ORGANOMETALLICS

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pubs.acs.org/Organometallics

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

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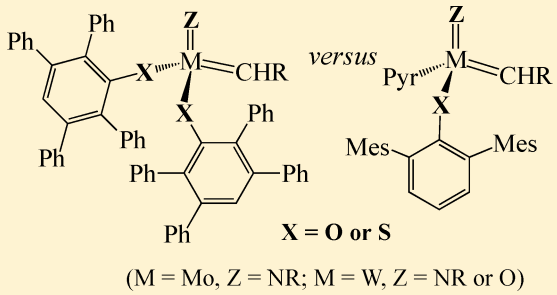
Supporting Information

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-Ph_4C_6H (STPP) and S-2,6-$(mesityl)_2C_6H_3$ (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, aryloxides, 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 coworkers[5] 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-dimesitylphenoxide (hexamethylterphenoxide 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, HMTSH[8] 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

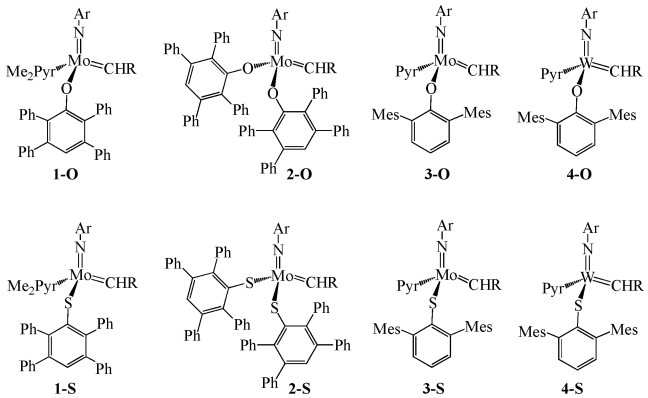


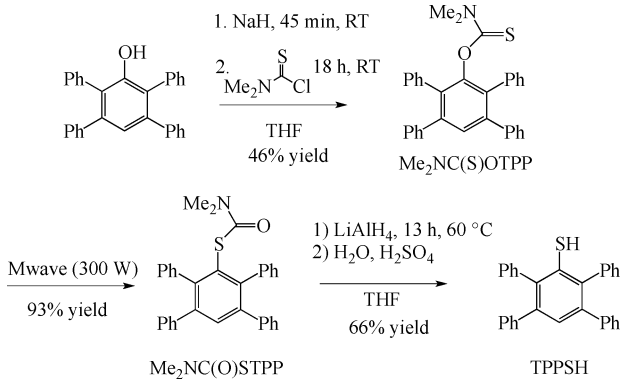
Figure 1. Imido complexes compared in this work (Ar = 2,6-*i*-$Pr_2C_6H_3$; R = CMe_2Ph; Pyr = pyrrolide; Me_2Pyr = 2,5-dimethylpyrrolide).

Received: June 19, 2014
Published: September 22, 2014

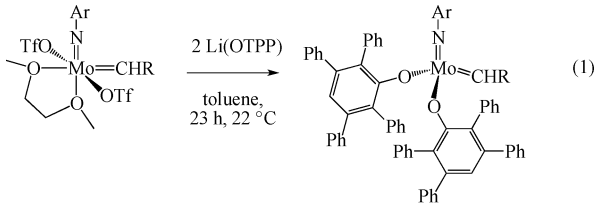
   dx.doi.org/10.1021/om500655n | *Organometallics* 2014, 33, 5334−5341

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

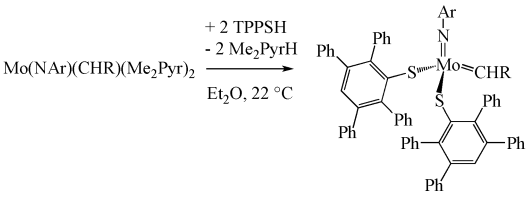
Scheme 1. Synthesis of 2,3,5,6-Tetraphenylthiophenol



Three MAP complexes shown in Figure 1 (**1-O**,[9] **3-O**,[10] and **4-O**[11]) have been prepared previously. Compound **2-O** was prepared straightforwardly in 78% isolated yield from Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(dme) and 2 equiv of LiOTPP in toluene (eq 1).



(1)



(2)

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)(CHCMe$_2$Ph)(Me$_2$Pyr)$_2$ 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)(CHCMe$_2$Ph)(Me$_2$Pyr)$_2$ 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 ^{1}H NMR spectrum with J_{CH} = 100–110 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),[9] which can be interpreted as a sign of a greater σ-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 π 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 π 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.

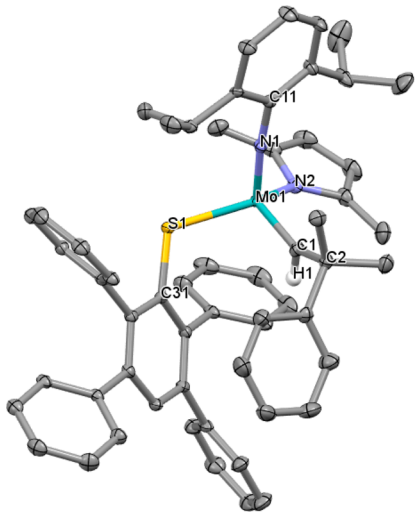


Figure 2. Thermal ellipsoid drawing of **1-S** (50% probability ellipsoids). Selected distances (Å) and angles (deg): Mo(1)–C(1) = 1.871(1), Mo(1)–N(1) = 1.7262(18), Mo(1)–N(2) = 2.0522(18), Mo(1)–S(1) = 2.3708(7); Mo(1)–S(1)–C(31) = 112.66(7).

