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

Jonathan C. Axtell, † Richard R. Schrock,* † Peter Müller, † Stacey J. Smith, † 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: Tungsten NArR alkylidene complexes have been prepared that contain the electron-withdrawing Ar groups 2,4,6-X3C6H2 (ArX3, X = Cl, Br), 2,6-Cl2-4-CF3C6H2 (ArCl2CF3), and 3,5-(CF3)2C6H3 (Ar(CF3)2). Reported complexes include W(NArR)2Cl2(dme) (dme = 1,2-dimethoxyethane), W(NArR)2(CH2CMe3)2, W(NArR)(CHCMe3)(OTf)2(dme), and W(NArR)(CHCMe3)(ODBMP)2 (DBMP = 4-Me-2,6-(CHPh2)C6H2). The W(NArR)(CHCMe3)(ODBMP)2 complexes were explored as initiators for the polymerization of 2,3-dicarbomethoxynorbornadiene (DCMNB).

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 ligand5 or variations in which the imido ligand is relatively electron withdrawing: e.g., NR = NC6F5,6 N-2,6-Cl2C6H3.7 Tungsten complexes that contain NC6F5 or N-2,6-Cl2C6H3 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 NR = NC6F5 or N-2,6-Cl2C6H3 failed due to decomposition of bis-imido dialkyl intermediates, even in the solid state, to give the anilines and unidentified 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-X3C6H2 (ArX3, X = Cl, Br), N-2,6-Cl2-4-CF3C6H2 (ArCl2CF3), or N-3,5-(CF3)2C6H3 (Ar(CF3)2) ligands (Figure 1).

RESULTS AND DISCUSSION

A typical procedure for synthesizing W-based imido alkylidene complexes begins with a reaction between WO2Cl2(dme),9 2 equiv of aniline, excess base (e.g., triethylamine), and TMSCl to afford complexes of the type W(NR)2Cl2(dme).10 This approach was unsuccessful in our hands for synthesizing W(NArR)2Cl2(dme) complexes in which NR is NArX3, NArCl2CF3, or NAr(CF3)2. We instead turned to an approach that we employed12a for the synthesis of [W(NR)2Cl2(RNH2)]2 (R = 1-Ad, t-Bu) complexes, in which WCl6 was treated with 4 equiv of a trimethylsilyl-substituted

Figure 1. New electron-withdrawing arylimido substituents.

Received: June 23, 2014
Published: September 17, 2014
aniline (eq 1), an approach that was employed first by Nielson. The required ArNH(TMS) (Ar = ArX3, ArCl2CF3, 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 WCl6, 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)2Cl2(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(CH2CMe3)2 (2a−d; eq 2). Addition of acetonitrile to 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(CH2CMe2Ph)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(CH2CMe3)2 (2d) stood out among this family of dineopentyl complexes. Whereas the others exhibited typical NMR spectra with well-defined JWH couplings for the WCH2 unit, 2d displayed broad resonances in C6D6 at room temperature. Cooling a CD2Cl2 solution of this complex to −20 °C resulted in the further broadening of the CH2 resonance, as well as broadening of the resonances for the protons at the 2- and 6-positions on the aryl ring. Heating a C7D8 solution of this same sample above 50 °C resulted in the sharpening of both the CH2 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).

Figure 2. Thermal ellipsoid drawing of the structure of [W-(NAr(CF3)2)2(CH2CMe3)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−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).

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-(CHPh2)2-4-MeC6H2 (ODBMP) ligand, which was introduced recently as a potentially useful bulky phenoxide ligand. Addition of 2 equiv of LiODBMP to the requisite bis-triflate complexes (eq 4) led to formation of bis-ODBMP complexes, which could be isolated readily in moderate to good yields. The fact that the bis-aryl oxide compounds of type 4 can be prepared readily at room temperature suggests that the ODBMP ligand is not as...
sterically demanding as the 2,6-dimesitylphenoxide (HMTO) and 2,6-(CF3)2C6H4 ligands, which do not form bis-aryloxide complexes readily.15,a,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(2), 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-dicarbomethoxyborbornadiene (DCMNBD) (eq 5) was chosen as the test metathesis reaction.15,16 The results of polymerization of 50 equiv of DCMNBD with various initiators in CDCl3 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 trans17 sequences) centered around the poly(DCMNBD) resonance at 5.41 ppm in CDCl3.

The fastest rates of polymerization were observed employing 4d, f,h. The estimated value (95% conversion in 5 min) for kobs 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 than for than 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.15,a,c,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 enantiotopic site control (to give cis, isotactic polymers) or stereogenic metal control (to give cis, syndiotactic polymers) in ROMP with Mo and W initiators.15,c,d

### CONCLUSIONS

A new class of tungsten imido complexes that contain strongly electron withdrawing imido ligands has been prepared directly from WCl6. 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.15,c,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.

