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Alkylidene and Metalacyclic Complexes of Tungsten that Contain a Chiral Biphenoxide Ligand. Synthesis, Asymmetric Ring-Closing Metathesis, and Mechanistic Investigations

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Abstract: Two complexes that contain the racemic or enantiomerically pure (*S*) form of the 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diolate (Biphen^{2-}) ligand, W(NAr)(CHCMe$_2$Ph)(Biphen) (**2a**) and W(NAr′)(CHCMe$_2$Ph)(Biphen) (**2b**) (Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$; Ar′ = 2,6-Me$_2$C$_6$H$_3$), were prepared and shown to be viable catalysts for several representative ring-closing reactions to give products in good yields in most cases and high % ee in asymmetric reactions. Exploration of the reaction between **2a** and a stoichiometric amount of one desymmetrization substrate allowed two intermediate tungstacyclobutane complexes to be observed, in addition to the final and quite stable tungstacyclobutane complex formed in a reaction between the ring-closed product and a tungsten methylene complex. Reactions involving ^{13}C labeled ethylene allowed for the observation of an unsubstituted tungstacyclobutane complex, an ethylene complex, an unsubstituted tungstacyclopentane complex, and a heterochiral dimeric form of a methylene complex. The tungstacyclopentane complex was found to catalyze the dimerization of ethylene to 1-butene slowly.

Introduction

Catalytic alkene metathesis in its simplest form consists of a redistribution of alkylidene fragments of olefins to give, at equilibrium, a mixture of all possible cis and trans olefins.[1] The reaction was known to be promoted by tungsten, molybdenum, and rhenium, although little was known about the catalysts in detail except that a carbene ligand almost certainly was present in the species that re-formed in this reaction.[2−7] It was clear that the carbene complexes generated in these "classical" systems were present in very low concentrations and that the carbene complexes known at the time (compounds that contained a heteroatom-stabilized carbene ligand) did not react with olefins in a catalytic metathesis-like fashion via propagating carbenes derived from the olefins.[3,8,9] Therefore, it was highly desirable to learn how to synthesize new types of carbene complexes that would react with olefins in a metathesis manner and how to prepare stable and active complexes, to be able to control the metathesis reaction at a molecular level. The discovery that alkoxide ligands would "turn on" metathesis of olefins by well-characterized "high oxidation state" tantalum alkylidene complexes[10,11] and the discovery of related high oxidation state oxo alkylidene complexes of tungsten[12] ultimately led to the conclusion that high oxidation state complexes[13] almost certainly were by far the most common, if not the only catalysts containing Mo or W that would sustain olefin metathesis. In 1986, a method of synthesizing stable tungsten imido alkylidene complexes of the type W(NAr)(CH-*t*-Bu)(OR′)$_2$ (Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$ and OR′ = O-*t*-Bu, OCMe(CF$_3$)$_2$,

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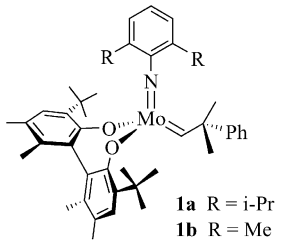
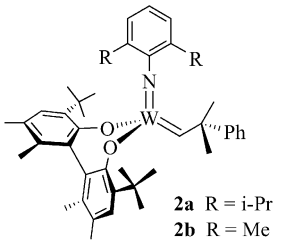
O-2,6-*i*-$Pr_2C_6H_3$, etc.) was discovered.[14,15] If the alkoxide is relatively electron withdrawing (e.g., OR′ = $OCMe(CF_3)_2$), these complexes are fully active for the metathesis of internal alkenes. Propagating alkylidene complexes and intermediate tungstacyclobutane complexes could be observed and, in some cases, isolated and characterized.[14] The relatively high stability of unsubstituted tungstacyclobutane complexes was believed to limit the utility of tungsten catalysts for the metathesis of terminal olefins at room temperature, although the metathesis of terminal olefins was not investigated extensively and, in particular, not at elevated temperatures. Recent developments in high oxidation state alkylidene chemistry can be found in a comprehensive review.[16]

In the mid 1980s, a relatively efficient synthesis of Mo(NAr)(CH-*t*-Bu)(OR′)$_2$ catalysts from various molybdates was developed.[17] It was believed, by analogy with earlier work concerning alkyne metathesis by tungsten[18] and molybdenum[19] alkylidyne trialkoxide complexes via intermediate metalacyclobutadiene complexes, that molybdacyclobutane complexes would be more likely to lose an olefin readily and re-form an alkylidene than would tungstacyclobutane complexes. Therefore, the possibility that metal would remain largely sequestered as an unsubstituted metalacyclobutane complex, which would be formed in any system in which a terminal olefin was present, would be diminished by employing molybdenum. In fact, it was found that even terminal alkenes could be metathesized readily at room temperature by Mo-based catalysts such as Mo(NAr)(CH-*t*-Bu)$[OCMe(CF_3)_2]_2$.[20−22] Applications to organic chemistry using Mo(NAr)$(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ also began to appear, most notably in 1992 in the form of the ring-closing metathesis (RCM) reaction.[23] It appeared that molybdenum catalysts would always be preferred over tungsten catalysts, in part because of the relative ease of synthesizing them, and because of their supposed lower sensitivity to certain functionalities, water, oxygen, etc. The development of well-characterized ruthenium-based catalysts in the mid 1990s led to a dramatic further expansion of interest in the application of metathesis to organic chemistry.[24,25]

In the last five years, a variety of molybdenum imido alkylidene catalysts of the type Mo(NAr)(CHR)(diolate) (R = CMe_3 or CMe_2Ph) have been prepared in which the diolate is optically pure.[26] When the diolate is a biphenolate or binaphtholate, these species have been shown to promote a variety of asymmetric metathesis reactions efficiently.[26a−p] Mo(NAr)(CHR)(diolate) complexes have a "modular" character in the sense that one now can choose from several imido groups and diolates and thereby optimize catalyst activity and selectivity.[26i] Complexes **1a** and **1b** were the first in the class of biphenolate or binaphtholate catalysts to be prepared.[26f] Because the first well-characterized olefin metathesis catalysts contained tungsten rather than molybdenum, we felt compelled to attempt to synthesize and test tungsten analogues of **1a** and **1b**, **2a** and **2b**. In this paper, we report the preparation of **2a** and **2b** and examine their viability in representative asymmetric metathesis reactions. Because ethylene is generated in many metathesis reactions and may play a significant role in determining catalyst longevity, we also have explored reactions between **2a** or **2b** and ethylene.



1a R = i-Pr
1b R = Me



2a R = i-Pr
2b R = Me

Results

Synthesis and Characterization of New Tungsten Biphenolate Complexes. Two precursors to tungsten diisopropylphenylimido alkylidene catalysts, W(NAr)$(CHCMe_2Ph)Cl_2$(DME) (**3a**,

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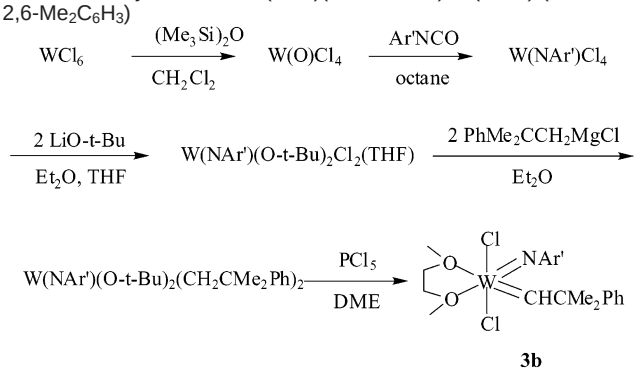
Scheme 1. Synthesis of W(NAr′)(CHCMe$_2$Ph)Cl$_2$(DME) (Ar′ = 2,6-Me$_2$C$_6$H$_3$)



3b

Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$) and W(NAr)(CHCMe$_2$Ph)(OTf)$_2$(DME) (**4**), can be synthesized from WCl_6 by methods reported in the literature.[27] Only **4** was employed in this work. A complex related to **3a**, W(NAr′)(CHCMe$_2$Ph)Cl$_2$(DME) (**3b**, Scheme 1, Ar′ = 2,6-Me$_2$C$_6$H$_3$), was prepared following a procedure similar to that used to synthesize **3a**. Addition of benzyl potassium[28,29] or potassium hydride to H$_2$(Biphen) (where Biphen^{2-} = 3,3′-di-*t*-Bu-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diolate) gave the dipotassium salt, K$_2$(Biphen). W(NAr)(CHCMe$_2$Ph)(Biphen) (**2a**) was then prepared by adding K$_2$(Biphen) to **4**, while W(NAr′)(CHCMe$_2$Ph)(Biphen) (**2b**) was prepared by adding K$_2$(Biphen) to **3b**.

The racemic complex, *rac*-**2b**,[30] was obtained free of coordinated THF, while *rac*-**2a** was isolated as a THF adduct. (Their molybdenum analogues were both isolated as THF-free species.[26f]) Attempts to synthesize THF-free **2a** by carrying out the reaction between K$_2$(Biphen) and **4** in toluene were unsuccessful. However, THF-free **2a** could be isolated by redissolving the THF adduct in toluene and removing all solvents in vacuo. The enantiomerically pure complexes, (*S*)-**2a** and (*S*)-**2b**, were prepared in a manner analogous to the methods used to synthesize the racemic compounds. Unfortunately, each could be isolated only as a "foam" by removing all solvent in vacuo. (It is not unusual to find that enantiomerically pure compounds are much more difficult to crystallize than racemic compounds.) The enantiopure complexes are essentially free of THF.

Both **2a** and **2b** exist as mixture of syn and anti isomers in benzene or toluene, with the syn isomer predominating in each case. (In the syn isomer, the alkylidene substituent points toward the imido ligand; in the anti isomer, the substituent points away from the imido ligand.) In the ^{1}H NMR spectrum of THF-free **2a** at 20 °C, the syn alkylidene H$_\alpha$ resonance was found at 7.91 ppm ($^2J_{WH}$ = 14.1 Hz), while the broad and weak anti resonance was located at 10.76 ppm; the syn/anti ratio was 22. The analogous syn and anti resonances for **2b** were found at 7.99 ($^2J_{WH}$ = 16.4 Hz) and 9.06 ($^2J_{WH}$ = 15.0 Hz) ppm, respectively; the syn/anti ratio was 88. The larger syn/anti ratio for **2b** is consistent with the presence of smaller *ortho*-substituents in the arylimido ligand. These alkylidene resonances are found at much higher field (by ~3 ppm) than the syn and anti resonances in **1a**.[26f] In the ^{13}C NMR spectrum of **2a**, a sharp downfield resonance was observed at 245.8 ppm ($^1J_{WC}$ = 202.1 Hz, $^1J_{CH}$ = 113.4 Hz), while a similar downfield resonance was observed at 247.7 ppm ($^1J_{CH}$ = 115.6 Hz) in the spectrum of **2b**. The $^1J_{CH}$ value in each case is characteristic of that for a syn isomer.[14] The anti alkylidene α carbon resonance is too weak to be observed in the spectrum of either **2a** or **2b**.

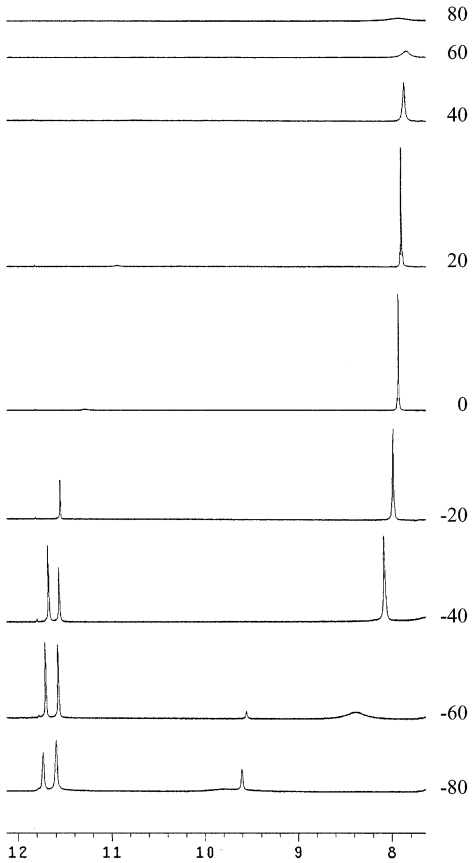


Figure 1. Variable-temperature 500 MHz ^{1}H NMR spectra of *rac*-**2a(THF)** in toluene-d_8. (Units are ppm; all temperatures are reported in °C.)

