Tungsten alkylidene complexes that contain the 2,6-dichlorophenylimido ligand (NArCl), W(NArCl)(CHCMe3)(ORF6)2 and W(NArCl)(CHCMe3)(Biphen)(THP) (ORF6 = OCMe(CF3)2; Biphen2− = 3,3′-di-t-Bu-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diolate; THP = tetrahydrofuran), have been prepared from W(NArCl)(CHCMe3)(OSSiMe3)2(dme). Reaction of W(NArCl)(CHCMe3)(ORF6)2 with excess ethylene gave the tungstacarbobutane complex W(NArCl)(ORF6)2(C2H4), while reaction of W(NArCl)(CHCMe3)(ORF6)2 with internal olefins gave the dimer, [W(μ-NArCl)(ORF6)2]2, W(NArCl)(CHCMe3)(Biphen)(THP) reacted with excess ethylene to give W(NArCl)(Biphen)(C2H4), which yielded W(NArCl)(Biphen)(C2H4)(THF) upon addition of THF. The tungstacarbopentane complex, W(NArCl)(Biphen)(C3H6), was formed upon treatment of W(NArCl)(Biphen)(C2H4)(THF) with ethylene. W(NArCl)(Biphen)(C2H4) decomposed to yield (inter alia) the dimeric, heterochiral methylidene complex, [W(NArCl)(Biphen)(μ-CH2CH2)]2, which decomposed further to yield homochiral [W(NArCl)(Biphen)]2(μ-CH2CH3). Finally, [W(NArCl)(Biphen)]2(μ-CH2CH3) loses ethylene reversibly to yield [W(NArCl)(Biphen)]2, which could not be isolated in pure form. [W(μ-NArCl)(OC(CF3)2)2Me]2, W(NArCl)(Biphen)(C2H4), W(NArCl)(Biphen)(C3H6)(THF), W(NArCl)(Biphen)(C4H8), [W(NArCl)(Biphen)(μ-CH2CH2)]2, and [W(NArCl)(Biphen)]2(μ-CH2CH3) were characterized through X-ray studies.

**Introduction**

Imido alkylidene bisalkoxide complexes of molybdenum or tungsten of the type Mo(NR)(CHR′)(OR′)2 are now established as well-defined high oxidation state olefin metathesis catalysts.1 The overall efficiencies shown by such catalysts are controlled to a dramatic degree by the electronic and steric characteristics of the NR and OR′ groups. Since the rate of decomposition is part of overall efficiency, the stability of the alkylidenes that are accessible during the catalytic reaction is an issue; for example, methylene species are likely to be formed in the presence of ethylene or terminal olefins, and they are especially susceptible to bimolecular decomposition to yield “reduced” metal species. In order to understand and predict the reactivity of Mo(NR)(CHR′)(OR′)2, species, catalysts that contain new imido and alkoxide (or diolate) groups are continually being synthesized and evaluated. Recently many catalysts for asymmetric metathesis reactions that contain an enantiomerically pure diolate ligand have been prepared and employed in a variety of asymmetric metathesis reactions.14

The most common imido ligands that have been employed in M(NR)(CHR′)(OR′)2 catalysts are N-2,6-i-Pr2C6H3, N-2,6-Me2C6H3, N-2-t-BuC6H4, N-2-CF3C6H4, N-2,6-C6H4, and N-1-adamantyl.14 Molybdenum catalysts that contain the 2,6-dichlorophenylimido (NArCl) ligand2 and an enantiomerically pure bifenpholate or binaphtholate ligand have shown reactivities with some substrates that are not duplicated in terms of conversion and % ee by other imido/diolate combinations that have been tried. The NArCl ligand is one of the smallest aryl substituents and is relatively electron withdrawing. The NArCl ligand also is likely to be a relatively robust ligand, since there is no opportunity for CH activation in substituents in the 2 or 6 positions of the aryl ring, a complicating feature of some recent chemistry involving 2,6-dimethylimido complexes.3 Finally, the only crystallographically characterized example of a Mo(NR)(CHR′)(OR′)2 (olefin) complex is a molybdenum complex that contains the NArCl ligand, namely, Mo(NArCl)(Biphen)(C2H4)(Et2O) (Biphen− = 3,3′-di-t-Bu-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diolate).4

W(NR)(CHR′)(OR′)2 catalysts were discovered and developed before Mo(NR)(CHR′)(OR′)2 catalysts.5 However, tungsten forms relatively stable tungstacarbobutane species, especially unsubstituted tungstacarbobutanes, a circumstance that has been proposed to limit alkylidenes that are available for metathesis at temperatures where the WC3 ring does not lose olefin readily. Molybdenum catalysts have gained favor over tungsten catalysts since molybducyclobutane species appear to lose an olefin more readily. However, that is not to say that tungsten catalysts would not be preferred in certain circumstances.

Reactions of W(NAr)(CHR′)(Biphen) (Ar = 2,6-i-Pr2C6H3) species with 13C-labeled ethylene revealed a relatively complete picture of the initiation, propagation, and decomposition reactions under ethylene.6 Unfortunately, several of the interesting species that were observed (ethylene, tungstacarbobutane, and tungstacarbopentane complexes) could not be isolated. The most...
interesting of the unisolated species observed in this study was a dimeric complex, \([\text{W(NAr)(Biphen)(μ-C}_2\text{H}_5)]\), in which an unsymmetrically bridging methylene ligand bound to one tungsten was proposed to behave as a “donor” toward the second tungsten. This species was proposed to be heterochiral, i.e., \([\text{W-(NAr)(S)-Biphen}(μ-C}_2\text{H}_5)]\) \([\text{W(NAr)(R)-Biphen}(μ-C}_2\text{H}_5)]\). \([\text{W(NAr)(Biphen)(μ-C}_2\text{H}_5)]\) was not observed in a system in which the Biphen\(^2\) ligand was enantiomerically pure.

We decided to attempt to synthesize tungsten species that contain the 2,6-dichlorophenylimido ligand in order to compare them with molybdenum species. Our goal was to prepare two prototypical tungsten alkylidene complexes of the type \([\text{W(NArCl)}-\text{(CHCMe}_3\text{)}\text{(OR)}_2\text{]}\), one in which \(\text{OR} = \text{OC(CF}_3\text{)}_2\text{Me}\) (OR\(_{\text{Me}}\)) and the other in which (OR\(_2\) = Biphen), and to explore their reactions with selected olefins. These experiments are the subject of this paper.

**Results**

**Syntheses of \([\text{W(NArCl)}-\text{(CHCMe}_3\text{)}\text{(OC(CF}_3\text{)}_2\text{Me})_2\]** and \([\text{W(NArCl)}-\text{(CHCMe}_3\text{)}\text{(Biphen)(THP)}\] (THP = tetrahydropyran).

The synthesis of \([\text{W(NAr)}\text{]}\text{ complexes follows the traditional route.}\) \([\text{W(NArCl)}-\text{Cl}_2\text{(DME)}\] (DME = 1,2-dimethoxyethane) is first prepared in a reaction between \(\text{Me}_3\text{SiCl}\), 2,6-lutidine, and \(\text{WO}_2\text{Cl}_2\) in dimethoxyethane.\(^7\) Alkylation of \([\text{W(NArCl)}-\text{Cl}_2\text{(DME)}\] with \(\text{Me}_2\text{CCH}_2\text{MgCl}\) to give \([\text{W(NArCl)}-\text{CH}_2\text{CMe}_3\text{]}\) proceeded without complication. \([\text{W(NArCl)}-\text{Cl}_2\text{(DME)}\] and \([\text{W(NArCl)}-\text{CH}_2\text{CMe}_3\text{]}\) have been reported in a recent Ph.D. thesis.\(^8\) Experimental details are reported in this paper for convenience.

