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Synthesis of Tungsten Imido Alkylidene Complexes that Contain an Electron-Withdrawing Imido Ligand

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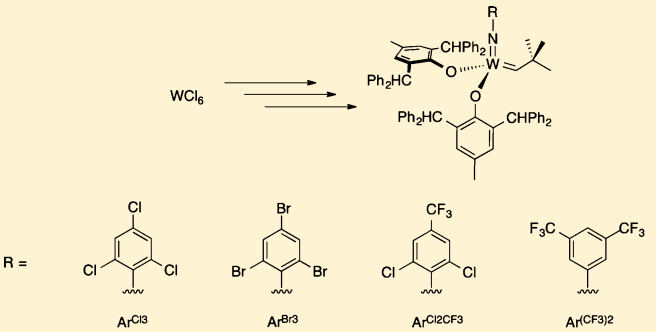
Supporting Information

ABSTRACT: Tungsten NAr^R alkylidene complexes have been prepared that contain the electron-withdrawing Ar^R groups 2,4,6-$X_3C_6H_2$ (Ar^{X3}, X = Cl, Br), 2,6-Cl_2-4-$CF_3C_6H_2$ (Ar^{Cl2CF3}), and 3,5-$(CF_3)_2C_6H_3$ ($Ar^{(CF3)2}$). Reported complexes include $W(NAr^R)_2Cl_2(dme)$ (dme = 1,2-dimethoxyethane), $W(NAr^R)_2(CH_2CMe_3)_2$, $W(NAr^R)(CHCMe_3)(OTf)_2(dme)$, and $W(NAr^R)(CHCMe_3)(ODBMP)_2$ (DBMP = 4-Me-2,6-$(CHPh_2)C_6H_2$). The $W(NAr^R)(CHCMe_3)(ODBMP)_2$ complexes were explored as initiators for the polymerization of 2,3-dicarbomethoxynorbornadiene (DCMNBD).



INTRODUCTION

Olefin metathesis by Mo-, W-, or Ru-based catalysts is a widely applied method for the catalytic formation of C=C bonds.[1,2] The success of metathesis reactions with high-oxidation-state catalysts that have the generic formula M(Z)(CHR)(X)(Y)[3] depends upon M (Mo or W), the electronic and steric nature of Z (an imido or oxo ligand), and the monoanionic ligands X and Y.[4] Most of the progress in the last several years has concerned complexes in which X and Y are pyrrolide or a 2,5-disubstituted pyrrolide and sterically demanding 2,6-terphenoxide ligands. It is becoming increasingly clear that a huge variety of catalysts can be prepared, their activities and selectivities for various reactions can be tuned over a wide range, and no single catalyst is optimal for all reactions.

One of the key variables in M(Z)(CHR)(X)(Y) catalysts is the nature of Z. Perhaps the most dramatic variations are those in which M is tungsten and Z is an oxo ligand[5] or variations in which the imido ligand is relatively electron withdrawing: e.g., NR = NC_6F_5,[6] N-2,6-$Cl_2C_6H_3$.[7] Tungsten complexes that contain NC_6F_5 or N-2,6-$Cl_2C_6H_3$ imido ligands have turned out to be the most successful in several circumstances concerned with the selective formation of (Z)-olefins.[4i,6b] Therefore, we have been interested in synthesizing Mo or W complexes that contain electron-withdrawing imido groups other than the few that are known. Past attempts to make Mo imido alkylidene complexes in which the imido group is NAr^{Cl3} or NAr^{Br3} (NAr^{X3} = N-2,4,6-$X_3C_6H_2$, where X = Cl, Br) failed due to decomposition of bis-imido dialkyl intermediates, even in the solid state, to give the anilines and unidentifiable metal-containing products.[8] The nature of that decomposition was not determined, and syntheses of tungsten complexes were not attempted at that time. In this paper we report the syntheses of tungsten complexes that contain N-2,4,6-$X_3C_6H_2$ (NAr^{X3}, X = Cl, Br), N-2,6-Cl_2-4-$CF_3C_6H_2$ (NAr^{Cl2CF3}), or N-3,5-$(CF_3)_2C_6H_3$ ($NAr^{(CF3)2}$) ligands (Figure 1).

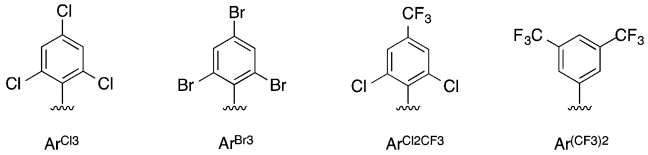


Figure 1. New electron-withdrawing arylimido substituents.

RESULTS AND DISCUSSION

A typical procedure for synthesizing W-based imido alkylidene complexes begins with a reaction between $WO_2Cl_2(dme)$,[9] 2 equiv of aniline, excess base (e.g., triethylamine), and TMSCl to afford complexes of the type $W(NR)_2Cl_2(dme)$.[10] This approach was unsuccessful in our hands for synthesizing $W(NC_6F_5)_2Cl_2(dme)$.[6a] We now find the same to be true for $W(NR)_2Cl_2(dme)$ species in which NR is NAr^{X3}, NAr^{Cl2CF3}, or $NAr^{(CF3)2}$. We propose that the electron-withdrawing nature of the anilines reduces their nucleophilicity to a degree that is insufficient to replace both oxo ligands on the metal. We also found that the *N*-sulfinylamine method reported by Sundermeyer and co-workers,[11] which was successful for preparing $W(NC_6F_5)_2Cl_2(dme)$, was not successful for preparing NAr^{X3}, NAr^{Cl2CF3}, or $NAr^{(CF3)2}$ complexes. We instead turned to an approach that we employed[12a] for the synthesis of $[W(NR)_2Cl_2(RNH_2)]_2$ (R = 1-Ad, *t*-Bu) complexes, in which WCl_6 was treated with 4 equiv of a trimethylsilyl-substituted

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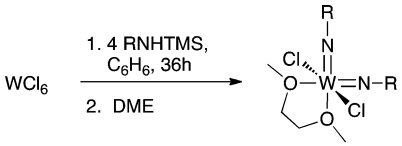
aniline (eq 1), an approach that was employed first by Nielson.[12b] The required ArNH(TMS) (Ar = Ar^{X3}, Ar^{Cl2CF3},

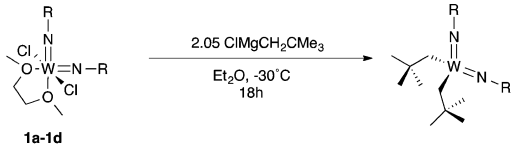


(1)

R = 2,4,6-$Cl_3C_6H_2$ (**1a**), 82%
2,4,6-$Br_3C_6H_2$ (**1b**), 74%
2,6-Cl_2-4-$(CF_3)C_6H_2$ (**1c**), 47%
3,5-$(CF_3)_2C_6H_3$ (**1d**), 65%

$Ar^{(CF3)2}$) reagents can be prepared on a large scale and in high purity through deprotonation of the parent aniline followed by addition of TMSCl (see the Experimental Section). The TMS-substituted aniline was then added to a benzene suspension of WCl_6, and the mixture was stirred for 1.5 days. The solvent was removed in vacuo and replaced by a mixture of DME and pentane, from which the $W(NR)_2Cl_2(dme)$ complexes **1a−d** were all isolated on a relatively large scale in good yields and high purity.