### EXPERIMENTAL SECTION

**General Procedures.** All manipulations of air- and moisture-sensitive materials were performed either in a Vacuum Atmospheres glovebox (N2 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(NArF)2(CHMe2)2(CHMe2)(OTf)2(dme),6a,18 W(NArCl)2(CHMe2)2(CHMe2)(OTf)2(dme),19 and W(NAr3,5Me2)(CHCMe2Ph)(OTf)2(dme)19 were prepared according to reported procedures. N-Trimethylsilyl-2,4,6-trimethoxyaniline20 and N-trimethylsilyl-2,6-dichloro-4-trifluoromethylaniline21 have been previously reported. All other reagents were used as received unless otherwise noted. Methylene chloride-d4, chloroform-d, and benzene-d3 were

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**Table 1. Polymerization of DCMNBD with Initiators 4a–h in CDCl3**

<table>
<thead>
<tr>
<th>Imido Substituent</th>
<th>kobs (M⁻¹ s⁻¹)</th>
<th>Polymer Structure</th>
</tr>
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<tbody>
<tr>
<td>2,6-Cl2C6H4 (4a)</td>
<td>0.59</td>
<td>84% cis, iso</td>
</tr>
<tr>
<td>2,6-Br2C6H4 (4b)</td>
<td>0.075</td>
<td>71% cis, iso</td>
</tr>
<tr>
<td>2,6-Cl2-(CF3)2C6H4 (4c)</td>
<td>1.1</td>
<td>85% cis</td>
</tr>
<tr>
<td>3,5-(CF3)2C6H4 (4d)</td>
<td>&gt;4.1 (est)</td>
<td>53% cis, iso</td>
</tr>
<tr>
<td>2,6-Cl2C5H4 (4e)</td>
<td>0.51</td>
<td>88% cis</td>
</tr>
<tr>
<td>C6F5 (4f)</td>
<td>&gt;4.1 (est)</td>
<td>85% cis</td>
</tr>
<tr>
<td>2,6-Me2C5H4 (4g)</td>
<td>0.005</td>
<td>75% cis (10% trans)</td>
</tr>
<tr>
<td>3,5-Me2C5H4 (4h)</td>
<td>&gt;4.1 (est)</td>
<td>55% cis</td>
</tr>
</tbody>
</table>

*Monomer and initiator concentrations were held constant at 0.002 and 0.1 M, respectively, across three trials for each initiator. Reactions were >95% complete within 5 min. Unless otherwise noted, <5% trans polymer sequences is observed.*
(10.0 mmol) was added via syringe under an argon syringe, and the solution was warmed to room temperature. The white slurry was stirred for 2 h; the slurry acquired a reddish tint over to that had been recrystallized from hot hexane. The solution was chilled (98%); $^1$H NMR (C$_6$D$_6$, 200 MHz) δ 11.51 (s, 1H, W=CH$_2$), 7.47 (s, 2H, Ar), 4.58 (s, 3H, CH$_3$), 4.39 (m, 1H, CH), 4.31 (m, 1H, CH), 4.11 (m, 1H, CH), 3.72 (s, 3H, CH$_3$), 3.72 (m, 1H, CH), 1.22 (s, 9H, CMe$_3$); $^{13}$C NMR (DP$_2$, 20 °C) δ 179.5, 141.3, 124.8, 123.6, 1.8.

W(NArCl$_3$)($^2$H$_2$CMe$_3$)$_2$ (2a). $W(NArCl_3)(^{2}H_{2}CMe_3)_2$ (10 g, 13.6 mmol) was charged with LiODBMP·$H_2$O (11.2 mmol) in DME and chilled to −78 °C. The solution was stirred for 2 h and then returned to room temperature. The precipitated orange solid was isolated by filtration. Analytically pure product was obtained by recrystallization from toluene: yield 86 mg (57%); $^1$H NMR (CD$_2$Cl$_2$, 20 °C) δ 9.29 (s, 1H, W=CH$_2$), 7.12 (m, 14H, Ar), 6.89−6.78 (m, 28H, Ar), 6.56 (s, 4H, Ar), 5.84 (s, 4H, CH$_2$Ph$_2$), 2.11 (s, 6H, CH$_3$), 1.13 (s, 9H, CMe$_3$); $^{13}$NMR (CD$_2$Cl$_2$, 20 °C) δ 255.0, 159.5, 149.8, 144.4, 143.5, 133.3, 133.3, 131.5, 130.4, 130.1, 129.9, 128.8, 127.6, 126.5, 126.4, 50.1, 45.9, 34.5, 21.3. Anal. Calcld. for C$_{22}$H$_{26}$Br$_6$N$_2$W: C, 24.45; H, 2.26; N, 1.59.