Addition of 3 equiv of triflic acid to \([\text{W(NArCl)}-\text{CH}_2\text{CMe}_3\text{]}\) in DME produced \([\text{W(NArCl)}-\text{CHCMe}_3\text{]}\text{(OTf)}_2\text{(DME)}\] as bright yellow microcrystals in 57% yield. NMR data are consistent with \([\text{W(NArCl)}-\text{CHCMe}_3\text{]}\text{(OTf)}_2\text{(DME)}\] being a 1:1 mixture of two isomers in \(\text{C}_6\text{D}_6\) (\(\delta_{\text{H}} = 11.80\) and 10.96 ppm) and a 5:1 mixture of two isomers in \(\text{C}_6\text{H}_6\) (\(\delta_{\text{H}} = 11.52\) and 10.83 ppm). The isomer in which the alkylidene proton resonance has the smaller chemical shift has mirror symmetry and is proposed to be that in which the triflate ligands are trans to one another.


A species of this type has been crystallographically characterized where the alkoxide is \(\text{OC(CF}_3\text{)}_2\text{Cl}_2\) and the imido ligand is 2,6-disopropylphenyl.\(^5\) Tungstacyclobutane species that contain the Biphen\(^2\)– ligand have also been crystallographically characterized.\(^6\) The α methylene resonances in the WC ring in \([\text{W(NAr)}\text{(OR)}_2\text{(C}_6\text{H}_6)]\) are found at 4.91 and 4.77 ppm in the proton NMR spectrum in \(\text{C}_6\text{D}_6\) while the β methylene resonances are found at −0.87 and −1.46 ppm. The \(\text{C}_6\text{H}_6\) NMR spectrum exhibits characteristic resonances at 103.4 ppm for the α carbon atoms in the WC ring (with \(\text{J}_{\text{CH}}\) values of 160.6
and 165.2 Hz) and at −4.7 ppm for the β carbon atom in the WC₃ ring (with Jₐ values of 162.0 and 166.2 Hz). The reaction between W(NAr)(CHCMe₃)(ORF₆)₂ and ethylene is proposed to yield an initial α-β-Bu-substituted tungstacyclobutane complex that loses tert-butylethylene to yield intermediate W(NAr)₂(CH₂)(ORF₆)₁. This methylene species is then trapped with ethylene to give the observed product, W(NAr)(C₆H₆)(ORF₆)₂. The presence of only one ¹⁹F resonance in the room-temperature ¹⁹F NMR spectrum of [W(N−NArCl)][OC(CF₃)₂Me]₂(C₆H₆) (06034) suggests that this structure is not maintained in solution on the NMR time scale. Recently, we have shown that [W(NR)₄]₂⁺ species are formed upon decomposition of W(NR)₂(CH₃)₂ species when the CH₃ ligand is relatively small (e.g., ethylidene or propylidene). We propose that ethylidene complexes formed in the reaction shown in eq 4 decompose most readily and lead to the observed dimeric species, although precise details are uncertain.

The structure of [W(NAr)(ORF₆)]₂ (Table 1) is shown in Figure 1. All non-hydrogen atoms of the imido group lie approximately in a plane that is orthogonal to the plane that contains both tungsten atoms and the four oxygen atoms. The geometry around each tungsten atom is approximately a trigonal bipyramid with one bridging chloride and one nitrogen atom in the apical position; the equatorial positions are occupied by the other bridging nitrogen and two alkoxide oxygens. The bridging geometry around each tungsten atom is approximately a trigonal bipyramid with one bridging chloride and one nitrogen atom in the apical position; the equatorial positions are occupied by the other bridging nitrogen and two alkoxide oxygens. The bridging nitrogen species observable in solution at any point during the reaction. The short W(1)−W(1) distance is similar to the Mo−Cl bond length (2.624(1) Å) in the Schiff base complex Mo(C₆H₅Cl)₂(NCl)CO, that contains 0.94 Å.

The presence of only one ¹⁹F resonance in the room-temperature ¹⁹F NMR spectrum of [W(N−NArCl)][OC(CF₃)₂Me]₂(C₆H₆) (06034) suggests that this structure is not maintained in solution on the NMR time scale. Recently, we have shown that [W(NR)₄]₂⁺ species are formed upon decomposition of W(NR)₂(CH₃)₂ species when the CH₃ ligand is relatively small (e.g., ethylidene or propylidene). We propose that ethylidene complexes formed in the reaction shown in eq 4 decompose most readily and lead to the observed dimeric species, although precise details are uncertain.

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metathesis of propylene) to yield the observed product. Is formed and trapped with ethylene (that is generated through a dative aryl Cl to Mo interaction. 13 The chlorides (Cl(1) and Cl(1′)) are bound in approximately axial positions trans to the imido nitrogens. [W(μ-NArCl)(ORF6)2] is the only complex in the category of [W(NR)(OR′)]2 complexes12 that does not contain an unsupported double bond. Formation of a species that contains a bridging NArCl group might be encouraged through binding of a chlorine. The interatomic W1−W′1 distance in [W(NArCl)(ORF6)2] (2.5297(3) Å) is slightly longer than in related tungsten complexes that contain unsupported double bonds (2.4445(3)−2.4925(3) Å).13 It is interesting to note that [Mo(μ-NAr)(OCMe3)]2 (Ar = 2,6-disisopropylphenyl) is a purple dimer that contains bridging imido ligands and that the Mo−Mo distance in this species is 2.654(1) Å.14

When a benzene solution of W(NArCl)(CHCMe3)(ORF6)2 is treated with an excess of propylene, the color of the solution changes rapidly from bright yellow to pale yellow. NMR spectra showed that the parent alkylidene complex had been converted into the unsubstituted tungstacyclobutane complex, W(NArCl)(C3H6)(ORF6)2. No intermediate tungsten complex were observed under these conditions. We presume that W(NArCl)(CH2)(ORF6)2 is formed and trapped with ethylene (that is generated through metathesis of propylene) to yield the observed product. In a reaction between W(NArCl)(CHCMe3)(ORF6)2 and 1 equiv of styrene the color of the solution changed from bright yellow to dark brown within 45 min. At this time 90% of the W(NArCl)(CHCMe3)(ORF6)2 had been converted into a mixture of W(NArCl)(C3H6)(ORF6)2 and (Me3C)CH═CHF and minor unidentified products. After 16 h at 25 °C, the yellow solution contained W(NArCl)(C3H6)(ORF6)2 as the only tungsten species along with a minor amount of [W(μ-NArCl)(ORF6)2] as a purple deposit.