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)(CHCMe$_2$Ph)(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

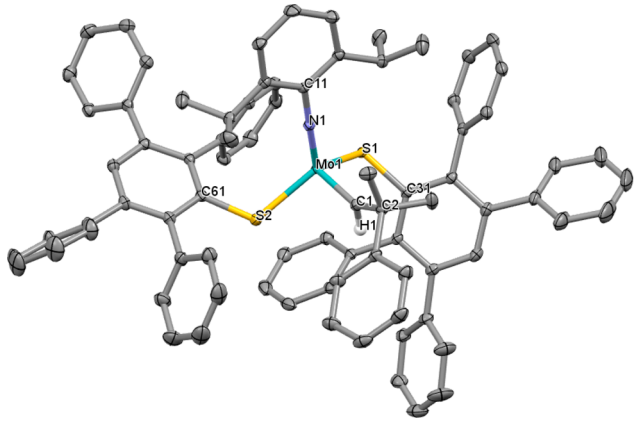


Figure 3. Thermal ellipsoid drawing of **2-S** (50% probability ellipsoids). Selected distances (Å) and angles (deg): Mo(1)–C(1) = 1.8766(11), Mo(1)–N(1) = 1.7308(10), Mo(1)–S(1) = 2.3935(3), Mo(1)–S(2) = 2.3713(3); Mo(1)–S(1)–C(31) = 108.99(4), Mo(1)–S(2)–C(61) = 116.13(4).

dx.doi.org/10.1021/om500655n | *Organometallics* 2014, 33, 5334–5341

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)(CHCMe$_2$Ph)(Pyr)$_2$(dme) 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-O**[13]) 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)(CH-*t*-Bu)Cl$_2$(PMe$_2$Ph)$_2$. 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)(CH-*t*-Bu)(Me$_2$Pyr)$_2$(PMe$_2$Ph), which was prepared for this purpose through addition of 2 equiv of LiMe$_2$Pyr to W(O)(CHCMe$_2$Ph)Cl$_2$(PMe$_2$Ph)$_2$; 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 = 0.62[14]). The W=O distance (1.690(3) Å) is consistent with those in the previously reported W(O)(CH-*t*-Bu)(Me$_2$Pyr)(OHIPT) (1.695(3) Å) and W(O)(CH-*t*-Bu)(Me$_2$Pyr)(OHMT)(PMe$_2$Ph) (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-d_6. The structure is displayed in Figure 6. The overall structure is similar to that of **2-S** described earlier.

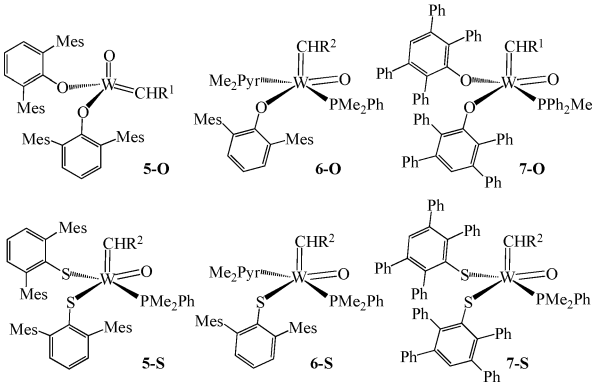


Figure 4. Oxo complexes compared in this work (R^1 = CMe_2Ph; R^2 = CMe_3; Me_2Pyr = 2,5-dimethylpyrrolide).

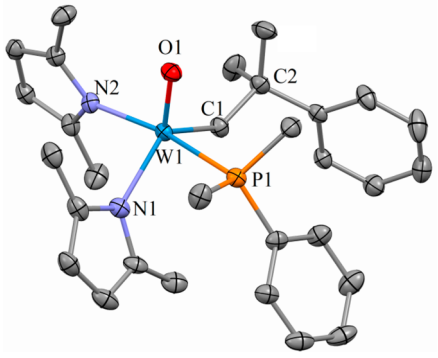


Figure 5. Thermal ellipsoid plot (50%) of W(O)(CHCMe$_2$Ph)(Me$_2$Pyr)$_2$(PMe$_2$Ph). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): W1–C1 = 1.901(5), W–O1 = 1.690(3), W1–N1 = 2.099(3), W1–N2 = 2.117(3), W1–P1 = 2.5776(10); W1–C(1)–C2 = 140.3(4).

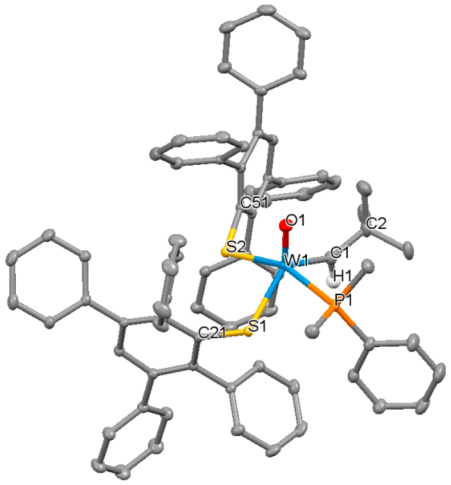


Figure 6. Thermal ellipsoid drawing of **7-S** (50% probability ellipsoids). Selected distances (Å) and angles (deg): W(1)–C(1) = 1.938(2), W(1)–O(1) = 1.6871(16), W(1)–S(1) = 2.4306(5), W(1)–S(2): 2.4228(5), W(1)–P(1) = 2.5488(6); W(1)–S(1)–C(21) = 116.08(6), W(1)–S(2)–C(51) = 106.14(6).

