Synthesis and Reactions of Tungsten Alkylidene Complexes That Contain the 2,6-Dichlorophenylimido Ligand

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Tungsten alkylidene complexes that contain the 2,6-dichlorophenylimido ligand (NAr_{Cl}), $W(NAr_{Cl})(CHCMe_3)(OR_{F6})_2$ and $W(NAr_{Cl})(CHCMe_3)(Biphen)(THP)$ ($OR_{F6} = OCMe(CF_3)_2$; $Biphen^{2-}$ = 3,3′-di-t-Bu-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diolate; THP = tetrahydropyran), have been prepared from $W(NAr_{Cl})(CHCMe_3)(OSO_2CF_3)_2(dme)$. Reaction of $W(NAr_{Cl})(CHCMe_3)(OR_{F6})_2$ with excess ethylene gave the tungstacyclobutane complex $W(NAr_{Cl})(OR_{F6})_2(C_3H_6)$, while reaction of $W(NAr_{Cl})(CHCMe_3)(OR_{F6})_2$ with internal olefins gave the dimer, $[W(\mu\text{-}NAr_{Cl})(OR_{F6})_2]_2$. $W(NAr_{Cl})(CHCMe_3)(Biphen)(THP)$ reacted with excess ethylene to give $W(NAr_{Cl})(Biphen)(C_3H_6)$, which yielded $W(NAr_{Cl})(Biphen)(C_2H_4)(THF)$ upon addition of THF. The tungstacyclopentane complex, $W(NAr_{Cl})(Biphen)(C_4H_8)$, was formed upon treatment of $W(NAr_{Cl})(Biphen)(C_2H_4)(THF)$ with ethylene. $W(NAr_{Cl})(Biphen)(C_3H_6)$ decomposed to yield (*inter alia*) the dimeric, heterochiral methylidene complex, $[W(NAr_{Cl})(Biphen)(\mu\text{-}CH_2)]_2$, which decomposed further to yield homochiral $[W(NAr_{Cl})(Biphen)]_2(\mu\text{-}CH_2CH_2)$. Finally, $[W(NAr_{Cl})(Biphen)]_2(\mu\text{-}CH_2CH_2)$ loses ethylene reversibly to yield $[W(NAr_{Cl})(Biphen)]_2$, which could not be isolated in pure form. $\{W(\mu\text{-}NAr_{Cl})[OC(CF_3)_2Me]_2\}_2$, $W(NAr_{Cl})(Biphen)(C_3H_6)$, $W(NAr_{Cl})(Biphen)(C_2H_4)(THF)$, $W(NAr_{Cl})(Biphen)(C_4H_6)$, $[W(NAr_{Cl})(Biphen)(\mu\text{-}CH_2)]_2$, and $[W(NAr_{Cl})(Biphen)]_2(\mu\text{-}CH_2CH_2)$ were characterized through X-ray studies.

Introduction

Imido alkylidene bisalkoxide complexes of molybdenum or tungsten of the type $M(NR)(CHR')(OR'')_2$ 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 $M(NR)(CHR')(OR'')_2$ 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.[1a]

The most common imido ligands that have been employed in $M(NR)(CHR')(OR'')_2$ catalysts are $N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3$, $N\text{-}2,6\text{-}Me_2C_6H_3$, $N\text{-}2\text{-}t\text{-}BuC_6H_4$, $N\text{-}2\text{-}CF_3C_6H_4$, $N\text{-}2,6\text{-}Cl_2C_6H_3$, and N-1-adamantyl.[1a] Molybdenum catalysts that contain the 2,6-dichlorophenylimido (NAr_{Cl}) ligand[2] and an enantiomerically pure biphenolate 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 NAr_{Cl} ligand is one of the smallest aryl substituents and is relatively electron withdrawing. The NAr_{Cl} 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 $M(NR)(OR'')_2(olefin)$ complex is a molybdenum complex that contains the NAr_{Cl} ligand, namely, $Mo(NAr_{Cl})(Biphen)(C_2H_4)(Et_2O)$ ($Biphen^{2-}$ = 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 tungstacyclobutane species, especially unsubstituted tungstacyclobutanes, a circumstance that has been proposed to limit alkylidenes that are available for metathesis at temperatures where the WC_3 ring does not lose olefin readily. Molybdenum catalysts have gained favor over tungsten catalysts since molybdacyclobutane 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) ($Ar = 2,6\text{-}i\text{-}Pr_2C_6H_3$) species with ^{13}C-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, tungstacyclobutane, and tungstacyclopentane complexes) could not be isolated. The most

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interesting of the unisolated species observed in this study was a dimeric complex, $[W(NAr)(Biphen)(\mu\text{-}CH_2)]_2$, 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., $\{W(NAr)[(S)\text{-}Biphen](\mu\text{-}CH_2)\}\{W(NAr)[(R)\text{-}Biphen](\mu\text{-}CH_2)\}$. $[W(NAr)(Biphen)(\mu\text{-}CH_2)]_2$ was not observed in a system in which the $Biphen^{2-}$ ligand was enantiomerically pure.

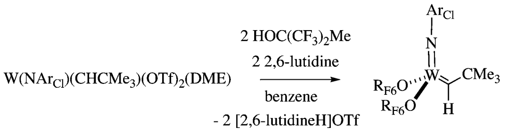
We decided to attempt to synthesize tungsten species that contain the 2,6-dichlorophenylimido ligand in order to compare them with molybdenum species. Our goal was to prepare two prototypical tungsten alkylidene complexes of the type $W(NAr_{Cl})(CHCMe_3)(OR'')_2$, one in which $OR'' = OC(CF_3)_2Me$ (OR_{F6}) 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 $W(NAr_{Cl})(CHCMe_3)[OC(CF_3)_2Me]_2$ and $W(NAr_{Cl})(CHCMe_3)(Biphen)(THP)$ (THP = tetrahydropyran). The synthesis of $W(NAr_{Cl})$ complexes follows the traditional route.[7] $W(NAr_{Cl})_2Cl_2(DME)$ (DME = 1,2-dimethoxyethane) is first prepared in a reaction between Me_3SiCl, 2,6-lutidine, and WO_2Cl_2 in dimethoxyethane.[7] Alkylation of $W(NAr_{Cl})_2Cl_2(DME)$ with Me_3CCH_2MgCl to give $W(NAr_{Cl})_2(CH_2CMe_3)_2$ proceeded without complication. $W(NAr_{Cl})_2Cl_2(DME)$ and $W(NAr_{Cl})_2(CH_2CMe_3)_2$ have been reported in a recent Ph.D. thesis.[8] Experimental details are reported in this paper for convenience.

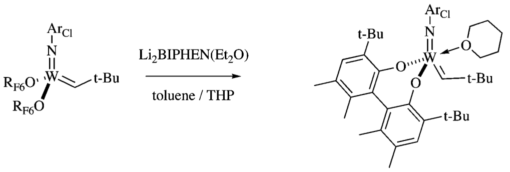
Addition of 3 equiv of triflic acid to $W(NAr_{Cl})_2(CH_2CMe_3)_2$ in DME produced $W(NAr_{Cl})(CHCMe_3)(OTf)_2(DME)$ as bright yellow microcrystals in 57% yield. NMR data are consistent with $W(NAr_{Cl})(CHCMe_3)(OTf)_2(DME)$ being a 1:1 mixture of two isomers in C_6D_6 (δ H_α = 11.80 and 10.96 ppm) and a 5:1 mixture of two isomers in CD_2Cl_2 (δ H_α = 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. (The molybdenum analogue, $Mo(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(CHCMe_3)(OTf)_2(DME)$, has this geometry.[9]) The isomer in which the alkylidene proton resonance has the larger chemical shift has no symmetry and is believed to be one of the possible species in which the triflate ligands are *cis* to one another; its precise structure is not known.

Bright yellow crystals of $W(NAr_{Cl})(CHCMe_3)(OR_{F6})_2$ ($OR_{F6} = OC(CF_3)_2Me$) could be isolated from the reaction between $W(NAr_{Cl})(CHCMe_3)(OTf)_2(DME)$ (as the mixture of isomers described above) and 2 equiv of $LiOR_{F6}$ in toluene (6 mmol scale, 80% yield). Alternatively, $W(NAr_{Cl})(CHCMe_3)(OR_{F6})_2$ can be prepared in a reaction between $W(NAr_{Cl})(CHCMe_3)(OTf)_2(DME)$ and 2 equiv of $(CF_3)_2MeCOH$ in the presence of 2,6-lutidine, as shown in eq 1. The method shown in eq 1 avoids the alkoxide anion, which in some circumstances leads to deprotonation of an alkylidene to give an alkylidyne species.[10] Only the *syn* isomer of $W(NAr_{Cl})(CHCMe_3)(OR_{F6})_2$ is observed in C_6D_6 at 25 °C. The neopentylidene α proton resonance was found at 8.91 ppm ($^2J_{WH}$ = 14.1 Hz, $^1J_{CH}$ = 115.2 Hz) in the ^1H NMR spectrum, and the α carbon resonance was found at 257.3 ppm ($^1J_{WC}$ = 195.9 Hz) in the ^{13}C NMR spectrum.



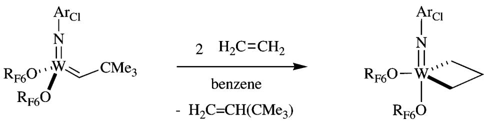
(1)

The $Biphen^{2-}$ complex, $W(NAr_{Cl})(CHCMe_3)(Biphen)(THP)$ (THP = tetrahydropyran), was prepared in a reaction between $W(NAr_{Cl})(CHCMe_3)(OR_{F6})_2$ and $Li_2Biphen$ in toluene in the presence of THP on a 2.6 mmol scale and isolated as a benzene-soluble pale yellow powder in 82% yield (eq 2). (It should be assumed that all $Biphen^{2-}$ complexes in this paper contain *rac*-$Biphen^{2-}$, unless otherwise noted.) Attempts to prepare $W(NAr_{Cl})(CHCMe_3)(Biphen)(THF)$ by adding $K_2Biphen$ to $W(NAr_{Cl})(CHCMe_3)(OTf)_2(DME)$ or $W(NAr_{Cl})(CHCMe_3)(OR_{F6})_2$ in the presence of THF failed. It appears that polyTHF is formed in either reaction, which compromises the yield and the ease of product isolation. In $W(NAr_{Cl})(CHCMe_3)(Biphen)(THP)$ the alkylidene H_α resonance in C_6D_6 at 25 °C is observed at 9.19 ppm ($^2J_{WH}$ = 8.3 Hz, $^1J_{CH}$ = 109.4 Hz) in the ^1H NMR spectrum. This resonance is assigned to a *syn* isomer on the basis of the low value for $^1J_{CH}$. The alkylidene α carbon atom resonance is found at 266.5 ppm in the ^{13}C NMR spectrum. The structure is likely to be one in which the imido and alkylidene ligands occupy equatorial positions in a trigonal bipyramid, a common structure for simple adducts.