The reaction between W(NArCl)(CHCMe3)(ORF6)2 and 1 equiv of trans-3-hexene after 40 min at 0 °C yielded a 2:1:1 mixture of W(NArCl)(CHCMe3)(ORF6)2, W(NArCl)(CHEt)(ORF6)2, and what appears to be a mixture of various tungstacyclobutanes. The alkylidyne resonance for W(NArCl)(CHEt)(ORF6)2 is found at 9.27 ppm in toluene-d8 at 0 °C. Proton resonances at −0.31, −0.41, −0.51, and −0.80 ppm are typical for β protons in TBP metallacyclobutanes of this type. After 24 h at 0 °C, the reaction solution contained a 1:1 mixture of unreacted W(NArCl)(CHCMe3)(ORF6)2 and various tungstacyclobutanes along with a purple deposit of [W(μ-NArCl)(ORF6)2]. After 3 days at 25 °C, only [W(μ-NArCl)(ORF6)2]2 was present. The amount of [W(μ-NArCl)(ORF6)2]2 formed in reactions between W(NArCl)(CHCMe3)(ORF6)2 and trans-3-hexene at 22 °C depends to a significant degree on the ratio of starting materials. A maximum amount of [W(μ-NArCl)(ORF6)2]2 is produced under approximately stoichiometric conditions. Only a trace of [W(μ-NArCl)(ORF6)2]2 was formed when 10 equiv of trans-3-hexene was added to W(NArCl)(CHCMe3)(ORF6)2, and [W(μ-NArCl)(ORF6)2]2 did not form when W(NArCl)(CHCMe3)(ORF6)2 was treated with neat trans-3-hexene. GC/MS analysis and 1H NMR spectroscopy of the orange solution that was obtained in this last experiment after 72 h at 25 °C indicated that ~25% of the trans-3-hexene had been converted into approximately a 1:1 mixture of C6H10 and C7H14 (4:1 ratio of trans and cis olefins). No further attempt was made to identify the hydrocarbon products. Clearly the presence of a high concentration of 3-hexene slows formation of the dimer dramatically, most likely because 3-hexene must be lost from some intermediate to yield [W(μ-NArCl)(ORF6)2]2.

Reactions of W(NArCl)(CHCMe3)(Biphen)(THP) with Ethylene. Exposure of a degassed solution of W(NArCl)(CHCMe3)(Biphen)(THP) in C6D6 (40 μmol/mL) to 1 atm of ethylene for 25 min led to consumption of 30% of the starting material and formation of W(NArCl)(C3H6)(Biphen), according to 1H NMR spectra (eq 5). After 24 h at 25 °C, only W(NArCl)-(C3H6)(Biphen), excess ethylene, tert-butylethylene, and free tetrahydropryn could be detected in the proton NMR spectrum. W(NArCl)(C3H6)(Biphen) could be isolated as a pale yellow powder upon lyophilization of the above NMR sample. Analytically pure W(NArCl)(C3H6)(Biphen) could be prepared from W(NArCl)(CHCMe3)(Biphen)(THP) and ethylene on a 0.8 mmol scale in virtually quantitative yield in a similar manner. The 1H NMR spectrum of W(NArCl)(C3H6)(Biphen) shows six multiplets at 4.71, 4.42, 4.35, 3.41, −0.03, and −0.27 ppm at 25 °C in C6D6 that can be ascribed to the six protons of the unsubstituted tungstacyclobutane ring in a TBP complex. Coupling constants for the methylene units of the tungstacyclobutane moiety (JCH values between 148.9 and 161.3 Hz) are typical of metallacyclobutane complexes of this general type.11

Single crystals of W(NArCl)(C3H6)(Biphen) (containing 0.25 equiv of CH2Cl2 of crystallization) suitable for X-ray structure

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References:
The larger C(1)–W–C(3) angle is less pronounced than in W(NAr Cl)(C3H6)(Biphen). The NAr Cl ligand, as there is in W(NAr Cl)(C3H6)(Biphen). The W–C(11)–C(11) angle is similar to what it is in Mo(NAr Cl)(Biphen)–(C2H4)(PMe3)2 (1.434(6) Å) and Mo(NAr Cl)(Biphen)–(C3H6)(Et2O) (1.400(13) Å).3,4 Bending of the NAr Cl ligand probably can be attributed largely to steric interactions between the CMe3 group attached to C(2) of the Biphen ligand and the NAr Cl ligand; Cl(2) is not within bonding distance of the metal (W(1)–Cl(2) = 3.5730(11) Å). The larger C(1)–W(1)–O(2) angle (143.49(16)°) relative to the C(3)–W(1)–O(2) angle (132.75(16)°) is consistent with Cl(2) being forced between O(2) and C(1) when the imido group is analogous to other known TBP metallacyclobutane species of this type, i.e., essentially planar with a short W–C distance (2.157(14) and 2.173(15) Å), while the W–C(3)–C(1) angle is larger (115.0(3)° versus 97.2(11)°). In short, the WC3 ring in the TBP species is more square with a W–Cβ distance = 2.762 Å. What this means in terms of olefin analysis were grown from a saturated CH2Cl2/Et2O solution at −30 °C. The complex was found to be a distorted trigonal bipyramid with the imido nitrogen and one oxygen of the Biphen ring is analogous to other known TBP metallacyclobutane species. The complex was found to be a distorted trigonal bipyramid with the imido nitrogen and one oxygen of the Biphen ligand and the NAr Cl ligand; Cl(2) is not within bonding distance of the metal (W(1)–Cl(2) = 3.5730(11) Å). The larger C(1)–W(1)–O(2) angle (143.49(16)°) relative to the C(3)–W(1)–O(2) angle (132.75(16)°) is consistent with Cl(2) being forced between O(2) and C(1) when the imido group bends. The W–N(1)–C(11) angle (158.9(3)°) is within the expected range. For example, in Mo(NAr Cl)(Biphen)–(C3H6)–(Et2O)4 Mo–N–C = 169.4(7)°, while in Mo(NAr Cl)(CHMe2)–((S)-Biphen)(THF) Mo–N–C = 149.8(8)°.2,3 Comparison of the structure of TBP W(NAr Cl)(C3H6)(Biphen) with that of SP W(NAr)(CH2CH2CMe3Ph)CH2]Biphen6 reveals differences in the tungstacyclobutane rings that are analogous to those found in other TBP versus SP metallacycles in this family of bisalkoxide complexes. The W–Cα distances in the TBP WC3 ring (2.078(4) and 2.016(4) Å) are approximately 0.1 Å shorter than the W–Cα distances in the SP WC3 ring (2.157(14) and 2.173(15) Å), while the W–Cα–Cβ angles are smaller (81.54(17)° and 82.6(2)° versus 95.7(9)° and 94.8(9)°) and the Cα–Cβ–Cγ angle is larger (115.0(3)° versus 97.2(11)°). In short, the WC3 ring in the TBP species is more diamond shaped with a shorter W–Cβ distance (2.398(4) Å), while the WC3 ring in the SP species is more square with a W–Cβ distance = 2.762 Å. What this means in terms of olefin loss from the WC3 ring versus β hydride rearrangement of the WC3 ring is a fundamental question that is still not known for any metallacyclobutane species in the general category of bisalkoxide species.