Compounds **1a−d** could be alkylated with neopentylmagnesium chloride to give the dineopentyl complexes $W(NR)_2(CH_2CMe_3)_2$ (**2a−d**; eq 2). Addition of acetonitrile to



(2)

R = 2,4,6-$Cl_3C_6H_2$ (**2a**) 75%
2,4,6-$Br_3C_6H_2$ (**2b**) 65%
2,6-Cl_2-4-$(CF_3)C_6H_2$ (**2c**) 78%
3,5-$(CF_3)_2C_6H_3$ (**2d**) 72%

the crude products (or pentane in the case of **2d**) followed by filtration yielded bright yellow, analytically pure **2a−d** in good yields (65−78%). The dineophyl complexes $W(NR)_2(CH_2CMe_2Ph)_2$ also could be prepared, but since the dineophyl complexes decomposed under the reaction conditions of the next step (addition of triflic acid), their syntheses were not pursued.

$W(NAr^{(CF3)2})_2(CH_2CMe_3)_2$ (**2d**) stood out among this family of dineopentyl complexes. Whereas the others exhibited typical NMR spectra with well-defined $^2J_{WH}$ couplings for the WCH_2 unit, **2d** displayed broad resonances in C_6D_6 at room temperature. Cooling a CD_2Cl_2 solution of this complex to −20 °C resulted in the further broadening of the CH_2 resonance, as well as broadening of the resonances for the protons at the 2- and 6-positions on the aryl ring. Heating a C_7D_8 solution of this same sample above 50 °C resulted in the sharpening of both the CH_2 and aryl resonances. An X-ray study of crystals grown from a diethyl ether solution at −30 °C revealed that this complex is, in fact, an imido-bridged dimer, as shown in Figure 2 (full details can be found in the Supporting Information).

The bond angles centered about the metal atoms give a τ parameter[13] of 0.86, indicating a trigonal-bipyramidal disposition of the ligands about each tungsten atom, where a value of 1 represents a perfect trigonal bipyramid and a value of 0 represents a perfect square pyramid. We suggest that a monomer/dimer interconversion is the cause of the temperature-dependent NMR behavior observed here.

Addition of 3 equiv of triflic acid to complexes **2a−d** resulted in formation of the desired $W(NR)(CHCMe_3)(OTf)_2(dme)$ complexes **3a−d** (eq 3) in good yields. Mixtures of cis and

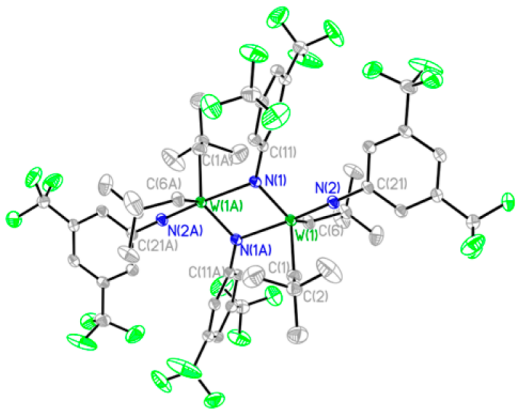
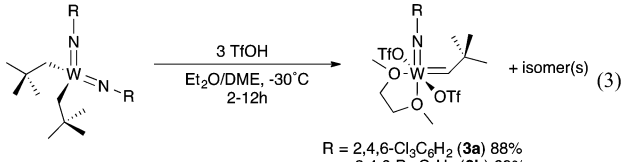


Figure 2. Thermal ellipsoid drawing of the structure of $[W(NAr^{(CF3)2})_2(CH_2CMe_3)_2]_2$ (**2d**). Selected bond distances (Å) and angles (deg): W1−N1 = 1.888(2), W1−N2 = 1.756(7), W1−C1 = 2.135(2), W1−C6 2.126(2), W1−N1A 2.262(2); W1−N1−C11 = 127.0(7), W1−N2−C21 = 179.2(7), W1−C1−C2 = 128.7(9), W1−C6−C7 = 129.1(9), W1−N1−W1A = 104.3(0).

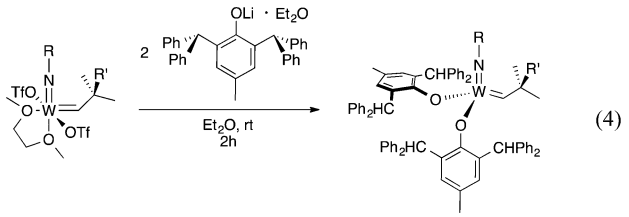


(3)

R = 2,4,6-$Cl_3C_6H_2$ (**3a**) 88%
2,4,6-$Br_3C_6H_2$ (**3b**) 69%
2,6-Cl_2-4-$(CF_3)C_6H_2$ (**3c**) 49%
3,5-$(CF_3)_2C_6H_3$ (**3d**) 84%

trans triflate isomers are observed in ^{1}H NMR spectra in C_6D_6 for **3a−c**, while only one isomer of **3d** is observed in C_6D_6. We do not know at this point why the neophylidene analogues of **3a−d** are not produced under the same conditions. An X-ray structural study of **3a** revealed the structure to be one in which the triflates are cis with respect to one another. All details can be found in the Supporting Information.

With the synthesis of **3a−d** we have the opportunity to prepare and evaluate a derivative in some metathesis reactions in order to compare electron-withdrawing imido groups more thoroughly. At the same time we decided to explore compounds that contain the O-2,6-$(CHPh_2)_2$-4-MeC_6H_2 (ODBMP) ligand, which was introduced recently[14] as a potentially useful bulky phenoxide ligand. Addition of 2 equiv of LiODBMP to the requisite bis-triflate complexes (eq 4) led



(4)

R = 2,4,6-$Cl_3C_6H_2$ (**4a**) 57%
2,4,6-$Br_3C_6H_2$ (**4b**) 69%
2,6-Cl_2-4-$(CF_3)C_6H_2$ (**4c**) 61%
3,5-$(CF_3)_2C_6H_3$ (**4d**) 65%
2,6-$Cl_2C_6H_3$ (**4e**) 63%
C_6F_5 (**4f**) 59%
2,6-$Me_2C_6H_3$ (**4g**) 75%
3,5-$Me_2C_6H_3$ (**4h**) 79%
R' = Me, **4a-g**; Ph, **4h**

to formation of bis-ODBMP complexes, which could be isolated readily in moderate to good yields. The fact that the bis-aryloxide compounds of type **4** can be prepared readily at room temperature suggests that the ODBMP ligand is not as

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sterically demanding as the 2,6-dimesitylphenoxide (HMTO) and 2,6-$(C_6F_5)_2C_6H_3$ ligands, which do not form bis-aryloxide complexes readily.[5a,6a,16] In all cases (**4a−d**) the alkylidene ligand was found to be in the syn orientation. Crystalline **4d** contains 2 equiv of DME that can be removed by dissolving **4d** in toluene and removing all solvent in vacuo. In order to compare **4a−d** with complexes that contain other electron-withdrawing imido groups or that contain more electron-donating groups, compounds **4e−h** were prepared in a similar manner (eq 4).