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

cat.	time (h)	conversion (%)	*Z* (%)
1-O	0.25/1/6/24	56/60/67/68	19/19/18/18
1-S	0.25/1/6/24	0/2/6/22	n.d./n.d./40/44
2-O	0.25/1/6/24	0/0/13/46	n.d./n.d./21/19
2-S	24	3	n.d.
3-O	0.25/1/6/24	64/62/67/78	19/21/23/24
3-S	0.25/1/6/24	0/0/7/19	n.d./n.d./52/54
4-O	0.25/1/6/24	34/52/66/72	86/75/46/43
4-S	0.25/1/6/24	0/1/4/14	n.d/n.d./69/62
5-O	0.25/1/6/24	8/17/47/67	94/92/91/78
5-S	0.25/1/6/24	0/0/9/18	–/–/38/36
6-O	0.25/1/6/24	35/45/55/63	99/99/99/99
6-S	0.25/1/6/24	0/0/5/6	–/–/18/17
7-O	0.25/1/6/24	30/57/75/83	42/38/21/20
7-S	0.25/1/6/24	0/2/8/14	–/29/39/39

dx.doi.org/10.1021/om500655n | *Organometallics* 2014, 33, 5334–5341

Catalyst **6-O** is known to be exceptionally *Z*-selective for the homocoupling of terminal olefins,[12,15] 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-O** (94/92/91/78), or **7-O** (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-O** 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-O**, **4-O**, and **6-O**.

Table 2. Polymerization of DCMNBD

cat.	time (h)	conversion (%)	major dyad structure[a]
1-O	0.25/1/24	0/7/75	43% c,s; 7% c,i
1-S	0.25/1/24	0/0/27	45% c,s; 11% c,i
2-O	0.25/1/24	0/2/97	27% c,s; 20% c,i
2-S	0.25/1/24	0/0/25	45% c,s; 10% c,i
3-O	0.25	100	99% c,s
3-S	0.25/1/24	2/20/97	64% c,s; 4% c,i
4-O	0.25	100	99% c,s
4-S	0.25/1/24	0/3/66	69% c,s; 4% c,i
5-O	1	100	90% c,s; 10% c,i[b]
5-S	0.33/1/24	18/23/81	29% c,s; 41% c,i
6-O	0.1	100	99% c,s[b]
6-S	0.33/1/24	1/3/17	70% c,s; 12% c,i
7-O	0.5	100	87% c,s; 5% c,i[b]
7-S	0.33/1/24	19/34/60	40% c,s; 29% c,i

[a]Abbreviations: c,s = cis,syndiotactic; c,i = cis,isotactic. [b]Reported in ref 12.

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,[1b] 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 surprsing 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 CH_2Cl_2 were sparged with nitrogen and passed through activated alumina prior to use. Chloroform-*d* and C_6D_6 were stored over molecular sieves. The following chemicals were purchased from Aldrich and used as received: sulfur, $LiAlH_4$, *n*-butyllithium, sodium hydride, *N*,*N*-dimethylthiocarbamoyl chloride, *N*,*N*-dimethylacetamide, benzaldehyde, and sulfuric acid. 1-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)(CHCMe$_2$Ph)(Me$_2$pyr)(OTPP)),[9] **3-O** (Mo(NAr)(CHCMe$_2$Ph)(Pyr)(OHMT)),[10] **4-O** (W(NAr)(CHCMe$_2$Ph)(Pyr)(OHMT)),[11] HOHMT,[16] HSHMT,[8] Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(dme),[17] Mo(NAr)(CHCMe$_2$Ph)(Me$_2$Pyr)$_2$,[18] Mo(NAr)(CHCMe$_2$Ph)(Pyr)$_2$,[19] W(NAr)(CHCMe$_2$Ph)(Pyr)$_2$(dme),[20] W(O)(CH-*t*-Bu)Cl$_2$(PMe$_2$Ph)$_2$,[21] 2,3-dicarbomethoxynorbornadiene (DCMNBD),[22] and HOTPP.[23] Li(OTPP) was prepared through addition of *n*-BuLi to a solution of HOTPP in THF at room temperature, followed by concentration, addition of pentane, and filtration (washing with pentane); the isolated Li(OTPP) contained 1.25 equiv of THF. Li(Me$_2$Pyr) was synthesized through addition of Li-*n*-Bu to 2,5-dimethylpyrrole in benzene, followed by removal of the solvents in vacuo. NMR spectra were obtained on spectrometers operating at either 300 or 500 MHz. NMR chemical shifts are reported as ppm relative to tetramethylsilane and are referenced to the residual proton or ^{13}C signal of the solvent (^{1}H $CDCl_3$, 7.27 ppm; ^{1}H C_6D_6, 7.16 ppm; ^{13}C $CDCl_3$, 77.16 ppm; ^{13}C C_6D_6, 128.06 ppm). All chemical shifts are reported in ppm referenced to the solvent.

***O*-(2,3,5,6-Tetraphenyl)phenyl-*N*,*N*-dimethylthiocarbamate (Me$_2$NC(S)OTPP).** This procedure was developed with the assistance of a literature report of a related compound.[24] Into an oven-dried 250 mL Schlenk flask were placed a stir bar and 5.0 g of HOTPP (12.55 mmol, 1.0 equiv). In this flask 150 mL of anhydrous THF was added under N_2. A separate flask was charged with 2.02 g of *N*,*N*-dimethylthiocarbamoyl chloride (16.31 mmol, 1.3 equiv) and 10 mL of anhydrous THF. The large flask was cooled in an ice bath (0 °C), and to it was added 600 mg of NaH (60% mineral oil dispersion, 15.06 mmol, 1.3 equiv) in four portions under a flow of nitrogen. The