Decomposition of W(NAr Cl)(Biphen)(C3H6) and Other W(Biphen) Species. When W(NAr Cl)(Biphen)(C3H6) is dissolved in THF–d8 (200 μmol/mL), the ethylene complex, W(NAr Cl)(Biphen)(C3H6)(THF–d8), and approximately a 2:1 mixture of propylene and ethylene are formed after 90 min. The formation of both propylene and ethylene from W(NAr Cl)(C3H6)(Biphen) suggests that both β hydride rearrangement of the tungstacyclobutane ring as well as formation and bimolecular decomposition of a transient methylidene complex are pathways for the generation of W(NAr Cl)(Biphen)(C3H6)(THF–d8) from W(NAr Cl)(Biphen)(C3H6). If we assume that the ratio of propylene to ethylene in solution is a good estimate of the relative amounts of each formed as decomposition products, then we can conclude that only ~25% of the W(NAr Cl)(Biphen)(C3H6) decomposes via β hydride rearrangement, as shown in eq 6. The major pathway of decomposition under these conditions is loss of ethylene to give transient W(NAr Cl)(CH2)–(Biphen) and ethylene, which evolve into a mixture of W(NAr Cl)(Biphen)(C3H6)(THF–d8) and ethylene (eq 6).

In the 1H NMR spectrum of W(NAr Cl)(Biphen)(C3H6)(THF–d8) in THF–d8 at 25 °C, the four ethylene protons appear as multiplets at 3.31, 3.01, 2.13, and 2.06 ppm. The 13C NMR spectrum of W(NAr Cl)(Biphen)(C3H6)(THF–d8) exhibits two resonances at 55.8 and 52.6 ppm that are assigned (through an HMOC study) to the ethylene carbons. The CH coupling constants (UCH = 152–158 Hz) are what one would expect. Yellow crystals of W(NAr Cl)(Biphen)(C3H6)(THF–d8) suitable for an X-ray structure were isolated in 55% yield from an NMR solution of W(NAr Cl)(C3H6)(Biphen) in THF–d8 that was allowed to stand for 48 h at 22 °C. The molecular structure of W(NAr Cl)(Biphen)(C3H6)(THF–d8) shown in Figure 3 closely resembles that of Mo(NAr Cl)(Biphen)(C3H6)(Et2O),3 hitherto the only crystallographically characterized ethylene adduct of a group 6 metal imido bis(alkoxide) complex. The coordination geometry around tungsten is best described as square pyramidal with the ethylene ligand in the apical position. The ethylene is symmetrically bound to tungsten (W–C(1) = 2.121(2) Å, W–C(2) = 2.143(2) Å) with the C(1)–C(2) distance (1.452(3) Å) similar to what it is in the related complexes W(NPh){x2–C2H4–(NSiMe3)2}(C2H4)(PMe3)2 (1.434(6) Å) and Mo(NAr Cl)(Biphen)(C3H6)(Et2O) (1.400(13) Å).4,5 Bending of the NAr Cl ligand in W(NAr Cl)(Biphen)(C3H6)(THF–d8) (W–N–(C–C(11)) = 170.27(14)°) is less pronounced than in W(NAr Cl)(C3H6)(Biphen) (158.9(3)°; vide supra), since there is no significant steric interaction of the NAr Cl ligand with a tert-butyl group in the Biphen2– ligand, as there is in W(NAr Cl)(C3H6)(Biphen). The W–N–C angle is similar to what it is in Mo(NAr Cl)(Biphen)(C3H6)(Et2O) (169.4(7)°).4

When W(NAr Cl)(Biphen)(C3H6)(THF–d8) in CD2Cl2 is treated with 13CH3=13CH3 (14 equiv), the color of the solution immediately changes from yellow to orange. Proton and carbon NMR spectra indicate that the tungstacyclopentane complex, W(NAr Cl)(13CH3=13CH3)(13CH3=13CH3)(13CH3)(Biphen) (eq 7), is formed.
Hydrogen and solvate atoms are omitted for clarity; thermal ellipsoids are drawn at 50% probability level. Selected bond lengths [Å] and angles [deg]: W–C(1) = 2.121(2), W–C(2) = 2.143(2), W–O(1) = 1.9684(13), W–O(2) = 2.0239(13), W–O(3) = 2.2462(14), W–N(1) = 1.7742(16), C(1)–C(2) = 1.452(3), N(1)–W–O(1) = 161.44(6), O(2)–W–O(3) = 152.52(5), W–C(1)–C(2) = 70.91(11), C(1)–C(2)–W = 69.28(11), C(2)–W–C(1) = 39.81(8), W–N(1)–C(11) = 170.27(14).

As found in the case of W(NAr)(Biphen)(C₃H₆)(THF) and ethylene, W(NArCl)(C₂H₆)(Biphen) was found to be stable for at least 24 h at 22 °C in the presence of ethylene. However, in the absence of ethylene W(NArCl)(C₂H₆)(Biphen) decomposes within 36 h in C₆D₆ (90 μmol/mL) at 22 °C. Decomposition of W(NArCl)(C₃H₆)(Biphen) led to formation of W(NArCl)(C₂H₄)(Biphen). The second tungsten species formed as a product of decomposition of W(NArCl)(C₂H₆)(Biphen) gave rise to a singlet resonance at 187.8 ppm that has two sets of tungsten satellites (1Jw = 52.6 Hz, 84.5 Hz), which is indicative of formation of a dimeric methylidene complex, [W(NArCl)(Biphen)(μ-CH₂CH₂)]₂, analogous to [W(NAr)(Biphen)(μ-CH₂)]₂. In the ¹H NMR spectrum, two resonances at 8.14 ppm (1JCH = 146.7 Hz, 2JHH = 6.1 Hz) and 7.62 ppm (2JHH = 6.3 Hz) are ascribed to the diastereotopic protons of two equivalent methylidene groups.

Decomposition of W(NArCl)(C₃H₆)(Biphen) at 40 °C in C₆D₆ (90 μmol/mL) was followed by ¹H NMR spectroscopy. During the first 3 h, [W(NArCl)(Biphen)(μ-CH₂)]₂ and W(NArCl)(C₂H₆)(Biphen) formed at the expense of W(NArCl)(C₃H₆)(Biphen). The ratio of propylene to ethylene in solution during the first 2 h of this reaction was found to be approximately 1.7–2.0, similar to what was found in THF (eq 6). The amount of propylene in solution never exceeded 2 equiv per W. All propylene was consumed over a period of 8 h. After 3 h, a maximum amount of [W(NArCl)(Biphen)(μ-CH₂)]₂ was formed with the species in solution being W(NArCl)(C₃H₆)(Biphen) (~30%), [W(NArCl)(Biphen)(μ-CH₂)]₂ (~20%), and W(NArCl)(C₂H₆)(Biphen) (~30%). At this point, no more ethylene could be detected in solution. It is clear that decomposition of W(NArCl)(C₃H₆)(Biphen) is accelerated in the absence of ethylene, the concentration of W(NArCl)(C₂H₆)(Biphen) reaches a steady state, and the [W(NArCl)(Biphen)(μ-CH₂)]₂ that is formed decomposes with time under the reaction conditions. In spite of the complexity of the decomposition reaction [W(NArCl)(Biphen)(μ-CH₂)]₂ could be isolated as purple microcrystals in 29% yield upon decomposition of a sample of W(NArCl)(C₃H₆)(Biphen) in benzene at 25 °C on a 0.5 mmol scale.