W(NArCl$_3$)($^{2}$H$_2$CMe$_3$)$_2$ (3a). W(NArCl$_3$)($^{2}$H$_2$CMe$_3$)$_2$ (7.15 g, 10.0 mmol) was charged with LiODBMP·Et$_2$O (101 mg, 0.227 mmol) in 10 mL of Et$_2$O 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$_2$Cl$_2$ 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$_2$Cl$_2$, 20 °C) δ 9.29 (s, 1H, W=CH$_2$), 7.12 (m, 14H, Ar), 6.89−6.78 (m, 28H, Ar), 6.56 (s, 4H, Ar), 5.84 (s, 4H, CH$_2$Ph$_2$), 2.11 (s, 6H, CH$_3$), 1.13 (s, 9H, CMe$_3$); $^{13}$NMR (CD$_2$Cl$_2$, 20 °C) δ 255.0, 159.5, 149.8, 144.4, 143.5, 133.3, 133.3, 131.5, 130.4, 130.1, 129.9, 128.8, 127.6, 126.5, 126.4, 50.1, 45.9, 34.5, 21.3. Anal. Calcld. for C$_{22}$H$_{26}$Br$_6$N$_2$W: C, 69.66; H, 5.01; N, 1.04. W(NArBr$_3$)Cl$_2$ (1b). WCl$_3$ (3.51 g, 8.87 mmol) was added to benzene (150 mL) in a round-bottom flask. N-Trimethylsilyl-2,6-dichloro-4-trifluoromethylaniline (19.26 g, 35.5 mmol) was added, and the dark red mixture was stirred for 3 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 (CD$_2$Cl$_2$, 20 °C) δ 7.37 (s, 2H, Ar), 6.56 (s, 4H, Ar), 5.84 (s, 4H, CH$_2$Ph$_2$), 2.11 (s, 6H, CH$_3$), 1.13 (s, 9H, CMe$_3$); $^{13}$NMR (CD$_2$Cl$_2$, 20 °C) δ 255.0, 159.5, 149.8, 144.4, 143.5, 133.3, 133.3, 131.5, 130.4, 130.1, 129.9, 128.8, 127.6, 126.5, 126.4, 50.1, 45.9, 34.5, 21.3. Anal. Calcld. for C$_{22}$H$_{26}$Br$_6$N$_2$W: C, 69.66; H, 5.01; N, 1.06. W(NArBr$_3$)(CH$_2$CMe$_3$)$_2$ (2b). A solution of W(NAr$_3$)(CH$_2$CMe$_3$)$_2$ (6.0 g, 6.0 mmol) in diethyl ether was chilled for 1 h, after which neopentylmagnesium chloride (1.55 M in Et$_2$O, 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 (CD$_2$Cl$_2$, 20 °C) δ 7.37 (s, 2H, Ar), 6.56 (s, 4H, Ar), 5.84 (s, 4H, CH$_2$Ph$_2$), 2.11 (s, 6H, CH$_3$), 1.21 (s, 18H, CMe$_3$); $^{13}$C NMR (CD$_2$Cl$_2$, 125 MHz) δ 152.6, 134.1, 121.6, 116.9, 97.3, 34.9, 34.1. Anal. Calcld. for C$_{22}$H$_{26}$Br$_6$N$_2$W: C, 72.69; H, 2.67; N, 2.85. Found: C, 72.77; H, 2.50; N, 2.96. W(NAr$_3$)(CH$_2$CMe$_3$)$_2$ (3b). W(NAr$_3$)(CH$_2$CMe$_3$)$_2$ (3.67 g, 3.74 mmol) was added to a mixture of 30 mL of Et$_2$O 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 −30 °C of Et$_2$O 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$_2$Cl$_2$, 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
trilate salts); 1H NMR (CDCl3, 20 °C) δ (major isomer) 11.47 (s, 1H, W=CH), 7.74 (s, 2H, Ar), 4.59 (s, 3H, CH3), 4.44 (m, 1H, CH), 4.31 (m, 1H, CH), 4.06 (m, 1H, CH), 3.75 (s, 3H, CH3), 3.73 (m, 1H, CH), 1.24 (s, 9H, CMe); 13C NMR (CDCl3, 20 °C) δ (major isomer) 303.2 (W=CCl, 150.4, 152.5, 124.0, 121.5, 120.0 (q, JCF = 316 Hz), 119.0 (q, JCF = 316 Hz), 62.0, 79.2, 71.8, 62.3, 48.5, 32.9; 19F NMR (CDCl3, 20 °C) δ −77.3 (major), −77.4 (minor), −77.1 (major). Anal. Calc for C14H9Br2F3NO2W: C, 63.31; H, 4.55; N, 0.96. Found: C, 63.63; H, 4.56; N, 0.89.