dx.doi.org/10.1021/om500655n | *Organometallics* 2014, 33, 5334−5341

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 N_2. 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 more 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 *N,N*-dimethylthiocarbamoyl chloride (621 mg) was added, and the solution was heated to 45 °C for 2 h, after which time a ^{1}H NMR aliquot showed ~75% conversion to product. Water was added to the flask, and the mixture was transferred to a larger flask. The THF was removed by rotary evaporation, and a solid precipitated. This solid was washed on a frit with water and dried, and a silica column was run using gradient elution ranging from 3/1 hexanes/CH_2Cl_2 to 1/3 hexanes/CH_2Cl_2. The first substance to elute was TPPOH, followed by pure product (2.74 g, 46% yield): ^{1}H NMR (C_6D_6, 20 °C, 500 MHz) δ 7.62 (s, 1H, H_{para}), 7.85−7.20 (br, 4H, aryl), 7.24 (m, 4H, aryl), 7.07−6.89 (overlapping m, 12H, aryl), 2.52 (s, 3H, NMe_2), 2.26 (s, 3H, NMe_2); ^{13}C{^{1}H} NMR (C_6D_6, 20 °C) δ 186.87, 150.26, 142.57, 141.27, 137.18, 134.59, 130.35, 128.11, 127.07, 126.89, 42.40, 37.48; HRMS calcd $[M + H]^+$ 486.1886, found $[M + H]^+$ 486.1885. Anal. Calcd for $C_{33}H_{27}NOS$: C, 81.62; H, 5.60; N, 2.88. Found: C, 81.27; H, 5.61; N, 2.92.

***S*-(2,3,5,6-Tetraphenyl)phenyl-*N,N*-dimethylthiocarbamate ($Me_2NC(O)STPP$).** This procedure was discovered with the assistance of a literature report of a related compound.[25] A 500 mg portion of $Me_2NC(S)OTPP$ (1.03 mmol) was placed in a 10 mL microwave pressure tube with 5 mL of anhydrous *N,N*-dimethylacetamide. The tube was set up in a microwave reactor and heated for 30 min at 275 °C (300 W power, 2 min ramp time, 200 psi pressure, 20 min cooling time). This procedure was repeated for four similarly prepared tubes for a total of 2.5 g of material. The resulting mixtures were combined on a frit and washed with a large amount of water. The solid was dissolved in dichloromethane. The solution was dried over $MgSO_4$ and filtered, and the solvents were removed in vacuo to obtain 2.32 g of pure product (93% yield): ^{1}H NMR (C_6D_6, 20 °C, 500 MHz) δ 7.69 (s, 1H, H_{para}), 7.46 (br, 4H, aryl), 7.20 (m, 4H, aryl), 7.07−6.89 (overlapping m, 12H, aryl), 2.29 (br s, 3H, NMe_2), 2.04 (br s, 3H, NMe_2); ^{13}C{^{1}H} NMR (C_6D_6, 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, 36.39 (one methyl signal because of interconversion); HRMS calcd $[M + H]^+$ 486.1886, found $[M + H]^+$ 486.1896. Anal. Calcd for $C_{33}H_{27}NOS$: C, 81.62; H, 5.60; N, 2.88. Found: C, 80.44; H, 5.36; N, 2.81.

2,3,5,6-Tetraphenylthiophenol (TPPSH). This procedure was discovered with the assistance of a literature report of a related compound.[25] In the glovebox, a 100 mL bomb was charged with a stir bar, 782 mg of $LiAlH_4$ (20.6 mmol, 5.0 equiv), and 15 mL of THF. In the bomb was placed 2.0 g of $Me_2NC(O)STPP$ (4.12 mmol, 1.0 equiv) and 55 mL of THF. The bomb was sealed, brought out of the glovebox, and heated in an oil bath at 60 °C for 13 h. The bomb was cooled to room temperature, and water was added slowly to quench excess $LiAlH_4$. The resulting mixture was poured into a slurry of ice, water, and H_2SO_4. The slurry was stirred until the ice melted and then filtered through a frit. The solid was washed with water and dissolved in dichloromethane. This solution was dried over $MgSO_4$ and filtered. The resulting solid was recrystallized from a mixture of hot toluene and hexane to afford 1.13 g of pure product (66% yield): ^{1}H NMR (C_6D_6, 20 °C, 500 MHz) δ 7.43 (s, 1H, H_{para}), 7.24 (m, 4H, aryl), 7.19 (m, 4H, aryl), 7.00 (m, 8H, aryl), 6.92 (m, 4H, aryl), 3.62 (s, 1H, S*H*); ^{13}C{^{1}H} NMR (C_6D_6, 20 °C) δ 142.02, 141.92, 140.56, 138.27, 135.11, 131.14, 130.06, 129.08, 128.73, 128.00, 127.61, 126.79; HRMS calcd $[M + NH_4]^+$ 432.18, found $[M + H]^+$ 432.1789. Anal. Calcd for $C_{30}H_{22}S$: C, 86.92; H, 5.35. Found: C, 86.34; H, 5.43.

Mo(NAr)($CHCMe_2Ph$)$(OTPP)_2$ (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)($CHCMe_2Ph$)$(OTf)_2$(dme) (containing ~12% $ArNH_3OTf$, 0.30 mmol, 1.0 equiv), and 317 mg of Li(OTPP)-$(THF)_{1.25}$ (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 as an orange solid (281 mg, 78% yield): ^{1}H NMR (C_6D_6, 20 °C, 500 MHz) δ 11.48 (s, 1H, C*H*CMe_2Ph), 7.34−7.08 (aryl, 17H), 7.03−6.86 (aryl, 33H), 2.90 (sept, 2H, *i*-Pr methines) J_{HH} = 7 Hz), 1.33 (s, 6H, $CHCMe_2Ph$), 0.91 (d, 12H, $CHMe_2$, J_{HH} = 7 Hz); ^{13}C{^{1}H} NMR (C_6D_6, 20 °C) δ 284.07, 162.44, 154.27, 150.31, 147.06, 142.83, 142.25, 137.71, 132.74, 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. Calcd for $C_{82}H_{71}MoNO_2$: C, 82.18; H, 5.97; N, 1.17. Found: C, 81.84; H, 6.30; N, 1.10.