An X-ray study of [W(NArCl)(Biphen)(μ-CH₂)]₂ (Table 2) showed it to have the centrosymmetric (heterochiral) structure shown in Figure 5. The coordination geometry around each W is a distorted trigonal bipyramid with the equatorial position occupied by one biphenoxide oxygen, a methylidene ligand, and an imido ligand. The W(CH₂)₂ core exhibits two short (1.982 Å) and two long (2.277 Å) interatomic W–C distances.

Table 2. Crystal Data and Structure Refinement for W(NArCl)(Biphen)(CH₂CH₂CH₂CH₃) (06179), [W(NArCl)(Biphen)(μ-CH₂)]₂ (06185), and [W(NArCl)(Biphen)]₂(μ-CH₂CH₂) (06208)

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<td>3.092(2) Å</td>
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<td></td>
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<td>c 11.1488(17) Å</td>
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α For all structures the temperature is 100(2) K, the wavelength is 0.71073 Å, the absorption correction is semiempirical from equivalents, and the refinement method is full-matrix least-squares on F².

The first is characteristic of a W≡C bond in bisalkoxide imido alkylidene species, while the latter is typical of a W≡CH bond. In short, [W(NArCl)(Biphen)(μ-CH₂)]₂ is essentially a dimer containing W(NArCl)(CH₂)]₂(R)-Biphen) and W(NArCl)(CH₂)]₂(S)-Biphen) in which each of the methylene ligands behaves as a donor toward the second tungsten in an apical position. The interatomic W(1)–W(1′) distance (3.121(6) Å) suggests that no W≡W bond is present, while the C(1)–C(1′) distance (2.913(12) Å) suggests that no C≡C bond is present. The W–C≡H distance (3.121(6) Å) suggests that no W≡C bond is present, while the C(1)–C(1′) distance (2.913(12) Å) suggests that no C≡C bond is present. The W–C≡H–H dihedral angle was found to be 131(7)°, while the W–C≡H–H dihedral angle was found to be 136(6)°. These dihedral angles for a sp³-hybridized carbon atom are expected to be 120° and for a sp²-hybridized carbon atom are expected to be 180°. Therefore these methylene ligands are slightly distorted from a planar structure, as one would expect as a consequence of their behavior as donors to another tungsten, but they retain many of the structural and spectroscopic characteristics we would expect of the methylene ligand in the unobservable monomeric species, W(NArCl)(CH₂)]₂(Biphen). The W₂(CH₂)]₂ core in [W(NArCl)-(Biphen)(μ-CH₂)]₂ contrasts with that in the centrosymmetric W(V) complex, [W(O)(μ²-C₆H₄Me₂)(μ-CH₂)]₂, in which the two W–C≡C bond lengths (2.076(6) and 2.078(4) Å) are essentially identical. The centrosymmetric titanium(V) methylene derivative, [Ti[N(C₆H₄Me₂)]₂]₂(μ-CH₂)]₂, also contains symmetrically bridging methylene groups (Ti–C = 2.025(5) and 2.016(5) Å). To our knowledge [W(NArCl)(Biphen)(μ-CH₂)]₂ is the only crystallographically characterized (WVI) methylene species.

Decomposition of W(NArCl)(C₆H₆)(Biphen) at 100 °C for 90 min in C₆D₆ under argon produces a new compound in 70% yield whose proton NMR spectrum contains resonances at 3.71 and 2.06 ppm, each with an area of one proton per Biphen ligand. A trace of W(NArCl)(C₆H₆)(Biphen) is also present. A 13C NMR spectrum reveals an ethylene resonance at 70.6 ppm for a carbon with two protons attached (CH(2) 140.8 and 151.4 Hz). An X-ray structure (Table 2, Figure 6) shows the product to be a homochiral “1,2-ditungstacyclobutane” dimer that contains a bridging ethylene and two bridging imido groups, i.e., W₂(Biphen)(μ-NArCl)(μ-CH₂CH₂). The W–C distance in the W₂C₂ ring is 2.152(5) Å, and the ethylene is slightly twisted. The C–C bond length of the ethylene is 1.556(10) Å, consistent with it being a long single bond. Since a C₂ axis passes through the middle of the ethylene C–C bond, two different sets of ethylene protons are present. It should be noted that neither chloride in the bridging imido ligands is coordinated to the metal, as found in [W(NArCl)(ORF₆)]₂ (Figure 1), and that the W₂N₂ unit is puckered, not planar (Figure 7). The two W–N bond distances are essentially the same (W(1)–N(1) = 1.974(4) Å, W(1)–N(1′) = 1.926(4) Å). A W–W single bond must be present on the basis of the W–W bond length (W(1)–W(1′) = 2.5782(6) Å). W₂(Biphen)(μ-NArCl)(μ-CH₂CH₂) is similar to the “1,2-ditungstacyclobutane” species with the formula W₂(N-2,3-Me₂C₆H₄)(OCMe₂CF₃)(μ-OCMe₂CF₃)(μ-CH₂CH₂) prepared by adding ethylene to the W≡W bond in [W(N-2,3-Me₂C₆H₄)(OCMe₂CF₃)](μ-OCMe₂CF₃)(μ-CH₂CH₂) prepared by adding ethylene to the W≡W bond in [W(N-2,3-Me₂C₆H₄)(OCMe₂CF₃)](μ-OCMe₂CF₃)(μ-CH₂CH₂) prepared by adding ethylene to the W≡W bond in [W(N-2,3-Me₂C₆H₄)(OCMe₂CF₃)](μ-OCMe₂CF₃)(μ-CH₂CH₂) prepared by adding ethylene to the W≡W bond in [W(N-2,3-Me₂C₆H₄)(OCMe₂CF₃)](μ-OCMe₂CF₃)(μ-CH₂CH₂) prepared by adding ethylene to the W≡W bond in [W(N-2,3-Me₂C₆H₄)(OCMe₂CF₃)](μ-OCMe₂CF₃)(μ-CH₂CH₂) prepared by adding ethylene to the W≡W bond in [W(N-2,3-Me₂C₆H₄)(OCMe₂CF₃)](μ-OCMe₂CF₃)(μ-CH₂CH₂). The fact that W₂(Biphen)(μ-NArCl)(μ-CH₂CH₂) is homochiral constitutes proof that it cannot form directly from heterochiral [W(NArCl)(Biphen)(μ-CH₂)]₂ without [W(NArCl)(Biphen)(μ-CH₂)]₂ breaking into monomeric units. Monomeric units with the same chirality then recombine to give homochiral W₂(Biphen)(μ-NArCl)(μ-CH₂CH₂).

A 27 µmol/mL suspension of [W(NArCl)(Biphen)(μ-CH₂)]₂ in C₆D₆ decomposes after 50 min at 100 °C to yield a mixture of decomposition products, ~25% of which consist of W₂-
Figure 5. Molecular structure of \([W(N\text{ArCl})(Biphen)]_2(\mu-\text{CH}_2\text{CH}_2)\). Hydrogen and solvate atoms are omitted for clarity; thermal ellipsoids are drawn at 50% probability level. Selected bond lengths [Å] and angles [deg]: \(W(1)−W(1)' = 1.944(4), W−O(1) = 1.930(4), W−N(1) = 1.753(5), W−C(1) = 2.277(6), W−C(1)' = 1.982(6), W−W = 3.121(1), C(11)−N(1)−W = 153.3(5), O(1)−W−C(1) = 169.76(19), O(2)−W−C(1) = 118.7(2), O(2)−W−N(1) = 133.7(2), C(1)'−W−N(1) = 104.3(3), W−C(1)−W' = 94.0(2), C(1)'−W−C(1) = 86.0(2).