Variable-temperature ^{1}H NMR studies of *rac*-**2a(THF)** (Figure 1) suggest that THF is not strongly bound to the metal. At 20 °C, a relatively sharp *syn*-alkylidene proton resonance (with ^{183}W and ^{13}C satellites) is observed at 7.9 ppm ($^2J_{WH}$ = 14.2 Hz; $^1J_{CH}$ = 113 Hz). (The ^{13}C satellites are observable only after many transients.) On the basis of the chemical shifts of the alkylidene α proton for the THF-free syn isomer of **2a**, the predominant syn isomer of **2a(THF)** is close to being THF-free at 20 °C at the concentrations employed. The anti alkylidene resonance at 11.15 ppm (weak) is broad and shifted slightly downfield from where it is found in THF-free **2a**. When the sample was warmed to 80 °C, THF dissociation and interconversion of the syn and anti isomers on the NMR time scale led to a reversible broadening of both resonances. When the sample was cooled to −80 °C, the alkylidene α proton resonances for two diastereomeric THF adducts of the anti isomer could be observed in roughly equal amounts near 11.6 ppm. (Two diastereomeric THF adducts form as a consequence of THF coordinating to the diastereotopic CNO faces.) Resonances were observed at 9.6 ppm (sharp, weak) and ~9.8 ppm (broad, weak) for the much more labile diastereomeric *syn*-THF adducts. At −80 °C, the amount of the syn isomer is much less than the amount of anti isomer. As the sample was warmed from −80 to 20 °C, the resonances for the syn diastereomers merged and

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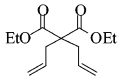
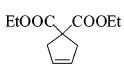
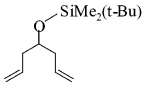
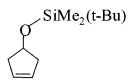
(30) For simplicity, we will use the *rac* or *S* label for the entire complex, even though it refers to the Biphen^{2-} ligand in the complex.

Table 1. Some Simple Ring-Closing Reactions Catalyzed by *rac*-**2a** and *rac*-**2b**[a]

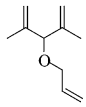
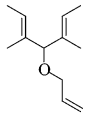
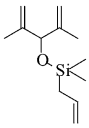
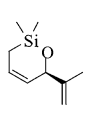
Entry	Substrate	Product	Catalyst	Temp (°C)	Time (h)	Conversion (%)
1			**2a**	75	0.5	>99
2			**2b**	22	8	>99
3	**5**		**2b**	60	0.5	>99
4			**2a**	60	4	>99
5			**2a**	75	1	>99
6	**6**		**2b**	60	0.5	>99
7			**2a**	75	1	>99
8			**2a(THF)**	75	1	>99
9	**7**		**2b**	60	1	>99
10			**2a**	60	0.5	16
11			**2a(THF)**	60	0.5	14
12	**8**		**2b**	60	0.5	14

[a] Solvent = benzene-d_6; 5% catalyst loading (0.01 M). Conversion was determined by the analysis of the 500 MHz ^{1}H NMR spectrum.

shifted upfield as a consequence of the loss of labile THF and generation of a significant amount of the THF-free syn complex (Figure 1). The same phenomenon leads to the resonances for the anti diastereomers broadening and merging, and the average resonance shifting upfield, although that process takes place at slightly higher temperatures than for the syn isomer. The syn/anti ratio increases significantly as the temperature increases. In the ^{13}C NMR spectrum of **2a** at −80 °C in the presence of 5 equiv of THF, the anti alkylidene α carbon resonances were found at 283.5 ($^1J_{CH}$ = 141 Hz) and 273.1 ($^1J_{CH}$ = 136 Hz) ppm. The alkylidene α carbon resonances for the syn isomers under these conditions could not be located with certainty. In the presence of 36 equiv of THF, the syn/anti ratio at 20 °C decreased from 22 to 1.4; at −80 °C, the *anti*-THF adducts (∼1:1) again were the dominant species. Under these circumstances, all four diastereomeric THF adducts could be observed at or below −60 °C, with the now sharp H_α resonance for the most labile syn adduct appearing at 9.8 ppm. All of this behavior for **2a** is broadly similar to what has been observed for **1a**,[26f] although it is clear that THF binds more strongly to W than to Mo, as one might expect.

Ring-Closing Metathesis Reactions and the Observation of Tungstacyclobutane Complexes. The results of some simple ring-closing metathesis reactions catalyzed by *racemic* **2a** and **2b** are listed in Table 1. (The THF adduct of **2a** is noted as **2a(THF)**.) *N*,*N*-Diallylsulfonamide (**5**) was cyclized slowly but completely by **2b** in 8 h at 22 °C. At elevated temperatures, **5** was fully ring-closed by **2a** (75 °C) and **2b** (60 °C) in 0.5 h. At 60 °C, substrates **6** and **7** both were ring-closed smoothly by **2b**. A slightly higher temperature (75 °C) was required for **2a** relative to **2b** (compare entries 4 and 6 in Table 1). For **7** at 75 °C, the rate of conversion is approximately the same whether the THF-free complex (**2a**) or the THF adduct (**2a(THF)**) was used (compare entries 7 and 8). Substrate **8** could not be ring-closed completely by **2a(THF)** or **2b** at 60 °C; a conversion of approximately 14% was observed after 0.5 h, and the reaction did not proceed further even upon heating for an additional 1.5 h. Attempts to ring-close **8** with the THF-free complex **2a** did not lead to significant improvement in the conversion. It seems likely that **8** and the ring-closed product both bind strongly to the metal and thereby inhibit reaction. However, we cannot exclude some destructive reaction between either catalyst and some component of the reaction. In general, **2b** seems to afford higher conversion at lower temperatures than **2a** with these selected substrates.

Table 2. Catalytic Asymmetric Ring-Closing Reactions with (*S*)-**2a** and (*S*)-**2b**

Entry	Substrate	Product	Catalyst	Temp (°C)	Time (h)	Conversion (%)	ee[b] (%)
1			**(*S*)-1a**	22	6	94	93
2			**(*S*)-2a**	75	12	91	96
3			**(*S*)-1b**	22	6	93	93
4	**9**		**(*S*)-2b**	75	8	88	95
5			**(*S*)-1b**	22	4	95	99
6			**(*S*)-2b**	60	0.5	30	93
	10						
7			**(*S*)-1b**	22	24	51	85
8			**(*S*)-2b**	60	12	96	>98
9			**(*S*)-2b**	75	5	>98	>98
	11						

[a] Solvent = benzene-d_6; 5% catalyst loading (0.01 M). Conversion was determined by the analysis of the 500 MHz ^{1}H NMR spectrum. The data for **1a** and **1b** were obtained from the literature.[26f] [b] Product enantioselectivity was determined by GLC analysis (Chiraldex-GTA by Alltech for entries 1−6, Betadex 120 for entries 7−9) in comparison to the authentic racemic ring-closed product. In all cases, the (*R*)-antipode was enriched.

The results of some preliminary catalytic desymmetrizations of **9**, **10**, and **11** by (*S*)-**2b** and (*S*)-**2a** are summarized in Table 2. The conversion of **10** to product by (*S*)-**2b** at 60 °C was unexpectedly low (30%), and the enantioselectivity (93% ee) was lower than that observed when (*S*)-**1b** was employed (99% ee).[26b] (The low conversion did not improve with time.) Both conversion and enantioselectivity were high with sterically less hindered substrates **9** and **11**. At 75 °C, substrate **11** was ring-closed to the six-membered product (>98% conversion and >98% ee) within 5 h. This result is particularly encouraging, as previous attempts to ring-close **11** by (*S*)-**1b** yielded only 51% product (85% ee) and 28% homocoupled product ("dimer") even when the reaction was performed at room temperature for 24 h.[26b] Multiplets characteristic of an unsubstituted tungstacyclobutane complex (vide infra) were observed at 4.02, 3.91, and 3.83 ppm when this reaction was periodically monitored by ^{1}H NMR at 20 °C. Substrate **9** was shown to be ring-closed by (*S*)-**2a** at 75 °C (entry 2, Table 2) to marginally greater conversion and % ee than by (*S*)-**2b** (entry 4, Table 2). On the basis of what has been observed in a molybdenum binaphtholate system,[31] the higher reaction temperatures are needed in general to eject ethylene from the unsubstituted tungstacyclobutane resting state and re-form an alkylidene (methylene) which can then continue the ring-closing reaction.

To identify possible intermediates, the *stoichiometric* reaction between *rac*-**2a** and **9** (mixed initially at −78 °C) was monitored by ^{1}H NMR at −40 °C. No alkylidene resonances, except those

(31) Tsang, W. C. P.; Schrock, R. R.; Hoveyda, A. H. *Organometallics* **2001**, *20*, 5658.

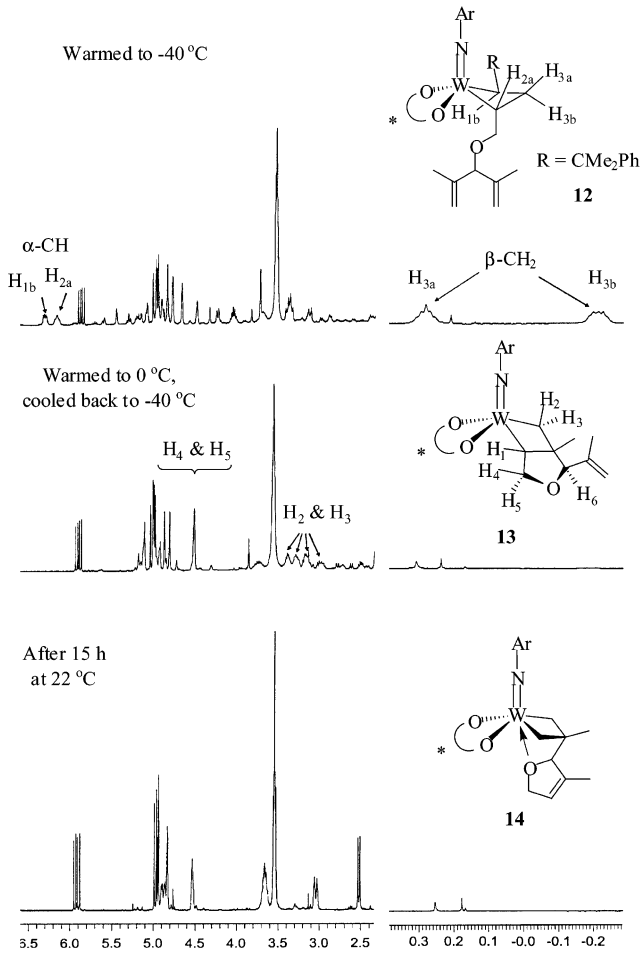
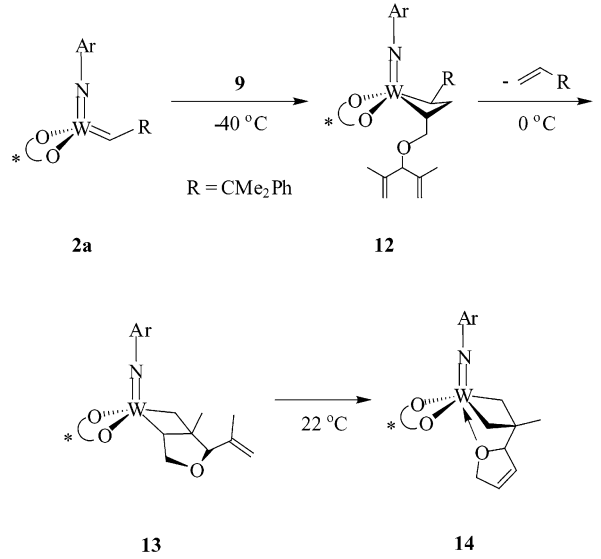


Figure 2. ^{1}H NMR spectra of the reaction mixture prepared from **2a** and **9** in toluene-d_8.

Scheme 2. Synthesis of Tungstacyclobutane **14**



of unreacted **2a**, were detected in these experiments. Two intermediates (**12** and **13**) were observed (Scheme 2, Figure 2). Complex **12** is believed to be the initial metalacycle formed from **2a** and **9** on the basis of two high field ^{1}H resonances at 0.34 (H_{3a}) and −0.17 (H_{3b}) ppm (see Figure 2 for numbering of protons), which are typical for β-protons in trigonal bipyramidal tungstacyclobutane complexes.[14] Resonances for the two α-protons (H_{2a} and H_{1b}) were observed at 6.21 and 6.37 ppm. On the basis of the coupling pattern observed in a homonuclear ^{1}H gCOSY experiment, we conclude that the substituents on the two α carbons are trans to one another. (The absolute arrangement is not known.) The equatorial β-proton (H_{3b}) is through-bond coupled to H_{3a} and H_{1b}; its coupling to H_{2a} is too weak to be observed. The axial β-proton (H_{3a}) is coupled to H_{3b} and H_{2a}; its coupling to H_{1b} is weak. In a ^{1}H−^{13}C HMQC experiment, the ^{13}C NMR resonances for the α carbons were located at 130.5 and 117.4 ppm; the β carbon resonance could not be located unambiguously. The resonance for the methine carbon next to the ethereal oxygen in **12** was shifted downfield to 90.5 ppm as compared with 85.9 ppm in **9**. The resonance for the methylene carbon attached to the metalacyclobutane α carbon was found at 75.9 ppm.

