br), 133.05, 131.15, 130.66, 130.06, 129.84, 128.72, 128.50, 126.38, 126.29, 125.96, 123.26, 125.76, 118.7, 55.05, 32.40, 30.21, 28.52, 26–21 (broad signals). Anal. Calc. for C₂₃H₂₆MoNS: C, 80.04; H, 5.36; N, 2.81.

**Mo(NAR)(CH(CMe₂Ph))(OTTP) (2-O).** In the glovebox, a 100 mL round-bottom flask was charged with a stir bar, 10 mL of toluene, 250 mg of Mo(NAR)(CH(CMe₂Ph))(OTTP) (dime) (containing ~12% ArN₂OTf, 0.30 mmol, 1.0 equiv), and 317 mg of Li(OTTP) (THF) (1.25, 0.641 mmol, 2.14 equiv). The flask was capped and the mixture stirred at room temperature for 23 h, after which time the mixture was filtered through Celite and the solvent removed from the filtrate in vacuo. Pentane was added and subsequently removed in vacuo. Another pentane addition and filtration led to the isolation of pure product (321 mg, 78% yield): 1 H NMR (CD₃OD, 20 °C, 500 MHz) δ 11.48 (s, 1H, CH(CMe₂Ph)), 7.34–7.08 (aryl, 17H), 7.03–6.86 (aryl, 33H), 2.90 (sept, 2H, ipr methines) JHH = 7 Hz), 1.33 (s, 6H, CH₂Me₂), 0.91 (d, 12H, CH₂Me₂, JHH = 7 Hz); 13C{1H} NMR (CD₃OD, 20 °C) δ 284.07, 162.44, 154.27, 150.31, 147.06, 142.83, 142.25, 137.71, 131.72, 131.55, 130.38, 130.22, 130.12, 128.51, 127.07, 126.62, 126.43, 126.05, 126.01, 123.56, 55.16, 31.71, 28.48, 24.62. Anal. Calc. for C₂₂H₂₆MoF₄: C, 82.18; H, 5.97; N, 1.17. Found: C, 81.84; H, 6.30; N, 1.10.
round-bottom flask was charged with 250 mg of W(NAr)(CHCMe2Ph)(Pyr)(SHMT)2(PMe2Ph) (0.300 mg, 1.0 equiv) and 15 mL of toluene. The solution was filtered through a bed of Celite to remove LiCl before the solvent was removed in vacuo to yield an orange solid. Trituration with pentane (5 mL) overnight resulted in an orange suspension, which was filtered, and the orange-solid was collected (0.116 mmol, 45% yield): 1H NMR (CD2Cl2, 20 °C, 500 MHz) δ 8.93 (s, 1H, WCH-Br), 7.11 (m, 2H, aryl), 7.03 (m, 3H, aryl), 6.97 (m, 5H, aryl), 6.92 (m, 2H, NC4H2), 2.79 (s, 6H, CHMTH, 2H, HMT CH3), 2.08 (s, 6H, HMT CH3), 2.04 (br s, 6H, NHCH2Me), 0.94 (overlapping signals, 15H, CH-CH2-tBu, PMe3); 13C{1H} NMR (CD2Cl2, 20 °C) δ 303.58, 147.97, 147.96, 142.57, 132.31, 131.69, 130.56, 130.52, 130.51, 128.69, 128.67, 127.62, 127.42, 126.42, 126.28, 122.69, 110.51, 54.16, 32.39, 32.30, 28.31, 24.14, 23.24, 21.67, 21.32, 20.97, 20.54. Anal. Calcld for C43H54NOPSW: C, 61.52; H, 6.47; N, 1.65. Found: C, 61.06; H, 6.42; N, 1.08.