Mo(NAr)($CHCMe_2Ph$)(Me_2Pyr)(STPP) (1-S). In the glovebox, a 50 mL round-bottom flask was charged with a stir bar, 275 mg of Mo(NAr)($CHCMe_2Ph$)$(Me_2Pyr)_2$ (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 TPPSH (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 (^{1}H NMR showed 95% pure product), and then recrystallized from benzene and pentane. Three crops were obtained for a total of 88 mg of pure product (20% yield): ^{1}H NMR (C_6D_6, 20 °C, 500 MHz) δ 11.82 (s, 1H, C*H*CMe_2Ph), 7.52 (s, 1H, H_{para} on STPP), 7.39 (m, 2H, aryl), 7.30−6.85 (15H, aryl), 6.81 (m, 2H, aryl), 5.71 (s, 2H, $NC_4H_2Me_2$), 3.25 (br d, 2H, C*H*Me_2), 2.04 (br s, 6H, $NC_4H_2Me_2$), 1.51 (s, 6H, $CHCMe_2Ph$), 1.20−0.65 (br d and sharp d, 12H, $CHMe_2$); ^{13}C{^{1}H} NMR (C_6D_6, 20 °C) δ 290.64, 153.60, 148.47, 145.67, 142.98, 142.61, 142.22, 140.42, 137.89, 132.31, 132.11, 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, 123.03, 108.76, 55.05, 32.40, 30.21, 28.52, 26−21 (broad signals). Anal. Calcd for $C_{58}H_{58}MoN_2S$: C, 76.43; H, 6.74; N, 3.02. Found: C, 76.83; H, 6.37; N, 3.05.

Mo(NAr)($CHCMe_2Ph$)$(STPP)_2$ (2-S). In the glovebox, a 50 mL round-bottom flask was charged with 275 mg of Mo(NAr)-($CHCMe_2Ph$)$(Me_2Pyr)_2$ (0.465 mmol, 1 equiv), 193 mg of TPPSH (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 TPPSH (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 TPPSH at the beginning of the reaction, rather than the portionwise addition described here, is a logical alternative that was not tried: ^{1}H NMR (C_6D_6, 20 °C, 500 MHz) δ 12.72 (s, 1H, C*H*CMe_2Ph), 7.35−6.90 (50H, aryl, many overlapping signals), 3.48 (sept, 2H, C*H*Me_2, J_{HH} = 7 Hz), 1.25 (br s, 6H, $CHCMe_2Ph$), 0.96 (d, 12 H, $CHMe_2$, J_{HH} = 7 Hz); ^{13}C{^{1}H} NMR (C_6D_6, 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, 56.64, 29.71 (br), 27.91, 23.88. Anal. Calcd for $C_{82}H_{71}MoNS_2$: C, 80.04; H, 5.82; N, 1.14. Found: C, 79.74; H, 5.77; N, 0.98.

Mo(NAr)($CHCMe_2Ph$)(Pyr)(SHMT) (3-S). In the glovebox, a 50 mL round-bottom flask was charged with 330 mg of Mo(NAr)-($CHCMe_2Ph$)$(Pyr)_2$ (0.616 mmol, 1.0 equiv), 214 mg of HMTSH (0.616 mmol, 1.0 equiv), a stir bar, and 15 mL of toluene. This flask was closed, and the mixture was stirred at room temperature for 15 h, after which time the solvent was removed in vacuo and pentane was added to the residue. Removal of solvent from this solution resulted in isolation of 329 mg of pure product (65% yield) as a foam. Recrystallization for elemental analysis was carried out using pentane: ^{1}H NMR (C_6D_6, 20 °C, 500 MHz) δ 11.06 (s, 1H, C*H*CMe_2Ph, $^1J_{CH}$

dx.doi.org/10.1021/om500655n | *Organometallics* 2014, 33, 5334−5341

= 110 Hz), 7.28 (m, 2H, aryl), 7.13 (m, 2H, aryl), 7.05−6.95 (m, 2H, aryl), 6.91−6.87 (overlapping, 5H, aryl), 6.79 (s, 2H, HMT aryls), 6.72 (s, 2H, HMT aryls), 6.50 (m, 2H, NC_4H_4), 6.26 (m, 2H, NC_4H_4), 3.25 (sept, 2H, $CHMe_2$, J_{HH} = 7 Hz), 2.22 (s, 6H, HMT CH_3), 2.21 (s, 6H, HMT CH_3), 2.10 (s, 6H, HMT CH_3), 1.51 (s, 3H, $CHCMe_2Ph$), 1.47 (s, 3H, $CHCMe_2Ph$), 1.02 (d, 6H, $CHMe_2$, J_{HH} = 7 Hz), 0.98 (d, 6H, $CHMe_2$, J_{HH} = 7 Hz); $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C) δ 281.35, 153.88, 147.96, 147.80, 144.44, 139.61, 139.31, 137.30, 136.25, 135.97, 130.71, 129.95, 129.86, 129.43, 129.34, 129.13, 128.93, 128.67, 128.60, 127.19, 126.69, 126.24, 123.08, 109.56, 55.73, 31.16, 30.49, 28.53, 24.16, 23.34, 21.59, 21.52, 20.94. Anal. Calcd for $C_{50}H_{58}MoN_2S$: C, 73.68; H, 7.17; N, 3.31. Found: C, 73.38; H, 7.20; N, 3.44.