Complex **12** was moderately stable at −60 °C, although it decomposed slowly to yield **13** and 3-methyl-3-phenyl-1-butene at −40 °C ($t_{1/2} \approx 200$ min). Conversion of **12** to **13** was complete at 0 °C within 15 min, as judged by the irreversible disappearance of the characteristic α- and β-proton resonances and the appearance of 3-methyl-3-phenyl-1-butene. On the basis of extensive NMR studies, we conclude that **13** is the bicyclic intermediate in the desymmetrization reaction (Scheme 2). The characteristic multiplet at 4.52 ppm in the ^{1}H NMR spectrum at −40 °C was assigned to the methylene protons next to the ethereal oxygen (H_4 and H_5) on the basis of a correlation between these protons and the methylene carbon at 75.8 ppm. The methylene protons in the tungstacyclobutane ring (H_2 and H_3) were observed as multiplets at 3.01 and 3.19 ppm. The resonance for H_1 was obscured by the *tert*-butyl resonance and a THF resonance at 1.4 ppm. The other methine proton in the ether ring (H_6) was observed as a broad resonance at approximately 5.0 ppm, which is partly obscured by an olefinic resonance from 3-methyl-3-phenyl-1-butene. The methine α carbon resonance was located at 12.2 ppm, while the resonance for the methine carbon on the ether ring was found at 93.1 ppm. The methylene α carbon resonance was located at 79.9 ppm by ^{1}H−^{13}C HMQC. Unfortunately, all attempts to obtain single crystals of **13** have failed.

Complex **13** showed no signs of decomposition after two weeks in solution at −30 °C, but it decomposed in a first-order manner ($k \approx 7.3 \times 10^{-5}$ s^{-1}, $t_{1/2} \approx 160$ min) at 22 °C to form the final tungstacyclobutane complex **14**. In the absence of excess **9**, complex **14** is stable both in solution and in the solid state. Resonances characteristic of **14** were still observed upon heating a sample to 90 °C. Spectroscopic data for **14** are consistent with a tungstacyclobutane formed between the tungsten methylene complex and the ring-closed product (Figure 2, Scheme 2); its solid-state structure was determined by X-ray crystallography (vide infra). The four α-protons were observed as two pairs of doublets at 2.53 ($^2J_{HH}$ = 9.7 Hz), 1.33 ($^2J_{HH}$ = 9.7 Hz), 1.79 ($^2J_{HH}$ = 10.0 Hz), and 1.17 ($^2J_{HH}$ = 10.0 Hz) ppm in the ^{1}H NMR spectrum. The two α carbons in the metalacyclic ring were found at 47.9 and 55.1 ppm in the ^{13}C NMR spectrum, consistent with a square-pyramidal structure.

When **2a** was mixed with stoichiometric amounts of 1,6-heptadiene or 3-allyl-(2,5-dimethyl-1-hexenyl) ether (**15**), the ring-closed product and the tungstacyclobutane complex **16** were observed as the major products (Scheme 3). Complex **16** is stable in the solid state but relatively unstable in C_6D_6; an orange

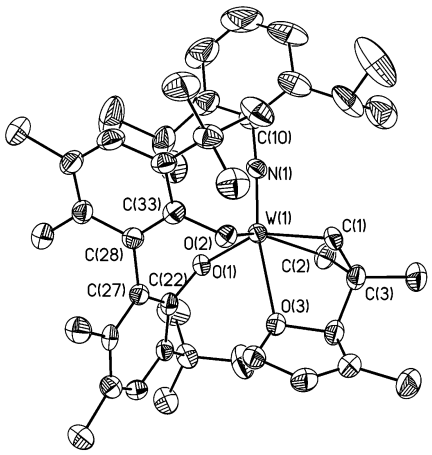
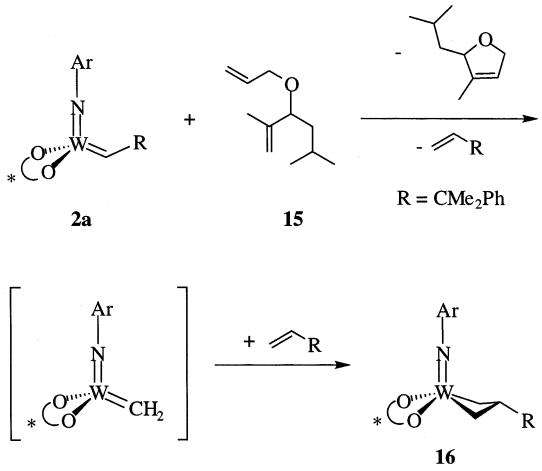


Figure 3. ORTEP diagram of **14**. Thermal ellipsoids are displayed at 50% probability level. Hydrogen atoms were omitted for clarity.

Scheme 3. Synthesis of Tungstacyclobutane **16**



solution of **16** immediately darkened at 20 °C, and free 3-methyl-3-phenyl-1-butene was observed within 2 h; the metal-containing decomposition products could not be identified. Compound **16** was isolated as orange crystals from pentane at −30 °C and identified in an X-ray study (vide infra). In a homonuclear ^{1}H gCOSY experiment, resonances for the α-protons were found at 2.97, 2.56, 1.32, and 1.26 ppm. The two downfield resonances (δ 2.97, 2.56) were assigned to the equatorial protons, and the upfield resonances (δ 1.32, 1.26) were assigned to the axial protons on the ring, consistent with previously observed chemical shift data in square pyramidal tungstacyclobutane complexes.[14] The β-proton resonance was found at 3.18 ppm.

X-ray Studies of Tungstacyclobutanes 14 and 16. Red crystals of **14** suitable for X-ray diffraction were obtained in a reaction between *rac*-**2a** and **9** in a concentrated pentane solution at room temperature. Orange crystals of **16** were prepared in the reaction between *rac*-**2a** and **15** in pentane at −20 °C. ORTEP diagrams of **14** and **16** are shown in Figures 3 and 4. Crystal data can be found in Table 3, and selected bond distances and angles are given in Table 4. Only one diastereomer of **14** was present, consistent with the observation of only one diastereomer in solution in NMR studies.

Complex **16** adopts approximately a square pyramidal geometry in which the two biphenolate oxygen atoms and the two metalacyclobutane α carbon atoms occupy the four basal

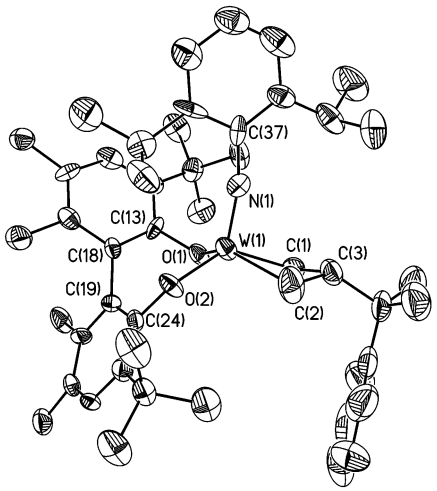


Figure 4. ORTEP diagram of **16**. Thermal ellipsoids are displayed at 50% probability level. Hydrogen atoms were omitted for clarity.

Table 3. Crystal Data and Structure Refinement for **14** and **16**[a]

	14	**16**
empirical formula	$WC_{45}H_{63}NO_3$	$WC_{50}H_{65}NO_2$
formula weight	849.81	895.88
crystal system	triclinic, $P\bar{1}$	monoclinic, $C2/c$
a	10.1880(16) Å	22.2675(15) Å
b	10.8869(17) Å	19.8014(14) Å
c	21.512(3) Å	22.5546(15) Å
α	75.914(3)	90
β	80.904(2)	113.5690(10)
γ	65.334(2)	90
volume, Z	2098.7(6) Å^3, 2	9115.3(11) Å^3, 8
density (calculated)	1.345 Mg/m^3	1.306 Mg/m^3
absorption coefficient	2.790 mm^{-1}	2.572 mm^{-1}
F(000)	876	3696
θ range for data collection	2.47 to 23.34	2.09 to 19.99
index ranges	$-11 \le h \le 11$ $-7 \le k \le 12$ $-18 \le l \le 23$	$-21 \le h \le 21$ $-12 \le k \le 19$ $-21 \le l \le 21$
reflections collected	8327	12 979
independent relections	5863 [$R_{int} = 0.0321$]	4250 [$R_{int} = 0.0635$]
completeness to θ	96.2%	99.8%
max. and min. transmission	0.5958 and 0.3937	0.4624 and 0.3419
data/restraints/ parameters	5863/0/452	4250/0/482
goodness-of-fit on F^2	1.120	1.427
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0280$, w$R_2 = 0.0699$	$R_1 = 0.0769$, w$R_2 = 0.1268$
R indices (all data)	$R_1 = 0.0292$, w$R_2 = 0.0705$	$R_1 = 0.0878$, w$R_2 = 0.1298$
extinction coefficient	0.0018(3)	0.00000(2)
largest diff. peak and hole	1.304 and −0.875 e Å^{-3}	1.026 and −1.651 e Å^{-3}

[a] Both experiments were carried out at 183(2) K using Mo Kα radiation (0.71073 Å), the absortpion correction was empirical, and the refinement method was full-matrix least-squares on F^2.

sites. The octahedral structure of **14** can be viewed as a related "solvated" square pyramid in which O(3) is coordinated trans to the imido nitrogen. In each compound, the C(1)−W−C(2) angle is relatively small (∼64°). The tungsten atom resides above the least-squares plane defined by O(1), O(2), C(1), and C(2) by 0.47 Å in **14** and 0.65 Å in **16**. Carbon C(3) points away from the imido ligand in **14** as a consequence of intramolecular coordination of the dihydrofuran side chain to the metal through O(3). In **16**, C(3) points toward the imido

Table 4. Selected Bond Distances (Å) and Angles (deg) in Tungstacyclobutanes **14** and **16**

	14	**16**[a]
W(1)−C(1)	2.204(4)	2.157(14)
W(1)−C(2)	2.160(4)	2.173(15)
W(1)−N(1)	1.739(3)	1.684(12)
W(1)−O(1)	1.936(3)	1.917(8)
W(1)−O(2)	1.975(3)	1.983(8)
W(1)−O(3)	2.381(3)	
C(1)−C(3)	1.541(6)	1.520(19)
C(2)−C(3)	1.526(6)	1.53(2)
W(1)−C(1)−C(3)	91.8(2)	95.7(9)
W(1)−C(2)−C(3)	94.0(3)	94.8(9)
W(1)−N(1)−C(10)	176.0(3)	168.0(10)
W(1)−O(1)−C(22)	125.1(2)	128.4(7)
W(1)−O(2)−C(33)	112.9(2)	106.7(7)
C(1)−W(1)−C(2)	63.75(17)	63.8(6)
C(1)−C(3)−C(2)	97.4(3)	97.2(11)
N(1)−W(1)−C(1)	102.79(16)	101.8(5)
N(1)−W(1)−C(2)	97.52(17)	97.8(6)
N(1)−W(1)−O(1)	104.81(14)	118.2(4)
N(1)−W(1)−O(2)	107.30(14)	111.1(4)
N(1)−W(1)−O(3)	168.63(13)	
O(1)−W(1)−C(1)	151.13(14)	137.0(5)
O(1)−W(1)−C(2)	104.04(15)	94.2(5)
O(1)−W(1)−O(2)	98.89(11)	99.5(3)
O(1)−W(1)−O(3)	80.68(10)	
O(2)−W(1)−C(1)	80.71(14)	78.6(4)
O(2)−W(1)−C(2)	140.42(14)	136.5(6)
O(2)−W(1)−O(3)	81.26(10)	
C(22)−C(27)−C(28)−C(33)	78.8(5)	81.1(16)

[a] Atom numbers were changed to correspond to the atom labels in **14**.

ligand. The dihedral angle between the planes defined by C(1), W, and C(2) and that by C(1), C(3), and C(2) is 37° in **14** and 29.5° in **16** (cf. 25° in W[CH(*t*-Bu)CH_2CH(CO_2Me)](NAr)-[$OCMe_2(CF_3)]_2$ (**17**)[32]). Metal−ligand bond lengths and angles around the metal are not unusual, and the C−C bond lengths (1.541(6) and 1.526(6) Å in **14**, 1.520(19) and 1.53(2) Å in **16**) in the tungstacyclobutane ring are similar to what have been observed in other square pyramidal tungstacyclobutane complexes.[14] The dihedral angles in the biphenolate ligands are 78.8-(5)° in **14** and 81.1(16)° in **16**, which are similar to angles that have been observed in five-coordinate molybdenum biphenolate or binaphtholate alkylidene complexes.[26c,f,33,34] The structure of **14** closely resembles that of **17**;[32] in both complexes, the tungsten atom adopts a distorted square pyramidal geometry with an additional oxygen donor binding weakly trans to the apical imido ligand. The W−O(3) bond lengths in **14** (2.381-(3) Å) and **17** (2.372(6) Å) are essentially identical. The angles around tungsten and within the tungstacyclobutane ring are similar in **14** and **17**, although **14** contains a bidentate biphenolate ligand.