(2)

Reactivity of $W(NAr_{Cl})(CHCMe_3)[OC(CF_3)_2Me]_2$ toward Olefins. $W(NAr_{Cl})(CHCMe_3)(OR_{F6})_2$ reacts readily with ethylene (1 atm) in benzene to yield the metallacyclobutane complex $W(NAr_{Cl})(C_3H_6)(OR_{F6})_2$ (eq 3); on a 0.3 mmol scale the product was isolated in 90% yield. A color change is observed immediately. NMR data suggest that the reaction is complete in less than 15 min with the only organic product being *tert*-butylethylene. NMR data are consistent with the product having a trigonal bipyramidal structure in solution with the alkoxides occupying equatorial and apical positions, as shown.[11]



(3)

A species of this type has been crystallographically characterized where the alkoxide is $OC(CF_3)_2(CF_2CF_2CF_3)$ and the imido ligand is 2,6-diisopropylphenyl.[5a] Tungstacyclobutane species that contain the $Biphen^{2-}$ ligand have also been crystallographically characterized.[6] The α methylene resonances in the WC_3 ring in $W(NAr_{Cl})(OR_{F6})_2(C_3H_6)$ are found at 4.91 and 4.77 ppm in the proton NMR spectrum in C_6D_6, while the β methylene resonances are found at −0.87 and −1.46 ppm. The ^{13}C NMR spectrum exhibits characteristic resonances at 103.4 ppm for the α carbon atoms in the WC_3 ring (with $^1J_{CH}$ values of 160.6

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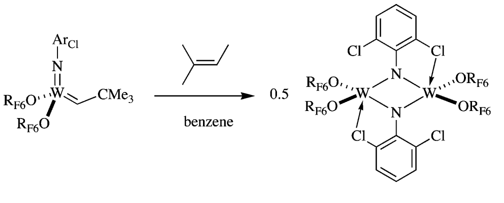
Table 1. Crystal Data and Structure Refinement for $\{W(\mu\text{-}NAr_{Cl})[OC(CF_3)_2Me]_2\}_2(C_6H_6)$ (06034), $W(NAr_{Cl})(Biphen)(CH_2CH_2CH_2)(CH_2Cl_2)_{0.25}$ (06135), and $W(NAr_{Cl})(Biphen)(CH_2CH_2)(THF\text{-}d_8)$ (06140)

	06034	06135	06140
empirical formula	$C_{34}H_{24}Cl_4F_{24}N_2O_4W_2$	$C_{33.25}H_{41.50}Cl_{2.50}NO_2W$	$C_{36}H_{47}Cl_2NO_3W$
fw	1490.05	759.65	796.50
cryst syst	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2(1)$	Pbca
unit cell dimens			
a	9.5827(8) Å	10.0730(12) Å	19.8794(11) Å
b	10.9540(9) Å	13.9931(16) Å	17.2218(9) Å
c	11.4344(10) Å	11.4971(14) Å	20.1976(11) Å
α	74.2250(10)°	90°	90°
β	82.7420(10)°	98.600(3)°	90°
γ	67.5280(10)°	90°	90°
volume	1067.00(16) $Å^3$	1602.3(3) $Å^3$	6914.8(6) $Å^3$
Z	1	2	8
density (calcd)	2.319 Mg/m^3	1.574 Mg/m^3	1.530 Mg/m^3
absorp coeff	5.785 mm^{-1}	3.843 mm^{-1}	3.531 mm^{-1}
$F(000)$	706	761	3216
cryst size	$0.17 \times 0.15 \times 0.04$ mm^3	$0.25 \times 0.10 \times 0.10$ mm^3	$0.25 \times 0.20 \times 0.05$ mm^3
θ range for data collection	2.07 to 29.57°	1.79 to 29.57°	1.86 to 29.57°
index ranges	$-13 \le h \le 13$	$-13 \le h \le 13$	$-27 \le h \le 27$
	$-15 \le k \le 15$	$-19 \le k \le 19$	$-23 \le k \le 23$
	$-15 \le l \le 15$	$-15 \le l \le 15$	$-28 \le l \le 28$
no. of reflns collected	23 920	31 950	149 111
no. of indep reflns	5953 [R(int) = 0.0257]	8943 [R(int) = 0.0467]	9686 [R(int) = 0.0441]
completeness to $\theta = 29.57°$	99.7%	100.0%	100.0%
max. and min. transmn	0.8016 and 0.4397	0.6999 and 0.4467	0.8432 and 0.4723
no. of data/restraints/params	5953/0/318	8943/77/407	9686/5/410
goodness-of-fit on F^2	1.054	1.051	1.044
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0173$, $wR_2 = 0.0414$	$R_1 = 0.0288$, $wR_2 = 0.0635$	$R_1 = 0.0207$, $wR_2 = 0.0494$
R indices (all data)	$R_1 = 0.0183$, $wR_2 = 0.0418$	$R_1 = 0.0404$, $wR_2 = 0.0680$	$R_1 = 0.0274$, $wR_2 = 0.0532$
largest diff peak and hole	1.572 and −0.585 e·$Å^{-3}$	2.988 and −1.591 e·$Å^{-3}$	1.292 and −0.380 e·$Å^{-3}$

[a] 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 F^2.

and 165.2 Hz) and at −4.7 ppm for the β carbon atom in the WC_3 ring (with $^1J_{CH}$ values of 162.0 and 166.2 Hz). The reaction between $W(NAr_{Cl})(CHCMe_3)(OR_{F6})_2$ and ethylene is proposed to yield an initial α-t-Bu-substituted tungstacyclobutane complex that loses *tert*-butylethylene to yield intermediate $W(NAr_{Cl})(CH_2)(OR_{F6})_2$. This methylene species is then trapped with ethylene to give the observed product. $W(NAr_{Cl})(C_3H_6)(OR_{F6})_2$ does not lose ethylene readily in the absence of excess ethylene at room temperature, since the resulting methylene species almost certainly would decompose readily in a bimolecular fashion and thereby provide a facile decomposition pathway for $W(NAr_{Cl})(C_3H_6)(OR_{F6})_2$ overall.

We were somewhat surprised to find that $W(NAr_{Cl})(CHCMe_3)(OR_{F6})_2$ reacts relatively readily with 1 equiv of 2-methyl-2-butene in benzene. After 15 min the bright yellow solution turned orange and purple microcrystals were deposited. After 7 days at 25 °C the purple product was isolated in 75% yield on a 0.3 mmol scale. According to ^1H and ^{19}F NMR spectra $W(NAr_{Cl})(CHCMe_3)(OR_{F6})_2$ was the only fluorine-containing species observable in solution at any point during the reaction. The purple microcrystals are insoluble in pentane, benzene, and dichloromethane and are only sparingly soluble in THF. On the basis of an X-ray structure (*vide infra*) the purple product was shown to be a dimeric species that contains bridging imido ligands, $[W(\mu\text{-}NAr_{Cl})(OR_{F6})_2]_2$, in which one of the ortho chlorides in each bridging imido group is bonded weakly to one of the tungsten centers, as shown schematically in eq 4.



(4)

The presence of only one ^{19}F resonance in the room-temperature ^{19}F NMR spectrum of $[W(\mu\text{-}NAr_{Cl})(OR_{F6})_2]_2$ at −79.0 ppm in THF-d_8 suggests that this structure is not maintained in solution on the NMR time scale. Recently, we have shown that $[W(NR)(OR'')_2]_2$ species are formed upon decomposition of $W(NR)(CHR')(OR'')_2$ species when the CHR′ ligand is relatively small (e.g., ethylidene or propylidene).[12] 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 $[W(NAr_{Cl})(OR_{F6})_2]_2$ (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 imido ligands are asymmetrically disposed with the "equatorial" W(1)−N(1) distance being shorter (1.897(17) Å) than the "axial" W(1)′−N(1) distance (2.0265(17) Å). A greater degree of π bonding to the nitrogen in an "equatorial" position around W(1) is believed to be the reason for the shorter W(1)−N(1) bond. The short W−Cl distance (W(1)−Cl(1) = 2.6136(5) Å) should be compared with the distance between the other tungsten center and the other ortho chloride in one aryl ring (W(1)′−Cl(2) = 3.5845(6) Å), which is clearly nonbonding. The W(1)−Cl(1) distance is similar to the Mo−Cl bond length (2.624(1) Å) in the Schiff base complex $Mo(C_{13}H_8Cl_2N)Cl(CO)_3$ that contains

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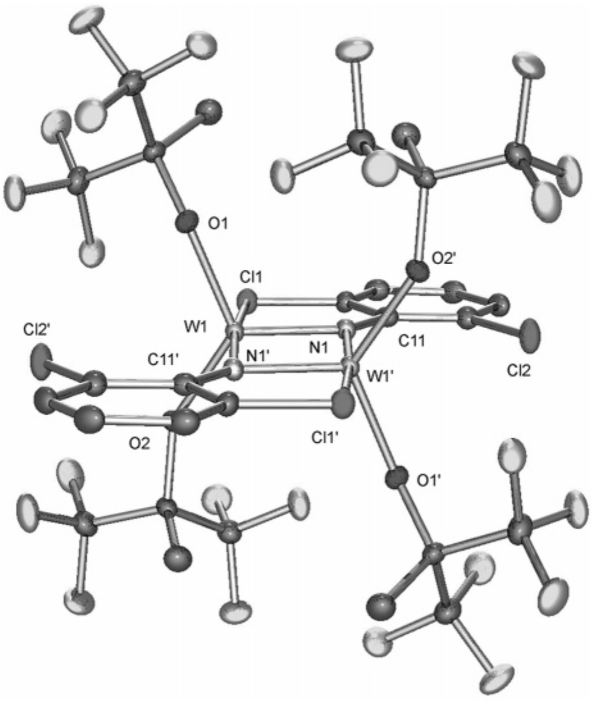


Figure 1. Molecular structure of $\{W(\mu\text{-}NAr_{Cl})[OC(CF_3)_2Me]_2\}_2$-$(C_6H_6)$. Hydrogen and solvate atoms are omitted for clarity; thermal ellipsoids are drawn at 50% probability level. Selected bond lengths [Å] and angles [deg]: W−N(1) = 1.8965(17), W−N(1)′ = 2.0265(17), W−O(1) = 1.9511(14), W−O(2) = 1.9214(14), W−Cl(1) = 2.6136(5), W−W′ = 2.5297(3), Cl(1)−W−N(1)′ = 173.31(5), O(1)−W−N(1) = 115.22(7), O(1)−W−O(2) = 122.36(6).

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. $[W(\mu\text{-}NAr_{Cl})(OR_{F6})_2]_2$ is the only complex in the category of $[W(NR)(OR'')_2]_2$ complexes[12] that does not contain an unsupported double bond. Formation of a species that contains a bridging NAr_{Cl} group might be encouraged through binding of a chlorine. The interatomic W1−W1′ distance in $[W(NAr_{Cl})(OR_{F6})_2]_2$ (2.5297(3) Å) is slightly longer than in related tungsten complexes that contain unsupported double bonds (2.4445(3)−2.4925(3) Å).[12] It is interesting to note that $[Mo(\mu\text{-}NAr)(OCMe_3)_2]_2$ (Ar = 2,6-diisopropylphenyl) is a purple dimer that contains bridging imido ligands and that the Mo−Mo distance in this species is 2.654(1) Å.[14]

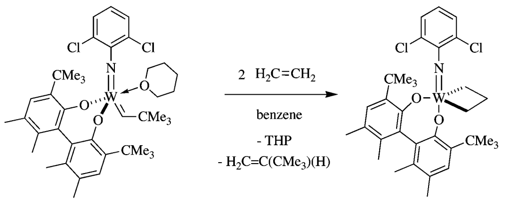
When a benzene solution of $W(NAr_{Cl})(CHCMe_3)(OR_{F6})_2$ is treated with an excess of propylene, the color of the solution changes rapidly from bright yellow to pale yellow. NMR spectra showed that the parent alkylidene complex had been converted into the unsubstituted tungstacyclobutane complex, $W(NAr_{Cl})(C_3H_6)(OR_{F6})_2$. No intermediate tungsten species were observed under these conditions. We presume that $W(NAr_{Cl})(CH_2)(OR_{F6})_2$ is formed and trapped with ethylene (that is generated through metathesis of propylene) to yield the observed product.

In a reaction between $W(NAr_{Cl})(CHCMe_3)(OR_{F6})_2$ 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 $W(NAr_{Cl})(CHCMe_3)(OR_{F6})_2$ had been converted into a mixture of $W(NAr_{Cl})(C_3H_6)(OR_{F6})_2$ and $(Me_3C)CH{=}CHPh$ and minor unidentified products. After 16 h at 25 °C, the yellow solution contained $W(NAr_{Cl})(C_3H_6)(OR_{F6})_2$ as the only tungsten species along with a minor amount of $[W(\mu\text{-}NAr_{Cl})(OR_{F6})_2]_2$ as a purple deposit.

The reaction between $W(NAr_{Cl})(CHCMe_3)(OR_{F6})_2$ and 1 equiv of *trans*-3-hexene after 40 min at 0 °C yielded a 2:1:1 mixture of $W(NAr_{Cl})(CHCMe_3)(OR_{F6})_2$, $W(NAr_{Cl})(CHEt)(OR_{F6})_2$, and what appears to be a mixture of various tungstacyclobutanes. The alkylidene resonance for $W(NAr_{Cl})(CHEt)(OR_{F6})_2$ is found at 9.27 ppm in toluene-d_8 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.[11] After 24 h at 0 °C, the reaction solution contained a 1:1 mixture of unreacted $W(NAr_{Cl})(CHCMe_3)(OR_{F6})_2$ and various tungstacyclobutanes along with a purple deposit of $[W(\mu\text{-}NAr_{Cl})(OR_{F6})_2]_2$. After 3 days at 25 °C, only $[W(\mu\text{-}NAr_{Cl})(OR_{F6})_2]_2$ was present.