(Biphen)$_2(\mu-\text{NArCl})_2(\mu-\text{CH}_2\text{CH}_2)$. The other products could not be identified conclusively. However, the mixture contains...
ligand is more electron withdrawing and sterically less bulky than the NAr ligand, it renders the metal more electrophilic as well as more accessible. It is perhaps for these reasons that NArCl complexes appear to decompose bimolecularly more readily than complexes that contain the NAr ligand. Bimolecular reactions also may be encouraged as a consequence of intermolecular coordination of an ortho chloride, a circumstance that appears in the structure of [W(μ-NArCl)(OR)]22 described in this work. In any case, we can now add tungsten 2,6-dichlorophenylimido complexes to the lengthening list of available variations of M(NR)(CHR)(OR)2 complexes. There does not appear to be any special feature of the 2,6-dichlorophenylimido species, aside from interaction of one of the chlorides with the metal in certain situations, that would differentiate the chemistry of 2,6-dichlorophenylimido species strongly from that of other imido complexes such as 2,6-diisopropylphenylimido. 2,6-Dichlorophenylimido species appear to be less soluble than 2,6-diisopropylphenylimido species (inter alia), a property that probably has assisted in the isolation of the six species that have been crystallographically characterized here.

The work described here presents the most complete picture of how W(VI) imido methane complexes decompose. It also serves as a model study for decomposition of other (e.g., monosubstituted) alkylidenes. Several of the intermediates on the decomposition pathway of monosubstituted alkylidenes for sterically either will not be formed or will lose a disubstituted olefin readily to yield (ultimately) a dimeric species that contains only imido and alkoxide groups.

Perhaps the most striking compound prepared and characterized in this work is [W(NArCl)(Biphen)(μ-CH2)]2. The analogous [W(NAr)(Biphen)(μ-CH2)]2 species was observed in solution, but since it was not isolated and crystallographically characterized, the proposal that it was indeed a relatively stable dimeric form of a methane complex remained unconfirmed. Since it has long been known that methane complexes decompose more readily in a bimolecular manner than any other alkylidene to give ethylene or ethylene complexes, we were astonished that an apparent intermediate in this process would actually be stable. We now know that heterochiral [W(NArCl)(Biphen)(μ-CH2)]2 is not an intermediate along a pathway to homochiral W2(Biphen)(μ-NArCl)(μ-CH2CH2). Instead, it breaks up to yield monomeric W(NAr)(Biphen)(μ-CH2)2 species, and homochiral monomers then combine to yield homochiral W2(Biphen)(μ-NArCl)(μ-CH2CH2), either directly or via homochiral [W(NArCl)(Biphen)(μ-CH2)]2 that is unstable with respect to rearrangement to yield W2(Biphen)(μ-NArCl)(μ-CH2CH2). Likewise, either heterochiral [W(NAr)(Biphen)(μ-CH2)]2 cannot rearrange intramolecularly in order to bring the methylenes close enough to form a “1,2-ditungstacyclobutane” species or else a C–C bond is formed in a more direct manner when homochiral W(NAr)(Biphen)(μ-CH2)2 complexes combine.

Although we have not yet confirmed that ethylene is lost from W2(Biphen)(μ-NArCl)(μ-CH2CH2) to form [W(Biphen)(μ-NArCl)]2, the structure of W2(Biphen)(μ-NArCl)(μ-CH2CH2) suggests that it is poised to lose ethylene as an ortho chloride coordinates to the metal, as shown in Figure 1 for the ORCl analogue. We have observed that ethylene is lost reversibly from the 1,2-ditungstacyclobutane species with the formula W2(N,2,3-Me2C6H3)(OCMe2CF3)(μ-OCMe2CF3)(μ-CH2CH2) to yield [W(N,2,3-Me2C6H3)(OCMe2CF3)]2, which contains an unbridged W=W bond.3 Does the chirality at each metal play an important role in decompositions of alkylidene complexes? Nothing is known, but it would be difficult to justify any sweeping statement at this juncture. Nevertheless, it would seem that chirality at least could be a determinant of an enantioselectively pure catalyst’s longevity or lack thereof.

We have obtained some evidence that alkylidenes can be regenerated from reduced metal species.19 We have been entertaining the possibility of regenerating alkylidene species from decomposition products, a circumstance that could lead to long-lived catalysts, possibly through reactions with main group alkylidene sources. However, the possibility of regenerating catalysts in this manner would seem to be most favorable if a single product of alkylidene decomposition were present. Unfortunately a single decomposition product is far from reality in the system that we have examined here and perhaps also in many other systems. Therefore regeneration of a catalyst employing a main group alkylidene may be possible only rarely, if ever. It remains to be seen whether that circumstance will change if a catalyst is attached to a silica surface where bimetallic species cannot form readily.20

Experimental Section

General Procedures. All operations were performed under a nitrogen atmosphere in the absence of oxygen and moisture in a glovebox or using standard Schlenk procedures. The glassware and NMR tubes were flame-dried or oven-dried prior to use. Benzene, ether, dichloromethane, pentane, and toluene were degassed with dinitrogen and passed through activated alumina columns. Dimethoxycyclohexane (DME) was distilled from a dark purple solution of sodium benzophenone ketyl and degassed three times by freeze–pump–thaw techniques.1,13,C, and 19F NMR spectra were acquired at room temperature (unless otherwise noted) using a Bruker Avance 400 spectrometer (1H 400 MHz, 13C 100 MHz, 19F 376 MHz) and referenced to the residual proton solvent peaks or external CF3O (=163.0 ppm). HMOC spectra were recorded on a Bruker Avance 600 spectrometer. Elemental analyses were performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany. Neopentylmagnesium chloride was titrated against propanol in a THF solution using 1,10-phenanthroline as an indicator immediately prior to use. WO2Cl2 was prepared from WCl6 and 2 equiv of hexamethyldisiloxane in dichloromethane. All other chemicals were purchased from commercial sources and used as received.

Xray Crystallography. Low-temperature diffraction data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), performing φ- and ω-scans. The structures were solved by direct methods using SHELXS11 and refined against F2 on all data by full-matrix least-squares with SHELXL-97.20 All non-hydrogen atoms were refined anisotropically. All hydrogen atoms (except the hydrogen atoms on carbon that binds directly to tungsten, which have been taken from the difference Fourier synthesis and refined semisfreely with the help of distance constraints) were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). Details of the data quality and a summary of the residual values of the refinements are listed in Tables 1 and 2.