X-ray-quality crystals of **4a** were obtained from a saturated methylene chloride solution at −30 °C. A drawing of the structure is shown in Figure 3. Bond distances and angles do not significantly deviate from those of known bis-aryloxide species. Details can be found in the Supporting Information.

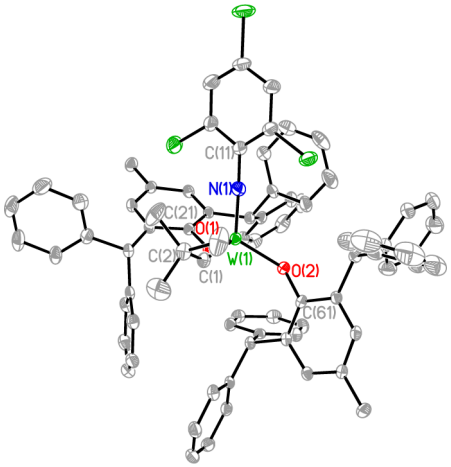
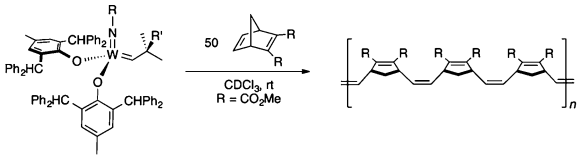


Figure 3. Thermal ellipsoid drawing of the structure of **4a**. Selected bond distances (Å) and angles (deg): W1−N1 = 1.741(2), W1−C1 = 1.897(3), W1−O1 = 1.906(0), W1−O2 = 1.907(2); W1−N1−C11 = 175.4(2), W1−C1−C2 = 144.8(4), W1−O1−C21 = 138.1(1), W1−O2−C61 = 140.8(9).

The ring-opening metathesis polymerization (ROMP) of 2,3-dicarbomethoxynorbornadiene (DCMNBD) (eq 5) was chosen



(5)

as the test metathesis reaction.[15,16] The results of polymerization of 50 equiv of DCMNBD with various initiators in $CDCl_3$ are summarized in Table 1. The resulting poly(DCMNBD) polymers have a relatively high cis content and a bias toward an isotactic microstructure, according to both proton (resonance at 5.41 ppm) and carbon (38.8 ppm) NMR spectra.[15] For example, *x*% cis,isotactic means *x*% of the integrated area of all olefinic resonances (for both cis and trans[17] sequences) centered around the poly(DCMNBD) resonance at 5.41 ppm in $CDCl_3$.

The fastest rates of polymerization were observed employing **4d,f,h**. The estimated value (95% conversion in 5 min) for k_{obs} is >4.1 in those cases. The rates decreased from there in the order **4c** > **4a** ≈ **4e** > **4b** > **4g**. The slowest reaction (employing **4g**) is approximately 2 orders of magnitude slower that for than

Table 1. Polymerization of DCMNBD with Initiators 4a−h in $CDCl_3$[a]

imido substituent	k_{obs} (M^{-1} s^{-1})	polymer structure[c]
2,4,6-$Cl_3C_6H_2$ (**4a**)	0.59	84% cis,iso
2,4,6-$Br_3C_6H_2$ (**4b**)	0.075	71% cis,iso
2,6-Cl_2-4-$(CF_3)C_6H_2$ (**4c**)	1.1	85% cis,iso
3,5-$(CF_3)_2C_6H_3$ (**4d**)	>4.1 (est)[b]	53% cis,iso
2,6-$Cl_2C_6H_3$ (**4e**)	0.51	88% cis,iso
C_6F_5 (**4f**)	>4.1 (est)[b]	85% cis,iso
2,6-$Me_2C_6H_3$ (**4g**)	0.005	75% cis,iso (10% trans)
3,5-$Me_2C_6H_3$ (**4h**)	>4.1 (est)[b]	55% cis,iso

[a]Monomer and initiator concentrations were held constant at 0.002 and 0.1 M, respectively, across three trials for each initiator. [b]Reactions were >95% complete within 5 min. [c]Unless otherwise noted, <5% trans polymer sequences is observed.

other initiators with substituents in the 2- and 6-positions (**4a−c,e**). In particular, initiators with the same substituents at the 2- and 6-positions polymerize DCMNBD at faster rates with more electron-withdrawing substituents at the 4-position (**4c** > **4a** ≈ **4e**). These are significant electronic effects, consistent with past findings that a more electrophilic metal center results in an increase in the metathesis activity of the catalyst.

The failure of these initiators to produce a polymer with a single structure (e.g., cis,isotactic) is typical of bis-alkoxides and bis-aryloxide initiators in general.[15c,d] The reason is that these initiators have mirror symmetry if all ligands are freely rotating at a rate that is faster than the rate of polymerization itself. Any degree of polymer regularity that is observed therefore must be ascribed to some form of chain end control, which in general is not as secure or as general a means of control as is enantiomorphic site control (to give cis,isotactic polymers) or stereogenic metal control (to give cis,syndiotactic polymers) in ROMP with Mo and W initiators.[15c,d]

■ CONCLUSIONS

A new class of tungsten imido complexes that contain strongly electron withdrawing imido ligands has been prepared directly from WCl_6. An exploration of bis-ODBMP complexes as initiators for ROMP suggests that more electron deficient and less sterically demanding arylimido substituents produce more reactive catalysts, as one would expect.[15c,d] In terms of preparing polymers with a stereoregular structure, the results suggest that the bis-ODBMP complexes containing the new electron-withdrawing imido groups do not differ dramatically as ROMP initiators in comparison with initiators that contain other imido ligands, relatively electron withdrawing or not. It remains to be seen whether these new electron-withdrawing imido groups are useful in other types of metathesis reactions.[4]

■ EXPERIMENTAL SECTION

General Procedures. All manipulations of air- and moisture-sensitive materials were preformed either in a Vacuum Atmospheres glovebox (N_2 atmosphere) or on an air-free dual-manifold Schlenk line. All solvents were sparged with nitrogen, passed through activated alumina, and stored over activated 4 Å molecular sieves. W(NAr^F)($CHCMe_3$)$(OTf)_2$(dme),[6a] W($NAr^{2,6Me2}$)($CHCMe_3$)$(OTf)_2$(dme),[18] W($NAr^{3,5Me2}$)($CHCMe_2Ph$)$(OTf)_2$(dme),[19] and W(NAr^{Cl})($CHCMe_3$)$(OTf)_2$(dme)[7b] were prepared according to reported procedures. *N*-Trimethylsilyl-2,4,6-tribromoaniline[20] and *N*-trimethylsilyl-2,6-dichloro-4-trifluoromethylaniline[21] have been previously reported. All other reagents were used as received unless otherwise noted. Methylene chloride-d_2, chloroform-*d*, and benzene-d_6 were

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stored over 4 Å molecular sieves. NMR measurements of air- and moisture-sensitive materials were carried out in Teflon-valve-sealed J. Young type NMR tubes. NMR spectra were recorded using spectrometers at 500 or 300 MHz (^{1}H), 125 MHz (^{13}C), and 282 (^{19}F) MHz, reported in δ (parts per million) relative to tetramethylsilane (^{1}H, ^{13}C) or fluorobenzene (^{19}F) and referenced to residual ^{1}H/^{13}C signals of the deuterated solvent (^{1}H (δ), benzene 7.160, methylene chloride 5.320, chloroform 7.260; ^{13}C (δ), benzene 128.06, methylene chloride 53.84, chloroform 77.16). Midwest Microlabs, Inc., and the CENTC Elemental Analysis Facility at the University of Rochester provided the elemental analysis results.