The amount of $[W(\mu\text{-}NAr_{Cl})(OR_{F6})_2]_2$ formed in reactions between $W(NAr_{Cl})(CHCMe_3)(OR_{F6})_2$ and *trans*-3-hexene at 22 °C depends to a significant degree on the ratio of starting materials. A maximum amount of $[W(\mu\text{-}NAr_{Cl})(OR_{F6})_2]_2$ is produced under approximately stoichiometric conditions. Only a trace of $[W(\mu\text{-}NAr_{Cl})(OR_{F6})_2]_2$ was formed when 10 equiv of *trans*-3-hexene was added to $W(NAr_{Cl})(CHCMe_3)(OR_{F6})_2$, and $[W(\mu\text{-}NAr_{Cl})(OR_{F6})_2]_2$ did not form when $W(NAr_{Cl})(CHCMe_3)(OR_{F6})_2$ 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 C_5H_{10} and C_7H_{14} (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 $[W(\mu\text{-}NAr_{Cl})(OR_{F6})_2]_2$.

Reactions of $W(NAr_{Cl})(CHCMe_3)$(Biphen)(THP) with Ethylene. Exposure of a degassed solution of $W(NAr_{Cl})(CHCMe_3)$(Biphen)(THP) in C_6D_6 (40 μmol/mL) to 1 atm of ethylene for 25 min led to consumption of 30% of the starting material and formation of $W(NAr_{Cl})(C_3H_6)$(Biphen), according to ^1H NMR spectra (eq 5). After 24 h at 25 °C, only $W(NAr_{Cl})(C_3H_6)$(Biphen), excess ethylene, *tert*-butylethylene, and free tetrahydropyran could be detected in the proton NMR spectrum. $W(NAr_{Cl})(C_3H_6)$(Biphen) could be isolated as a pale yellow powder upon lyophilization of the above NMR sample. Analytically pure $W(NAr_{Cl})(C_3H_6)$(Biphen) could be prepared from $W(NAr_{Cl})(CHCMe_3)$(Biphen)(THP) and ethylene on a 0.8 mmol scale in virtually quantitative yield in a similar manner. The ^1H NMR spectrum of $W(NAr_{Cl})(C_3H_6)$(Biphen) shows six multiplets at 4.71, 4.42, 4.35, 3.41, −0.03, and −0.27 ppm at 25 °C in C_6D_6 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 ($^1J_{CH}$ values between 148.9 and 161.3 Hz) are typical of metallacyclobutane complexes of this general type.[11]



(5)

Single crystals of $W(NAr_{Cl})(C_3H_6)$(Biphen) (containing 0.25 equiv of CH_2Cl_2 of crystallization) suitable for X-ray structure

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[13] Harrison, R.; Arif, A. M.; Wulfsberg, G.; Lang, R.; Ju, T.; Kiss, G.; Hoff, C. D.; Richmond, T. G. *J. Chem. Soc., Chem. Commun.* **1992**, 1374.

[14] Robbins, J.; Bazan, G. C.; Murdzek, J. S.; O'Regan, M. B.; Schrock, R. R. *Organometallics* **1991**, *10*, 2902.

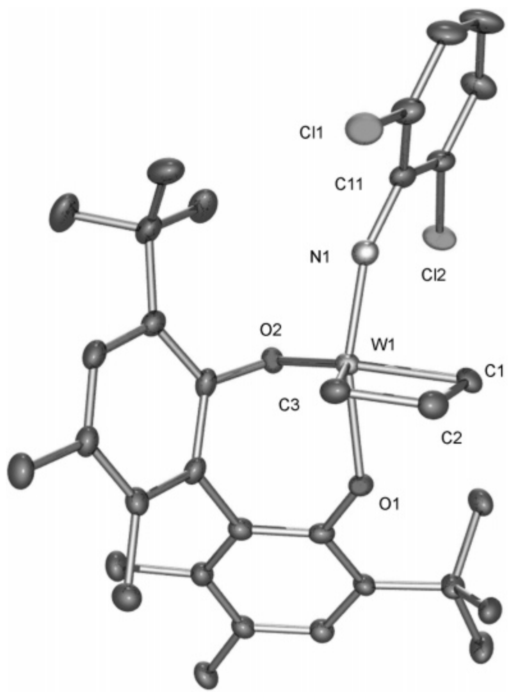
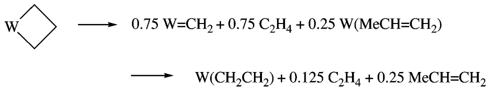


Figure 2. Molecular structure of W(NAr_{Cl})(Biphen)(CH_2CH_2-CH_2)(CH_2Cl_2)$_{0.25}$. Hydrogen and solvate atoms are omitted for clarity; thermal ellipsoids are drawn at 50% probability level. Selected bond lengths [Å] and angles [deg]: W−O(1) = 1.983(3), W−O(2) = 1.967(3), W−N(1) = 1.766(4), W−C(1) = 2.078(4), W−C(2) = 2.398(4), W−C(3) = 2.016(4), N(1)−W−O(1) = 161.75(14), C(1)−W−O(2) = 143.49(16), C(1)−W−C(3) = 81.54-(17), W−C(3)−C(2) = 82.6(2), C(1)−C(2)−C(3) = 115.0(3), C(2)−C(1)−W = 80.5(2), W−N(1)−Cl(11) = 158.9(3).

analysis were grown from a saturated CH_2Cl_2/Et_2O solution at −30 °C. The complex was found to be a distorted trigonal bipyramid with the imido nitrogen and one oxygen of the Biphen ligand adopting axial positions (Table 1, Figure 2). The WC_3H_6 ring is analogous to other known TBP metallacyclobutane species of this type, i.e., essentially planar with a short W−C_β distance (2.398(4) Å) and a C_α−C_β−C_α angle of 115.0(3)°. The bending of the NAr_{Cl} ligand probably can be attributed largely to steric interactions between the CMe_3 group attached to C(42) 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)−O2 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)(C_2H_4)-(Et_2O)[4] Mo−N−C = 169.4(7)°, while in Mo(NAr_{Cl})($CHCMe_3$)-((S)-Biphen)(THF) Mo−N−C = 149.8(8)°.[2]

Comparison of the structure of TBP W(NAr_{Cl})(C_3H_6)(Biphen) with that of SP W(NAr)[$CH_2CH(CMe_2Ph)CH_2$](Biphen)[6] reveals differences in the tungstacyclobutane rings that are analogous to those found in other TPB versus SP metallacycles in this family of bisalkoxide complexes. The W−C_α distances in the TBP WC_3 ring (2.078(4) and 2.016(4) Å) are approximately 0.1 Å shorter than the W−C_α distances in the SP WC_3 ring (2.157(14) and 2.173(15) Å), while the W−C_α−C_β angles are smaller (81.54(17)° and 82.6(2)° versus 95.7(9)° and 94.8(9)°) and the C_α−C_β−C_α angle is larger (115.0(3)° versus 97.2(11)°). In short, the WC_3 ring in the TBP species is more diamond shaped with a shorter W−C_β distance (2.398(4) Å), while the WC_3 ring in the SP species is more square with a W−C_β distance = 2.762 Å. What this means in terms of olefin loss from the WC_3 ring versus β hydride rearrangement of the WC_3 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)(C_3H_6) and Other W(Biphen) Species. When W(NAr_{Cl})(Biphen)(C_3H_6) is dissolved in THF-d_8 (200 μmol/mL), the ethylene complex, W(NAr_{Cl})(Biphen)(C_2H_4)(THF-d_8), 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})-(C_3H_6)(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)(C_2H_4)(THF-d_8) from W(NAr_{Cl})(Biphen)(C_3H_6). 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)-(C_3H_6) 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})(CH_2)-(Biphen) and ethylene, which evolve into a mixture of W(NAr_{Cl})-(Biphen)(C_2H_4)(THF-d_8) and ethylene (eq 6).



$$\longrightarrow 0.75\ W{=}CH_2 + 0.75\ C_2H_4 + 0.25\ W(MeCH{=}CH_2)$$

$$\longrightarrow W(CH_2CH_2) + 0.125\ C_2H_4 + 0.25\ MeCH{=}CH_2 \qquad (6)$$

In the ^{1}H NMR spectrum of W(NAr_{Cl})(Biphen)(C_2H_4)(THF-d_8) in THF-d_8 at 25 °C, the four ethylene protons appear as multiplets at 3.31, 3.01, 2.13, and 2.06 ppm. The ^{13}C NMR spectrum of W(NAr_{Cl})(Biphen)(C_2H_4)(THF-d_8) exhibits two resonances at 55.8 and 52.6 ppm that are assigned (through an HMQC study) to the ethylene carbons. The CH coupling constants ($^{1}J_{CH}$ = 152−158 Hz) are what one would expect.

Yellow crystals of W(NAr_{Cl})(Biphen)(C_2H_4)(THF-d_8) suitable for an X-ray structure were isolated in 55% yield from an NMR sample of W(NAr_{Cl})(C_3H_6)(Biphen) in THF-d_8 that was allowed to stand for 48 h at 22 °C. The molecular structure of W(NAr_{Cl})-(Biphen)(C_2H_4)(THF-d_8) shown in Figure 3 closely resembles that of Mo(NAr_{Cl})(Biphen)(C_2H_4)(Et_2O),[4] 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){κ^2-C_6H_4-($NSiMe_3)_2$}(C_2H_4)(PMe_3)$_2$ (1.434(6) Å) and Mo(NAr_{Cl})(Biphen)-(C_2H_4)(Et_2O) (1.400(13) Å).[4,15] Bending of the NAr_{Cl} ligand in W(NAr_{Cl})(Biphen)(C_2H_4)(THF-d_8) (W−N(1)−C(11) = 170.27-(14)°) is less pronounced than in W(NAr_{Cl})(C_3H_6)(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 $Biphen^{2-}$ ligand, as there is in W(NAr_{Cl})(C_3H_6)(Biphen). The W═N−C angle is similar to what it is in Mo(NAr_{Cl})(Biphen)-(C_2H_4)(Et_2O) (169.4(7)°).[4]

When W(NAr_{Cl})(Biphen)(C_2H_4)(THF-d_8) in CD_2Cl_2 is treated with $^{13}CH_2{=}^{13}CH_2$ (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})($^{13}CH_2{}^{13}CH_2{}^{13}CH_2{}^{13}CH_2$)(Biphen) (eq 7), is formed.

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[15] Wang, S. Y. S.; van der Lende, D. D.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1998**, *17*, 2628.

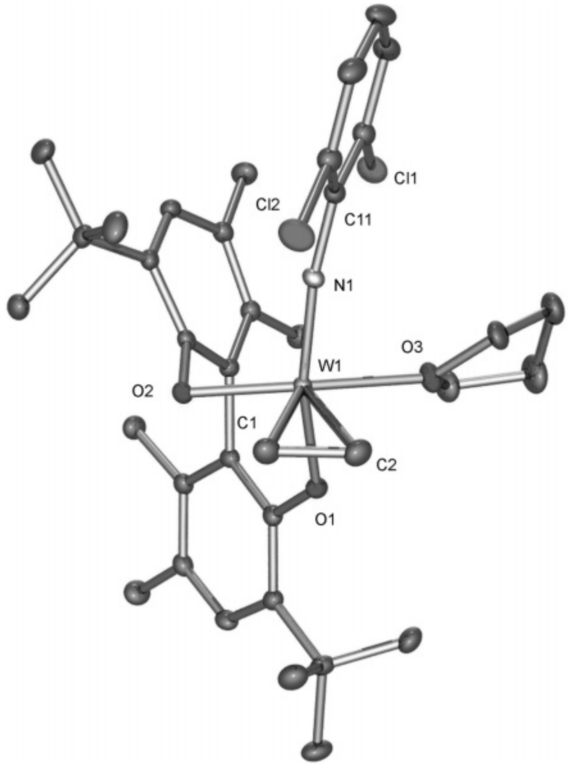
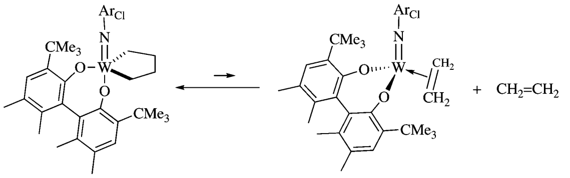


Figure 3. Molecular structure of W(NAr$_{Cl}$)(Biphen)(C$_2$H$_4$)(THF). Hydrogen and solvate atoms are omitted for clarity; thermal ellipsoids are drawn at 50% probability level. Selected bond lengths [Å] and angles [deg]: W−C(1) = 2.121(2), W−C(2) = 2.143(2), W−O(1) = 1.9684(13), W−O(2) = 2.0239(13), W−O3 = 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)(^{13}CH$_2$^{13}CH$_2$^{13}CH$_2$^{13}CH$_2$)[6] and W(NPh){κ^2-C$_6$H$_4$(NSiMe$_3$)$_2$}(C$_4$H$_8$),[15] the ^{13}C NMR spectrum of W(NAr$_{Cl}$)(^{13}CH$_2$^{13}CH$_2$^{13}CH$_2$^{13}CH$_2$)(Biphen) exhibits two doublets at 86.4 ppm ($^1J_{CC}$ = 35.4 Hz, α-CH$_2$) and 75.3 ppm ($^1J_{CC}$ = 34.5 Hz, α-CH$_2$) as well as one higher order multiplet at 37.6 ppm for the two β-CH$_2$ groups. In the ^{1}H NMR spectrum, the methylene protons of the WC$_4$H$_8$ moiety appear as broad multiplets in the region 2.56 to 3.33 ppm. Although formation of the tungstacyclopentane complex from W(NAr$_{Cl}$)(Biphen)(C$_2$H$_4$)(THF-d_8) and ethylene is reversible in the presence of THF, it was possible to isolate W(NAr$_{Cl}$)(C$_4$H$_8$)(Biphen) on a 1 mmol scale as an orange powder through lyophilization of a benzene solution of W(NAr$_{Cl}$)(Biphen)(C$_2$H$_4$)(THF) that had been treated with excess ethylene. Isolated W(NAr$_{Cl}$)(C$_4$H$_8$)(Biphen) showed no signs of decomposition in benzene (90 μmol/mL) at 60 °C over a period of 12 h. This result suggests that solvent-free "W(NAr$_{Cl}$)(C$_2$H$_4$)(Biphen)" is highly reactive, and in the absence of THF the equilibrium between W(NAr$_{Cl}$)(CH$_2$CH$_2$CH$_2$CH$_2$)(Biphen) and "W(NAr$_{Cl}$)(CH$_2$=CH$_2$)(Biphen)" must lie far toward W(NAr$_{Cl}$)(CH$_2$CH$_2$CH$_2$CH$_2$)(Biphen) (eq 7). Heating a sample of W(NAr$_{Cl}$)(C$_4$H$_8$)(Biphen) to 100 °C for 90 h in benzene leads to ~20% decomposition to yield ethylene and a mixture of unidentified tungsten compounds.