### WO(CH-t-Bu)(Me2Pyr)(HMTSH) (5-S).

In the glovebox, a 20 mL vial was charged with 102 mg of HMTSH (0.394 mmol, 2.42 equiv), a stir bar, and 5 mL of toluene. Partly precipitated 2.67 M Li-n-Bu (0.297 mmol, 2.26 equiv) in hexanes was added dropwise. The volatiles were removed from the solution under reduced pressure. W(O)(CH-t-Bu)-Cl2(PMe2Ph) (0.131 mmol, 1.0 equiv, 81 mg) of HMTSH (0.231 mmol, 1.43 equiv), a stir bar, and 11 mL of benzene. The solution was sealed, and the solution was stirred at 75 °C for 4 h. After that, the volatiles were removed under reduced pressure, yielding an orange solid. Trituration with 1 mL of pentane for 30 min resulted in formation of an orange powder, which was collected by filtration. The title product (8 mg, 0.086 mmol) was obtained as an orange powder in 42% yield: 1H NMR (CD2Cl2, 20 °C, 500 MHz) δ 10.12 (br s, 1H, CH-t-Bu, JCH = 115 Hz), 7.11 (m, 2H, aryl), 7.03 (m, 3H, aryl), 6.97 (m, 5H, aryl), 6.92 (m, 2H, NC4H2), 2.79 (s, 6H, NC4H2), 2.08 (s, 6H, HMT CH3), 2.04 (br s, 6H, NHCH2Me), 0.94 (overlapping signals, 15H, CH-CH2-tBu, PMe3); 13C{1H} NMR (CD2Cl2, 20 °C) δ 303.58, 147.97, 147.96, 142.57, 132.31, 131.69, 130.56, 130.52, 130.51, 128.69, 128.67, 127.62, 127.42, 126.42, 126.28, 122.69, 110.51, 54.16, 32.39, 32.30, 28.31, 24.14, 23.24, 21.67, 21.32, 20.97, 20.54. Anal. Calcld for C43H54NOPSW: C, 61.52; H, 6.47; N, 1.65. Found: C, 61.12; H, 6.63; N, 1.08.

### WO(CH-t-Bu)(CHCMe2Ph)(Me2Pyr)(Pyr)(SHMT)2(PMe2Ph) (5-S).

In the glovebox, a 20 mL vial was charged with 102 mg of TPSPh (0.246 mmol, 2.30 equiv) and 15 mL of toluene. The solution was heated to 65 °C for 4 h. The vials were removed under reduced pressure, yielding an orange oil. Trituration with pentane (5 mL) overnight resulted in an orange suspension, which was filtered, and the orange-solid was collected (0.116 mmol, 45% yield): 1H NMR (CD2Cl2, 20 °C, 500 MHz) δ 8.99 (s, 1H, WCH-Br), 7.14 (d, 2H, CH=CMe2Ph, 2JPH = 115 Hz), 7.04 (2H, CH=CMe2Ph, 2JPH = 115 Hz), 7.20 (d, 2H), 7.14–7.10 (t, 2H), 7.04–6.88 (multiplets, 6H), 6.15 (broad s, 4H), 2.27 (broad s, 12H), 1.60 (broad s, 6H), 1.06 (merged singlets, 6H); 13C{1H} NMR (CD2Cl2, 20 °C) δ 142.1 (d, WCH=CH2, JCH = 24 Hz), 149.8, 134.2, 133.9, 131.0, 130.3, 128.9, 126.7, 126.2, 109.6, 51.2, 31.0, 18.2, 13.2; 31P NMR (CD2Cl2, 20 °C) δ 5.32 (broad s). Anal. Calcld for C43H54NOPSW: C, 65.97; H, 6.85; N, 4.33. Found: C, 65.63; H, 6.56; N, 4.13.
In the glovebox, a 4 mL vial was charged with 5 mg, 1.0 equiv) and 1 mL of CDCl3. A second vial was charged with 0.005 2726. (i) Kiesewetter, E. T.; O

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Associate content
Supporting information
Text, figures, tables, and CIF files giving NMR spectra of poly(DCMNBDB) and details of the four X-ray structural studies. This material is available free of charge via the Internet at http://pubs.acs.org.

Author information
Corresponding author
*E-mail for R.R.S.: rrs@mit.edu.

Notes
The authors declare no competing financial interest.

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