***N*-(Trimethylsilyl)-2,4,6-trichloroaniline.** Et_2O (50 mL) was placed in a Schlenk flask under argon containing 2,4,6-trichloroaniline that had been recrystallized from hot hexane. The solution was chilled to −78 °C, *n*-butyllithium (2.0 M in cyclohexane, 4.03 mL, 8.06 mmol) was added via syringe under an argon flow, and the resulting white slurry was stirred for 2 h; the slurry acquired a reddish tint over time. Trimethylsilyl chloride (1.86 mL, 14.6 mmol) was added via syringe, and the solution was warmed to room temperature. The solvent was removed, and the orange residue was charged with CH_2Cl_2. The mixture was filtered over Celite, the Celite washed with CH_2Cl_2, and the filtrate concentrated under reduced pressure to give an analytically pure orange oil: yield 90% (1.776 g, 6.61 mmol); ^{1}H NMR (C_6D_6, 20 °C) δ 6.95 (s, 2H, Ar), 3.76 (s, 1H, N*H*), 0.16 (s, 9H, SiMe_3); ^{13}C NMR (C_6D_6, 20 °C) δ 179.5, 141.3, 124.8, 123.6, 1.8. Anal. Calcd for $C_9H_{12}Cl_3NSi$: C, 40.24; H, 4.50; N, 5.21. Found: C, 40.01; H, 4.39; N, 5.22.

***N*-(Trimethylsilyl)-2, 6-dichloro-4-trifluoromethylaniline.** Diethyl ether (200 mL) was placed in a Schlenk flask under nitrogen containing 2,6-dichloro-4-trifluoromethylaniline (14.39 g, 62.6 mmol) and was cooled to −78 °C. *n*-Butyllithium (2.5 M in henxane, 26.3 mL, 65.7 mmol) was added over 15 min to the stirred solution. The solution was stirred at −78 °C for 2 h and then taken out of the cold bath, during which time a dark red-brown color evolved. Trimethylsilyl chloride (15.9 mL, 125 mmol) was then added dropwise to afford a light yellow slurry. This mixture was warmed to room temperature and was filtered through Celite. The yellow filtrate was concentrated under reduced pressure to give an analytically pure orange oil: yield 18.90 g (98%); ^{1}H NMR (C_6D_6, 20 °C) δ 7.24 (s, 2H, Ar), 4.21 (bs, 1H, N*H*), 0.16 (s, 9H, TMS); ^{13}C NMR (C_6D_6, 20 °C) δ 145.7, 125.4 (m), 123.9 (q, $^1J_{CF}$ = 271 Hz), 123.4, 121.3 (q, $^2J_{CF}$ = 33.8 Hz), 2.2 (m); ^{19}F NMR (C_6D_6, 20 °C) δ −61.8. Anal. Calcd for $C_{10}H_{12}Cl_2F_3NSi$: C, 39.75; H, 4.00; N, 4.64; Found: C, 40.06; H, 3.84; N, 4.42.

W(NAr^{Cl3})$_2$Cl$_2$(dme) (1a). WCl_6 (0.568 g, 0.143 mmol) was added to toluene (25 mL) in a round-bottom flask. A solution of *N*-trimethylsilyl-2,4,6-trichloroaniline (1.539 g, 0.572 mmol) in toluene was added to the stirred WCl_6 solution. The red-orange mixture was stirred for 2 days, after which the solvent was removed in vacuo. Pentane (20 mL) and 2 mL of DME were added to the viscous residue, and the mixture was stirred. The precipitated orange solid was isolated by filtration: yield 82% (757 mg, 0.118 mmol);: ^{1}H NMR (C_6D_6, 20 °C) δ 6.93 (s, 4H, Ar), 3.61 (s, 6H, CH_3), 3.16 (s, 4H, CH_2); ^{13}C NMR (C_6D_6, 20 °C) δ 149.0, 132.9, 130.4, 127.8, 71.5, 64.9. Anal. Calcd for $C_{16}H_{14}Cl_8N_2O_2W$: C, 26.19; H, 1.92; N, 3.82. Found: C, 26.26; H, 1.96; N, 3.75.

W(NAr^{Cl3})$_2$(CH$_2$CMe$_3$)$_2$ (2a). W(NAr^{Cl3})$_2$(dme)Cl$_2$ (10g, 13.6 mmol) was charged in a round-bottom flask with 200 mL of Et_2O, and the flask was chilled to −30 °C for 1 h. Neopentylmagnesium chloride (1.68 M, 16.6 mL, 27.9 mmol) was added dropwise via syringe. The resulting mixture was stirred overnight. The suspension was filtered over Celite, and the Celite cake was washed thoroughly with Et_2O. The volatiles were removed from the filtrate under vacuum to afford a red oil. Acetonitrile and minimal diethyl ether were added to the viscous residue, and the mixture was stirred. The precipitated yellow solid was filtered off and rinsed once with acetonitrile: yield 75% (7.322 g); ^{1}H NMR (C_6D_6, 20 °C) δ 9.94 (s, 4H, Ar), 2.19 (s, 4H, CH_2), 1.16 (s, 18H, CMe_3); ^{13}C NMR (C_6D_6, 20 °C) δ 149.7, 131.4, 129.5, 127.9, 95.6, 35.4, 34.1. Anal. Calcd for $C_{22}H_{26}Cl_6N_2W$: C, 36.96; H, 3.67; N, 3.92. Found: C, 37.11; H, 3.78; N, 4.02.