An X-ray study of W(NAr$_{Cl}$)(Biphen)(C$_4$H$_8$) (Table 2, Figure 4) showed it to have structural parameters reminiscent of W(NPh){κ^2-C$_6$H$_4$(NSiMe$_3$)$_2$}(C$_4$H$_8$),[15] i.e., a slightly distorted square pyramid geometry around W with the imido ligand in the axial position. The W−C(1) and W−C(4) bond lengths (2.129(8) and 2.112(8) Å) are marginally shorter than those found in other crystallographically characterized tungstacyclopentane complexes (2.173(6)−2.191(12) Å).[15,16] The C−C distances (1.504(12)−1.535(11) Å) in the WC$_4$ ring suggest that they are essentially single bonds, as expected for complexes of this type. The NAr$_{Cl}$ ligand is only slightly bent (W−N(1)−C(11) = 175.5(6)°).



(7)

When generated in C$_6$D$_6$ from W(NAr$_{Cl}$)(CHCMe$_3$)(Biphen)(THP) and ethylene, W(NAr$_{Cl}$)(C$_3$H$_6$)(Biphen) was found to be stable for at least 24 h at 22 °C in the presence of excess ethylene. However, in the absence of ethylene W(NAr$_{Cl}$)(C$_3$H$_6$)(Biphen) decomposes within 36 h in C$_6$D$_6$ (90 μmol/mL) at 22 °C. Decomposition of W(NAr$_{Cl}$)(^{13}C$_3$H$_6$)(Biphen) led to formation of W(NAr$_{Cl}$)(^{13}C$_4$H$_8$)(Biphen). The second tungsten species formed as a product of decomposition of W(NAr$_{Cl}$)(^{13}C$_3$H$_6$)(Biphen) gave rise to a singlet resonance at 187.8 ppm that has two sets of tungsten satellites ($^1J_{WC}$ = 52.6 Hz, 84.5 Hz), which is indicative of formation of a dimeric methylidene complex, [W(NAr$_{Cl}$)(Biphen)(μ-^{13}CH$_2$)]$_2$, analogous to [W(NAr)(Biphen)(μ-^{13}CH$_2$)]$_2$.[6] In the ^{1}H NMR spectrum, two resonances at 8.14 ppm ($^1J_{CH}$ = 146.7 Hz, $^2J_{HH}$ = 6.1 Hz) and 7.62 ppm ($^2J_{HH}$ = 6.3 Hz) are ascribed to the diastereotopic protons of two equivalent methylidene groups.

Decomposition of W(NAr$_{Cl}$)(C$_3$H$_6$)(Biphen) at 40 °C in C$_6$D$_6$ (90 μmol/mL) was followed by ^{1}H NMR spectroscopy. During the first 3 h, [W(NAr$_{Cl}$)(Biphen)(μ-CH$_2$)]$_2$ and W(NAr$_{Cl}$)(C$_4$H$_8$)(Biphen) formed at the expense of W(NAr$_{Cl}$)(C$_3$H$_6$)(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(NAr$_{Cl}$)(Biphen)(μ-CH$_2$)]$_2$ was formed with the species in solution being W(NAr$_{Cl}$)(C$_3$H$_6$)(Biphen) (~30%), [W(NAr$_{Cl}$)(Biphen)(μ-CH$_2$)]$_2$ (~20%), and W(NAr$_{Cl}$)(C$_4$H$_8$)(Biphen) (~30%). At this point, no more ethylene could be detected in solution. It is clear that decomposition of W(NAr$_{Cl}$)(C$_3$H$_6$)(Biphen) is accelerated in the absence of ethylene, the concentration of W(NAr$_{Cl}$)(C$_4$H$_8$)(Biphen) reaches a steady state, and the [W(NAr$_{Cl}$)(Biphen)(μ-CH$_2$)]$_2$ that is formed decomposes with time under the reaction conditions. In spite of the complexity of the decomposition reaction [W(NAr$_{Cl}$)(Biphen)(μ-CH$_2$)]$_2$ could be isolated as purple microcrystals in 29% yield upon decomposition of a sample of W(NAr$_{Cl}$)(C$_3$H$_6$)(Biphen) in benzene at 25 °C on a 0.5 mmol scale.

An X-ray study of [W(NAr$_{Cl}$)(Biphen)(μ-CH$_2$)]$_2$ (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$_2$(CH$_2$)$_2$ core exhibits two short (1.982(6) Å) and two long (2.277(6) Å) interatomic W−C distances.

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(16) (a) Chisholm, M. H.; Huffman, J. C.; Hampden Smith, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 5284. (b) Giannini, L.; Guillemot, G.; Solari, E.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1999**, *121*, 2797.

Table 2. Crystal Data and Structure Refinement for W(NAr$_{Cl}$)(Biphen)($CH_2CH_2CH_2CH_2$) (06179), [W(NAr$_{Cl}$)(Biphen)(μ-CH_2)]$_2$ (06185), and [W(NAr$_{Cl}$)(Biphen)]$_2$(μ-CH_2CH_2) (06208)

	06185	06179	06208
empirical formula	$C_{62}H_{74}Cl_4N_2O_4W_2$	$C_{34}H_{43}Cl_2NO_2W$	$C_{62}H_{74}Cl_4N_2O_4W_2$
fw	1420.73	752.44	1420.73
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
unit cell dimens			
a	10.3917(15) Å	10.080(5) Å	32.092(2) Å
b	11.1488(17) Å	12.753(6) Å	10.7957(7) Å
c	14.478(2) Å	13.233(6) Å	20.7966(14) Å
α	96.419(4)°	70.799(11)°	90°
β	110.987(4)°	87.085(11)°	127.4120(10)°
γ	108.135(4)°	72.710(11)°	90°
volume	1440.4(4) Å^3	1531.7(12) Å^3	5722.9(6) Å^3
Z	1	2	4
density (calcd)	1.638 Mg/m^3	1.631 Mg/m^3	1.649 Mg/m^3
absorp coeff	4.224 mm^{-1}	3.977 mm^{-1}	4.252 mm^{-1}
F(000)	708	756	2832
cryst size	0.15 × 0.10 × 0.04 mm^3	0.15 × 0.03 × 0.03 mm^3	0.10 × 0.10 × 0.02 mm^3
θ range for data collection	1.56 to 29.13°	1.97 to 27.48°	1.96 to 29.13°
index ranges	$-14 \leq h \leq 14$	$-13 \leq h \leq 12$	$-43 \leq h \leq 43$
	$-15 \leq k \leq 15$	$-16 \leq k \leq 16$	$-14 \leq k \leq 14$
	$-19 \leq l \leq 19$	$-17 \leq l \leq 17$	$-28 \leq l \leq 28$
no. of reflns collected	42 252	22 375	59 487
no. of indep reflns	7742 [R(int) = 0.0544]	7001 [R(int) = 0.0890]	7704 [R(int) = 0.1033]
completeness to θ = 29.13°	99.8%	99.8%	100.0%
max. and min. transmn	0.8492 and 0.5699	0.8900 and 0.5869	0.9198 and 0.6758
no. of data/restraints/params	7742/2/350	7001/0/371	7704/666/676
goodness-of-fit on F^2	1.088	1.043	1.019
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0451$, $wR_2 = 0.1161$	$R_1 = 0.0526$, $wR_2 = 0.1073$	$R_1 = 0.0380$, $wR_2 = 0.0714$
R indices (all data)	$R_1 = 0.0562$, $wR_2 = 0.1223$	$R_1 = 0.0922$, $wR_2 = 0.1220$	$R_1 = 0.0746$, $wR_2 = 0.0831$
largest diff peak and hole	6.597 and −1.236 e·Å^{-3}	1.814 and −4.199 e·Å^{-3}	1.317 and −0.915 e·Å^{-3}

[a] 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 F^2.

The first is characteristic of a W═C bond in bisalkoxide imido alkylidene species, while the latter is typical of a 2e donor ligand bound in the axial position. In short, [W(NAr$_{Cl}$)(Biphen)(μ-CH_2)]$_2$ is essentially a dimer containing W(NAr$_{Cl}$)(CH_2)[(R)-Biphen] and W(NAr$_{Cl}$)(CH_2)[(S)-Biphen] in which each of the methylidene groups behaves as a donor toward the second tungsten in an apical position. The interatomic W(1)−W(1′) distance (3.1211(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$_a$−H$_b$ dihedral angle was found to be 131(7)°, while the W−C−H$_b$−H$_a$ dihedral angle was found to be 136(6)°. These dihedral angles for a sp^3-hybridized carbon atom are expected to be 120° and for a sp^2-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(NAr$_{Cl}$)(CH_2)(Biphen). The $W_2(CH_2)_2$ core in [W(NAr$_{Cl}$)(Biphen)(μ-CH_2)]$_2$ contrasts with that in the centrosymmetric W(V) complex, [W(O)(η^5-C_5Me_5)(μ-CH_2)]$_2$, in which the two W−C bond lengths (2.076(4) and 2.078(4) Å) are essentially identical.[17] The centrosymmetric titanium(IV) methylene derivative, [Ti{N(C_6H_{11})$_2$}$_2$(μ-CH_2)]$_2$, also contains symmetrically bridging methylidene groups (Ti−C = 2.020(5) and 2.016(5) Å).[18] To our knowledge [W(NAr$_{Cl}$)(Biphen)(μ-CH_2)]$_2$ is the only crystallographically characterized W(VI) methylene species.

Decomposition of W(NAr$_{Cl}$)(C_3H_6)(Biphen) at 100 °C for 90 min in C_6D_6 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(NAr$_{Cl}$)(C_4H_8)(Biphen) is also present. A ^{13}C NMR spectrum reveals an ethylene resonance at 70.6 ppm for a carbon with two protons attached ($^1J_{CH}$ = 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., W_2(Biphen)$_2$(μ-NAr$_{Cl}$)$_2$(μ-CH_2CH_2). The W−C distance in the W_2C_2 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 C_2 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(NAr$_{Cl}$)(OR$_{F6}$)$_2$]$_2$ (Figure 1), and that the W_2N_2 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). W_2(Biphen)$_2$(μ-NAr$_{Cl}$)$_2$(μ-CH_2CH_2) is similar to the "1,2-ditungstacyclobutane" species with the formula W_2(N-2,3-$Me_2C_6H_3$)$_2$($OCMe_2CF_3$)$_3$(μ-$OCMe_2CF_3$)(μ-CH_2CH_2) prepared by adding ethylene to the W═W bond in [W(N-2,3-$Me_2C_6H_3$)($OCMe_2CF_3$)$_2$]$_2$.[3] The fact that W_2(Biphen)$_2$(μ-NAr$_{Cl}$)$_2$(μ-CH_2CH_2) is homochiral constitutes proof that it cannot form directly from heterochiral [W(NAr$_{Cl}$)(Biphen)(μ-CH_2)]$_2$ without [W(NAr$_{Cl}$)(Biphen)(μ-CH_2)]$_2$ breaking into monomeric units. Monomeric units with the same chirality then recombine to give homochiral W_2(Biphen)$_2$(μ-NAr$_{Cl}$)$_2$(μ-CH_2CH_2).