W(NAr)(CHCMe$_2$Ph)(Pyr)(SHMT) (4-S). In the glovebox, a 50 mL round-bottom flask was charged with 250 mg of W(NAr)-$(CHCMe_2Ph)(Pyr)_2$(dme) (0.350 mmol, 1.0 equiv), 122 mg of HMTSH (0.350 mmol, 1.0 equiv), a stir bar, and 15 mL of toluene. This mixture was stirred at room temperature for 4 h, after which time the solvent was removed under vacuum to give a foam. The ^{1}H NMR spectrum of the foam showed 76% conversion to product; therefore, an additional 35 mg of HMTSH (0.100 mmol, 0.29 equiv) was added along with 12 mL of toluene. This mixture was stirred for 3 h at room temperature, after which time the solvent was removed in vacuo. The resulting residue was dissolved in pentane, and the pentane was removed in vacuo. The residue was dissolved in diethyl ether for an attempted recrystallization. The solid that resulted contained no alkylidene (according to NMR analysis); therefore, it was discarded. An attempted recrystallization from pentane also resulted in precipitation of an unwanted product, which was filtered off. The filtrate was dried in vacuo to a yellow foam that was analytically pure product (220 mg, 70% yield). This unusual workup procedure is similar to that found in the previously reported synthesis of **4-O**:[1] ^{1}H NMR (C_6D_6, 20 °C, 500 MHz) δ 8.40 (s, 1H, $CHCMe_2Ph$, $^2J_{WH}$ = 15 Hz, $^1J_{CH}$ = 100 Hz), 7.35 (m, 2H, aryl), 7.16 (m, 2H, aryl), 7.05−6.98 (m, 2H, aryl), 6.97−6.82 (overlapping, 5H, aryl), 6.78 (s, 2H, HMT aryls), 6.69 (s, 2H, HMT aryls), 6.44 (m, 2H, NC_4H_4), 6.22 (m, 2H, NC_4H_4), 3.20 (sept, 2H, $CHMe_2$, J_{HH} = 7 Hz), 2.21 (s, 6H, HMT CH_3), 2.19 (s, 6H, HMT CH_3), 2.10 (s, 6H, HMT CH_3), 1.52 (s, 3H, $CHCMe_2Ph$), 1.47 (s, 3H, $CHCMe_2Ph$), 1.05 (d, 6H, $CHMe_2$, J_{HH} = 7 Hz), 0.99 (d, 6H, $CHMe_2$, J_{HH} = 7 Hz); $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C) δ 260.65, 152.03, 149.92, 146.25, 145.09, 139.12, 138.77, 137.47, 136.14, 136.05, 131.50, 130.17, 129.35, 128.98, 128.48, 127.69, 127.42, 126.42, 126.28, 122.69, 110.51, 54.16, 32.39, 32.00, 28.31, 24.14, 23.24, 21.67, 21.52, 20.97, 20.54. Anal. Calcd for $C_{50}H_{58}WN_2S$: C, 66.51; H, 6.47; N, 3.10. Found: C, 66.44; H, 6.53; N, 3.07.

W(O)(CH-*t*-Bu)(SHMT)$_2$(PMe$_2$Ph) (5-S). In the glovebox, a 20 mL vial was charged with 102 mg of HMTSH (0.294 mmol, 2.24 equiv), a stir bar, and 5 mL of toluene. Previously titrated 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. $W(O)(CH\text{-}t\text{-}Bu)Cl_2(PMe_2Ph)_2$ (0.131 mmol, 1.0 equiv, 81 mg) and 2.5 mL of toluene were added to the residue, and the mixture was stirred at room temperature for 1.5 h. The cloudy yellow solution was filtered through a bed of Celite, and the solvent was removed from the filtrate under reduced pressure to yield an orange oil. Trituration with pentane (1 mL) for 30 min resulted in an orange suspension, which was filtered. The product (92 mg; 0.084 mmol) was obtained as a yellow powder in 64% yield: ^{1}H NMR (C_6D_6, 20 °C, 500 MHz) δ 8.93 (br s, 1H, C*H*-*t*-Bu), 7.37 (m, 1H, aryl), 7.32 (m, 1H, aryl), 7.13 (m, 2H, aryl), 7.00 (m, 1H, aryl), 6.89−6.85 (overlapping, 10H, aryl), 6.83 (m, 4H, aryl), 2.25 (s, 12H, HMT CH_3), 2.13 (s, 12H, HMT CH_3), 2.11 (s, 12H, HMT CH_3), 1.07−1.04 (overlapping, 15H, CHC-*t*-*Bu*, PMe_2); $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C) δ 284.29, 147.97, 144.29, 142.11, 138.81, 137.21, 136.96, 136.64, 135.78, 135.37, 131.04, 130.89, 129.45, 129.33, 128.74, 128.68, 128.35, 127.42, 125.70, 45.23, 30.51, 30.13, 21.78, 21.64, 21.32, 20.55, 14.65, 14.57; ^{31}P NMR (C_6D_6, 20 °C, 300 MHz, 40 mM) −45.85 (broad s). Attempted recrystallization from pentane afforded decomposition products and free thiol that thwarted several attempted elemental analyses.