W(NAr^{Cl3})(CHCMe$_3$)(OTf)$_2$(dme) (3a). W(NAr^{Cl3})(CH$_2$CMe$_3$)$_2$ (7.15 g, 10.0 mmol) was charged in a flask with 50 mL of Et_2O and 25 mL of DME and chilled to −30 °C for 2 h. A solution of triflic acid (4.50 g, 30.0 mmol) in 5 mLof chilled Et_2O was added dropwise to the stirred mixture. The resulting mixture was stirred for 1.5 h and warmed to room temperature. The solvents were removed in vacuo from the resulting mixture, and CH_2Cl_2 was added. The salts were removed by filtration through Celite, and the filtrate was taken to dryness in vacuo to give the desired product: yield 7.37 g (88%); ^{1}H NMR (CD_2Cl_2, 20 °C) (major isomer) δ 11.51 (s, 1H, W=C*H*), 7.47 (s, 2H, Ar), 4.58 (s, 3H, CH_3), 4.39 (m, 1H, C*H*), 4.31 (m, 1H, C*H*), 4.11 (m, 1H, C*H*) 3.72 (s, 3H, CH_3), 3.72 (m, 1H, C*H*), 1.22 (s, 9H, CMe_3); ^{13}C NMR (C_6D_6, 20 °C) δ (2 isomers) 302.6 ($^1J_{WC}$ = 169 Hz), 294.7 ($^1J_{WC}$ = 169 Hz), 147.6, 147.4, 135.2, 133.5, 132.9, 128.4, 128.3, 120.6 (q, $^1J_{CF}$ = 315 Hz), 119.8 (q, $^1J_{CF}$ = 315 Hz), 119.7 (q, $^1J_{CF}$ = 315 Hz), 81.3, 78.4, 74.4, 70.6, 70.2, 67.2, 63.0, 61.3, 48.4, 48.2, 33.3, 33.1; ^{19}F NMR (CD_2Cl_2, 20 °C) (major isomer) δ −77.4, −78.2. Anal. Calcd for $C_{17}H_{22}Cl_3F_6NO_8S_2W$: C, 24.40; H, 2.65; N, 1.67. Found: C, 24.25; H, 2.32; N, 1.59.

W(NAr^{Cl3})(CHCMe$_3$)(ODBMP)$_2$ (4a). Compound **3a** (95 mg, 0.114 mmol) was charged with LiODBMP·Et_2O (101 mg, 0.227 mmol) in 10 mL of Et_2O at room temperature. The mixture was stirred for 2 h to yield an orange solution with a precipitate. The solvent was removed in vacuo, and CH_2Cl_2 was added to the residue. The mixture was filtered through a Celite plug, and solvents were removed from the filtrate in vacuo. Pentane was added to the orange residue, and the mixture was stirred for 1 h to give a yellow solid, which was isolated by filtration. Analytically pure product was obtained by recrystallization from toluene: yield 86 mg (57%); ^{1}H NMR (CD_2Cl_2, 20 °C) δ 9.29 (s, 1H, W=C*H*), 7.12 (m. 14H, Ar), 6.89−6.78 (m, 28H, Ar), 6.56 (s, 4H, Ar), 5.84 (s, 4H, C*H*Ph$_2$), 2.11 (s, 6H, CH_3), 1.13 (s, 9H, CMe_3); ^{13}C NMR (CD_2Cl_2, 20 °C) δ 255.0, 159.5, 149.8, 144.4, 143.5, 133.3, 133.3, 131.5, 130.4, 130.1, 130.1, 129.9, 128.5, 128.4, 127.6, 126.5, 126.4, 50.1, 45.9, 34.5, 21.3. Anal. Calcd for $C_{77}H_{66}Cl_3NO_2W$: C, 69.66; H, 5.01; N, 1.06. Found: C, 69.52; H, 4.81; N, 1.04.

W(NAr^{Br3})$_2$Cl$_2$(dme) (1b). WCl_6 (3.51 g, 8.87 mmol) was added to benzene (150 mL) in a round-bottom flask. *N*-Trimethylsilyl-2,4,6-tribromoaniline (19.26 g, 35.5 mmol) was added, and the dark red mixture was stirred for 36 h, after which the solvent was removed in vacuo. Minimal DME was added to the red viscous solid, and the resulting yellow solid was isolated by filtration and washed twice with minimal DME: yield 6.53 g (74%); ^{1}H NMR (C_6D_6, 20 °C) δ 7.37 (s, 4H, Ar), 3.60 (s, 6H, CH_3), 3.07 (s, 4H, CH_2); ^{13}C NMR (C_6D_6, 20 °C) δ 151.8, 134.2, 122.1, 118.5, 71.4, 65.0. Anal. Calcd for $C_{16}H_{14}Br_6Cl_2N_2O_2W$: C, 19.21; H, 1.41; N, 2.80. Found: C, 19.65; H, 1.26; N, 2.86.

W(NAr^{Br3})$_2$(CH$_2$CMe$_3$)$_2$ (2b). A solution of W(NAr^{Br3})$_2$Cl$_2$(dme) (6.0 g, 6.0 mmol) in diethyl ether was chilled for 1 h, after which neopentylmagnesium chloride (1.55 M in Et_2O, 7.91 mL, 12.3 mmol) was added. After 2 h, 2 mL of dioxane was added. The mixture was stirred for 20 min and filtered through Celite. The Celite pad was washed thoroughly with dichloromethane, and the solvents were removed from the filtrate in vacuo. Acetonitrile was added to the residue, and the resulting yellow solid was isolated by filtration: yield 3.81 g (65%); ^{1}H NMR (C_6D_6, 20 °C) δ 7.36 (s, 4H, Ar), 2.27 (s, 4H, CH_2), 1.21 (s, 18H, CMe_3); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 152.6, 134.1, 121.6, 116.9, 97.3, 34.9, 34.1. Anal. Calcd for $C_{22}H_{26}Br_6N_2W$: C, 26.92; H, 2.67; N, 2.85. Found: C, 27.27; H, 2.50; N, 2.96.

W(NAr^{Br3})(CHCMe$_3$)(OTf)$_2$(dme) (3b). W(NAr^{Br3})$_2$(CH$_2$CMe$_3$)$_2$ (3.67 g, 3.74 mmol) was added to a mixture of 30 mL of Et_2O and 20 mL of DME, and the solution was cooled to −30 °C for 1 h. A solution of trifluoromethanesulfonic acid (1.68 g, 11.2 mmol) in ∼4 mL of Et_2O was added dropwise to yield a deep red-orange solution. The solution was stirred for 1 h, after which the volatiles were removed in vacuo. The residue was dissolved in CH_2Cl_2, and the solution was filtered through Celite. The solvents were removed from the filtrate in vacuo. The residue was triturated with pentane, and the resulting yellow solid was isolated by filtration: yield 2.50 g (69%) (repeated isolations may be necessary in order to remove all anilinium

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triflate salts); ^{1}H NMR (CD_2Cl_2, 20 °C) δ (major isomer) 11.47 (s, 1H, W=C*H*), 7.48 (s, 2H, Ar), 4.59 (s, 3H, CH_3), 4.44 (m, 1H, C*H*), 4.31 (m, 1H, C*H*), 4.06 (m, 1H, C*H*), 3.75 (s, 3H, CH_3), 3.73 (m, 1H, C*H*), 1.24 (s, 9H, CMe_3); ^{13}C NMR (CD_2Cl_2, 20 °C) δ (major isomer) 303.2 (W=C), 150.4, 135.2, 124.0, 121.5, 120.0 (q, J_{CF} = 316 Hz), 119.0 (q, $^1J_{CF}$ = 316 Hz), 82.0, 79.2, 71.8, 62.3, 48.5, 32.9; ^{19}F NMR (CD_2Cl_2, 20 °C) δ −77.3 (major), −77.4 (minor), −77.1 (major). Anal. Calcd for $C_{17}H_{22}Br_3F_6NO_8S_2W$: C, 21.05; H, 2.29; N, 1.44. Found: C, 21.00; H, 2.15; N, 1.23.