Observation of Unsubstituted Metalacyclobutane Complexes. Because ethylene is formed to a greater or lesser extent in all ring-closing reactions that have been explored here, we became interested in exploring reactions between **2a** or **2b** and ethylene. When 4 equiv of ethylene was added to a sample of *rac*-**2b** in C_6D_6, several well-defined resonances were observed in the ^{1}H NMR spectrum that could be attributed to the six protons in an unsubstituted trigonal bipyramidal tungstacyclobutane complex, W(NAr′)(C_3H_6)(Biphen) (TBP-**18b**; eq 1), on the basis of a comparison of these chemical shift values with those in unsubstituted metalacyclobutane complexes in the literature.[14] (Minor amounts of other compounds were detected

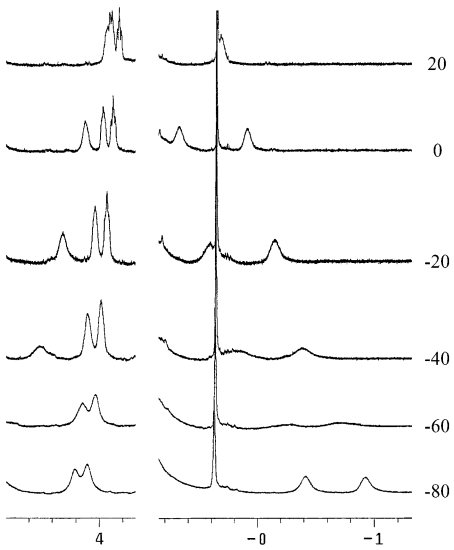
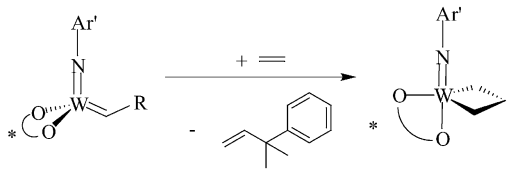


Figure 5. Variable-temperature ^{1}H NMR (500 MHz) spectra of W(NAr′)-($CH_2CH_2CH_2$)(Biphen) (**18b**) in toluene-d_8. (Units are ppm; temperatures are reported in °C.)



2b TBP-**18b** (1)

that were characterized by employing $^{13}C_2H_4$, as discussed in the following section.) Five of the six proton resonances are shown in the spectrum at 0 °C in Figure 5; the one near 3.0 ppm is not shown. Each has a relative intensity of one proton. All resonances split into two when $^{13}C_2H_4$ was employed. All six protons on the tungstacyclobutane ring could be observed as discrete contour circles in the ^{1}H−^{13}C HMQC spectrum at 20 °C, and each carbon was through-bond coupled to two protons. The proton NMR data for TBP-**18b** at 20 °C are listed in Table 5. When a toluene-d_8 sample of **18b** was cooled (Figure 5), the metalacycle proton resonances first broadened and then shifted, but sharpened again at −80 °C. Several resonances were shifted dramatically at −80 °C; only four are shown (each with relative area 1) in Figure 5. Complex **18b** was stable enough to be precipitated in pentane from a mixture of **2b** and 4 equiv of 1,6-heptadiene. (Note that the addition of only 1 equiv of 1,6-heptadiene to **2a** allowed **16** to be isolated, as described earlier.) In the solid state, **18b** is relatively stable under dinitrogen and could be analyzed satisfactorily.

Three broadened resonances centered at 86.9, 79.4, and 3.7 ppm were observed in the ^{13}C spectrum of a ^{13}C-labeled sample of **18b** at 20 °C (Figure 6); carbon−proton coupling constants were found to be 136, 149, and 149 Hz, respectively. Upon cooling the sample to −80 °C, we found that these resonances broadened, shifted, and sharpened to yield sharp resonances at 99.2, 87.4, and −3.2 ppm with J_{CH} values of 155, 156, and 152

(32) Feldman, J.; Murdzek, J. S.; Davis, W. M.; Schrock, R. R. *Organometallics* **1989**, *8*, 2260.
(33) Totland, K. M.; Boyd, T. J.; Lavoie, G. G.; Davis, W. M.; Schrock, R. R. *Macromolecules* **1996**, *29*, 6114.
(34) Schrock, R. R.; Jamieson, J. Y.; Dolman, S. J.; Miller, S. A.; Bonitatebus, P. J., Jr.; Hoveyda, A. H. *Organometallics* **2002**, *21*, 409.

Table 5. Chemical Shift and Coupling Values for Unsubstituted Tungstacyclobutane Complexes

	^{13}C δ (ppm)	^{1}H δ (ppm)	$^{1}J_{CH}$ (Hz)
W(NAr′)(C_3H_6)(biphen)	86.9 (99.2[c])	4.02, 3.91	136 (155[c])
18b[a]	79.4 (87.4[c])	3.83, 3.00	149 (156[c])
	3.7 (−3.2[c])	0.70, 0.10	149 (152[c])
W(NAr)(C_3H_6)(biphen)	73.5 (99.1[c])	3.39, 3.20	147 (153[c])
18a[b]	69.1 (86.5[c])	3.49, 2.47	145 (151[c])
	9.0 (−2.6[c])	1.77, 1.10	143 (147[c])

[a] All values are reported at 20 °C in C_6D_6 unless otherwise stated; Ar′ = 2,6-$Me_2C_6H_3$. [b] All values are reported at 20 °C in toluene-d_8 unless otherwise stated; Ar = 2,6-*i*-$Pr_2C_6H_3$. [c] Data are reported at −80 °C in toluene-d_8.

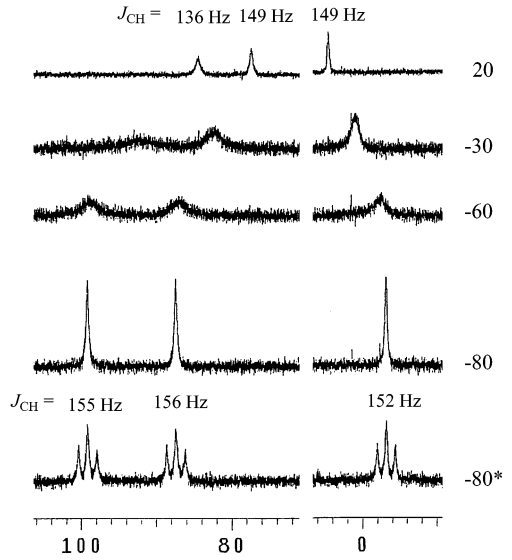
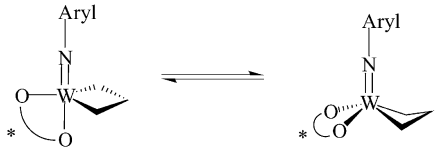


Figure 6. Variable-temperature ^{13}C NMR (125 MHz) spectra of W(NAr′)($CH_2CH_2CH_2$)(Biphen) (**18b**) in toluene-d_8. *J_{CH} values were determined from the ^{1}H-coupled ^{13}C NMR spectrum. (Units are ppm; all temperatures are reported in °C.)

Hz. The positions of the three sharp resonances observed at −80 °C are characteristic of a trigonal bipyramidal (TBP) tungstacyclobutane complex.[14] Unfortunately, the resonances at −80 °C were still too broad to observe $^{13}C-^{13}C$ coupling. On the basis of previous studies of tungstacyclobutane complexes,[14] we assign the two downfield resonances to the α carbons and the upfield resonance to the β carbon in a TBP species. A resonance for free ethylene could be observed at 123 ppm in all ^{13}C NMR spectra; therefore, ethylene is not a part of the temperature-dependent process observed in Figure 6.

When a sample of **2a** in toluene-d_8 was exposed to 2.5 equiv of $^{13}C_2H_4$, an unsubstituted tungstacyclobutane complex analogous to **18b**, W(NAr)(C_3H_6)(Biphen) (**18a**), was observed. Three broadened resonances centered at 73.5, 69.1, and 9.0 ppm were observed in the ^{13}C spectrum at 20 °C. A list of all of the correlated protons of **18a**, obtained from a $^{1}H-^{13}C$ HMQC experiment, is summarized in Table 5. Temperature-dependent behavior similar to that of **18b** was observed when **18a** was cooled to −80 °C. The chemical shifts (99.1, 86.5, −2.6 ppm) and J_{CH} values (153, 151, 147 Hz) of the three sharp resonances observed at −80 °C are characteristic of a TBP tungstacyclobutane complex.[14]

We ascribe the temperature dependence in the proton and the carbon NMR spectra of **18a** and **18b** to the same phenomenon. At the lowest temperature, each tungstacyclobutane complex is essentially a pure TBP species. As the sample is warmed, increasing amounts of a square pyramidal species forms (SP-**18**; eq 2) and the two metalacycles begin to interconvert on the NMR time scale starting at approximately −60 °C. Free

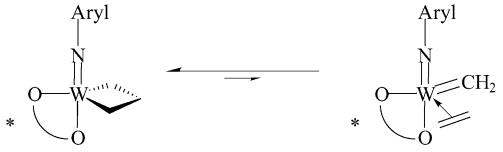


(2)

TBP-**18** SP-**18**

ethylene is *not* involved in the temperature-dependent process. The square pyramidal form cannot be observed at low temperature, as too little is present, or above −60 °C, as it is interconverting with the TBP form. Above −30 °C, the three metalacycle carbon resonances (Figure 6) sharpen and shift toward the 20−40 ppm region, where resonances for α and β carbon atoms in unsubstituted square pyramidal metalacycles are found.[14] On the basis of the average chemical shifts at 20 °C, we estimate that roughly 25% of the SP form is present in the mixture at 20 °C. At 20 °C, the average chemical shifts of the three broad labeled metalacycle carbon resonances of **18a** are nearly 10 ppm closer to the 20−40 ppm region than the resonances in **18b**, suggesting a more significant contribution of SP-**18a** to the interconverting mixture of tungstacyclobutane complexes (TBP-**18a** and SP-**18a**). It is not possible to obtain spectra at temperatures significantly above 20 °C, as the metalacycles decompose (vide infra). It should be noted that the two α carbons and the β carbon retain their identities when the two metalacycle isomers are interconverting rapidly, which is inconsistent with interconversion via loss of ethylene.

A second possible explanation for the temperature dependence is that the TBP metalacycle is in equilibrium with a distinct ethylene/methylene complex (eq 3). This possibility must be



(3)

TBP-**18**

considered in view of the fact that high oxidation state alkene/alkylidene complexes have been observed in cationic tungsten systems explored by Osborn and Kress.[35] If a methylene/ethylene complex were an intermediate, the ethylene could not rotate by 180° at a rate of the order of the NMR time scale at 20 °C, or else C_α and C_β would exchange. On the other hand, a nonrotating ethylene seems unlikely, because cycloheptene rotation was found to be rapid above 240 K in the tungsten system studied by Osborn and Kress.[35] Therefore, we prefer the explanation that the temperature dependence involves the formation of increasing amounts of a SP tungstacyclobutane complex and the interconversion of it with the TBP form.

Other Species Observed in Reactions between 2a or 2b and ^{13}C-Labeled Ethylene. Several other species are present

(35) Kress, J.; Osborn, J. A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1585.

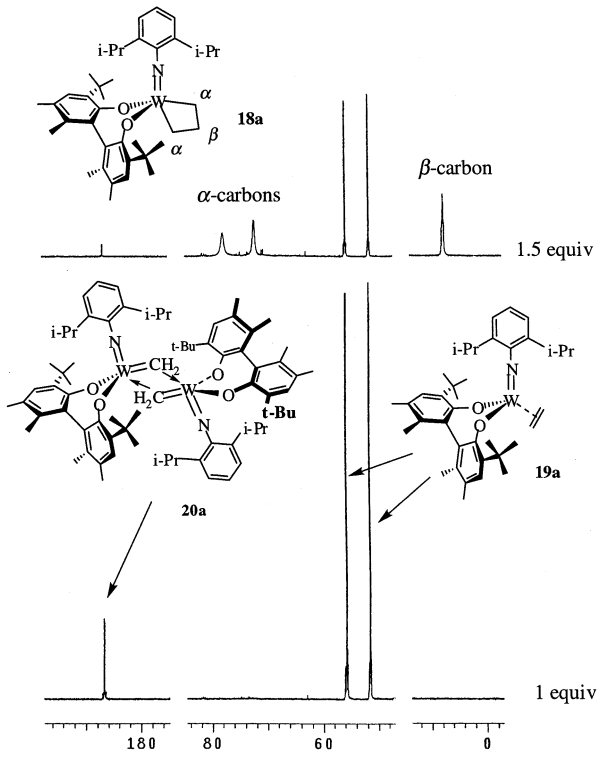


Figure 7. Observation of a mixture of **18a**, **19a**, and **20a** generated by treating **2a** with 1 or 1.5 equiv of $^{13}C_2H_4$.

in reactions in which **18a** and **18b** are observed. They can be identified most readily by employing $^{13}C_2H_4$.