A 27 μmol/mL suspension of [W(NAr$_{Cl}$)(Biphen)(μ-CH_2)]$_2$ in C_6D_6 decomposes after 50 min at 100 °C to yield a mixture of decomposition products, ∼25% of which consist of W_2-

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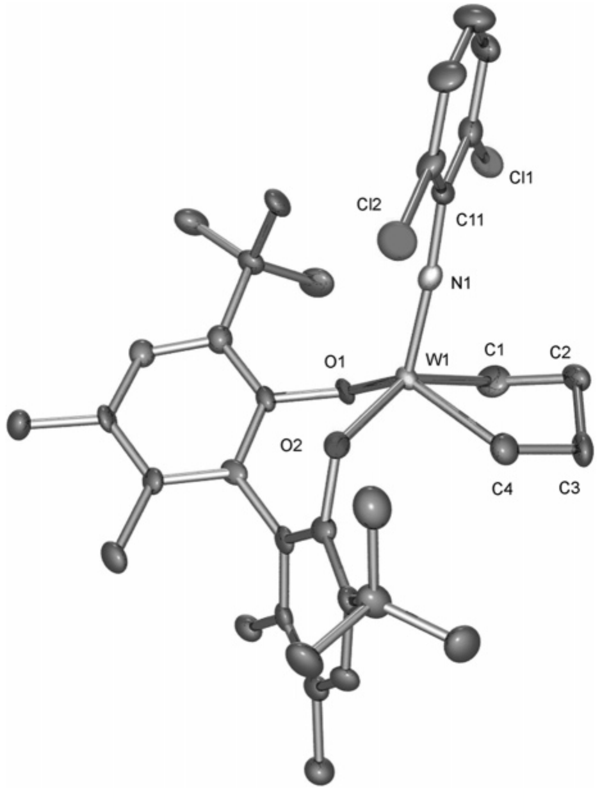

Figure 4. Molecular structure of W(NAr_{Cl})(Biphen)(C_4H_8). Hydrogen and solvate atoms are omitted for clarity; thermal ellipsoids are drawn at 50% probability level. Selected bond lengths [Å] and angles [deg]: $W-N(1) = 1.712(7)$, $W-O(1) = 1.917(5)$, $W-O(2) = 1.913(6)$, $W-C(1) = 2.129(8)$, $W-C(4) = 2.112(8)$, $C(1)-C(2) = 1.504(12)$, $C(2)-C(3) = 1.508(12)$, $C(3)-C(4) = 1.535(11)$, $W-N(1)-C(11) = 175.5(6)$, $N(1)-W-C(1) = 96.2(3)$, $N(1)-W-C(4) = 100.0(3)$, $N(1)-W-O(1) = 120.4(3)$, $N(1)-W-O(2) = 115.4(3)$, $O(1)-W-C(1) = 78.0(3)$, $C(1)-W-C(4) = 75.2(3)$, $C(4)-W-O(2) = 86.2(3)$, $O(1)-W-O(2) = 95.6(2)$.

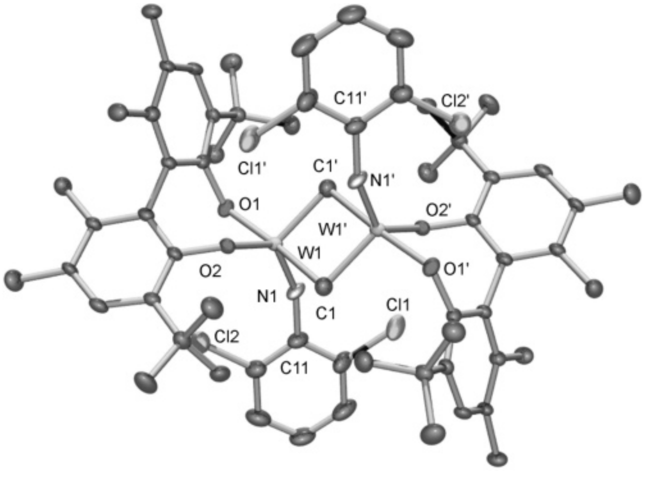

Figure 5. Molecular structure of [W(NAr_{Cl})(Biphen)(μ-CH_2)]$_2$. Hydrogen and solvate atoms are omitted for clarity; thermal ellipsoids are drawn at 50% probability level. Selected bond lengths [Å] and angles [deg]: $W-O(1) = 1.944(4)$, $W-O(2) = 1.930(4)$, $W-N(1) = 1.753(5)$, $W-C(1) = 2.277(6)$, $W-C(1)' = 1.982(6)$, $W-W' = 3.1211(6)$, $C(11)-N(1)-W = 153.3(5)$, $O(1)-W-C(1) = 169.76(19)$, $O(2)-W-C(1)' = 118.7(2)$, $O(2)-W-N(1) = 133.7(2)$, $C(1)'-W-N(1) = 104.3(3)$, $W-C(1)-W' = 94.0(2)$, $C(1)'-W-C(1) = 86.0(2)$.

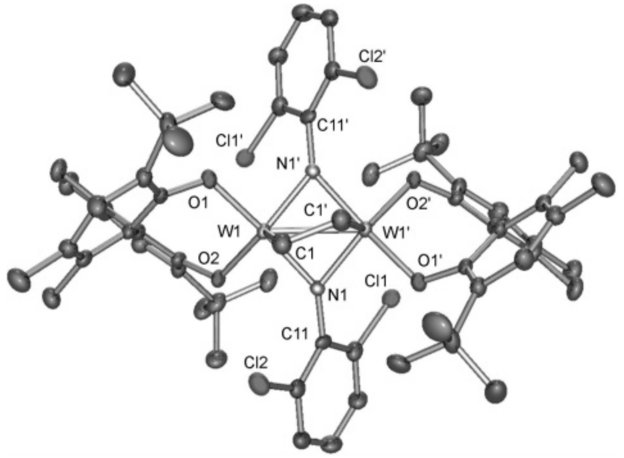

Figure 6. Molecular structure of [W(NAr_{Cl})(Biphen)]$_2$(μ-CH_2CH_2). Hydrogen and solvate atoms are omitted for clarity; thermal ellipsoids are drawn at 50% probability level. Selected bond lengths [Å] and angles [deg]: $W(1)-W(1)' = 2.5782(6)$, $W(1)-C(1) = 2.152(5)$, $C(1)-C(1)' = 1.556(10)$, $W(1)-N(1) = 1.974(4)$, $W(1)-N(1)'$ 1.926(4), $W(1)-O(1) = 1.934(3)$, $W(1)-O(2) = 1.960(3)$, $O(1)-W(1)-N(1) = 172.28(18)$, $O(2)-W(1)-C(1) = 124.3(2)$, $O(2)-W(1)-N(1)' = 138.7(2)$, $N(1)'-W(1)-C(1) = 96.6(2)$, $O(1)-W(1)-O(2) = 95.71(14)$, $O(1)-W(1)-N(1)' = 91.94(16)$, $O(1)-W(1)-C(1) = 87.11(19)$, $W(1)-N(1)-W(1)' = 82.77(15)$, $W(1)'-W(1)-C(1)-C(1)' = -153.3(6)$.

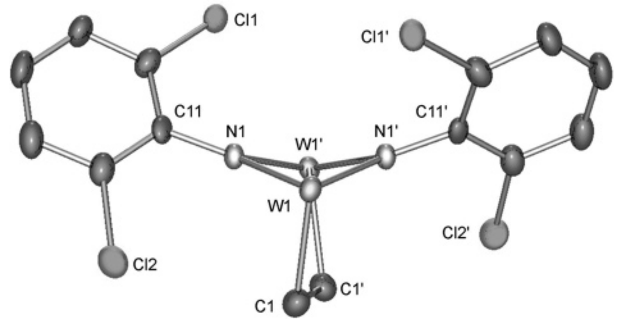

Figure 7. View of the structure of [W(NAr_{Cl})(Biphen)]$_2$(μ-CH_2-CH_2) down the W−W axis with the Biphen^{2-} ligands removed.

(Biphen)$_2$(μ-NAr_{Cl})$_2$(μ-CH_2CH_2). The other products could not be identified conclusively. However, the mixture contains resonances that are consistent with [W(Biphen)(μ-NAr_{Cl})]$_2$, formed through loss of ethylene from W_2(Biphen)$_2$(μ-NAr_{Cl})$_2$(μ-CH_2CH_2). These resonances disappear upon addition of ethylene, while the intensities of the resonances for W_2(Biphen)$_2$(μ-NAr_{Cl})$_2$(μ-CH_2CH_2) correspondingly increase. Although we cannot eliminate the possibility that the Biphen^{2-} ligand is not intact in some of the unidentified decomposition products, a significant fraction of the product appears to be [W(Biphen)(NAr_{Cl})]$_2$, although we cannot confirm that it has a structure analogous to the species shown in Figure 1. The main points are that homochiral W_2(Biphen)$_2$(μ-NAr_{Cl})$_2$(μ-CH_2CH_2) can form from heterochiral [W(NAr_{Cl})(Biphen)(μ-CH_2)]$_2$, that the process must involve scission of [W(NAr_{Cl})(Biphen)(μ-CH_2)]$_2$ into monomeric units and recombination of homochiral monomers, and that W_2(Biphen)$_2$(μ-NAr_{Cl})$_2$(μ-CH_2CH_2) appears to lose ethylene reversibly to yield a [W(Biphen)(NAr_{Cl})]$_2$ species whose structure has not been confirmed.

Discussion

We have shown in this work that tungsten 2,6-dichlorophenylimido complexes are accessible and that the chemistry of tungsten 2,6-dichlorophenylimido (NAr_{Cl}) alkylidene bisalkoxide complexes does not differ dramatically from that of NAr (N-2,6-diisopropylphenyl) complexes.[6] However, since the NAr_{Cl}

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 NAr_{Cl} 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 $[W(\mu\text{-}NAr_{Cl})(OR_{F6})_2]_2$ 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 methylene 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 steric reasons 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 $[W(NAr_{Cl})(Biphen)(\mu\text{-}CH_2)]_2$. The analogous $[W(NAr)(Biphen)(\mu\text{-}CH_2)]_2$ species was observed in solution,[6] but since it was not isolated and crystallographically characterized, the proposal that it was indeed a relatively stable dimeric form of a methylene complex remained unconfirmed. Since it has long been known that methylene 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 $[W(NAr_{Cl})(Biphen)(\mu\text{-}CH_2)]_2$ is *not* an intermediate along a pathway to homochiral $W_2(Biphen)_2(\mu\text{-}NAr_{Cl})_2(\mu\text{-}CH_2CH_2)$. Instead, it breaks up to yield monomeric $W(NAr_{Cl})(Biphen)(\mu\text{-}CH_2)$ species, and homochiral monomers then combine to yield homochiral $W_2(Biphen)_2(\mu\text{-}NAr_{Cl})_2(\mu\text{-}CH_2CH_2)$, either directly or via homochiral $[W(NAr_{Cl})(Biphen)(\mu\text{-}CH_2)]_2$ that is unstable with respect to rearrangement to yield $W_2(Biphen)_2(\mu\text{-}NAr_{Cl})_2(\mu\text{-}CH_2CH_2)$. Likewise, either heterochiral $[W(NAr_{Cl})(Biphen)(\mu\text{-}CH_2)]_2$ 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 $W(NAr_{Cl})(Biphen)(\mu\text{-}CH_2)$ complexes combine.

Although we have not yet confirmed that ethylene is lost from $W_2(Biphen)_2(\mu\text{-}NAr_{Cl})_2(\mu\text{-}CH_2CH_2)$ to form $[W(Biphen)(\mu\text{-}NAr_{Cl})]_2$, the structure of $W_2(Biphen)_2(\mu\text{-}NAr_{Cl})_2(\mu\text{-}CH_2CH_2)$ suggests that it is poised to lose ethylene as an ortho chloride coordinates to the metal, as shown in Figure 1 for the OR_{F6} analogue. We have observed that ethylene is lost reversibly from the 1,2-ditungstacyclobutane species with the formula $W_2(N\text{-}2,3\text{-}Me_2C_6H_3)_2(OCMe_2CF_3)_3(\mu\text{-}OCMe_2CF_3)(\mu\text{-}CH_2CH_2)$ to yield $[W(N\text{-}2,3\text{-}Me_2C_6H_3)(OCMe_2CF_3)_2]_2$, 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 enantiomerically pure catalyst’s longevity or lack thereof.

