Organometallics 1990, *9*, 2535–2548

Preparation and Reactivity of Tungsten(VI) Metallacyclobutane Complexes. Square Pyramids versus Trigonal Bipyramids

Jerald Feldman, William M. Davis, Julie K. Thomas, and Richard R. Schrock*

Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received February 23, 1990

Neopentylidene complexes of the type $W(CH\text{-}t\text{-}Bu)(NAr)(OR)_2$ ($Ar = 2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$; $OR = O\text{-}t\text{-}Bu$, $OCMe_2(CF_3)$, OAr) react with ethylene to give trigonal-bipyramidal or square-pyramidal tungstacyclobutane complexes. A square-pyramidal form is observed when $OR = O\text{-}t\text{-}Bu$. Both forms are present when $OR = OCMe_2(CF_3)$ or OAr, and they interconvert at a rate that is on the order of the NMR time scale. A complex of the type $W[CH_2CH(R)CH_2](NAr)(OAr)_2$ is a square pyramid when $R = t\text{-}Bu$ but a trigonal bipyramid when $R = SiMe_3$. Square-pyramidal tungstacycles are characterized by comparable chemical shifts for α- and β-protons, chemical shifts for α- and β-carbon atoms that differ by only ~25 ppm, and aliphatic J_{CH} values, as opposed to large differences in chemical shifts between α- and β-carbons and α- and β-hydrogens and olefinic J_{CH} values in TBP tungstacycles. Unsubstituted metallacycles react with excess neohexene to give square-pyramidal $W[CH_2CH(t\text{-}Bu)CH_2](NAr)(OR)_2$ complexes ($OR = O\text{-}t\text{-}Bu$, $OCMe_2(CF_3)$, OAr). $W[CH_2CH(t\text{-}Bu)CH_2](NAr)[OCMe_2(CF_3)]_2$ has been characterized crystallographically (space group $P4_2/n$, $a = 25.26$ (2) Å, $c = 9.720$ (5) Å, $V = 6202$ Å^3, $M_r = 711.48$, ρ(calcd) = 1.524 g cm^{-3}, $Z = 8$, $\mu = 40.05$ cm^{-1}, $R = 0.056$, $R_w = 0.082$). The most characteristic feature of the WC_3 ring in the SP complex is the relatively normal W---C_β distance of ~2.8 Å and W–C_α bond lengths of 2.15–2.20 Å, as opposed to a short W---C_β distance of ~2.4 Å and W–C_α bond lengths of 2.05–2.10 Å in TBP complexes. It is proposed that square-pyramidal complexes form in order to avoid competition between a relatively basic axial alkoxide and an axial imido ligand in a trigonal bipyramid. The reaction between $W[CH_2CH(t\text{-}Bu)CH_2](NAr)(OAr)_2$ and ethylene to give $W[CH_2CH_2CH_2](NAr)(OAr)_2$ and *tert*-butylethylene is zero order in ethylene and first order in tungsten between 9 and 34 °C with $\Delta H^\ddagger = 19.7$ kcal mol^{-1} and $\Delta S^\ddagger = -6$ eu. Reactions between ethylene and trigonal-bipyramidal $W[CH_2CH(Me_3Si)CH_2](NAr)(OAr)_2$, $W[CH_2CH(Me_3Si)CH_2](NAr)[OCMe(CF_3)_2]_2$, and $W[CH_2CH(Me_3Si)CH_2](NAr)[OC(CF_3)_2(CF_2CF_2CF_3)]_2$ are analogous but have positive values for $\Delta S^\ddagger$ (11–23 eu). It is proposed that square-pyramidal *tert*-butoxide complexes are relatively stable toward loss of an olefin because the WC_3 ring is further from an "olefin/alkylidene" transition state than is the WC_3 ring in a trigonal bipyramid and in general for that reason complexes that contain relatively electron-withdrawing alkoxides will lose an olefin more readily than those that contain relatively electron-donating alkoxides.