(22) Sheldrick, G. M. SHELXL 97; Universität Göttingen: Göttingen, Germany, 1997.
The shape of the anisotropic displacement ellipsoids in W(NArCl)₂(CH₃C₆H₄)(OTf)(DME) is deuterated. The deuteria were refined as hydrogens (same scattering factor). The highest two residual density maxima are off from a red solution. The solvent was removed from the red solution after 1 h. The charcoal was filtered off, and the volatiles were removed under reduced pressure to give a yellow foam. Recrystallization from ether (400 mL, −78 °C) gave analytically pure W(NArCl)(CHCMe₃)(OTf)(DME) (17.65 g, 57%) as bright yellow microcrystals. The NMR spectroscopic data are consistent with approximately a 1:1 mixture of two isomers in CDCl₃ and a 5:1 mixture of two isomers in C₆D₆, respectively: ¹H NMR (CDCl₃) δ 11.80, 10.96 (s, 1 H, WCH), 6.60 (br m, 2 H, NArCl-3 and NArCl-5), 6.25 (br m, 1 H, NArCl-4); 3.95, 3.84, 3.23, 3.18, 2.86, 2.78, 2.34 (br, 10 H, DME), 1.52, 1.29 (s, 9 H, CHCMe₃); ¹H NMR (CDCl₃) major isomer, OTf⁻ ligands in cisoid arrangement δ 11.52 (s, JCH = 121.0 Hz, 1 H, WCH), 7.45 (d, JHH = 8.3 Hz, 2 H, NArCl-3 and NArCl-5), 7.16 (t, JHH = 8.3 Hz, 1 H, NArCl-4), 4.58 (s, 3 H, DME), 4.38 (m, 2 H, DME), 4.15 (m, 1 H, DME), 3.76 (m, 3 H, DME), 3.72 (s, 3 H, DME), 1.22 (s, 9 H, CHCMe₃); minor isomer, OTf⁻ ligands in transoid arrangement δ 10.83 (s, JCH = 115.7 Hz, 1 H, WCH), 7.39 (d, JHH = 8.1 Hz, 2 H, NArCl-3 and NArCl-5), 4.35 (s, 3 H, DME), 4.09 (m, 2 H, DME), 3.87 (m, 2 H, DME), 3.67 (s, 3 H, DME), 1.25 (s, 9 H, CHCMe₃). The NArCl⁻ resonance of the minor isomer was obscured by the major isomer; ¹³C¹(H) NMR (CDCl₃) major isomer, OTf⁻ ligands in cisoid arrangement δ 302.5 (WCH), 148.8, 135.2, 129.2, 128.9, (NArCl), 120.2 (quart, JCH = 317.3 Hz, CF₃), 119.3 (quart, JCH = 318.7 Hz, CF₃); 82.3, 79.5, 71.9, 62.3 (DME), 48.5 (CMe₃), 33.2 (CMe₃); minor isomer, OTf⁻ ligands in transoid arrangement δ 294.7 (WCH); ¹³C NMR (CDCl₃) major isomer, OTf⁻ ligands in cisoid arrangement δ −76.2 (m), 77.1 (m); minor isomer, OTf⁻ ligands in transoid arrangement δ −76.4 (s). Anal. Calcld for C₃H₇F₃Cl₂N₂O₅S₂W: C, 25.45; H, 2.89; N, 1.75. Found: C, 25.38; H, 2.95; N, 1.77.

W(NArCl)(CHCMe₃)(OC(CF₃)₂)₂Me. Method A: A suspension of W(NArCl)(CHCMe₃)(OTf)(DME) (5.00 g, 6.23 mmol) in toluene (200 mL) was warmed until the compound completely dissolved. A solution of LiOC(CF₃)₂Me (2.34 g, 12.47 mmol) in Et₂O (50 mL) was added dropwise to the chilled (~30 °C) toluene solution while it was stirred. The yellow-orange-yellow solution was stirred for 12 h at 25 °C, then the volatiles were removed under reduced pressure (10⁻² Torr for 12 h to remove all DME). The yellow powder was suspended in pentane (200 mL), and after stirring it for 30 min at 25 °C the mixture was filtered through Celite and the solid was washed with pentane (3 × 50 mL). The yellow filtrate was reduced in volume and stored at −30 °C to give yellow crystals of W(NArCl)(CHCMe₃)(OResk). The pure product was obtained by washing powdered W(NArCl)(CHCMe₃)(OResk) with chilled (~30 °C) pentane; yield of bright yellow powder (3 crops) 3.80 g (80%).

Method B: Neat HOC(CF₃)₂Me (4.09 g, 22.44 mmol) was added dropwise to a stirred solution of W(NArCl)(CHCMe₃)(OTf)(DME) (9.00 g, 11.22 mmol) and 2,6-lutidine (2.41 g, 22.50 mmol) in benzene (200 mL). After the yellow suspension was stirred for 12 h at 25 °C, the volatiles were removed by lyophilization to yield a yellow powder. Pentane (150 mL) was added, and the yellow suspension was stirred at 25 °C for 30 min. The colorless deposit was filtered off and washed with pentane (3 × 50 mL). The volatiles were removed under reduced pressure, and the crude product was recrystallized from pentane to give bright yellow crystals; yield 6.41 g (74%) in 3 crops: ¹H NMR (CDCl₃) δ 8.91 (s, JCH = 14.1 Hz, 1CH); 115.2 Hz, 1 H, WCH), 6.82 (d, JHH = 8.1 Hz, 2 H, NArCl-3 and NArCl-5), 6.25 (t, JHH = 8.1 Hz, 1 H, NArCl-4), 1.37 (s, 2 × 3 H, OCCH₃), 1.06 (s, 9 H, CHCMe₃); ¹³C¹(H) NMR (CDCl₃) δ 257.3 (JCH = 195.9 Hz, WCH), 150.5, 133.7, 127.4.
was stirred under ethylene (1 atm) at 25 °C for 12 h and then stored at 30 °C for a further 24 h. This material was yellow microcrystals, which were isolated by filtration and washed with pentane (5 mL); yield 700 mg (65%): 1H NMR (THF-d8) δ 7.15–7.05 (br, 1 H, biphenyl, and 2 × 1 H, NArCl-3 and NArCl-5), δ 7.00 (s, 1 H, biphenyl), 6.72 (t, JHH = 8.1 Hz, 1 H, NArCl-4), 3.99 (br, 2 × 2 H, α-CH3, THF), 3.34, 3.13 (m, 2 × 1 H, WC4H12), 2.27, 2.15, 1.86 (s, 3 × 3 H, biphenyl-CH3), 1.83 (br, 2 × 2 H, β-CH2, THF), 1.42 (s, 3 × 3 H, biphenyl-CH3), 1.28, 1.17 (s, 2 × 9 H, biphenyl-CH2). Two protons in the ethylene group were obscured by other resonances.

W(NArCl)2(CH2)(Biphen)(THF-1,2). An orange solution of W(NArCl)2(CH2)(Biphen) (150 mg, 203 μmol) in THF-d6 was kept for 90 min at 25 °C before the NMR spectra were recorded. After 48 h the solvent was decanted to leave yellow crystals of W(NArCl)2(CH2)(Biphen)(THF-d6) (90 mg, 55%): 1H NMR (THF-d6) δ 7.08 (s, 1 H, biphenyl and d, JHH = 8.1 Hz, 2 × 1 H, NArCl-3 and NArCl-5), 0.94 (s, 1 H, biphenyl), 6.72 (t, JHH = 8.1 Hz, 1 H, NArCl-4), 3.31, 3.01 (m, JCH = 154.4 Hz, 157.9 Hz, 2 × 1 H, WC4H12), 2.27, 2.21 (s, 2 × 3 H, biphenyl-CH3), 2.13, 2.06 (m, JCH = 151.7 Hz, 152.6 Hz, 2 × 1 H, WC4H12), 1.87, 1.43 (s, 3 × 3 H, biphenyl-CH3), 1.29, 1.17 (s, 2 × 9 H, biphenyl-CMe2); 13C{1H} NMR (THF-d6) δ 160.5 (aryl), 155.7 (aryl), 151.3 (aryl), 140.3 (aryl), 135.8 (aryl), 134.4 (aryl), 133.2 (aryl), 131.5 (aryl), 131.4 (aryl), 130.6 (aryl), 128.7 (aryl), 128.4 (aryl), 127.2 (aryl), 127.0 (aryl), 123.9 (aryl), 55.8 (JCH = 152.6 Hz, 151.7 Hz, JwC = 37.9 Hz, WC4H12), 52.6 (JCH = 157.9 Hz, 154.4 Hz, JwC = 34.5 Hz, WC4H12), 36.0, 34.7, 31.3, 30.7, 20.5, 20.2, 17.0, 16.9. The coupling constants JCH were determined in an HMOC experiment. Anal. Calcd for C26H20Cl2N2O2W: C, 53.74; H, 6.89; N, 1.74. Found: C, 53.68; H, 6.95; N, 1.68.