W(NAr^{Br3})(CHCMe$_3$)(ODBMP)$_2$ (4b). Solid LiODBMP·Et_2O (144 mg, 0.276 mmol) and **3b** (134 mg, 0.138 mmol) were added to 10 mL of Et_2O at room temperature. Workup and isolation of the product followed the same procedure as for **4a**. Analytically pure product was obtained by recrystallization from toluene/pentane: yield 139 mg (69%); ^{1}H NMR (CD_2Cl_2, 20 °C) δ 9.82 (s, 1H, W=C*H*), 7.50 (s, 2H, Ar), 7.13 (m, 12H, Ar), 6.94 (m, 12H, Ar), 6.86 (m, 8H, Ar), 6.80 (m, 8H, Ar), 6.62 (s, 4H, Ar), 6.01 (s, 4H, C*H*Ph$_2$), 2.14, (s, 6H, CH_3), 1.13 (s, 9H, CMe$_3$); ^{13}C NMR (CD_2Cl_2, 20 °C) δ 260.6, 159.8, 144.4, 143.6, 134.2, 133.6, 133.4, 131.5, 130.2, 130.1, 130.0, 128.5, 128.4, 126.5, 126.4, 123.6, 50.2, 46.0, 34.4, 21.3. Anal. Calcd for $C_{77}H_{66}Br_3NO_2W$: C, 63.31; H, 4.55; N, 0.96. Found: C, 63.63; H, 4.56; N, 0.89.

W(NAr^{Cl2CF3})$_2$Cl$_2$(dme) (1c). *N*-Trimethylsilyl-2,6-dichloro-4-(trifluoromethyl)aniline (44.65 g, 148 mmol) was added to a solution of WCl_6 (14.6 g, 36.9 mmol) in 400 mL of benzene. The mixture was stirred for 48 h, and all solvents were removed in vacuo. Miminal DME was added to the residue, followed by pentane. The precipitate was isolated on a glass frit and washed with pentane: yield 24.98 g (85%); ^{1}H NMR (C_6D_6, 20 °C) δ 7.21 (s, 4H, Ar), 3.54 (s, 6H, CH_3), 3.05 (s, 4H, CH_2); ^{13}C NMR (C_6D_6, 20 °C) δ 132.7, 127.0, 125.1 (q), 124.6, 121.0, 71.4, 64.9. Anal. Calcd for $C_{18}H_{14}N_2F_6Cl_4O_2W$: C, 26.99; H, 1.76; N, 3.50. Found: C, 26.92; H, 1.72; N, 3.23.

W(NAr^{Cl2CF3})$_2$(CHCMe$_3$)$_2$ (2c). A solution of **1c** (4.21g, 5.25 mmol) in 150 mL of Et_2O was chilled for 1 h. Neopentylmagnesium chloride (1.555 M in Et_2O, 6.93 mL, 10.8 mmol) was added dropwise to the mixture. After 2 h, the suspension was filtered through Celite and the Celite pad was washed with Et_2O until the filtrate ran colorless. The solvents were removed from the filtrate in vacuo. A small quantity of acetonitrile was added to the residue, and the resulting yellow solid was isolated by filtration: yield 3.21 g (78%); ^{1}H NMR (C_6D_6, 20 °C) δ 7.27 (s, 4H, Ar), 2.25 (s, 4H, CH_2), 1.15 (s, 18H, CMe_3); ^{13}C NMR (CD_2Cl_2, 20 °C) δ 153.2, 131.7, 126.5, 125.3, 123.4, 97.4, 35.6, 34.1; ^{19}F NMR (C_6D_6, 20 °C) δ −62.5. Anal. Calcd for $C_{24}H_{26}Cl_4F_6N_2W$: C, 36.86; H, 3.35; N, 3.58. Found: C, 37.26; H, 3.28; N, 3.53.

W(NAr^{Cl2CF3})$_2$(CHCMe$_3$)(OTf)$_2$(dme) (3c). A solution of W(NAr^{Cl2CF3})$_2$(CH_2CMe$_3$)$_2$ (2.23 g, 2.85 mmol) in a mixture of 30 mL of Et_2O and 15 mL of DME was chilled to −30 °C overnight. HOTf (1.28g, 8.55 mmol) in 5 mL of cold Et_2O was added dropwise to the red solution. After 1.5 h, the volatiles were removed in vacuo and minimal dichloromethane was added to the residue. The mixture was filtered through Celite, and the solvents were removed from the filtrate in vacuo. Pentane was added to the residue, and the insoluble product was isolated by filtration: yield 1.22 g (49%); ^{1}H NMR (CD_2Cl_2, 20 °C) δ 11.52 (s, 1H, W=C*H*), 7.72 (s, 2H, Ar), 4.61 (s, 3H, CH_3), 4.38 (m, 2H, C*H*), 4.16 (m, 1H, C*H*), 3.73 (s, 3H, CH_3), 3.73 (m, 1H, C*H*), 1.23 (s, 9H, CMe_3); ^{13}C NMR (CD_2Cl_2, 20 °C) δ 303.8 (W=C, $^1J_{WC}$ = 170 Hz), 150.9, 135.7, 129.8 (q, $^2J_{CF}$ = 34.4 Hz), 126.2, 120.0 (q, $^1J_{CF}$ = 315 Hz), 119.2 ($^1J_{CF}$ = 315 Hz), 119.1 ($^1J_{CF}$ = 315 Hz), 82.4, 79.6, 71.7, 62.2, 48.5, 33.0; ^{19}F NMR (CD_2Cl_2, 20 °C) δ −77.4, −78.2. Anal. Calcd for $C_{18}H_{22}Cl_2F_9NO_8S_2W$: C, 24.84; H, 2.55; N 1.61. Found: C, 24.78; H, 2.38; N 1.47.

W(NAr^{Cl2CF3})(CHCMe$_3$)(ODBMP)$_2$ (4c). A mixture of **3c** (112 mg, 0.129 mmol) and LiODBMP·Et_2O (134 mg, 0.257 mmol) in 10 mL of Et_2O was stirred overnight. Workup and isolation followed the procedure employed for isolation of **4a**. Analytically pure product was obtained by recrystallization from a mixture of toluene and pentane: yield 106 mg (61%); ^{1}H NMR (CD_2Cl_2, 20 °C) δ 9.31 (s, 1H, W=C*H*), 7.38 (s, 2H, Ar), 7.15−7.09 (m, 12H, Ar), 6.93−6.86 (m, 12H, Ar), 6.84−6.74 (m, 16H, Ar), 6.57 (s, 4H, Ar), 5.85 (s, 4H, C*H*Ph$_2$), 2.11 (s, 6H, CH_3), 1.11 (s, 9H, CMe_3); ^{13}C NMR (CD_2Cl_2, 20 °C) δ 256.4, 144.3, 143.5, 133.3, 133.3, 131.8, 130.0, 129.9, 129.7, 128.9, 128.6, 128.5, 128.4, 126.5, 126.5, 124.9 ($^2J_{CF}$ = 3.75 Hz), 123.3 ($^1J_{CF}$ = 270 Hz), 50.1, 45.9, 34.5, 21.3; ^{19}F NMR (C_6D_6, 20 °C) δ −62.5. Anal. Calcd for $C_{78}H_{66}Cl_2F_3NO_2W$: C, 68.83; H, 4.89; N, 1.03. Found: C, 69.08; H, 4.82; N 1.00.