Introduction

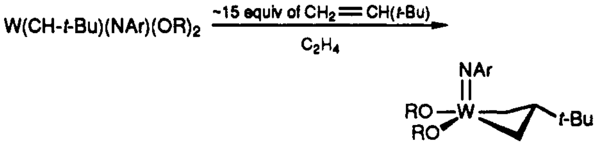
The activity of olefin metathesis catalysts of the type $W(CHR')(NAr)(OR)_2$ ($Ar = 2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$; R′ = alkyl; R = alkyl, fluoroalkyl, aryl)[1] depends dramatically upon the nature of OR, e.g. from ~10^3 turnovers min^{-1} when $OR = OCMe(CF_3)_2$ to virtually none when $OR = O\text{-}t\text{-}Bu$.[2] The rate also depends dramatically on the size of R′, the difference between R′ = *t*-Bu and R′ = Et being perhaps 2 orders of magnitude.[1] Tungstacyclobutane complexes $W[CH(Me_3Si)CH(Me_3Si)CH_2](NAr)[OCMe(CF_3)_2]_2$ and $W(CH_2CH_2CH_2)(NAr)[OC(CF_3)_2(CF_2CF_2CF_3)]_2$ have been isolated and shown to be approximately trigonal bipyramids in which the WC_3 ring is located in the equatorial plane.[1a] Further investigations have now shown that square-pyramidal tungstacyclobutane complexes are an important second major type of metallacycle formed in these systems and that only square-pyramidal metallacycles are observable for the least active catalysts ($OR = O\text{-}t\text{-}Bu$). This paper will be concerned with a comparison of the synthesis, structure, and reactivity of several trigonal-bipyramidal and square-pyramidal tungstacyclobutane complexes and how metallacycle structure fits into the general mechanism of olefin metathesis with tungsten complexes of this type. Preliminary accounts of portions of this work have been published.[3]

Table I. Selected Bond Distances (Å) and Angles (deg) in $W[CH_2CH(t\text{-}Bu)CH_2](NAr)[OCMe_2(CF_3)]_2$ (1b)

W–C(21)	2.17 (1)	C(22)–C(23)	1.55 (1)
W---C(22)	2.79 (1)	W–O(1)	1.869 (7)
W–C(23)	2.14 (1)	W–O(2)	1.886 (6)
C(21)–C(22)	1.57 (1)	W–N(1)	1.736 (7)
C(21)–W–C(23)	63	N(1)–W–O(1)	113.9 (3)
C(21)–C(22)–C(23)	93	N(1)–W–O(2)	111.7 (3)
W–C(21)–C(22)	95	N(1)–W–C(23)	98.4 (3)
W–C(23)–C(22)	97	N(1)–W–C(21)	99.4 (4)
O(1)–W–O(2)	99.6 (3)	W–O(1)–C(3)	164.4 (7)
O(2)–W–C(21)	87.4 (3)	W–O(2)–C(4)	158.6 (7)
O(1)–W–C(23)	89.2 (3)	W–N(1)–C(11)	167.9 (7)

Results

Square-Pyramidal $W[CH_2CH(t\text{-}Bu)CH_2](NAr)[OCMe_2(CF_3)]_2$. The reaction shown in eq 1 yields the β-*tert*-butyl-substituted tungstacyclobutane complex **1b**.



(1)

1b

OR = OCMe₂(CF₃)

An X-ray study (Figure 1) showed that **1b** is best described as a square pyramid. (Selected bond angles and distances are listed in Table I.) The nitrogen atom of the imido ligand occupies the apical position, and the two oxygen atoms and C(21) and C(23) occupy the basal positions. The tungsten atom resides 0.58 Å above the least-squares plane defined by the two oxygen and two carbon atoms. The angles between adjacent ligands in the basal plane vary greatly, with the C(21)–W–C(23) angle (63.4 (4)°)

---

[1] (a) Schrock, R. R.; DePue, R.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423. (b) Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Krüger, C.; Betz, P. *Organometallics*, in press.

[2] Schrock, R. R.; Feldman, J.; Grubbs, R. H.; Cannizzo, L. *Macromolecules* **1987**, *20*, 1169.

[3] (a) Feldman, J.; DePue, R. T.; Schaverien, C. J.; Davis, W. M.; Schrock, R. R. In *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer: Boston, MA, 1989. (b) Feldman, J.; Schrock, R. R. *Organometallics* **1989**, *8*, 2266.