W(NArCl)2(H2)(Biphen). W(NArCl)2(H2)(Biphen)(THF) (600 mg, 813 μmol) was suspended in benzene (50 mL), and the degassed reaction mixture was stirred under ethylene (1 atm) at 25 °C for 15 min. Upon addition of ethylene, the yellow suspension immediately dissolved to yield an orange-red solution. The reaction mixture was frozen, and the volatiles were removed by lyophilization to give an approximate 6:1 mixture of W(NArCl)2(C2H4)(Biphen) and unreacted W(NArCl)2(Biphen)(CH2)(THF). This material was redissolved in benzene (50 mL), and the above procedure was repeated (addition of ethylene, lyophilization) to yield W(NArCl)2(C2H4)(Biphen) as an orange powder (500 mg, 82%): 1H NMR (CDCl3) δ 7.32, 7.13 (s, 2 × 1 H, biphenyl), 6.78 (d, JHH = 8.1 Hz, 2 × 1 H, NArCl-3 and NArCl-5), 6.09 (t, JHH = 8.1 Hz, 1 H, NArCl-4), 3.75 (m, JCH = 124.4 Hz, 1 H, α-CH2, WC4H12), 3.46 (m, JCH = 123.3 Hz, 1 H, α-CH2, WC4H12), 3.41 (m, JCH = 136.7 Hz, 1 H, β-CH2, WC4H12), 3.37 (m, JCH = 128.5 Hz, 1 H, α-CH2, WC4H12).
WC\textsubscript{4}H\textsubscript{8}), 3.37 (m, J\textsubscript{CH} = 137.9 Hz, 1 H, \beta-CH\textsubscript{2}, WC\textsubscript{4}H\textsubscript{8}), 3.32 (m, J\textsubscript{CH} = 126.8 Hz, 1 H, \alpha-CH\textsubscript{2}, WC\textsubscript{4}H\textsubscript{8}), 3.07 (m, J\textsubscript{CH} = 135.6 Hz, 1 H, \beta-CH\textsubscript{2}, WC\textsubscript{4}H\textsubscript{8}), 2.09, 2.05, 1.73, 1.61 (s, 4 \times 3 H, Biphen-CH\textsubscript{3}), 1.60 (s, 9 H, CMe\textsubscript{3}), 1.49 (s, 9 H, CMe\textsubscript{3}). 1\textsuperscript{H} NMR (CD\textsubscript{3}OD) \delta 160.4, 158.0, 150.3, 140.9, 136.5, 136.4, 134.6, 133.6, 133.2, 132.6, 131.2, 130.9, 129.6, 128.9, 127.8, 126.7, 126.1, 85.3 (J\textsubscript{WC} = 79.3 Hz, 1 J\textsubscript{CH} = 123.3 Hz, 128.5 Hz, \alpha-CH\textsubscript{3}), 77.5 (J\textsubscript{WC} = 79.3 Hz, 1 J\textsubscript{CH} = 124.4 Hz, 126.8 Hz, \alpha-CH\textsubscript{3}), 38.3 (J\textsubscript{CH} = 132.1 Hz, 135.6 Hz, \beta-CH\textsubscript{3}), 38.1 (J\textsubscript{CH} = 136.7 Hz, 137.9 Hz, \beta-CH\textsubscript{3}), 35.6, 35.5, 32.0, 31.0, 20.7, 20.5, 17.4, 17.2. One aromatic carbon resonance could not be located. The coupling constants J\textsubscript{CH} were determined in an HMQC experiment. Anal. Calcd for C\textsubscript{34}H\textsubscript{43}Cl\textsubscript{2}NO\textsubscript{2}W: C, 54.27; H, 5.76; N, 1.86. Found: C, 54.18; H, 5.71; N, 1.84.

W(NArCl\textsubscript{3})\textsubscript{2}(Biphen) was observed when 1\textsuperscript{H}NMR (CD\textsubscript{2}Cl\textsubscript{2}) showed 3.97 ppm (3 H, CMe\textsubscript{3}); 3.83 ppm (15 H, C\textsubscript{2}H\textsubscript{4}NArCl\textsubscript{3} and CMe\textsubscript{3}); 3.31 ppm (1 H, C\textsubscript{2}H\textsubscript{4}NArCl\textsubscript{3} and CMe\textsubscript{3}). 1\textsuperscript{H}NMR (CD\textsubscript{2}Cl\textsubscript{2}) showed 2.09 ppm (3 H, \alpha-CH\textsubscript{3}), 1.61 ppm (3 H, \alpha-CH\textsubscript{3}).

Reaction of W(NArCl\textsubscript{3})\textsubscript{2}(CHCMe\textsubscript{3})[OC(CF\textsubscript{3})\textsubscript{2}Me\textsubscript{2}] with Excess 1\textsuperscript{H}NMR (CD\textsubscript{2}Cl\textsubscript{2}) showed 2.21 ppm (3 H, \alpha-CH\textsubscript{3}), 2.11 ppm (3 H, \alpha-CH\textsubscript{3}).

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Supporting Information Available: Labeled thermal ellipsoid drawings, crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, and anisotropic displacement parameters for all crystallographically characterized compounds. This material is available free of charge via the Internet at http://pubs.acs.org. Data for (\mu-\textsubscript{H}NArCl\textsubscript{3})(OC(CF\textsubscript{3})\textsubscript{2}Me\textsubscript{2})\textsubscript{2}(CMe\textsubscript{3}) (06034), W(NArCl\textsubscript{3})(Biphen)-(HC\textsubscript{2}H\textsubscript{4})(CMe\textsubscript{3})(06135), W(NArCl\textsubscript{3})(Biphen)(C\textsubscript{2}H\textsubscript{4})(THF-d\textsubscript{2}) (06140), W(NArCl\textsubscript{3})(Biphen)(C\textsubscript{2}H\textsubscript{4}) (06179), W(NArCl\textsubscript{3})(Biphen)-(\mu-\textsubscript{H}C\textsubscript{2}H\textsubscript{4}) (06185), and W(Biphen)(\mu-\textsubscript{N}ArCl\textsubscript{3})(\mu-\textsubscript{H}C\textsubscript{2}H\textsubscript{4}) (06208) are also available to the public at http://www.reciprocalnet.org/.

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