When 1 equiv of $^{13}C_2H_4$ was added to a sample of *rac*-**2a**, a singlet was observed for the ^{13}C label in the initial cleavage product, $PhMe_2CCH{=}^{13}CH_2$, along with resonances for two other compounds (Figure 7). The major species gives rise to a set of two doublets at 55.4 ($^1J_{WC}$ = 59.0, $^1J_{CC}$ = 6.9, $^1J_{CH}$ = 132 Hz) and 51.3 ($^1J_{WC}$ = 46.1, $^1J_{CC}$ = 6.9, $^1J_{CH}$ = 133 Hz) ppm. Both resonances can be ascribed to methylene carbons that are through-bond coupled to protons at 2.93 (δ 55.4), 2.48 (δ 51.3), 1.23 (δ 51.3), and 1.21 (δ 55.4) ppm, according to a $^1H-^{13}C$ HMQC experiment. On the basis of comparison with a crystallographically characterized ethylene complex of this general type and extensive NMR studies of that species,[36] these doublets are assigned to the ethylene complex, **19a** (Scheme 4). (In Scheme 4, the compound number is a generic number that refers to the species derived either from **2a** or from **2b**. All compounds except **20** are drawn with the (*S*)-Biphen ligand, although both enantiomers are present.) Note that for **19a** to be formed quantitatively, 1.5 equiv of ethylene would be required.

The second (minor) compound gives rise to a singlet at 185.9 ppm. In the ^1H-coupled ^{13}C spectrum, this resonance becomes two overlapping doublets as a consequence of that carbon being coupled to two inequivalent protons by different amounts ($^1J_{CH}$ = 148, 131 Hz). The two correlated proton resonances were located at 8.20 and 7.37 ppm; each was split into two resonances because of ^{13}C labeling. Importantly, *two* sets of tungsten satellites were observed ($^1J_{WC}$ = 78.9, 36.7 Hz) in the ^1H-decoupled ^{13}C spectrum (Figure 8), which is possible only if the carbon is coupled to two different ^{183}W nuclei. The

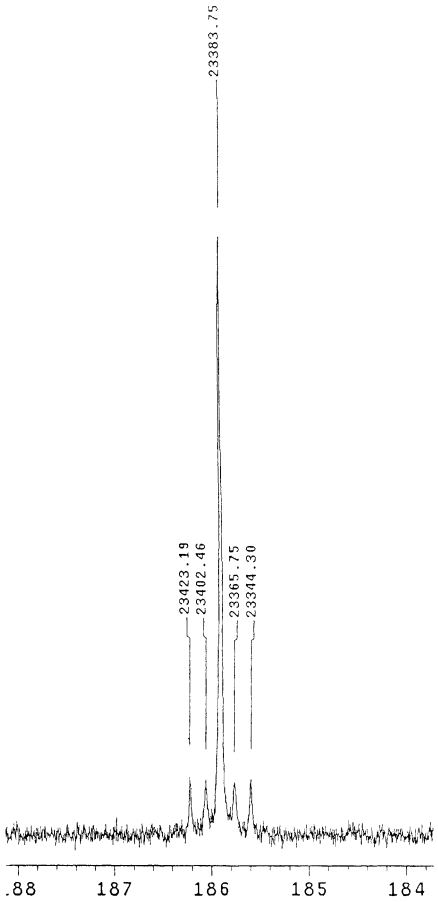


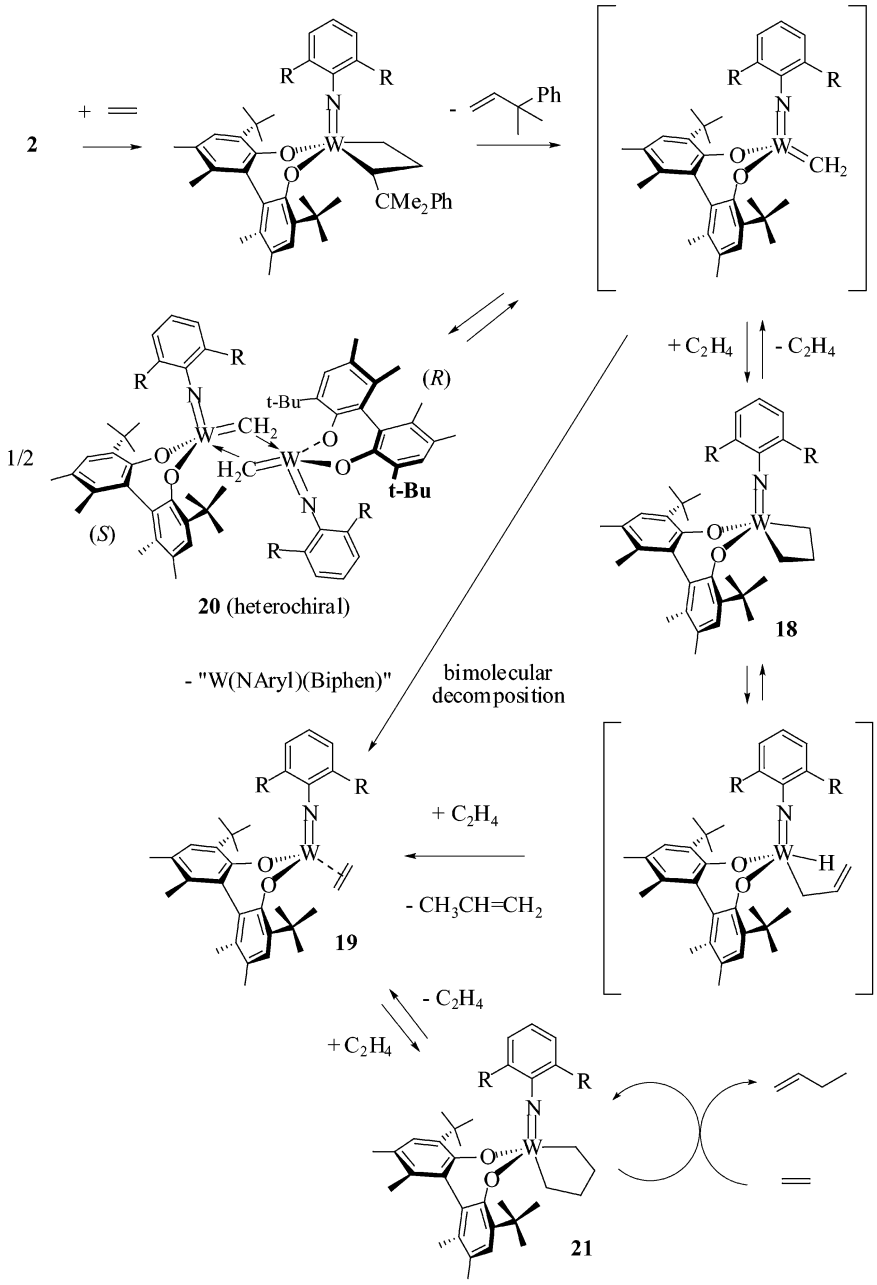
Figure 8. ^{13}C spectrum (125 MHz) of labeled **20a** showing two sets of ^{13}C satellites for the methylene carbon atom.

relatively large chemical shift and low $^1J_{WC}$ values are consistent with that species being a dimeric complex, [W(NAr)(Biphen)-$(CH_2)]_2$ (**20a**; Figure 7 and Scheme 4), that contains either a C_2 axis or a center of inversion that makes the two methylenes equivalent. In Scheme 4, compound **20** has been drawn with the methylene behaving as a "donor" toward the second tungsten on one (face "A") of the two possible CNO faces, where donors are known to bind. The left half of the molecule contains the (*S*)-Biphen^{2-} ligand and the methylene coordinated through face A, while the right half of the molecule contains the (*R*)-Biphen^{2-} ligand and the methylene coordinated through face B. As drawn, **20** is a heterochiral species that contains an inversion center that makes the two methylene carbons equivalent. Proposals concerning the mechanism of formation of **19a** and other species (Scheme 4) will be deferred to the discussion section. The mixture of **19a** and **20a** was stable for at least 12 h. Because dimeric methylene complexes of this general type have never been observed before, it is difficult to know if the different couplings to tungsten (78.9 and 36.7 Hz) in **20a** are characteristic of a dimeric methylene complex and therefore if they would be present even if two symmetric alkoxide ligands were present on each metal, or whether they are a consequence solely of the unsymmetric nature of the biphenolate ligands in **20a**.

When 0.92 equiv of $^{13}C_2H_4$ was added to a sample of (*S*)-**2a**, almost exclusively **19a** was observed. In particular, *no resonance for* **20a** *was observed*. The failure to observe any **20a** in the enantiomerically pure system leads us to conclude

(36) The isolated ethylene complex that has been crystallographically characterized is Mo(*N*-2,6-$Cl_2C_6H_3$)(C_2H_4)(Biphen) (Jamieson, J.; Aeilts, S.; Tsang, P., unpublished results). These results will be published in due course.

Scheme 4. A Plausible Relationship between Compounds Formed from Ethylene



that the **20a** observed in the racemic system is, in fact, a *heterochiral* dimer. (See Discussion section.)

When 1.5 equiv of $^{13}C_2H_4$ was added to a sample of *rac*-**2a**, broad resonances characteristic of tungstacyclobutane complex **18a** were observed in addition to resonances for **19a** and a trace of **20a** (Figure 7).

When 2.5 equiv of $^{13}C_2H_4$ was added to **2a** in toluene-d_8, largely **18a** was observed. With time, **18a** appears to decompose, and propylene (with resonances at 134, 116, and 20 ppm), 1-butene (with resonances at 141, 114, 27, 14 ppm), and a compound that is characterized by two small sets of doublets at 78 ($^1J_{CC}$ = 35.4 Hz, $^1J_{CH}$ = 126 Hz) and 77 ($^1J_{CC}$ = 34.7 Hz, $^1J_{CH}$ = 127 Hz) ppm and a non first-order multiplet at 37 ppm are formed. The doublets and multiplet are ascribed to an unsubstituted tungstacyclo*pentane* complex (**21a**; Scheme 4). 1-Butene appeared to form more rapidly than propylene, although the amounts were comparable. A maximum of 1 equiv of propylene can be generated, while 1-butene can be generated catalytically.

Introduction of >3 equiv of $^{13}C_2H_4$ into a sample of **2a** led immediately to the formation of some **18a**, along with propylene, 1-butene, and **21a**. Thereafter, ethylene was slowly and catalytically dimerized to 1-butene. The resonances for **20a** remained weak throughout this dimerization process.

When a sample of **2b** in C_6D_6 was exposed to 2−4 equiv of $^{13}C_2H_4$, the **18b** that was formed was found to be stable for at least 12 h at room temperature; resonances characteristic of free propylene were observed to grow in slowly (over a period of days) thereafter. However, propylene was observed immediately when **18b** was prepared using >4 equiv (e.g., 6 or 8 equiv) of labeled ethylene. After 24 h at 20 °C, a mixture of **18b**, propylene, 1-butene, and an unsubstituted tungstacyclopentane complex (**21b**) was clearly observed (Scheme 4). Two sets of doublets, which can be ascribed to the two α carbons of **21b**,

Table 6. Chemical Shift and Coupling Values for Tungsten Methylene Dimer, Ethylene Adduct, and Unsubstituted Metalacyclopentane Complexes

	^{13}C δ (ppm)	^{1}H δ (ppm)	$^{1}J_{CC}$ (Hz)	$^{1}J_{CH}$ (Hz)
$[W(NAr)(CH_2)(biphen)]_2$ **20a**[a,b]	185.9	8.20, 7.37		148, 131
$W(NAr)(C_2H_4)(biphen)$ **19a**[c]	55.4[c]	2.93, 1.21	6.9	132
	51.3[c]	2.48, 1.23	6.9	133
$W(NAr')(C_2H_4)(biphen)$ **19b**[d]	56.2	2.92, 1.22	7.0	132
	51.2	2.60, 1.26	7.0	135
$W(NAr')(C_4H_8)(biphen)$ **21b**[d]	79.9	3.43, 2.93	34.5	125
	76.0	3.39, 3.04	34.3	125
	38.5	3.15, 3.15	34.5, 33.9	126
	37.2	3.10, 2.99	34.3, 33.9	125

[a] All values are reported at 20 °C in toluene-d_8 unless otherwise stated; Ar = 2,6-*i*-$Pr_2C_6H_3$. [b] $^{1}J_{WC}$ values were determined from ^{13}C NMR; $^{1}J_{WC}$ = 78.9, 36.7 Hz. [c] $^{1}J_{WC}$ = 59.0 (δ 55.4), 46.1 (δ 51.3) Hz. [d] All values are reported at 20 °C in C_6D_6 unless otherwise stated; Ar′ = 2,6-$Me_2C_6H_3$.

were observed at 79.9 ($^{1}J_{CC}$ = 34.5 Hz, $^{1}J_{CH}$ = 125 Hz) and 76.0 ($^{1}J_{CC}$ = 34.3 Hz, $^{1}J_{CH}$ = 125 Hz) ppm. Two sets of triplets which can be ascribed to the two β carbons of **21b** were observed at 38.5 ($^{1}J_{CC}$ = 34.5, 33.9 Hz, $^{1}J_{CH}$ = 126 Hz) and 37.2 (J_{CC} = 34.3, 33.9 Hz, $^{1}J_{CH}$ = 125 Hz) ppm. Homonuclear ^{13}C gCOSY and $^{1}H-^{13}C$ HSQC experiments completely supported the tungstacyclopentane proposal; all data are gathered in Table 6. Upon close inspection of the ^{13}C NMR spectrum, two small doublets, which can be ascribed to a tungsten ethylene adduct **19b**, were observed at 56.2 ($^{1}J_{CC}$ = 7.0 Hz, $^{1}J_{CH}$ = 132 Hz) and 51.2 ($^{1}J_{CC}$ = 7.0 Hz, $^{1}J_{CH}$ = 135 Hz) ppm. The chemical shifts of the correlated protons are very similar to those observed for ethylene adduct **19a** (Table 6).