0276-7333/90/2309-2535$02.50/0

Table II. ^1H and ^{13}C NMR Data for Square-Pyramidal Tungstacyclobutane Complexes[a]

compd	$\delta(H_\alpha)$[b]	$\delta(H_\beta)$	$\delta(C_\alpha)$ (J_{CH})	$\delta(C_\beta)$ (J_{CH})	$J_{C_\alpha C_\beta}$
$W[CH(t\text{-}Bu)CH_2CH_2](NAr)[OCMe_2(CF_3)]_2$ (**1a**)	2.28 1.80	4.11 2.60	48.2 (127)[c]	24.1 (128)	32
$W[CH_2CH(t\text{-}Bu)CH_2](NAr)[OCMe_2(CF_3)]_2$ (**1b**)[d]	2.36 (eq) 1.12 (ax)	2.62	47.1 (126)	46.0 (127)	
$W(CH_2CH_2CH_2)(NAr)[OCMe_2(CF_3)]_2$ (**1c**)	2.29	4.30 2.78	43.6 (134)	24.2 (134)	28
$W[CH_2CH(t\text{-}Bu)CH_2](NAr)(OAr)_2$ (**2b**)[d]	2.39 1.2[e]	2.71	48.5 (133)	45.1 (133)	
$W(CH_2CH_2CH_2)(NAr)(OAr)_2$ (**2c**)	2.35 3.02	4.43	43.5 (138)	22.6 (133)	29
$W[CH(t\text{-}Bu)CH_2CH_2](NAr)(O\text{-}t\text{-}Bu)_2$ (**3a**)	2.35 1.52	4.30 2.72	45.4 (131)[c]	24.9 (132)	33
$W[CH_2CH(t\text{-}Bu)CH_2](NAr)(O\text{-}t\text{-}Bu)_2$ (**3b**)[d]	2.36 1.10	2.68	44.9 (130)	46.8 (125)	
$W(CH_2CH_2CH_2)(NAr)(O\text{-}t\text{-}Bu)_2$ (**3c**)	2.3 2.8	4.4	41.9	24.5	30

[a] In toluene-d_8 unless otherwise noted. All J values are in hertz. [b] In some instances not all the α-proton resonances were located due to interference by other signals. [c] Only the CH_2 C_α resonance is reported. [d] Spectrum recorded in C_6D_6. [e] Approximate chemical shift according to a COSY spectrum.

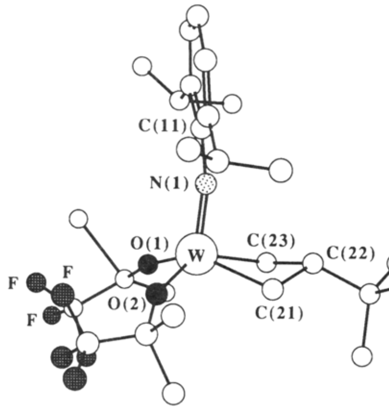


Figure 1. View of the structure of $W[CH_2CH(t\text{-}Bu)CH_2](NAr)[OCMe_2(CF_3)]_2$ (**1b**).

being the smallest and the O(1)–W–O(2) angle (99.6 (3)°) being the largest. The large O(1)–W–O(2) angle and the relatively large N(1)–W–O(1) (113.9 (3)°) and N(1)–W–O(2) (111.7 (3)°) angles can be ascribed to the bulk of the $OCMe_2(CF_3)$ ligands. The phenyl ring of the imido ligand is oriented such that the plane of the ring approximately bisects the two O–W–C_α bond angles, thereby minimizing steric interactions between an isopropyl group and the β-carbon of the metallacycle. The WC_3 ring is bent, with a dihedral angle of 33.4° between the plane defined by W, C(21), and C(23) and that defined by C(21), C(22), and C(23). The degree to which a metallacycle ligand is bent is potentially of interest because puckering of metallacycles has been invoked as a possible explanation for stereospecificity in olefin metathesis.[4]