We have obtained some evidence that alkylidenes can be regenerated from reduced metal species.[3,19] 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. Dimethoxyethane (DME) was distilled from a dark purple solution of sodium benzophenone ketyl and degassed three times by freeze−pump−thaw techniques. ^1H, ^{13}C, and ^{19}F NMR spectra were acquired at room temperature (unless otherwise noted) using a Bruker Avance 400 spectrometer (^1H 400 MHz, ^{13}C 100 MHz, ^{19}F 376 MHz) and referenced to the residual protio solvent peaks or external C_6F_6 (−163.0 ppm). HMQC 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. WO_2Cl_2 was prepared from WCl_6 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 ($\lambda = 0.71073$ Å), performing ϕ- and ω-scans. The structures were solved by direct methods using SHELXS[21] and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.[22] 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 semifreely with the help of distance restraints) 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.

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The shape of the anisotropic displacement ellipsoids in $\mathrm{W(NAr_{Cl})(C_3H_6)(Biphen)(CH_2Cl_2)_{0.25}}$ for atoms C(12) to C(16), Cl(1), and Cl(2) suggest some disorder for the dichlorinated aryl ring. A refinement of this disorder was attempted but was not stable. The solvent molecule was refined with 1/4 occupancy, leading to noninteger values for the elements C, H, and Cl in the empirical formula. The THF molecule in $\mathrm{[W(NAr_{Cl})(Biphen)(CH_2)_2(THF\text{-}}d_8\mathrm{)]}$ is deuterated. The deuteria were refined as hydrogens (same scattering factor). The highest two residual density maxima are much higher than the others. Taking into account the symmetry equivalents of those maxima, two possible additional components can be hypothesized (the distance between Q(1) and Q(2A) is about the same as the distance between the two W atoms of the main component). Refinement as a three-component whole molecule disorder is surprisingly stable as long as only the W positions are split. Even though this interpretation gives an explanation for the two highest residual electron density maxima, it was abandoned, as no general improvement of the model was gained. The structure of $\mathrm{[W(NArCl)(Biphen)]_2(-CH_2-CH_2-)}$ shows whole molecule disorder, which refines relatively well. The occupancies of the two components were refined freely, while constraining the sum of the occupancies of the components to unity. The ratio converged at a value of 0.895(2). The disorder was refined with the help of similarity restraints on 1−2 and 1−3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters, but no ADP restraints were used for the main component. All bond distances and angles of this structure as given in this publication refer to the main component of the whole molecule disorder.

$\mathbf{W(NAr_{Cl})_2Cl_2(DME)}$. This synthesis was adapted from that reported by P. Tsang.[8] A mixture of $\mathrm{SiMe_3Cl}$ (96 mL, 750 mmol) and 2,6-lutidine (58 mL, 500 mmol) was added dropwise to a stirred suspension of $\mathrm{WO_2Cl_2}$ (40.45 g, 125 mmol) and 2,6-dichloroaniline (40.50 g, 250 mmol) in DME (120 mL). The yellow suspension was stirred for 48 h at 60 °C, and an orange powder was filtered off from a red solution. The solvent was removed from the red solution *in vacuo*, and the orange residue was extracted with DME (4 × 500 mL). The volume of the combined solutions was reduced *in vacuo* to approximately 50 mL. The supernatant was decanted, and the orange crystalline mass of $\mathrm{W(NAr_{Cl})_2Cl_2(DME)}$ was washed with pentane (100 mL); yield 62.78 g (76%): ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 7.29 (d, $^3J_{\mathrm{HH}} = 8.1$ Hz, 2 × 2 H, $\mathrm{NAr_{Cl}}$-3 and $\mathrm{NAr_{Cl}}$-5), 6.79 (t, $^3J_{\mathrm{HH}} = 8.1$ Hz, 2 × 1H, $\mathrm{NAr_{Cl}}$-4), 4.11, 4.07 (br s, 10 H, DME); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 150.7, 133.1, 127.9, 126.1 ($\mathrm{NAr_{Cl}}$), 71.7, 65.2 (DME). Anal. Calcd for $\mathrm{C_{16}H_{16}Cl_6N_2O_2W}$: C, 28.90; H, 2.43; N, 4.21. Found: C, 28.86; H, 2.52; N, 4.20.

$\mathbf{W(NAr_{Cl})_2(CH_2CMe_3)_2}$. This synthesis was adapted from that reported by P. Tsang.[8] A solution of $\mathrm{ClMg(CH_2CMe_3)}$ (51.3 mL of a 1.76 M ether solution, 90 mmol) was added dropwise to a stirred ether solution (300 mL) of $\mathrm{W(NAr_{Cl})_2Cl_2(DME)}$ (30.0 g, 45 mmol). After the reaction mixture was stirred for 16 h, an off-white solid was filtered off and extracted with ether (3 × 100 mL). The volatiles were removed under reduced pressure from the combined solutions to give a yellow foam. Trituration with pentane gave a bright yellow powder of $\mathrm{W(NAr_{Cl})_2(CH_2CMe_3)_2}$ (24.46 g, 91%): ^{1}H NMR ($\mathrm{C_6D_6}$) δ 6.94 (d, $^3J_{\mathrm{HH}} = 8.1$ Hz, 2 H, $\mathrm{NAr_{Cl}}$-3 and $\mathrm{NAr_{Cl}}$-5), 6.23 (t, $^3J_{\mathrm{HH}} = 8.1$ Hz, 1 H, $\mathrm{NAr_{Cl}}$-4), 2.27 (s, 2 × 2 H, $\mathrm{WCH_2}$), 1.20 (s, 2 × 9 H, $\mathrm{CH_2CC}H_3$); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 151.4, 131.7, 128.7, 125.2 ($\mathrm{NAr_{Cl}}$), 95.4 ($\mathrm{WCH_2}$), 35.6, 34.5 ($\mathrm{CMe_3}$). Anal. Calcd for $\mathrm{C_{22}H_{28}Cl_4N_2W}$: C, 40.90; H, 4.37; N, 4.34. Found: C, 41.11; H, 4.32; N, 4.28.

$\mathbf{W(NAr_{Cl})(CHCMe_3)(OTf)_2(DME)}$. A suspension of triflic acid (17.42 g, 116.1 mmol) in pentane (10 mL) was added dropwise at −78 °C to a stirred solution of $\mathrm{W(NAr_{Cl})_2(CH_2CMe_3)_2}$ (25.00 g, 38.7 mmol) in DME (300 mL). The stirred reaction mixture was allowed to warm to 25 °C to give a dark yellow solution after 16 h at this temperature. Activated charcoal was added and the reaction mixture stirred at 25 °C for 1 h. The charcoal was filtered off, and the volatiles were removed under reduced pressure to give an oil that solidified upon trituration with toluene. The suspension was kept under dynamic vacuum at 60 °C until the pressure reached 15 × 10^{-3} Torr (∼6 h). Toluene (200 mL) was added to the yellow solid and the suspension stirred for 1 h at 25 °C. The reaction mixture was filtered over Celite and the deposit extracted with toluene (2 × 100 mL) to give a dark yellow filtrate. The volatiles were removed under reduced pressure to give the crude product as a yellow foam. Recrystallization from ether (400 mL, −78 °C) gave analytically pure $\mathrm{W(NAr_{Cl})(CHCMe_3)(OTf)_2(DME)}$ (17.65 g, 57%) as bright yellow microcrystals. The NMR spectroscopic data are consistent with approximately a 1:1 mixture of two isomers in $\mathrm{C_6D_6}$ and a 5:1 mixture of two isomers in $\mathrm{CD_2Cl_2}$, respectively: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 11.80, 10.96 (s, 1 H, WCH), 6.80 (br m, 2 H, $\mathrm{NAr_{Cl}}$-3 and $\mathrm{NAr_{Cl}}$-5), 6.25 (br m, 1 H, $\mathrm{NAr_{Cl}}$-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, $\mathrm{CHCC}H_3$); ^{1}H NMR ($\mathrm{CD_2Cl_2}$) major isomer, $\mathrm{OTf^-}$ ligands in *cisoid* arrangement δ 11.52 (s, $^1J_{\mathrm{CH}} = 121.0$ Hz, 1 H, WCH), 7.45 (d, $^3J_{\mathrm{HH}} = 8.3$ Hz, 2 H, $\mathrm{NAr_{Cl}}$-3 and $\mathrm{NAr_{Cl}}$-5), 7.16 (t, $^3J_{\mathrm{HH}} = 8.3$ Hz, 1 H, $\mathrm{NAr_{Cl}}$-4), 4.58 (s, 3 H, DME), 4.38 (m, 2 H, DME), 4.15 (m, 1 H, DME), 3.76 (m, 1 H, DME), 3.72 (s, 3 H, DME), 1.22 (s, 9 H, $\mathrm{CHCC}H_3$); minor isomer, $\mathrm{OTf^-}$ ligands in *transoid* arrangement δ 10.83 (s, $^1J_{\mathrm{CH}} = 115.7$ Hz, 1 H, WCH), 7.39 (d, $^3J_{\mathrm{HH}} = 8.1$ Hz, 2 H, $\mathrm{NAr_{Cl}}$-3 and $\mathrm{NAr_{Cl}}$-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, $\mathrm{CHCC}H_3$). The $\mathrm{NAr_{Cl}}$-4 resonance of the minor isomer was obscured by the major isomer; ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$) major isomer, $\mathrm{OTf^-}$ ligands in *cisoid* arrangement δ 302.5 (WCH), 148.8, 135.2, 129.2, 128.9, ($\mathrm{NAr_{Cl}}$), 120.2 (quart, $^1J_{\mathrm{FC}} = 317.3$ Hz, $\mathrm{CF_3}$), 119.3 (quart, $^1J_{\mathrm{FC}} = 318.7$ Hz, $\mathrm{CF_3}$), 82.3, 79.5, 71.9, 62.3 (DME), 48.5 ($C\mathrm{Me_3}$), 33.2 ($\mathrm{C}Me_3$); minor isomer, $\mathrm{OTf^-}$ ligands in transoid arrangement δ 294.7 (WCH); ^{19}F NMR ($\mathrm{CD_2Cl_2}$) major isomer, $\mathrm{OTf^-}$ ligands in *cisoid* arrangement δ −76.2 (m), 77.1 (m); minor isomer, $\mathrm{OTf^-}$ ligands in *transoid* arrangement δ −76.4 (s). Anal. Calcd for $\mathrm{C_{17}H_{23}Cl_2F_6NO_8S_2W}$: C, 25.45; H, 2.89; N, 1.75. Found: C, 25.38; H, 2.95; N, 1.77.

$\mathbf{W(NAr_{Cl})(CHCMe_3)[OC(CF_3)_2Me]_2}$. Method A: A suspension of $\mathrm{W(NAr_{Cl})(CHCMe_3)(OTf)_2(DME)}$ (5.00 g, 6.23 mmol) in toluene (200 mL) was warmed until the compound completely dissolved. A solution of $\mathrm{LiOC(CF_3)_2Me}$ (2.34 g, 12.47 mmol) in $\mathrm{Et_2O}$ (50 mL) was added dropwise to the chilled (−30 °C) toluene solution while it was stirred. The clear yellow-orange 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 $\mathrm{W(NAr_{Cl})(CHCMe_3)(OR_{F6})_2}$. The pure product was obtained by washing powdered $\mathrm{W(NAr_{Cl})(CHCMe_3)(OR_{F6})_2}$ with chilled (−30 °C) pentane; yield of bright yellow powder (3 crops) 3.80 g (80%).

Method B: Neat $\mathrm{HOC(CF_3)_2Me}$ (4.09 g, 22.44 mmol) was added dropwise to a stirred solution of $\mathrm{W(NAr_{Cl})(CHCMe_3)(OTf)_2(DME)}$ (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: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 8.91 (s, $^2J_{\mathrm{WH}} = 14.1$ Hz, $^1J_{\mathrm{CH}} = 115.2$ Hz, 1 H, WCH), 6.82 (d, $^3J_{\mathrm{HH}} = 8.1$ Hz, 2 H, $\mathrm{NAr_{Cl}}$-3 and $\mathrm{NAr_{Cl}}$-5), 6.25 (t, $^3J_{\mathrm{HH}} = 8.1$ Hz, 1 H, $\mathrm{NAr_{Cl}}$-4), 1.37 (s, 2 × 3 H, $\mathrm{OCCH_3}$), 1.06 (s, 9 H, $\mathrm{CHCC}H_3$); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$) δ 257.3 ($^1J_{\mathrm{WC}} = 195.9$ Hz, WCH), 150.5, 133.7, 127.4

(NAr$_{Cl}$), 124.2 (quart, $^1J_{FC}$ = 287.5 Hz, CF$_3$), 82.4 (sept, $^2J_{FC}$ = 30.5 Hz, O*C*CH$_3$), 46.0 (*C*Me$_3$), 33.6 (C*Me*$_3$), 19.3 (OC*C*H$_3$); one carbon resonance of the NAr$_{Cl}$ ligand was obscured by C$_6$D$_6$; ^{19}F NMR (C$_6$D$_6$) δ −76.8 (br m), −76.9 (br m). Anal. Calcd for C$_{19}$H$_{19}$Cl$_2$F$_{12}$NO$_2$W: C, 29.40; H, 2.47; N, 1.80. Found: C, 29.21; H, 2.43; N, 1.79.