W(O)(CH-*t*-Bu)(Me$_2$Pyr)$_2$(PMe$_2$Ph). Li(Me_2Pyr) (0.028 g, 0.277 mmol) was added to a benzene solution (7 mL) of W(O)(CH-*t*-Bu)$Cl_2(PMe_2Ph)_2$ (0.160 g, 0.26 mmol). The reaction mixture was stirred at room temperature for 30 min, and then a second solid portion of Li(Me_2Pyr) (0.027 g, 0.0277 mmol) was added and the reaction mixture was stirred overnight. The cloudy orange 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 (3 mL) overnight resulted in an orange suspension, which was filtered. The orange solid was collected (0.068 g, 0.116 mmol, 45% yield): ^{1}H NMR (C_6D_6) δ 9.83 (s, 1H, WC*H*-*t*-Bu, $^1J_{CH}$ = 115 Hz, $^2J_{HW}$ = 12 Hz), 7.03 (m, 5H, PMe_2Ph), 6.12 (broad s, 4H), 2.31 (broad s, 12H), 1.11 (broad s, 9H, WCH-*t*-*Bu*), 1.10 (broad s, 6H, PMe_2Ph; ^{31}P NMR (C_6D_6) 4.46 (broad s). Anal. Calcd for $C_{24}H_{37}N_2OPW$: C, 49.33; H, 6.38; N, 4.79. Found: C, 49.54; H, 6.33; N, 4.81. This compound was used in the synthesis of **6-S** below.

W(O)(CHCMe$_2$Ph)(Me$_2$Pyr)$_2$(PMe$_2$Ph). A solid portion of Li-(Me_2Pyr) (0.047 g, 0.470 mmol, 1.05 equiv) was added to a benzene solution (10 mL) of $W(O)(CHCMe_2Ph)Cl_2(PMe_2Ph)_2$ (0.300 g, 0.440 mmol). The reaction mixture was stirred at room temperature for 30 min. A second solid portion of Li(Me_2Pyr) (0.048 g, 0.47 mmol, 1.05 equiv) was added, and the reaction mixture was stirred overnight. The cloudy orange solution was filtered directly 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-yellow solid was collected (0.220 g, 0.33 mmol, 75% yield): ^{1}H NMR (C_6D_6) δ 9.83 (s, 1H, WC*H*CMe$_2$Ph, $^1J_{CH}$ = 115 Hz, $^2J_{HW}$ = 15 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); ^{13}C NMR (C_6D_6) δ 286.3 (d, WCHCMe$_2$Ph, $^2J_{CP}$ = 12 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; ^{31}P NMR (C_6D_6) 5.32 (broad s). Anal. Calcd for $C_{29}H_{39}N_2OPW$: C, 53.88; H, 6.08, N, 4.33. Found: C, 53.61, H, 5.65, N, 4.13.

W(O)(CH-*t*-Bu)(Me$_2$Pyr)(SHMT)(PMe$_2$Ph) (6-S). A 100 mL Schlenk flask was charged with 96 mg of W(O)(CH-*t*-Bu)-(Me_2Pyr)$_2$(PMe_2Ph) (0.161 mmol, 1.0 equiv), 80 mg of HSHMT (0.231 mmol, 1.43 equiv), a stir bar, and 11 mL of benzene. The flask was sealed, and the mixture 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 (58 mg; 0.068 mmol) was obtained as an orange powder in 42% yield: ^{1}H NMR (C_6D_6, 20 °C, 500 MHz) δ 10.12 (br s, 1H, C*H*-*t*-Bu, $^1J_{CH}$ = 118 Hz), 7.11 (m, 2H, aryl), 7.03 (m, 3H, aryl), 6.97 (m, 5H, aryl), 6.92 (m, 2H, aryl), 5.97 (s, 2H, $NC_4H_2Me_2$), 2.41 (s, 6H, HMT CH_3), 2.32 (s, 6H, HMT CH_3), 2.08 (s, 6H, HMT CH_3), 2.04 (br s, 6H, $NC_4H_2Me_2$), 0.94 (overlapping signals, 15H, CH-*t*-*Bu*, PMe_2); $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C) δ 303.58, 147.97, 146.97, 142.57, 139.21, 137.21, 136.59, 136.06, 135.52, 135.37, 131.61, 130.88, 130.78, 129.71, 129.62, 128.67, 128.59, 128.52, 128.48, 128.41, 128.35, 127.14, 110.58, 106.52, 45.33, 34.46, 30.85, 22.76, 21.77, 21.33, 21.16, 20.55, 17.03, 14.32, 14.03, 13.94, 13.13; ^{31}P NMR (C_6D_6, 20 °C, 300 MHz, 45 mM) −9.70 (broad s). Anal. Calcd for $C_{43}H_{54}NOPSW$: C, 60.92; H, 6.42; N, 1.65. Found: C, 61.12; H, 6.63; N, 1.08.

W(O)(CH-*t*-Bu)(STPP)$_2$(PMe$_2$Ph) (7-S). In the glovebox, a 20 mL vial was charged with 102 mg of TPPSH (0.246 mmol, 2.20 equiv), a stir bar, and 5 mL of benzene. To this solution was added previously titrated 2.5 M Li-*n*-Bu in hexanes dropwise (0.263 mmol, 2.35 equiv). $W(O)(CH\text{-}t\text{-}Bu)Cl_2(PMe_2Ph)_2$ (0.112 mmol, 1.0 equiv, 69 mg) was added, and the reaction mixture was stirred at room temperature for 3 h. The volatiles were removed under reduced pressure. NMR analysis showed that the starting material was consumed. The residue was dissolved in benzene (2 mL), the solution was filtered through a bed of Celite, and the filtrate was concentrated under reduced pressure. The residue was dissolved in 1.5 mL of toluene, and the solution was stored at −20 °C for 2 h. The resulting precipitate was collected by filtration. The product (80 mg, 0.0647 mmol) was obtained as an off-white powder in 58% yield as a mixture of two isomers: ^{1}H NMR (C_6D_6, 20 °C, 500 MHz; major isomer) δ 9.40 (d, 1H, C*H*-*t*-Bu, $^3J_{PH}$ = 4.3 Hz, $^1J_{CH}$ = 117.1 Hz), 7.96 (m, 1H, aryl), 7.90 (m, 1H, aryl), 7.81 (m, 1H,