In the sample in which **2b** was treated with $^{13}C_2H_4$, the resonances for 1-butene slowly intensified at the expense of that for ethylene. Warming the reaction mixture to 60 °C for 10 h led to the disappearance of **18b** and an increase in the intensity of propylene, 1-butene, and **21b** with respect to the solvent internal standard; a large decrease in the intensity of the ethylene resonance was also observed. Some **21b** was still observable after all of the solvent and ethylene were removed and fresh C_6D_6 was added. Upon standing this solution at room temperature for 24 h, we observed a small amount of labeled ethylene. Warming the sample at 60 °C for 8 h resulted in a decrease in the intensity of the resonances for **21b** and a small increase in the amount of free ethylene, although **21b** was still the major labeled product.

Discussion

We were not surprised by the stability of tungstacyclobutane complexes in general, at least relative to molybdacyclobutane complexes, as this is the trend that has been observed for imido bisalkoxide complexes of molybdenum and tungsten that have been investigated previously.[14] However, we were surprised by the relatively high stability of what must be highly strained **13** (Figure 2). We have assumed in the Mo-catalyzed ring-closing of **9** that the molybdacycle analogous to **13** is the *least* stable metalacycle in the catalytic cycle.[26f] That is no longer likely to be the case. It is easier to understand why **12** is relatively unstable in view of the presence of two α substituents. In a species in which the CMe_2Ph group points toward the imido ligand, steric interaction between the diisopropylphenylimido group and the CMe_2Ph group would encourage loss of 3-methyl-3-phenyl-1-butene and formation of **13**. We also were surprised to find that by simply raising the temperature of a metathesis reaction that even unsubstituted metalacycles would break up to give an alkylidene at a rate fast enough to make metathesis by tungsten viable.

Although several unsubstituted molybdacyclobutane complexes have been observed previously, none has been stable enough to isolate.[17,37] The molybdacycle formed upon treating $Mo(NAr)(CH\text{-}t\text{-}Bu)[OCMe(CF_3)_2]_2$ with ethylene is stable at 25 °C under ethylene for hours, but it decomposes over a period of ~12 h under ethylene to yield a molybdacyclopentane complex, $Mo(NAr)[OCMe(CF_3)_2]_2(C_4H_8)$ (δ C_α = 76.8 ppm, δ C_β = 38.6 ppm, $J_{C\alpha C\beta}$ = 32 Hz, $J_{C\alpha H}$ = 128 Hz, $J_{C\beta H}$ = 141 Hz; cf. 79.9, 76.0, 38.5, and 37.2 ppm in **21b**; Table 6).[17] On the basis of the chemical shifts for the α carbon atoms at 104.1 ppm and the β carbon atom at −2.28 ppm, and by analogy with crystallographically characterized tungstacyclobutane complexes,[14] $Mo(NAr)[OCMe(CF_3)_2]_2(C_3H_6)$ was proposed to have a trigonal bipyramidal structure. Treatment of $Mo(NAr)(CH\text{-}t\text{-}Bu)(OAr)_2$ (Ar = 2,6-*i*-$Pr_2C_6H_3$) with ethylene yields primarily (95%) square pyramidal $Mo(NAr)(OAr)_2(C_3H_6)$ (δ C_α = 39.9 ppm, δ C_β = 26.5 ppm) mixed with 5% trigonal bipyramidal $Mo(NAr)(OAr)_2(C_3H_6)$ (δ C_α = 100.1 ppm, δ C_β = −0.7 ppm). Addition of ethylene to $Mo(NAr)(CH\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2$ was proposed to yield a third molybdacyclobutane complex, square pyramidal $Mo(NAr)(O\text{-}t\text{-}Bu)_2(C_3H_6)$ (δ C_α = 34.9 ppm, δ C_β = 29.1 ppm, J_{CC} = 32 Hz, J_{CH} = 140 and 129 Hz) in low yield (~25%).[37] $Mo(NAr)(O\text{-}t\text{-}Bu)_2(C_3H_6)$ decomposed to yield crystallographically characterized $[Mo(NAr)(O\text{-}t\text{-}Bu)_2]_2$, in which the imido ligands bridge symmetrically between the metals.

Molybdacyclobutane complexes have also been observed recently in binaphtholate imido systems.[31] Evidence suggested that these molybdacyclobutane complexes decomposed (hours to days) in two ways, either by rearrangement of the metalacycle to yield propylene or by bimolecular decomposition of the methylene complex formed upon loss of ethylene from the metalacycle. The decomposition product was not identified in this case. It is important to note that decomposition appeared to be accelerated in the presence of ethylene (possibly by ethylene-induced β hydride rearrangement of the metalacycle) and in the absence of ethylene (by loss of ethylene from the metalacycle and decomposition of the resulting methylene species).

One of the interesting results reported here is the observation of **20**. In Scheme 4, **20** is drawn as a heterochiral dimer; that is, in the left half, the $Biphen^{2-}$ ligand has the *S* configuration, and the methylene "donor" is bound to one of the two possible CNO faces (say face A), while in the right half, the $Biphen^{2-}$ ligand has the *R* configuration, and the methylene "donor" is bound to the other possible CNO face (B). As drawn, **20** then has the configuration "SABR" and an inversion center. The homochiral dimer would have the configuration SAAS and a C_2 axis that passes through the W_2C_2 ring. Other possible dimers in a racemic system would have configurations SABS, SABR, etc., and in them the methylene carbons would *not* be equivalent. The proposal that **20** is a heterochiral dimer is consistent with the following: (i) donors are known to bind to Mo complexes through a CNO face in a manner that is determined solely by

(37) Robbins, J.; Bazan, G. C.; Murdzek, J. S.; O'Regan, M. B.; Schrock, R. R. *Organometallics* **1991**, *10*, 2902.

the chirality of the biphenolate or binaphtholate ligand in the six known adducts;[34] (ii) only one methylene carbon atom resonance is observed in **20**; and (iii) **20** was not observed when reactions were carried out with (*S*)-**2a**. Therefore, we suspect that the homochiral analogue of **20** is unstable and, in particular, it is unstable with respect to decomposition to yield **19** and "W(NAryl)(Biphen)."

It is important to understand the details of the reaction between **2a** or **2b** and ethylene and how various species that are formed in the presence of ethylene decompose, however qualitative those details might be at this stage. The following is only one of several consistent scenarios, but it provides a point of departure and a basis for discussion and future investigations. In the ethylene reactions, there will be issues concerning the mixing of ethylene throughout the solution versus reactions in one portion of the solution. These issues will have to be ignored for now, along with issues concerning the TBP or SP nature of various metallacycles, syn versus anti isomer interconversion, and relative rates of reaction of syn and anti isomers.

We propose that the (unobserved) initial metalacycle that is formed upon reaction of **2** (**a** or **b**) with ethylene readily loses 3-methyl-3-phenyl-1-butene to give $PhMe_2CCH{=}CH_2$ and unobservable monomeric W(NAryl)(Biphen)(CH_2) (Scheme 4). W(NAryl)(Biphen)(CH_2) then reacts bimolecularly with itself to give either heterochiral **20** (perhaps entirely reversibly) or to give **19** and "W(NAryl)(Biphen)" irreversibly via homochiral **20** (not observable). "W(NAryl)(Biphen)" then rapidly scavenges any remaining ethylene that is present to yield more **19**. The mechanism of formation of **19** is analogous to that proposed for the formation of $Cp_2Ta(CH_2CH_2)Me$ upon decomposition of $Cp_2Ta(CH_2)Me$ in the presence of ethylene.[38]

In the presence of a larger amount of ethylene, much of the W(NAryl)(Biphen)(CH_2) is captured by ethylene to give **18**. Compound **18** is quite stable toward rearrangement to give propylene in the absence of ethylene. Although it can lose ethylene to regenerate W(NAryl)(Biphen)(CH_2), that process is relatively slow at the temperatures employed in the NMR experiments, and the equilibrium lies far toward **18**. We might propose that intramolecular rearrangement of a tungstacyclobutane complex would proceed via an intermediate allyl hydride (Scheme 4) that is in equilibrium with **18**. We believe that it is this allyl hydride that is transformed into **19** and propylene (up to 1 equiv) upon reaction with ethylene. This is the reason more propylene is generated if a relatively large amount of ethylene is added initially. This proposal is analogous to that published recently in which acceleration of β hydride rearrangement of unsubstituted molybdacyclobutane complexes has been observed in similar types of complexes.[31]

Compound **19** can react with ethylene to give **21**, possibly in an equilibrium that lies largely toward **21**, and **21** can rearrange slowly to give "W(NAryl)(Biphen)(1-butene)", from which 1-butene is displaced by ethylene, etc., thereby allowing 1-butene to be formed catalytically. Documented examples of alkene dimerization via a metalacyclopentane intermediate are rare. Perhaps the best examples are monocyclopentadienyl tantalacyclopentane complexes.[39−43] A metalacyclopentane intermediate has also been proposed in the relatively efficient dimerization of ethylene to 1-butene when ethylene is added to $Ta(CH\text{-}t\text{-}Bu)_2(CH_2\text{-}t\text{-}Bu)(PMe_3)_2$.[44] Therefore, it is not surprising that tungstacyclopentane complexes can rearrange to give 1-butene. What we do not know is whether the formation of 1-butene from **21** is also accelerated in the presence of ethylene.

How rapidly the reactions in Scheme 4 and analogous reactions involving other alkylidenes lead to catalyst decomposition in real catalytic reactions in which ethylene is formed is not known at present. The answer is likely to depend on conditions. If it is true that ethylene in fact promotes decomposition of **18**, then carrying out metathesis reactions in which ethylene is generated in a closed reaction vessel would lead to low rates (because little W(NAryl)(Biphen)(CH_2) is available from **18**) and catalyst decomposition (by ethylene-induced decomposition of **18**). It should be noted that most of the ethylene would be evolved from solution in a vented reaction vessel, especially if that reaction is heated. Therefore, heating tungsten-catalyzed reactions in vessels from which ethylene can escape might turn out to be relatively beneficial in the long run for long-lived metathesis by tungsten complexes. Compound **18** is clearly a central feature of tungsten-catalyzed metathesis chemistry; it is essentially a way of sequestering W(NAryl)(Biphen)(CH_2) in a usable form and preventing bimolecular decomposition, *if* rearrangement of **18** to give propylene is slow under the reaction conditions relative to loss of ethylene to regenerate W(NAryl)(Biphen)(CH_2).

The tungsten systems examined here and the analogous molybdenum systems show many similarities. In both Mo and W systems, rearrangement of unsubstituted metalacyclobutane complexes to yield propylene appears to be faster in the sterically more crowded NAr complexes and possibly accelerated in the presence of ethylene. Two notable differences between tungsten and molybdenum that have surfaced so far are that **20** can be observed in the tungsten system and that metalacyclopentane complexes formed in the tungsten systems act as catalysts for the (slow) formation of 1-butene. It should be noted that if 1-butene builds up before the metathesis reaction of interest is complete, then the desired reaction could be complicated to a significant degree by metathesis reactions that involve 1-butene.

We assume that no alkylidene can be re-formed once **19** or **21** forms and that catalytic metathesis therefore ceases. However, it is now known that an olefin complex can rearrange to an alkylidene in high oxidation state tantalum[45−47] and niobium[48] chemistry. Therefore, we cannot exclude the possibility completely at this stage that some tungsten olefin complexes can rearrange to alkylidene complexes under certain conditions.

Finally, we do not know the nature of the final decomposition product or products in the tungsten metathesis systems. At this

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stage, we assume that a W(IV) complex that contains bridging imido ligands is formed from "W(NAryl)(Biphen)", as has been documented in one molybdenum system, and that this dimeric species does not readily react with ethylene to give **19**.[37] We also do not know how reactions involving other types of alkenes or donor functionalities might alter decomposition pathways.

Both tungsten(VI)[49] and molybdenum(VI)[50,51] phenylimido dineopentyl and neopentylidene complexes (as PMe_3 adducts) have been prepared that contain bisamido ligands of the type $[o\text{-}(Me_3SiN)_2C_6H_4]^{2-}$. The tungsten dineopentyl complex will react slowly with ethylene at temperatures above 70 °C to give neopentane (from the initial α hydrogen abstraction reaction), *tert*-butylethylene (from the reaction of the intermediate neopentylidene complex with ethylene), and a structurally characterized (distorted square pyramidal) tungstacyclopentane complex with carbon resonances at 61.25 (C_α) and 35.23 ppm (C_β). These chemical shifts are similar to what we have found in the complexes described here. In reactions between W(NPh)[*o*-$(Me_3SiN)_2C_6H_4$](CH-*t*-Bu)(PMe_3) and ethylene, the initial α *tert*-butyl-substituted tungstacyclobutane complex was observed in solution, as were the unsubstituted tungstacyclobutane and ethylene complexes. All were converted into the tungstacyclopentane complex with time in the presence of ethylene. These results are similar to what we propose in Scheme 4, although the reactions of the bisamido complexes are much slower than those in the biphenoxide complexes as a consequence of deactivation of the metal by σ and π electron donation from the amido nitrogens. (Molybdenum imido alkylidene complexes that contain a *N*,*N*′-disubstituted-2,2′-bisamido-1,1′-binaphthyl ligand also were shown to be unreactive toward ethylene and even benzaldehyde at room temperature.[52]) However, in the Boncella complexes, the tungstacyclobutane complex did not appear to rearrange to propylene, and the tungstacyclopentane complex did not appear to rearrange to 1-butene. Therefore, it appears that both metathesis and β hydride processes are slowed in bisamido complexes relative to bisphenoxide complexes.