W(NAr$^{(CF3)2}$)$_2$Cl$_2$(dme) (1d). *N*-Trimethylsilyl-3,5-bis-(trifluoromethyl)aniline (65 g, 215 mmol) was added over 10 min to a solution of WCl_6 (21.33 g, 53.8 mmol) in 400 mL of benzene in a round-bottom flask. The red-orange mixture was stirred for 36 h, and the mixture was filtered through a glass frit. The solid was washed with minimal DME and pentane to give a yellow-orange solid: three crops gave a total yield of 30.2 g (70%); ^{1}H NMR (C_6D_6, 20 °C) δ 7.52 (s, 2H, Ar), 7.29 (s, 1H, Ar), 3.29 (s, 6H, CH_3), 2.93 (s, 4H, CH_2); ^{13}C NMR (C_6D_6, 20 °C) δ 156.2, 132.4 (q, $^2J_{CF}$ = 33.8 Hz), 123.8, 123.6 (q, $^1J_{CF}$ = 271 Hz), 119.0, 71.5, 64.6; ^{19}F NMR (C_6D_6, 20 °C) δ −63.6. Anal. Calcd for $C_{20}H_{16}Cl_2F_{12}N_2O_2W$: C, 30.06; H, 2.02; N, 3.51. Found: C, 29.98; H, 2.09; N, 3.38.

W(NAr$^{(CF3)2}$)$_2$(CH$_2$CMe$_3$)$_2$ (2d). A solution of W(NAr$^{(CF3)2}$)-Cl$_2$(dme) (1.00 g, 1.25 mmol) in Et_2O was chilled for 1 h. Neopentylmagnesium chloride (1.06 mL, 2.57 mmol, 2.42 M in Et_2O) was added dropwise, and the mixture was stirred overnight. The solvents were removed from the mixture. Diethyl ether was added to the residue, and the mixture was filtered through Celite. Toluene was added to the filtrate, and all volatiles were removed in vacuo. Pentane was added to the resulting yellow solid, and the solid was filtered off to give the product. Analytically pure product was obtained by recrystallization from CH_2Cl_2/pentane: yield 699 mg (72%); ^{1}H NMR (C_6D_6, 20 °C) δ 7.49 (s, 4H, Ar), 7.45 (s, 2H, Ar), 1.75 (s, 4H, CH_2), 0.99 (s, 18H, CMe_3); ^{13}C NMR (CD_2Cl_2, 20 °C) δ 157.5, 132.4 (q, $^2J_{CF}$ = 33.8 Hz), 124.7, 123.5 (q, $^1J_{CF}$ = 271 Hz), 118.5, 97.2, 37.3, 34.3; ^{19}F NMR (C_6D_6, 20 °C) δ −63.5. Anal. Calcd for $C_{26}H_{28}F_{12}N_2W$: C, 40.02; H, 3.62; N, 3.59. Found: C, 39.93; H, 3.57; N, 3.43.

W(NAr$^{(CF3)2}$)(CHCMe$_3$)(OTf)$_2$(dme) (3d). A solution of **2d** (289 mg, 0.370 mmol) in a mixture of 7 mL of DME and 7 mL of Et_2O was chilled to −30 °C for 2 h. A chilled solution of HOTf (166 mg, 1.11 mg) in 4 mL of Et_2O was added dropwise. After the reaction mixture was stirred overnight, the solvent was removed in vacuo. Toluene was added to the residue, and the mixture was filtered through Celite. The solvents were remived from the filtrate in vacuo, and pentane was added to the residue. The yellow product was isolated on a glass frit: yield 321 mg (84%); ^{1}H NMR (C_6D_6, 20 °C) δ 10.45 (s, 1H, W=C*H*), 8.40 (s, 2H, Ar), 7.53 (s, 1H, Ar), 3.07 (s, 3H, CH_3), 2.96 (t, 2H, CH_2), 2.80 (s, 3H, CH_3), 2.43 (t, 2H, CH_2), 1.35 (s, 9H, CMe_3); ^{13}C NMR (C_6D_6, 20 °C) δ 291.2 (W=C), 154.9, 133.0 (q, $^2J_{CF}$ = 33.8 Hz), 128.5 (m), 123.3 (q, $^1J_{CF}$ = 272 Hz), 121.5 (m), 119.8 (q, $^1J_{CF}$ = 376 Hz), 74.5, 69.8, 64.5, 62.3, 48.8, 33.7; ^{19}F NMR (C_6D_6, 20 °C) δ −63.5, −77.2. Anal. Calcd for $C_{19}H_{23}F_{12}NO_8S_2W$: C, 26.25; H, 2.67; N, 1.61. Found: C, 25.86; H, 2.45; N, 1.50.

W(NAr$^{(CF3)2}$)(CHCMe$_3$)(ODBMP)$_2$·2 DME (4d). Compound **3d** (75 mg, 0.086 mmol) and LiODBMP·Et_2O (90 mg, 0.173 mmol) were added to 10 mL of Et_2O at room temperature, and the mixture was stirred overnight. Solvents were removed from the mixture in vacuo. The residue was dissolved in toluene, and the mixture was filtered through Celite. The solvents were removed from the filtrate in vacuo, ∼1 mL of DME was added, and the mixture was cooled to −30 °C overnight to give a yellow-orange crystalline product. The mother liquor was drawn off, the solid was washed once with cold DME, and the solid was dried in vacuo: yield 86 mg (65%); ^{1}H NMR (CD_2Cl_2, 20 °C) δ 7.13−7.03 (m, 25H, Ar + W=C*H*), 6.98−6.88 (m, 17H, Ar), 6.75 (s, 2H, Ar), 6.59 (s, 4H, Ar), 5.94 (s, 4H, C*H*Ph$_2$), 3.47 (s, 8H, CH_2), 3.32 (s, 12H, CH_3), 2.12 (s, 6H, CH_3), 0.83 (s, 9H, CMe_3); ^{13}C NMR (CD_2Cl_2, 20 °C) δ 248.0, 158.3, 156.5, 144.1, 143.4, 132.6, 131.4, 131.3 (q, $^2J_{CF}$ = 33.75 Hz), 130.0, 129.9, 129.7, 128.68, 128.65, 126.8, 126.7, 126.2 (m), 123.6 (q, $^1J_{CF}$ = 271 Hz), 118.0 (m), 72.2, 59.1, 50.5, 45.2, 33.5, 21.3; ^{19}F NMR (CD_2Cl_2, 20 °C) δ −65.4. Anal. Calcd for $C_{87}H_{87}F_6NO_6W$: C, 67.83; H, 5.69; N, 0.91. Found: C, 68.04; H, 5.37; N, 1.06.