dx.doi.org/10.1021/om500655n | *Organometallics* 2014, 33, 5334−5341

aryl), 7.68 (m, 1H, aryl), 7.58 (m, 2H, aryl), 7.50 (m, 1H, aryl), 7.42 (m, 2H, aryl), 7.34−7.32 (aryl, 3H), 7.27−7.22 (aryl, 2H), 7.07−6.98 (aryl, 20H), 6.95−6.88 (aryl, 7H), 6.84 (m, 5H, aryl), 6.51 (m, 1H, aryl), 0.95 (d, 3H, P*Me*, J_{PH} = 9.9 Hz), 0.89 (app s, 9H, CH-*t*-Bu), 0.86 (d, 3H, P*Me*, J_{PH} = 9.8 Hz). NMR samples (for ^{13}C NMR) of the product contained a minor isomer (38% relative to the major isomer) (^{1}H NMR alkylidene resonance at 11.89 for the minor isomer, doublet, $^3J_{PH}$ = 3.5 Hz, $^1J_{CH}$ = 124.0 Hz); ^{13}C{^{1}H} NMR (C_6D_6, 20 °C) δ (mixture of isomers) 304.97 (d, J_{PC} = 12 Hz), 148.72, 146.31, 145.79, 144.97, 144.57, 144.35, 144.02, 143.78, 143.31, 143.14, 142.95, 142.69, 142.37, 141.92, 141.74, 141.37, 141.00, 140.85, 140.56, 140.41, 140.23, 139.88, 139.73, 139.00, 138.81, 138.27, 135.11, 134.11, 134.02, 133.55, 133.45, 133.17, 133.02, 132.35, 132.10, 131.56, 131.48, 131.51, 131.33, 131.28, 131.22, 131.19, 131.14, 131.03, 131.00, 130.90, 130.63, 130.50, 130.40, 130.32, 130.06, 129.92, 129.08, 128.94, 128.59, 128.57, 128.59, 127.78, 127.64, 127.61, 127.53, 126.93, 126.78, 126.53, 126.45, 126.39, 126.16, 125.83, 125.77, 125.70, 45.45, 45.31, 32.20, 31.94, 31.92, 31.57, 17.40, 17.15, 15.86, 15.60, 15.41, 15.16; ^{31}P NMR (C_6D_6, 20 °C) δ 10.0 ($^1J_{PW}$ = 298.8 Hz); resonance at 8.2 ppm ($^1J_{PW}$ = 282.3 Hz) amounts to 35% relative to resonance at 10.0 ppm. Anal. Calcd for $C_{73}H_{63}OPS_2W$: C, 70.98; H, 5.14. Found: C, 71.39; H, 5.40.

General Procedure for 1-Octene Homocoupling Experiments. In the glovebox, a 4 mL vial was charged with ∼5 mg of 4,4′-di-*tert*-butylbiphenyl (as an internal standard), 0.5 mL of C_6D_6, 63 μL of 1-octene (0.400 mmol, 100 equiv), and a stir bar. A separate 2 mL vial was charged with 0.004 mmol of catalyst (3−5 mg, 1.0 equiv) and 0.45 mL of C_6D_6. The contents of the small vial were added to the 4 mL vial. The 4 mL vial was then placed into a 20 mL vial on a stir plate. The 20 mL vial was capped, and the reaction mixture was stirred at room temperature. The 20 mL vial was opened only to remove aliquots. Aliquots (∼100 μL) were removed at the designated times and immediately quenched with benzaldehyde (∼2.5 μL). These aliquots were added to 2 mL of $CDCl_3$ for NMR analysis. Conversion and percent *Z* were determined by ^{1}H NMR.[2b] Evaporation of 1-octene from the system was shown to be negligible for our purposes (<5%) over a period of 24 h; therefore, conversion could be estimated by monitoring the disappearance of the starting material.

General Procedure for ROMP of DCMNBD. In the glovebox, a 4 mL vial was charged with a stir bar, 52 mg of DCMNBD (0.25 mmol, 50.0 equiv), and 1 mL of $CDCl_3$. A second vial was charged with 0.005 mmol of catalyst (3−6 mg, 1.0 equiv) and 1 mL of $CDCl_3$. The contents of the second vial were added to the first, the first vial was sealed, and the contents were stirred at room temperature. Aliquots (∼200 μL) were taken at the designated time points and immediately quenched with benzaldehyde (∼2.5 μL). Conversion and polymer composition were determined by ^{1}H NMR spectroscopy. Cis,syndiotactic polymer, cis,isotactic polymer, and trans,syndiotactic polymer were identified according to the data found in a literature report.[12] Key resonances for cis,syndiotactic polymer: ^{1}H NMR 5.33 ppm (multiplet, olefinic protons); ^{13}C NMR 38.06 ppm (C7 from DCMNBD). Key resonances for cis,isotactic polymer: ^{1}H NMR 5.41 ppm (multiplet, olefinic protons); ^{13}C NMR 38.80 ppm (C7 from DCMNBD). Key resonances for trans,syndiotactic polymer: ^{1}H NMR 5.47 ppm (multiplet, olefinic protons); ^{13}C NMR 37.87 ppm (C7 from DCMNBD).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the National Institutes of Health (Grant GM-59426 to R.R.S. and A.H.H.) for financial support. We thank Gregory Gutierrez for assistance with the microwave reaction. J.H. thanks the Experientia Foundation for a postdoctoral fellowship. We thank the National Science Foundation for departmental X-ray diffraction instrumentation (CHE-0946721).

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