Tungsten has potential as an asymmetric metathesis catalyst in the right circumstances for several reasons. First, no five-coordinate tungstacyclobutane complex that we have observed so far is too stable for ready turnover in ring-closing reactions at some readily accessible temperature where catalyst decomposition is not rapid. Second, the enantioselectivities and conversions can be high. Third, there are some hints that tungsten catalyst systems may be more stable at higher temperatures than molybdenum catalyst systems, and possibly longer lived, and that substrates that are resistant to reactions with Mo catalysts therefore may be transformed successfully with W catalysts. We look forward in future studies to an exploration of asymmetric reactions involving viable substrates by the catalysts described here, and others. We also hope to devise conditions that would allow us to isolate and structurally characterize **20** (especially), or (more realistically) **19** or **21**, or related species. If the nature of the metal (Mo or W) along with the diolate and the imido group is a variable that must be considered in a search for a suitable catalyst for a given substrate, then the number of available catalysts in theory increases from approximately two dozen (for Mo) to twice that.

Experimental Section

General. All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon. Commercially available chemicals were obtained from Aldrich Co. or Lancaster Synthesis. 2,6-Dimethylphenyl isocyanate was stirred over P_2O_5 for 24 h, vacuum distilled, and stored over molecular sieves (4 Å) at −25 °C. Liquid reagents were distilled from CaH_2 under nitrogen and stored over molecular sieves (4 Å) before use. Ether, pentane, toluene, benzene, THF, and DME were dried with columns of activated alumina. Dichloromethane was distilled from calcium hydride. Benzyl potassium,[28,29] $W(O)Cl_4$, $W(NAr')Cl_4$, and $W(NAr)(CHCMe_2Ph)(OTf)_2(DME)$[27,53] were synthesized according to published procedures.

Conversions were determined by ^{1}H NMR of the unpurified reaction mixtures. Enantiomeric ratios were determined by chiral GLC analyses with an Alltech Associates Chiraldex GTA column (30 m × 0.25 mm) or Betadex 120 column (30 m × 0.25 mm) in comparison with authentic samples. Microanalyses were performed by Kolbe Microanalytical Laboratories (Mülheim an der Ruhr, Germany).

Representative Procedures for Ring-Closing Reactions in Tables 1 and 2. Diallyl sulfonamide (25 mg, 0.10 mmol) was loaded in a J-Young tube. W(NAr′)($CHCMe_2Ph$)(Biphen) (12 mg) was dissolved in benzene-d_6 (1.5 mL) to obtain a 0.01 M catalyst solution. The catalyst solution (0.5 mL) was added to the substrate via syringe, and the J-Young tube was sealed, attached to a dinitrogen line, and immersed into a 60 °C oil bath. The tube was opened to the dinitrogen line, and the ethylene was vented to a fast flowing stream of dinitrogen through the line. Periodically, the tube was resealed, and the reaction was monitored by ^{1}H NMR at room temperature.

Representative Procedure for Reactions Involving Ethylene. A toluene-d_8 solution (0.6 mL) of W(NAr)($CHCMe_2Ph$)(Biphen) (20 mg) was loaded in a J-Young tube, sealed, and attached to a gas transfer setup equipped with a 760 Torr gauge. The volume of the setup was calibrated immediately before the experiment (24.23 mL). The sample was degassed by freeze−pump−thaw and resealed with the J-Young cap. Ethylene (45 Torr) was passed into the setup by slowly opening the regulator attached to the ethylene tank. All of the ethylene in the setup was condensed into the frozen sample (with liquid nitrogen) by opening the J-Young seal. The sample was then brought to the spectroscopy facility under liquid nitrogen before it is thawed and immediately inserted into the NMR probe.

***rac*-W(NAr)($CHCMe_2Ph$)(Biphen)(THF) (*rac*-2a-THF).** Potassium hydride (470 mg, 11.7 mmol) was added in small portions to a solution of H_2(Biphen) (1.17 g, 3.3 mmol) in THF (20 mL). The solution was cooled to −20 °C after being stirred for 2 h and was added to a chilled solution (−20 °C) of W(NAr)($CHCMe_2Ph$)$(OTf)_2$(DME) (2.9 g, 3.3 mmol) in THF (20 mL). The reaction mixture was warmed to room temperature and stirred for 12 h. Concentration in vacuo gave a brown solid, which was extracted with pentane (4 × 10 mL) and filtered. The filtrate was concentrated in vacuo to approximately 5 mL. Upon being cooled at −25 °C, a yellow-brown crystalline solid was obtained, yield 2.05 g (68%). ^{1}H NMR (C_6D_6): δ 11.04 (s, 1, anti W=CH), 7.90 (s, 1, syn W=CH, J_{WH} = 14.2 Hz, J_{CH} = 113 Hz), 7.50 (d, 2, aryl, J_{HH} = 7.6 Hz), 7.41 (s, 1, aryl), 7.21 (t, 2, aryl, J_{HH} = 7.8 Hz), 7.04 (t, 1, aryl, J_{HH} = 7.4 Hz), 7.01 (d, 2, aryl, J_{HH} = 7.3 Hz), 6.93 (m, 1, aryl), 3.61 (sept, 2, C*H*$(CH_3)_2$, J_{HH} = 6.7 Hz), 3.57 (s, br, 4, THF), 2.10 (s, 3, Ar−CH_3), 2.03 (s, 3, Ar−CH_3), 1.87 (s, 3, CHC(C*H*$_3$)$_2$Ph), 1.69 (s, 3, Ar−CH_3), 1.61 (s, 3, Ar−CH_3), 1.60 (s, 9, C$(CH_3)_3$), 1.50 (s, 9, C$(CH_3)_3$), 1.17 (s, 3, CHC(C*H*$_3$)$_2$Ph), 1.14 (d, 6, CH(C*H*$_3$)$_2$, J_{HH} = 6.7 Hz), 0.92 (d, 6, CH(C*H*$_3$)$_2$, J_{HH} = 6.7 Hz). ^{13}C NMR (100 MHz,

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C_6D_6): δ 245.5, 153.4, 153.0, 152.2, 151.9, 144.9, 139.7, 137.7, 135.9, 135.2, 131.7, 131.5, 131.0, 130.5, 129.5, 129.4, 127.0, 126.3, 125.8, 123.0, 51.1, 35.6, 35.3, 34.6, 30.5, 30.3, 28.5, 25.7, 24.3, 24.1, 20.4, 20.3, 16.8, 16.3. Anal. Calcd for $WC_{50}H_{69}NO_3$: C, 65.57; H, 7.59; N, 1.53. Found: C, 65.79; H, 7.40; N, 1.56.

***rac*-W(NAr)(CHCMe$_2$Ph)(Biphen) (*rac*-2a).** To a 25 mL scintillation vial was added W(NAr)(CHCMe$_2$Ph)(Biphen)(THF) (500 mg, 0.55 mmol). The complex was dissolved in toluene (5−10 mL), and the solution was filtered through Celite. All volatiles were removed in vacuo. The sample was redissolved in toluene (5−10 mL), and all volatiles were removed. In the final cycle, benzene (5−10 mL) was added, and all volatiles were removed in vacuo to obtain a bright orange-yellow dry foam, yield 480 mg (96%). ^{1}H NMR (C_6D_6): δ 10.76 (s, br, 1, anti W=CH), 7.91 (s, 1, syn W=CH, J_{WH} = 14.11 Hz, J_{CH} = 113.36 Hz), 7.52 (d, 2, aryl), 7.43 (s, 1, aryl), 7.23 (t, 2, aryl), 7.18 (s, 1, aryl), 7.06 (t, 2, aryl), 7.02 (d, 2, aryl), 6.95 (t, 1, aryl), 3.63 (sept, 2, C*H*(CH$_3$)$_2$), 2.12 (s, 3, Ar−CH$_3$), 2.04 (s, 3, Ar−CH$_3$), 1.89 (s, 3, Ar−CH$_3$), 1.71 (s, 3, Ar−CH$_3$), 1.63 (s, 3, CHC(C*H*$_3$)$_2$Ph), 1.62 (s, 9, C(CH$_3$)$_3$), 1.52 (s, 9, C(CH$_3$)$_3$), 1.19 (s, 3, CHC(C*H*$_3$)$_2$Ph), 1.16 (d, 6, CH(C*H*$_3$)$_2$), 0.94 (d, 6, CH(C*H*$_3$)$_2$). ^{13}C NMR (125 MHz, C_6D_6): δ 245.8, 153.83, 153.39, 152.55, 152.24, 145.31, 140.11, 138.13, 136.34, 135.57, 132.10, 131.94, 131.43, 130.88, 129.94, 129.82, 128.93, 127.43, 126.71, 126.17, 123.41, 51.45, 36.04, 35.71, 34.97, 31.94, 30.93, 30.72, 28.90, 24.69, 24.46, 20.78, 20.71, 17.20, 16.70. Anal. Calcd for $WC_{46}H_{61}NO_2$: C, 65.45; H, 7.29; N, 1.66. Found: C, 65.58; H, 7.35; N, 1.58.

***(S)*-W(NAr)(CHCMe$_2$Ph)(Biphen) ((*S*)-2a).** Potassium hydride (220 mg, 5.48 mmol) was added in small portions to a solution of (*S*)-H_2(Biphen) (712 mg, 2.01 mmol) in THF (15 mL). After 18 h, the suspension was cooled to −20 °C and added to a chilled solution (−20 °C) of W(NAr)(CHCMe$_2$Ph)(OTf)$_2$(DME) (1.77 g, 2.01 mmol) in THF (15 mL). The brown mixture was warmed to room temperature and stirred for 12 h. Concentration in vacuo gave a brown solid, which was extracted with benzene (3 × 5 mL) and filtered. The filtrate was dried to give a brown foam, yield 1.51 g (89%).

***rac*-W(NAr′)(CHCMe$_2$Ph)(Biphen) (*rac*-2b).** Benzyl potassium (533 mg, 4.1 mmol) was added to a THF (40 mL) solution of *rac*-H_2-(Biphen) (708 mg, 2 mmol). After 15 min, W(NAr′)(CHCMe$_2$Ph)Cl$_2$-(DME) (1.191 g, 2 mmol) was added, and the reaction mixture was stirred for 2 h at room temperature. All volatiles were removed to give a yellow powder which was extracted with benzene (20 mL). The suspension was filtered through Celite, and the residue was washed with additional benzene (30 mL) until colorless. Volatiles were removed in vacuo, and the residue was redissolved in diethyl ether (10 mL). The bright yellow powder precipitated was collected by filtration, yield 1.09 g (69%). ^{1}H NMR (mixture of isomers, $K_{syn/anti}$ = 88): δ 9.06 (s, 1, anti W=CH, J_{WH} = 15 Hz), 7.99 (s, 1, syn W=CH, J_{WH} = 16.5 Hz, J_{CH} = 115 Hz), 7.44 (s, 1, aryl), 7.40 (d, 2, aryl, J_{HH} = 7.5 Hz), 7.17 (s, 1, aryl), 7.14 (t, 2, aryl, J_{HH} = 7.5 Hz), 6.98 (t, 1, aryl, J_{HH} = 7.5 Hz), 6.83 (d, 2, aryl, J_{HH} = 7.5 Hz), 6.74 (t, 1, aryl, J_{HH} = 7.5 Hz), 2.31 (s, 6, Ar−CH$_3$), 2.12 (s, 3, Ar−CH$_3$), 2.00 (s, 3, Ar−CH$_3$), 1.72 (s, 3, Ar−CH$_3$/CHC(C*H*$_3$)$_2$Ph), 1.67 (s, 3, Ar−CH$_3$/CHC(C*H*$_3$)$_2$Ph), 1.60 (s, 3, Ar−CH$_3$/CHC(C*H*$_3$)$_2$Ph), 1.58 (s, 9, C(CH$_3$)$_3$), 1.54 (s, 9, C(CH$_3$)$_3$), 1.33 (s, 3, CHC(C*H*$_3$)$_2$Ph). ^{13}C NMR (125 MHz, C_6D_6): δ 247.70, 155.12, 153.25, 152.67, 152.02, 140.29, 138.32, 136.58, 135.76, 135.48, 132.38, 131.95, 131.28, 130.89, 130.04, 129.86, 128.91, 128.10, 127.30, 126.19, 126.10, 51.75, 36.04, 35.45, 34.91, 33.92, 30.94, 30.85, 20.79, 20.71, 19.60, 17.30, 16.80. Anal. Calcd for $WC_{42}H_{53}NO_2$: C, 64.04; H, 6.78; N, 1.78. Found: C, 64.12; H, 6.71; N, 1.74.