W(NAr$_{Cl}$)(CH$_2$CH$_2$CH$_2$)[OC(CF$_3$)$_2$Me]$_2$. A stirred solution of W(NAr$_{Cl}$)(CHCMe$_3$)(OR$_{F6}$)$_2$ (250 mg, 322 μmol) in benzene (5 mL) was exposed to 1 atm of ethylene for 2 min. The resulting pale yellow solution was stirred for 30 min at 25 °C. The reaction mixture was frozen, and the volatiles were removed by lyophilization to give a pale brown powder (213 mg, 90%): ^{1}H NMR (C$_6$D$_6$) δ 6.70 (d, $^3J_{HH}$ = 8.1 Hz, 2 H, NAr$_{Cl}$-3 and NAr$_{Cl}$-5), 6.01 (t, $^3J_{HH}$ = 8.1 Hz, 1 H, NAr$_{Cl}$-4), 4.91, 4.77 (m, $^1J_{CH}$ = 165.2 Hz, 160.6 Hz, 2 × 2 H, α-CH$_2$), 1.59, 1.55 (br s, 2 × 3 H, OCCH$_3$), −0.87, −1.46 (m, $^1J_{CH}$ = 166.2 Hz, 162.0 Hz, 2 × 1 H, β-CH$_2$); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 147.1, 134.2, 128.9, 127.3 (NAr$_{Cl}$), 124.7 (quart, $^1J_{FC}$ = 287.9 Hz, CF$_3$), 103.4 ($^1J_{CH}$ = 160.6 Hz, 165.2 Hz, $^1J_{WC}$ = 64.7 Hz, α-CH$_2$), 84.5, 81.7 (O*C*CH$_3$), 17.8, 17.6 (OC*C*H$_3$), −4.7 ($^1J_{CH}$ = 162.0 Hz, 166.2 Hz, β-CH$_2$); $^1J_{CH}$ values were determined in an HMQC experiment; ^{19}F NMR (C$_6$D$_6$) δ −77.4 (s), −77.5 (s). Anal. Calcd for C$_{17}$H$_{15}$Cl$_2$F$_{12}$NO$_2$W: C, 27.30; H, 2.02; N, N, 1.87. Found: C, 27.08; H, 1.89; N, 1.81.

{W(μ-NAr$_{Cl}$)[OC(CF$_3$)$_2$Me]$_2$}$_2$. Amylene (40 μL, 376 μmol) was added to a stirred solution of W(NAr$_{Cl}$)(CHCMe$_3$)(OR$_{F6}$)$_2$ (250 mg, 322 μmol) in benzene (5 mL). After 15 min the bright yellow solution turned orange, and purple microcrystals started to be deposited. After the reaction mixture was stirred for 7 days at 25 °C, the purple product was filtered off and washed with pentane (3 × 2 mL); yield 170 mg (75%): ^{1}H NMR (THF-*d*$_8$) δ 7.96 (d, $^3J_{HH}$ = 8.1 Hz, 2 × 2 H, NAr$_{Cl}$-3 and NAr$_{Cl}$-5), 7.18 (t, $^3J_{HH}$ = 8.1 Hz, 2 × 1 H, NAr$_{Cl}$-4), 0.88 (s, 4 × 3 H, OCCH$_3$); the ^{13}C NMR spectrum could not be obtained due to the limited stability and solubility of [W(μ-NAr$_{Cl}$)(OR$_{F6}$)$_2$]$_2$ in common NMR solvents; ^{19}F NMR (THF-*d*$_8$) δ −79.0 (s). Anal. Calcd for C$_{28}$H$_{18}$Cl$_4$F$_{24}$N$_2$O$_4$W$_2$: C, 23.82; H, 1.28; N, 1.98. Found: C, 24.03; H, 1.22; N, 2.01.

W(NAr$_{Cl}$)(CHCMe$_3$)(Biphen)(THP). A solution of Biphen(Li$_2$)(Et$_2$O) (1.14 g mg, 2.58 mmol) in toluene (20 mL) was added dropwise to a stirred solution of W(NAr$_{Cl}$)(CHCMe$_3$)(OR$_{F6}$)$_2$ (2.00 g, 2.58 mmol) in toluene (50 mL) at −30 °C. The orange solution was stirred at 25 °C for 12 h and then stored at −30 °C for 3 h. The colorless deposit was filtered off and washed with chilled toluene (10 mL, −30 °C) to give an orange solution, to which THP (4 mL) was added. After all volatiles were removed under reduced pressure, the yellow-brownish residue was suspended in pentane (40 mL) to precipitate W(NAr$_{Cl}$)(CHCMe$_3$)(Biphen)(THP) as a pale yellow powder, which was washed with pentane (10 mL) and dried under reduced pressure (1.80 g, 82%): ^{1}H NMR (C$_6$D$_6$) δ 9.19 (s, $^2J_{WH}$ = 8.3 Hz, $^1J_{CH}$ = 109.4 Hz, 1 H, WCH), 7.28, 7.12 (s, 2 × 1 H, Biphen), 7.03, 6.87 (d, $^3J_{HH}$ = 8.1 Hz, 2 × 1 H, NAr$_{Cl}$-3 and NAr$_{Cl}$-5), 6.15 (t, $^3J_{HH}$ = 8.1 Hz, 1 H, NAr$_{Cl}$-4), 3.24 (br, 2 × 2 H, α-CH$_2$, THP), 2.33, 2.03, 1.90, 1.76 (s, 4 × 3 H, Biphen-CH$_3$), 1.72, 1.55, 1.49 (s, 3 × 9 H, CMe$_3$), 1.04 (s, 3 × 2 H, β- and γ-CH$_2$, THP); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 266.5 (WCH), 160.5 (aryl), 158.1 (aryl), 151.2 (aryl), 136.7 (aryl), 136.5 (aryl), 136.0 (aryl), 135.4 (aryl), 132.0 (aryl), 131.6 (aryl), 130.1 (aryl), 129.2 (aryl), 128.3 (aryl), 126.9 (aryl), 126.8 (aryl), 123.9 (aryl), 69.8, 46.4, 36.2, 35.3, 34.2, 33.1, 32.8, 26.1, 22.8, 20.9, 20.6, 20.0, 17.6, 17.3. Fifteen out of 18 carbon resonances were observed. Anal. Calcd for C$_{40}$H$_{55}$Cl$_2$NO$_3$W: C, 56.35; H, 6.50; N, 1.64. Found: C, 56.22; H, 6.37; N, 1.57.

W(NAr$_{Cl}$)(C$_3$H$_6$)(Biphen). A yellow solution of W(NAr$_{Cl}$)(CHCMe$_3$)(Biphen)(THP) (672 mg, 788 μmol) in benzene (20 mL) was stirred under ethylene (1 atm) at 25 °C for 16 h. The reaction mixture was frozen, and the volatiles were removed by lyophilization. The analytically pure product was obtained as a pale yellow powder (553 mg, 95%): ^{1}H NMR (C$_6$D$_6$) δ 7.31 (s, 2 × 1 H, Biphen), 6.82 (d, $^3J_{HH}$ = 8.1 Hz, 2 × 1 H, NAr$_{Cl}$-3 and NAr$_{Cl}$-5), 6.09 (t, $^3J_{HH}$ = 8.1 Hz, 1 H, NAr$_{Cl}$-4), 4.71, 4.42, 4.35, 3.41 (m, $^1J_{CH}$ = 148.9 Hz, 161.3 Hz, 153.8 Hz, 151.4 Hz, 4 × 1 H, α-CH$_2$), 2.16, 1.79 (s, 4 × 3 H, Biphen-CH$_3$), 1.57 (s, 2 × 9 H, Biphen-CMe$_3$), −0.03, −0.27 (m, $^1J_{CH}$ = 151.4 Hz, 153.8 Hz, 2 × 1 H, β-CH$_2$); ^{13}C{^{1}H} NMR (toluene-*d*$_8$) δ 149.0, 134.2, 129.2, 128.1, 125.9, 96.6 ($^1J_{CH}$ = 148.9 Hz, 153.8 Hz, α-CH$_2$), 86.5 ($^1J_{CH}$ = 151.4 Hz, 161.3 Hz, α-CH$_2$), 31.4, 20.7, 17.1, −0.1 ($^1J_{CH}$ = 151.4 Hz, 153.8 Hz, β-CH$_2$). The resonances of the quarternary carbons of the Biphen ligand could not be assigned unambiguously. The coupling constants $^1J_{CH}$ were determined in an HMQC experiment. Anal. Calcd for C$_{33}$H$_{41}$Cl$_2$NO$_2$W: C, 53.68; H, 5.60; N, 1.90. Found: C, 53.52; H, 5.54; N, 1.82.

W(NAr$_{Cl}$)(^{13}CH$_2$^{13}CH$_2$^{13}CH$_2$)(Biphen) was observed when ^{13}CH$_2$=^{13}CH$_2$ was employed: ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 97.7 (br d, α-CH$_2$), 87.5 (br d, α-CH$_2$), −0.5 (br t, β-CH$_2$).

W(NAr$_{Cl}$)(C$_2$H$_4$)(Biphen)(THF). Complex W(NAr$_{Cl}$)(C$_3$H$_6$)(Biphen) (1.00 g, 1.35 mmol) was suspended in THF (4 mL), and the mixture was stirred at 25 °C. The yellow suspended powder dissolved to yield an orange-red solution within 2 min. After the reaction mixture was stirred for 16 h, the product precipitated as yellow microcrystals, which were isolated by filtration and washed with pentane (5 mL); yield 700 mg (65%): ^{1}H NMR (CD$_2$Cl$_2$) δ 7.15−7.05 (br, 1 H, Biphen and, 2 × 1 H, NAr$_{Cl}$-3 and NAr$_{Cl}$-5), δ 7.00 (s, 1 H, Biphen), 6.72 (t, $^3J_{HH}$ = 8.1 Hz, 1 H, NAr$_{Cl}$-4), 3.99 (br, 2 × 2 H, α-CH$_2$, THF), 3.34, 3.13 (m, 2 × 1 H, WC$_2$H$_4$), 2.27, 2.15, 1.86 (s, 3 × 3 H, Biphen-CH$_3$), 1.83 (br, 2 × 2 H, β-CH$_2$, THF), 1.42 (s, 3 H, Biphen-CH$_3$), 1.28, 1.17 (s, 2 × 9 H, Biphen-CMe$_3$). Two protons in the ethylene group were obscured by other resonances.

W(NAr$_{Cl}$)(C$_2$H$_4$)(Biphen)(THF-*d*$_8$). An orange solution of W(NAr$_{Cl}$)(C$_3$H$_6$)(Biphen) (150 mg, 203 μmol) in THF-*d*$_8$ was kept for 90 min at 25 °C before the NMR spectra were recorded. After 48 h the solvent was decanted to leave behind yellow crystals of W(NAr$_{Cl}$)(C$_2$H$_4$)(Biphen)(THF-*d*$_8$) (90 mg, 55%): ^{1}H NMR (THF-*d*$_8$) δ 7.08 (s, 1 H, Biphen and d, $^3J_{HH}$ = 8.1 Hz, 2 × 1 H, NAr$_{Cl}$-3 and NAr$_{Cl}$-5), δ 6.94 (s, 1 H, Biphen), 6.72 (t, $^3J_{HH}$ = 8.1 Hz, 1 H, NAr$_{Cl}$-4), 3.31, 3.01 (m, $^1J_{CH}$ = 154.4 Hz, 157.9 Hz, 2 × 1 H, WC$_2$H$_4$), 2.27, 2.21, (s, 2 × 3 H, Biphen-CH$_3$), 2.13, 2.06 (m,$^1J_{CH}$ = 151.7 Hz, 152.6 Hz, 2 × 1 H, WC$_2$H$_4$), 1.87, 1.43 (s, 2 × 3 H, Biphen-CH$_3$), 1.29, 1.17 (s, 2 × 9 H, Biphen-CMe$_3$); ^{13}C{^{1}H} NMR (THF-*d*$_8$) δ 160.5 (aryl), 155.7 (aryl), 151.3 (aryl), 140.3 (aryl), 135.8 (aryl), 134.4 (aryl), 134.2 (aryl), 132.1 (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 ($^1J_{CH}$ = 152.6 Hz, 151.7 Hz, $^1J_{WC}$ = 37.9 Hz, WC$_2$H$_4$), 52.6 ($^1J_{CH}$ = 157.9 Hz, 154.4 Hz, $^1J_{WC}$ = 34.5 Hz, WC$_2$H$_4$), 36.0, 34.7, 31.3, 30.7, 20.5, 20.2, 17.0, 16.9. The coupling constants $^1J_{CH}$ were determined in an HMQC experiment. Anal. Calcd for C$_{36}$H$_{39}$D$_8$Cl$_2$NO$_3$W: C, 53.74; H, 6.89; N, 1.74. Found: C, 53.68; H, 6.95; N, 1.68.