Proton and carbon NMR spectra of **1b** (Figure 2; Table II) are fully consistent with the results of the X-ray study but significantly different from those typically observed for trigonal-bipyramidal metallacyclobutane complexes.[1]

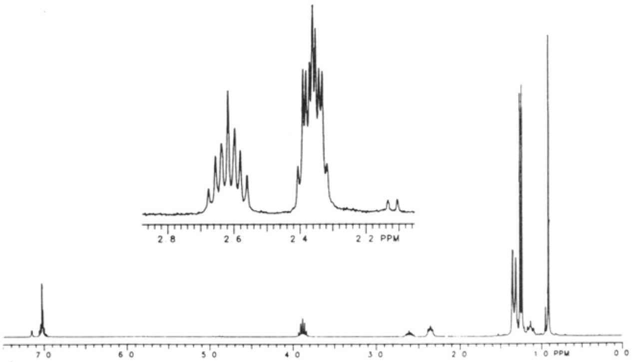


Figure 2. ^1H NMR spectrum (C_6D_6, 25 °C) of $W[CH_2CH(t\text{-}Bu)CH_2](NAr)[OCMe_2(CF_3)]_2$ (**1b**).

A multiplet at 2.62 ppm in the ^1H NMR spectrum can be assigned to H_β coupled to two pairs of α-protons (J_{HH} = 3,6 Hz), while two multiplets of area 2 each at 2.36 and 1.12 ppm can be assigned to the two inequivalent sets of α-protons. Homonuclear decoupling experiments show that $J_{H_\alpha H_\beta}$ is larger for the H_α resonance at 1.12 ppm than for the H_α resonance at 2.36 ppm. If we assume that axial/axial coupling is larger than axial/equatorial coupling,[5] we can assign the resonance at 1.12 ppm to H_α(axial) and that at 2.36 ppm to H_α(equatorial). (In square-pyramidal $W[CH(t\text{-}Bu)CH_2CH(CO_2Me)](NAr)(O\text{-}t\text{-}Bu)_2$ the axial H_α resonance was found at 1.98 ppm and the equatorial H_α resonance at 2.39 ppm.[6]) In the ^{13}C NMR spectrum of **1b**, the α-carbon resonance is a triplet at 47.1 ppm (J_{CH} = 126 Hz), and the β carbon resonance is a doublet at 46.0 ppm (J_{CH} = 127 Hz). The near equivalence of α- and β-carbon resonances in the case of **1b** is circumstantial; in unsubstituted rings to be described below, α- and β-carbon resonances differ by ~20 ppm (Table II). In trigonal-bipyramidal metallacyclobutane complexes α- and β-carbon resonances differ by ~100 ppm and J_{CH} values are generally ~150 Hz.[1]

Metallacycles Formed in Reactions of Ethylene with Neopentylidene Complexes. W(CH-t-Bu)-

---

[4] (a) Katz, T. J.; McGinnis, J. *J. Am. Chem. Soc.* **1975**, *97*, 1592. (b) Casey, C. P.; Albin, L. D.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2533. (c) Leconte, M.; Basset, J. M.; Quignard, F.; Larroche, C. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum Press: New York, 1986. (d) Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983. (e) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 8. (f) Dragutan, V.; Balaban, A. T.; Dimonie, M. *Olefin Metathesis and Ring-opening Polymerization of Cyclo-Olefins*, 2nd ed.; Wiley-Interscience: New York, 1985.

[5] (a) Bovey, F. A. *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Academic Press: San Diego, 1988. (b) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; Wiley-Interscience: New York, 1981.

[6] Feldman, J.; Murdzek, J. S.; Davis, W. M.; Schrock, R. R. *Organometallics* **1989**, *8*, 2260.