W(Na[Cl2]3)2(C5H5)(dme) (1c). N-Trimethylsilyl-3,5-bis(trifluoromethyl)aniline (65 g, 215 mmol) was added over 10 min to a solution of WCl6 (21.33 g, 53.8 mmol) in 400 mL of benzene in a round-bottom flask. The red-orange mixture was stirred for 3 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%); 

1H NMR (CDCl3, 20 °C) δ 7.52 (s, 2H, Ar), 7.29 (s, 1H, Ar), 3.29 (s, 6H, CH3), 2.93 (s, 4H, CH2); 13C NMR (CDCl3, 20 °C) δ 156.2, 123.4 (q, JCF = 33.8 Hz), 123.8, 123.6 (q, JCF = 271 Hz), 119.0, 71.5, 64.6; 

19F NMR (CDCl3, 20 °C) δ −63.6. Anal. Calc for C18H22Cl2F9NO8S2W: C, 24.84; H, 2.25; N, 3.75; S, 3.3.

W(Na[Cl2]3)2(C5H5)(CF3)(2d).

A solution of W(Na[Cl2]3)2(C5H5)(dme) (1.00 g, 1.25 mmol) in Et2O was chilled for 1 h. Neopentylmagnesium chloride (1.06 mL, 2.57 mmol, 2.42 M in Et2O) was added dropwise, and the mixture was stirred overnight. The yellow product was added to the filtrate, and all volatiles were removed in pentane. The residue was added to the filtrate, and all volatiles were removed in pentane. The residue was added to the filtrate, and all volatiles were removed in pentane. W(Na[Cl2]3)2(C5H5)(CF3)(2d).

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**Organometallics**

A mixture of W(NArF)3(CH2Ph)(OTf)2, (dme) (97 mg, 0.121 mmol) and LiODMBP (127 mg, 0.244 mmol) in 10 mL of Et2O was stirred at room temperature for 2 h. Workup and isolation followed the procedure employed for 4a. Analytically pure product was obtained by crystallization from a mixture of toluene and pentane: yield 99 mg (65%); 1H NMR (CDCl3, 20 °C) δ 7.93 (s, 1H, W=CH), 7.16−7.95 (m, 14H, Ar), 6.90−6.76 (m, 28H, Ar), 6.54 (s, 4H, Ar), 5.31 (s, 4H, CFPPh), 2.10 (s, 6H, CH3), 1.07 (s, 9H, CMe3); 13C NMR (CDCl3, 20 °C) δ 158.7, 158.4, 154.1, 153.5, 145.4, 143.6, 135.2, 133.3, 131.1, 130.15, 129.27, 128.4, 128.3, 127.4, 126.5, 126.4, 125.9, 50.0, 46.1, 43.6, 21.2, 18.9. Anal. Calcd for C85H75NO2W: C, 76.76; H, 6.00; N, 0.93.

A mixture of W(NArF)3(CH2Ph)(OTf)2, (dme) (93 mg, 0.123 mmol) and LiODMBP (127 mg, 0.244 mmol) in 10 mL of Et2O was stirred for 2 h. Workup and isolation followed the procedure employed for 4a: yield 118 mg (59%); 1H NMR (CD2Cl2, 20 °C) δ 7.20 (m, 14H, Ar), 7.05−6.85 (30H, Ar), 6.32 (s, 4H, CFPPh), 1.83 (s, 6H, CH3), 1.14 (s, 9H, CMe3); 13C NMR (CD2Cl2, 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, 128.55, 126.7, 126.5, 50.1, 45.3, 33.7, 21.3; 19F NMR (CD2Cl2, 20 °C) δ −147.1 (t, 2F), −160.3 (d, 2F), −164.6 (s, 1F). Anal. Calcd for C84H75NO2W: C, 70.13; H, 4.83; N, 0.86. Found: C, 70.37; H, 4.91; N, 1.07. Found: C, 71.72; H, 4.10; N, 1.12. Found: C, 71.38; H, 5.15; N, 0.86.

**REFERENCES**


**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 alkylidyne complexes. This material is available free of charge via the Internet at http://pubs.acs.org.