***(S)*-W(NAr′)(CHCMe$_2$Ph)(Biphen) ((*S*)-2b).** To a solution of (*S*)-H_2(Biphen) (357 mg, 1.01 mmol) in THF (10 mL) was added benzyl potassium (262 mg, 2.02 mmol). After 15 min, the suspension was added to a solution of W(NAr′)(CHCMe$_2$Ph)Cl$_2$(DME) (602 mg, 1.01 mmol) in THF (10 mL). The yellow-brown solution was stirred for 2 h and chilled at −20 °C for 12 h. Removal of volatiles in vacuo gave a yellow-brown solid, which was extracted with pentane (3 × 5 mL) and filtered. The filtrate was concentrated in vacuo to give a yellow-brown foam, yield 676 mg (85%).

W(NAr′)(O-*t*-Bu)$_2$Cl$_2$(THF). W(NAr′)Cl$_4$ was recrystallized as a solvent adduct from diethyl ether before use. Lithium *tert*-butoxide (13.1 g, 164 mmol) suspended in diethyl ether (100 mL) was added to a chilled solution (−25 °C) of W(NAr′)Cl$_4$(Et$_2$O) (42.5 g, 82 mmol) in diethyl ether (300 mL) and THF (100 mL) over 20 min. After being stirred for 20 h, the mixture was filtered through Celite; the solid residue was washed with diethyl ether (100 mL) until colorless. All volatiles were removed in vacuo, and the orange solid was extracted with diethyl ether (250 mL). The solution was concentrated to approximately 200 mL and stored at −25 °C for 18 h. Orange crystals were collected by filtration and dried in vacuo, yield 32.3 g (66%). ^{1}H NMR (C_6D_6): δ 6.90 (d, 2, aryl, J_{HH} = 7.8 Hz), 6.58 (t, 1, aryl, J_{HH} = 7.8 Hz), 4.20 (t, br, 4, THF), 3.02 (s, 6, Ar−CH$_3$), 1.46 (s, 18, OC(CH$_3$)$_3$), 1.42 (t, br, 4, THF). ^{13}C NMR (125 Hz, C_6D_6): δ 151.18, 140.29, 128.68, 128.04, 86.65, 71.21, 31.05, 25.79, 21.16. Anal. Calcd for $WC_{20}H_{35}Cl_2NO_2$: C, 40.56; H, 5.96; N, 2.36. Found: C, 40.39; H, 5.88; N, 2.43.

W(NAr′)(O-*t*-Bu)$_2$(CH$_2$CMe$_2$Ph)$_2$. An ether solution of PhMe$_2$-CCH$_2$MgCl (95 mL, 109 mmol, 1.15 M) was slowly added to a cold solution of W(NAr′)(O-*t*-Bu)$_2$Cl$_2$(THF) (32.3 g, 54.6 mmol) in diethyl ether (120 mL, −25 °C). The mixture was stirred for 20 h at room temperature. The mixture was filtered through Celite, and the residue was washed with diethyl ether (100 mL) until colorless. The combined solution was concentrated to approximately 50 mL. Orange needles were observed upon overnight cooling at −25 °C. The crystals were collected by filtration and dried in vacuo, yield 20 g (51%). ^{1}H NMR (C_6D_6): δ 7.55 (d, 4, aryl, J_{HH} = 7.5 Hz), 7.23 (t, 4, aryl, J_{HH} = 7.5 Hz), 7.05 (t, 2, aryl, J_{HH} = 7.5 Hz), 6.92 (d, 2, aryl, J_{HH} = 7.5 Hz), 6.63 (t, 1, aryl, J_{HH} = 7.5 Hz), 2.45 (s, 6, Ar−CH$_3$), 2.21 (s, br, 4, C*H*$_2$CMe$_2$Ph), 1.66 (s, 12, CH$_2$C(C*H*$_3$)$_2$Ph), 1.34 (s, 18, OC(CH$_3$)$_3$). ^{13}C NMR (125 Hz, C_6H_6): δ 156.96, 152.99, 137.50, 128.74, 127.84, 126.29, 126.09, 125.78, 42.09, 33.36, 32.09, 19.98, 14.64. Anal. Calcd for $WC_{36}H_{53}NO_2$: C, 60.42; H, 7.40; N, 1.96. Found: C, 60.58; H, 7.54; N, 2.04.

W(NAr′)(CHCMe$_2$Ph)Cl$_2$(DME) (3b). Phosphorus pentachloride (4.41 g, 21.2 mmol) was added to a rapidly stirring solution of W(NAr′)-(O-*t*-Bu)$_2$(CH$_2$CMe$_2$Ph)$_2$ (14.7 g, 20.6 mmol) in cold (−25 °C) DME (125 mL). After 1 h, all volatiles were removed in vacuo. The residue was extracted in diethyl ether (30 mL), and the orange precipitate was collected by filtration, triturated with diethyl ether (2 × 10 mL), and dried in vacuo, yield 5.4 g (44%). ^{1}H NMR (C_6H_6): δ 10.25 (s, 1, W=CH), 7.71 (d, 2, aryl, J_{HH} = 7.7 Hz), 7.27 (t, 2, aryl, J_{HH} = 7.7 Hz), 7.05 (t, 1, aryl, J_{HH} = 7.7 Hz), 6.86 (d, 2, aryl, J_{HH} = 7.7 Hz), 6.76 (t, 1, aryl, J_{HH} = 7.7 Hz), 3.16 (s, 6, OCH$_3$), 3.12 (s, 4, OCH$_2$), 2.86 (s, 6, Ar−CH$_3$), 1.76 (s, 6, CHC(C*H*$_3$)$_2$Ph). ^{13}C NMR (125 Hz, C_6D_6): δ 282.00, 155.32, 139.97, 128.92, 128.58, 127.13, 127.03, 126.44, 71.94, 62.64, 53.78, 33.00, 21.22.

Procedures for Observation of Intermediates 12 and 13. An NMR tube was charged with *rac*-**2a** (52 mg, 57 μmol) and toluene-d_8 (0.5 mL). The tube was cooled to −78 °C, and triene **9** (8 mg, 53 μmol) was added by syringe. The tube was flame-sealed in vacuo and was immediately inserted into the NMR probe cooled to −60 °C. The sample was warmed to −40 °C to allow for complete consumption of the starting materials. The sample was cooled back to −60 °C after 30 min, and the spectra for **12** were collected. Warming to 0 °C for 15 min resulted in complete decomposition of **12**, and spectra for species **13** were collected at −40 °C. The sample was warmed to 20 °C, and the decomposition of **13** was monitored by ^{1}H NMR spectroscopy.

Metalacyclobutane 14. A saturated solution of *rac*-**2a** (185 mg, 202 μmol) in pentane (2.5 mL) was added to triene **9** (35 mg, 230 μmol) at room temperature. The red reaction mixture was left without stirring for 16 h, after which the supernatant was decanted from the ruby red cubes. The crystals were dried in vacuo to give **14**, yield 137 mg (80%). ^{1}H NMR (tol-d_8): δ 7.24 (s, 1, aryl), 7.06 (s, 1, aryl), 7.00 (d, 2, aryl, J_{HH} = 7.7), 6.81 (t, 1, aryl, J_{HH} = 7.7 Hz), 4.88 (m, 1, CH$_2$O), 4.83 (s,

br, 1, OCH_2CH═CMe), 4.53 (m, br, 1, CHO), 3.67 (m, br, 2, $CH(CH_3)_2$), 3.05 (m, 1, CH_2O), 2.53 (d, 1, WCH_2, J_{HH} = 9.7 Hz), 2.23 (s, 3, Ar−CH_3), 2.18 (s, 3, Ar−CH_3), 1.79 (d, 1, WCH_2, J_{HH} = 10.0 Hz), 1.75 (s, 3, Ar−CH_3), 1.73 (s, 3, Ar−CH_3), 1.57 (s, 9, $C(CH_3)_3$), 1.41 (s, 9, $C(CH_3)_3$), 1.37 (m, br, 3, $OCHC(CH_3)$═CH), 1.33 (d, 1, WCH_2, J_{HH} = 9.6 Hz), 1.27 (s, 3, $WCH_2C(CH_3)(C_5H_7O)CH_2$), 1.23 (d, 6, $CH(CH_3)_2$, J_{HH} = 6.8 Hz), 1.17 (d, 1, WCH_2, J_{HH} = 10.0 Hz), 1.11 (d, 6, $CH(CH_3)_2$, J_{HH} = 6.8 Hz). ^{13}C NMR (100 MHz, tol-d_8): δ 158.6, 156.7, 150.5, 137.6, 135.8, 134.6, 134.5, 134.0, 131.7, 130.1, 128.9, 128.5, 127.9, 127.4, 126.7, 124.4 (OCH_2CH═CMe), 122.5, 99.1 (CHO), 74.3 (CH_2O), 55.1, 47.9 (WCH_2), 37.5 ($WCH_2C(CH_3)(C_5H_7O)CH_2$), 35.2, 34.9, 31.6, 31.4 ($WCH_2C(CH_3)(C_5H_7O)CH_2$), 30.4, 27.7, 25.0, 24.7, 20.7, 20.4, 17.4, 16.8, 14.1. Anal. Calcd for $WC_{45}H_{63}NO_3$: C, 63.60; H, 7.47; N, 1.65. Found: C, 63.46; H, 7.58; N, 1.61.

Metalacyclobutane 16. A solution of *rac*-**2a** (100 mg, 109 μmol) in pentane (5 mL) was added to freshly distilled and degassed 1,6-heptadiene (10.5 mg, 109 μmol) at room temperature. The solution was stirred for 2 h and filtered through Celite. The red solution was concentrated to approximately 1 mL and cooled to −30 °C for 12 h. Some orange crystals of **16** and a small amount of unidentified purple-black powder were observed in the vial; the total dry weight was 65 mg. The orange crystals were carefully picked out for further analysis. ^{1}H NMR: δ 7.35 (d, 2, aryl), 7.31 (s, 1, aryl), 7.29 (t, 1, aryl), 7.19 (d, 2, aryl), 7.13 (s, 1, aryl), 7.02 (t, 2, aryl), 6.93 (t, 1, aryl), 3.41 (sept, 2, $CHCMe_2$), 3.18 (m, 1, β-CH), 2.95 (m, 1, α-CH_{eq}), 2.55 (m, 1, α-CH_{eq}), 2.08 (s, 3, Ar−CH_3), 2.03 (s, 3, Ar−CH_3), 1.65 (s, 3, Ar−CH_3), 1.64 (s, 3, Ar−CH_3), 1.52 (s, 9, $C(CH_3)_3$), 1.39 (s, 3, $CHC(CH_3)_2Ph$), 1.38 (s, 9, $C(CH_3)_3$), 1.32 (m, 1, α-CH_{ax}), 1.29 (s, 3, $CHC(CH_3)_2Ph$), 1.26 (m, 1, α-CH_{ax}), 1.22 (d, 6, $CH(CH_3)_2$), 1.07 (d, 6, $CH(CH_3)_2$). Anal. Calcd for $WC_{48}H_{65}NO_2$: C, 66.10; H, 7.52; N, 1.61. Found: C, 66.22; H, 7.46; N, 1.57.

***rac*-W(NAr′)(C_3H_6)(Biphen) (*rac*-18b).** Four equivalents of 1,6-heptadiene was added to a slurry of *rac*-W(NAr′)($CHCMe_2Ph$)(Biphen) (150 mg, 0.191 mmol) in pentane (1 mL). The vial was immediately capped, and the suspension became homogeneous. The reaction was cooled to −25 °C for 6 days. The yellow-orange precipitate was collected by decanting the supernatant and drying the precipitate in vacuo, yield 125 mg (95%). ^{1}H NMR (C_6D_6): δ 7.17 (s, 2, aryl), 6.81 (d, 2, aryl), 6.65 (t, 1, aryl), 4.10−3.80 (m, 3, α-CH_2), 3.00 (m, 1, α-CH_2), 2.27 (s, 6, Ar−CH_3), 2.15 (s, 6, Ar−CH_3), 1.78 (s, 6, Ar−CH_3), 1.54 (s, 18, $C(CH_3)_3$), 0.70 (s, br, 1, β-CH_2), 0.10 (s, br, 1, β-CH_2). ^{13}C NMR (125 MHz, C_6D_6): δ 152.22, 136.69 (br), 134.83, 129.55 (br), 127.90, 126.14, 86.9 (br), 79.4 (br), 35.82 (br), 34.76, 33.08, 31.74 (br), 30.53, 28.71, 23.48, 23.06, 20.71, 19.76, 19.22, 17.18, 14.63, 3.7 (br), 3.51. Anal. Calcd for $WC_{35}H_{47}NO_2$: C, 60.26; H, 6.79; N, 2.01. Found: C, 60.44; H, 6.73; N, 1.95.

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Supporting Information Available: Fully labeled ORTEP drawing, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **14** and **16** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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