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W(NAr^{Cl})(CHCMe$_3$)(ODBMP)$_2$ (4e). A mixture of W(NAr^{Cl})(CHCMe$_3$)(OTf)$_2$(dme) (97 mg, 0.121 mmol) and LiODBMP·Et$_2$O (126 mg, 0.242 mmol) in 10 mL of Et$_2$O at room temperature was stirred overnight. Workup and isolation followed the procedure employed for **4a**. Analytically pure product was obtained by recrystallization from a mixture of toluene and pentane: yield 99 mg (63%); ^{1}H NMR (CD$_2$Cl$_2$, 20 °C) δ 9.32 (s, 1H, W=C*H*), 7.16−7.08 (m, 14H, Ar), 9.94 (t, 1H, Ar), 6.90−6.76 (m, 28H, Ar), 6.54 (s, 4H, Ar), 5.84 (s, 4H, C*H*Ph$_2$), 2.10 (s, 6H, C*H*$_3$), 1.13 (s, 9H, C*Me*$_3$); ^{13}C NMR (CD$_2$Cl$_2$, 20 °C) δ 254.6, 159.5, 150.9, 144.5, 143.6, 133.4, 133.0, 131.3, 130.1, 130.0, 129.9, 128.4, 128.3, 127.7, 126.5, 126.4, 126.1, 50.0, 45.9, 34.5, 21.3. Anal. Calcd for C$_{77}$H$_{67}$Cl$_2$NO$_2$W: C, 71.52; H, 5.22; N, 1.08. Found: C, 71.38; H, 5.15; N, 0.86.

W(NAr^{F})(CHCMe$_3$)(ODBMP)$_2$ (4f). A mixture of W(NAr^{F})(CHCMe$_3$)(OTf)$_2$(dme) (126 mg, 0.153 mmol) and LiODBMP·Et$_2$O (159 mg, 0.306 mmol) in 10 mL of Et$_2$O was stirred for 2 h. Workup and isolation followed the procedure employed for **4a**: yield 118 mg (59%); ^{1}H NMR (C$_6$D$_6$, 20 °C) δ 7.20 (m, 14H, Ar), 7.05−6.85 (30H, Ar), 6.32 (s, 4H, C*H*Ph$_2$), 1.83 (s, 6H, C*H*$_3$), 1.14 (s, 9H, C*Me*$_3$); ^{13}C NMR (CD$_2$Cl$_2$, 20 °C) δ 251.7, 144.6, 144.1, 144.0, 143.3, 142.7, 138.8, 136.5, 132.8, 130.00, 129.98, 129.7, 128.9, 128.57, 128.55, 126.7, 126.5, 50.1, 45.3, 33.7, 21.3; ^{19}F NMR (C$_6$D$_6$, 20 °C) δ −147.1 (t, 2F), −160.3 (d, 2F), −164.6 (s, 1F). Anal. Calcd for C$_{77}$H$_{64}$F$_5$NO$_2$W: C, 70.37; H, 4.91; N, 1.07. Found: C, 70.13; H, 4.83; N, 0.98.

W(NAr^{2,6Me2})(CHCMe$_3$)(ODBMP)$_2$ (4g). A mixture of W(NAr′)(CHCMe$_3$)(OTf)$_2$(dme) (133 mg, 0.175 mmol) and LiODBMP·Et$_2$O (182 mg, 0.349 mmol) in 10 mL of Et$_2$O was stirred for 2 h. Workup and isolation followed the procedure employed for **4a**: yield 164 mg (75%); ^{1}H NMR (CD$_2$Cl$_2$, 20 °C) δ 9.12 (s, 1H, W=C*H*), 7.15−7.08 (m, 12H, Ar), 6.90−6.74 (m, 31H, Ar), 6.56 (s, 4H, Ar), 5.82 (s, 4H, C*H*Ph$_2$), 2.10 (s, 6H, C*H*$_3$), 1.86 (s, 6H, C*H*$_3$), 1.07 (s, 9H, C*Me*$_3$); ^{13}C NMR (CD$_2$Cl$_2$, 20 °C) δ 249.7, 159.3, 155.3, 144.5, 143.6, 135.2, 133.3, 131.1, 130.10, 130.05, 129.7, 128.4, 128.3, 127.4, 126.5, 126.4, 125.9, 50.0, 46.1, 34.6, 21.2, 19.8. Anal. Calcd for C$_{79}$H$_{73}$NO$_2$W: C, 75.77; H, 5.88; N, 1.12. Found: C, 76.16; H, 6.00; N, 0.93.

W(NAr^{3,5Me2})(CHCMe$_2$Ph)(ODBMP)$_2$ (4h). A mixture of W(NAr^{3,5Me2})(CHCMe$_2$Ph)(OTf)$_2$(dme) (93 mg, 0.123 mmol) and LiODBMP·Et$_2$O (127 mg, 0.244 mmol) in 10 mL of Et$_2$O was stirred for 2 h. Workup and isolation followed the procedure employed for **4a**: yield 118 mg (79%); ^{1}H NMR (CD$_2$Cl$_2$, 20 °C) δ 7.11−6.81 (m, 39H, W=C*H* + Ar), 6.74 (d, 2H, Ar), 6.68 (s, 1H, Ar), 6.60 (s, 4H, Ar), 6.12 (s, 2H, Ar), 5.90 (s, 4H, C*H*Ph$_2$), 2.16 (s, 6H, C*H*$_3$), 2.01 (s, 6H, C*H*$_3$), 1.33 (s, 6H, C*Me*$_2$Ph); ^{13}C NMR (CD$_2$Cl, 20 °C) δ 242.8, 158.7, 156.0, 152.1, 144.4, 143.7, 137.7, 133.0, 131.0, 130.1, 130.0, 129.5, 128.6, 128.5, 128.0, 127.9, 126.6, 126.6, 126.5, 125.6, 124.6, 51.7, 50.3, 34.2, 21.3, 21.1. Anal. Calcd for C$_{84}$H$_{75}$NO$_2$W: C, 76.76; H, 5.75; N, 1.07. Found: C, 77.13; H, 5.90; N, 0.76.

Procedure for Polymerization using W(R)(CHMe$_2$R′)(ODBMP)$_2$ as the Initiator. From a 0.2 M stock solution in CDCl$_3$, 1 mL (50 equiv) of dicarbomethoxynorbornadiene (DCMNBD) was charged with 1 mL of a 0.004 M stock solution of the catalyst in CDCl$_3$. Aliquots were taken out of the reaction vial approximately every 6−9 min for three to four cycles, brought outside the glovebox in a capped vial, and quenched with wet CDCl$_3$. Integrations of polymer were measured with respect to the monomer peak at 6.92 ppm in CDCl$_3$. The rate constants were determined by plotting ln[([M] + [P])/[M] vs time, where [M] and [P] represent integration of the monomer peak and all polymer peaks (approximately 5.50−5.20 ppm), respectively, and where time is measured in seconds. The slope of this curve was divided by the concentration of catalyst to give the polymerization rate constant.

■ ASSOCIATED CONTENT

Supporting Information

Text, figures, tables, and CIF files giving experimental details for single-crystal X-ray studies, NMR studies involving **2d**, and NMR spectra of polymers and alkylidene complexes. 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.

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