W(NAr$_{Cl}$)(C$_4$H$_8$)(Biphen). W(NAr$_{Cl}$)(Biphen)(C$_2$H$_4$)(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(NAr$_{Cl}$)(C$_4$H$_8$)(Biphen) and unreacted W(NAr$_{Cl}$)(Biphen)(C$_2$H$_4$)(THF). This material was redissolved in benzene (50 mL), and the above procedure was repeated (addition of ethylene, lyophilization) to yield W(NAr$_{Cl}$)(C$_4$H$_8$)(Biphen) as an orange powder (500 mg, 82%): ^{1}H NMR (C$_6$D$_6$) δ 7.32, 7.13 (s, 2 × 1 H, Biphen), 6.78 (d, $^3J_{HH}$ = 8.1 Hz, 2 × 1 H, N NAr$_{Cl}$-3, N NAr$_{Cl}$-5), 6.09 (t, $^3J_{HH}$ = 8.1 Hz, 1 H, N NAr$_{Cl}$-4), 3.75 (m, $^1J_{CH}$ = 124.4 Hz, 1 H, α-CH$_2$, WC$_4$H$_8$), 3.46 (m,$^1J_{CH}$ = 123.3 Hz, 1 H, α-CH$_2$, WC$_4$H$_8$), 3.41 (m, $^1J_{CH}$ = 136.7 Hz, 1 H, β-CH$_2$, WC$_4$H$_8$), 3.37 (m, $^1J_{CH}$ = 128.5 Hz, 1 H, α-CH$_2$,

WC_4H_8), 3.37 (m, $^1J_{CH}$ = 132.1 Hz, 1 H, β-CH_2, WC_4H_8), 3.34 (m, $^1J_{CH}$ = 137.9 Hz, 1 H, β-CH_2, WC_4H_8), 3.32 (m, $^1J_{CH}$ = 126.8 Hz, 1 H, α-CH_2, WC_4H_8), 3.07 (m, $^1J_{CH}$ = 135.6 Hz, 1 H, β-CH_2, WC_4H_8), 2.09, 2.05, 1.73, 1.61 (s, 4 × 3 H, Biphen-CH_3), 1.60 (s, 9 H, CMe_3), 1.49 (s, 9 H, CMe_3); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 160.4, 150.8, 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 ($^1J_{WC}$ = 79.3 Hz, $^1J_{CH}$ = 123.3 Hz, 128.5 Hz, α-CH_2), 77.5 ($^1J_{WC}$ = 79.3 Hz, $^1J_{CH}$ = 124.4 Hz, 126.8 Hz, α-CH_2), 38.3 ($^1J_{CH}$ = 132.1 Hz, 135.6 Hz, β-CH_2), 37.8 ($^1J_{CH}$ = 136.7 Hz, 137.9 Hz, β-CH_2), 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 $^1J_{CH}$ were determined in an HMQC experiment. Anal. Calcd for $C_{34}H_{43}Cl_2NO_2W$: C, 54.27; H, 5.76; N, 1.86. Found: C, 54.18; H, 5.71; N, 1.84.

$W(NAr_{Cl})(^{13}CH_2)_4$(Biphen) was observed when $^{13}CH_2{=}^{13}CH_2$ was employed; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 85.4 (d, $^1J_{CC}$ = 33.6 Hz, α-CH_2), 77.4 (d, $^1J_{CC}$ = 32.8 Hz, α-CH_2), 38.3, 37.7 (dt, $^1J_{CC}$ = 33.6 and 32.8 Hz, β-CH_2).

[W(NAr$_{Cl}$)(Biphen)(μ-CH$_2$)]$_2$. A solution of $W(NAr_{Cl})(C_3H_6)$(Biphen) (400 mg, 542 μmol) in benzene (2 mL) was stirred for 24 h at 25 °C, and pentane (8 mL) was added. Purple microcrystals of $[W(NAr_{Cl})(Biphen)(\mu\text{-}CH_2)]_2$ were isolated by filtration and washed with pentane (2 mL); yield 112 mg (29%). Due to the insolubility of isolated $[W(NAr_{Cl})(Biphen)(\mu\text{-}CH_2)]_2$, a complete set of NMR spectroscopic data could not be obtained.

[W(NAr$_{Cl}$)(Biphen)]$_2$(μ-CH$_2$CH$_2$)]$_2$. A degassed solution of $W(NAr_{Cl})(C_3H_6)$(Biphen) (500 mg, 677 μmol) in benzene (10 mL) was stirred in a sealed thick-walled glass vessel for 90 min at 100 °C to give a dark orange solution, which was filtered through Celite. The volatiles were removed by lyophilization to leave behind a brown powder that was approximately a 5:1 mixture of [W(NArCl)(Biphen)]$_2$(μ-CH_2CH_2) and [W(NArCl)(Biphen)]$_2$, along with a trace of $W(NAr_{Cl})(C_4H_8)$(Biphen). The product mixture was washed with pentane (50 mL) to extract all $W(NAr_{Cl})(C_4H_8)$(Biphen). After all volatiles were removed under reduced pressure, the brown powder was suspended in benzene (~2 mL) and exposed to ethylene (1 atm) for 2 h. The supernatant was decanted from the orange microcrystalline product, which was then washed with pentane (5 mL); yield 140 mg (29%): ^1H NMR (C_6D_6) δ 7.28 (s, 4 × 1 H, Biphen), 7.02 (d, $^3J_{HH}$ = 8.1 Hz, 2 × 1 H, NAr_{Cl}-3), 6.47 (d, $^3J_{HH}$ = 8.1 Hz, 2 × 1 H, NAr_{Cl}-5), 6.14 (t, $^3J_{HH}$ = 8.1 Hz, 2 × 1 H, NAr_{Cl}-4), 3.71 (m, $^1J_{CH}$ = 151.4 Hz, 2 × 1 H, WCH_2), 2.21, 2.11 (s, 4 × 3 H, Biphen-CH_3), 2.06 (m, $^1J_{CH}$ = 140.8 Hz, 2 × 1 H, WCH_2), 1.95, 1.61 (s, 4 × 3 H, Biphen-CH_3), 1.34, 1.21 (s, 4 × 9 H, Biphen-CMe_3); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 162.6, 161.6, 161.5, 136.3 (2 × s), 136.1, 134.3, 131.8, 130.7, 130.6, 130.5, 129.9, 128.7, 127.9, 126.9, 70.6 ($^1J_{CH}$ = 140.8 Hz, 151.4 Hz, WCH_2), 36.6, 35.7, 33.3, 31.9, 23.8, 21.2, 18.0 (2 × s). The WCH_2 coupling constants $^1J_{CH}$ were determined in an HMQC experiment. Anal. Calcd for $C_{31}H_{37}Cl_2NO_2W$: C, 52.41; H, 5.25; N, 1.97. Found: C, 52.35; H, 5.31; N, 1.85.

Reaction of W(NAr$_{Cl}$)(CHCMe$_3$)[OC(CF$_3$)$_2$Me]$_2$ with *trans*-3-Hexene. A bright yellow solution of $W(NAr_{Cl})(CHCMe_3)(OR_{F6})_2$ (25 mg, 32 μmol) in toluene-d_8 was treated with *trans*-3-hexene (4 μL, 32 μmol), and the sample was kept at −78 °C until the NMR spectra were recorded. After 40 min at 0 °C, the yellow solution contained a 2:1:1 mixture of $W(NAr_{Cl})(CHCMe_3)(OR_{F6})_2$, $W(NAr_{Cl})(CHEt)(OR_{F6})_2$, and $W(NAr_{Cl})(OR_{F6})_2(CHEt)_3$. $W(NAr_{Cl})(CHEt)(OR_{F6})_2$ resonances were observed in the ^1H NMR spectrum (toluene-d_8, 0 °C) at 9.27 (br, 1 H, WCH), 6.69 (d, $^3J_{HH}$ = 8.1 Hz, 2 H, NAr_{Cl}-3 and NAr_{Cl}-5), 6.00 (t, $^3J_{HH}$ = 8.1 Hz, 1 H, NAr_{Cl}-4), 3.56 (m, 2 H, $WCHCH_2$), 1.81 (s, 2 × 3 H, $OCCH_3$), and 0.75 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, $WCHCH_2CH_3$) ppm. The tungstacyclobutane resonances were observed in the ^1H NMR spectrum (toluene-d_8, 0 °C) at −0.31, −0.41, −0.51, and −0.80 ppm (m, 5:1:3:1 mixture of 4 isomers, 1 H, β-CH). Other resonances could not be assigned unambiguously.

After 24 h at 0 °C, the above solution contained a 1:1 mixture of unreacted starting material and tungstacyclobutanes, along with insoluble $[W(\mu\text{-}NAr_{Cl})(OR_{F6})_2]_2$.

Reaction of W(NAr$_{Cl}$)(Biphen)(CH$_2$CH$_2$)(THF-*d*$_8$) with Excess ^{13}CH$_2$=^{13}CH$_2$: Observation of W(NAr$_{Cl}$)(Biphen)(^{13}C$_4$H$_8$). At −196 °C, $^{13}CH_2{=}^{13}CH_2$ (600 μmol) was condensed into an NMR tube that was charged with a yellow solution of $W(NAr_{Cl})$(Biphen)$(CH_2)_2$(THF-d_8) (35 mg, 44 μmol) in CD_2Cl_2 (0.7 mL). After the sealed NMR tube was allowed to warm to 25 °C, the color of the solution rapidly changed to orange. NMR spectra recorded after the sample was kept for 30 min at 25 °C indicated that $W(NAr_{Cl})$(Biphen)$(CH_2)_2$(THF-d_8) had been completely converted into $W(NAr_{Cl})$(Biphen)$(^{13}CH_2)_4$: ^1H NMR (CD_2Cl_2) δ 7.07 (d, s, 3 × 1 H, NAr_{Cl}-3, NAr_{Cl}-5 and Biphen) 6.94 (s, 1 H, Biphen), 6.70 (t, $^3J_{HH}$ = 8.1 Hz, 1 H, NAr_{Cl}-4), 5.23 (m, 40 H, $^{13}CH_2{=}^{13}CH_2$), 3.33−2.56 (m, 8 H, $W^{13}C_4H_8$), 2.07, 1.98, 1.52 (s, 3 × 3 H, Biphen-CH_3), 1.32 (s, 3 + 9 H, Biphen-CH_3 and CMe_3), 1.15 (s, 9 H, CMe_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 123.4 (s, $^{13}CH_2{=}^{13}CH_2$), 86.4 (d, $^1J_{CC}$ = 35.4 Hz, α-CH_2), 75.3 (d, $^1J_{CC}$ = 34.5 Hz, α-CH_2), 37.6 (m, β-CH_2). Coupling constants $^2J_{HH}$ and chemical shifts of the methylidene resonances in the ^1H NMR spectrum were determined in an experiment employing unlabeled ethylene instead of $^{13}CH_2{=}^{13}CH_2$. Since the methylidene resonance at 7.61 ppm in the ^1H NMR spectrum of $W(NAr_{Cl})(Biphen)(\mu\text{-}^{13}CH_2)_2$ was obscured, $^1J_{CH}$ could not be determined.

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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 $\{W(\mu\text{-}NAr_{Cl})[OC(CF_3)_2Me]_2\}_2(C_6H_6)$ (06034), $W(NAr_{Cl})$(Biphen)$(C_3H_6)(CH_2Cl_2)_{0.25}$ (06135), $W(NAr_{Cl})$(Biphen)(C_2H_4)(THF-d_8) (06140), $W(NAr_{Cl})$(Biphen)(C_4H_6) (06179), $[W(NAr_{Cl})(Biphen)(\mu\text{-}CH_2)]_2$ (06185), and $W_2(Biphen)_2(\mu\text{-}NAr_{Cl})_2(\mu\text{-}CH_2CH_2)$ (06208) are also available to the public at http://www.reciprocalnet.org/.

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