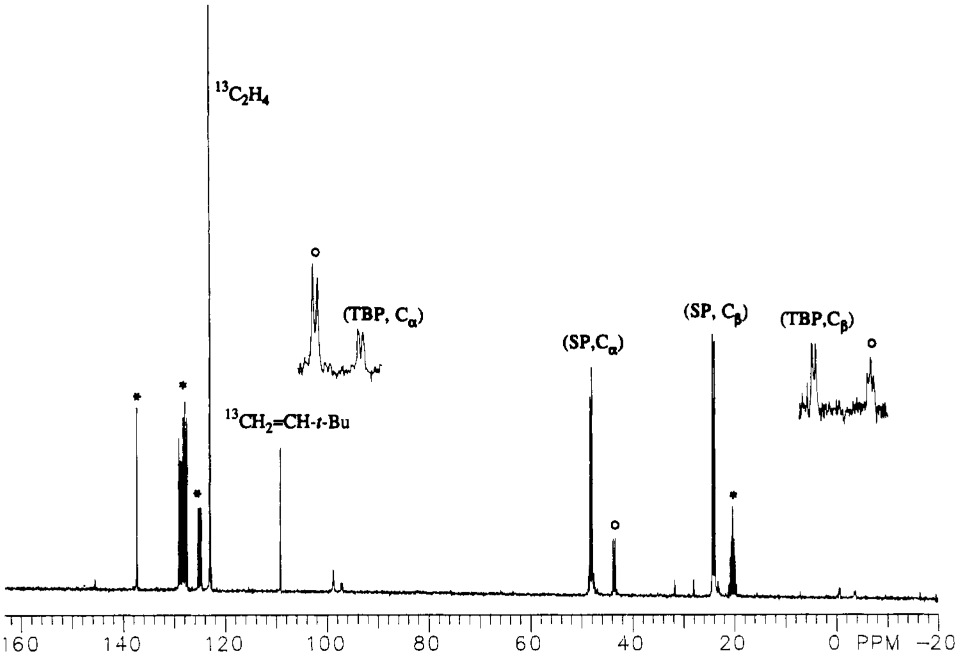
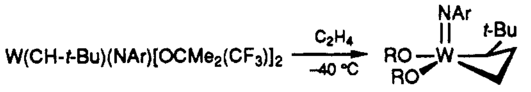


Figure 3. $^{13}C\{^1H\}$ NMR spectrum (toluene-d_8, −40 °C) of W[CH(t-Bu)$^{13}CH_2{}^{13}CH_2$](NAr)[OCMe$_2$(CF$_3$)]$_2$ (**1a**) showing trigonal-bipyramidal and square-pyramidal isomers. Resonances due to solvent are indicated by asterisks, and those due to W($^{13}C_3H_6$)(NAr)[OCMe$_2$(CF$_3$)]$_2$ (**1b**) are indicated by open circles.

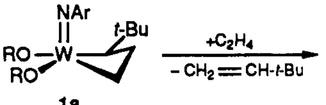
(NAr)[OCMe(CF$_3$)$_2$]$_2$ reacts with ethylene too quickly to follow by NMR spectroscopy. In one experiment, 5 equiv of ethylene was added to a frozen solution of W(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (0.045 M, toluene-d_8) in an NMR tube. The sample was thawed quickly and placed in a probe that had been precooled to −70 °C; the only observable products were *tert*-butylethylene and W(CH$_2$CH$_2$CH$_2$)(NAr)[OCMe(CF$_3$)$_2$]$_2$.[1]

In contrast, the reaction between W(CH-*t*-Bu)(NAr)[OCMe$_2$(CF$_3$)]$_2$ and ethylene is sufficiently slow to be followed by NMR at low temperature. When W(CH-*t*-Bu)(NAr)[OCMe$_2$(CF$_3$)]$_2$ in toluene-d_8 is treated with ethylene at −40 °C, an intermediate (**1a**) is observed before any *tert*-butylethylene is produced (eq 2; OR = OCMe$_2$(CF$_3$)). **1a** is characterized by multiplet resonances at 4.11, 2.60, 2.28, and 1.80 ppm in a 1:1:1:2 ratio. Comparison of the data for **1a** and **1b** in Table II shows that they are likely to be similar square-pyramidal species. When the NMR sample of **1a** is warmed to −20 °C, it rapidly loses *tert*-butylethylene and, in the presence of excess ethylene, gives the highly fluxional, unsubstituted metallacyclobutane complex **1c** (eq 3; OR = OCMe$_2$(CF$_3$)).



(2)

1a



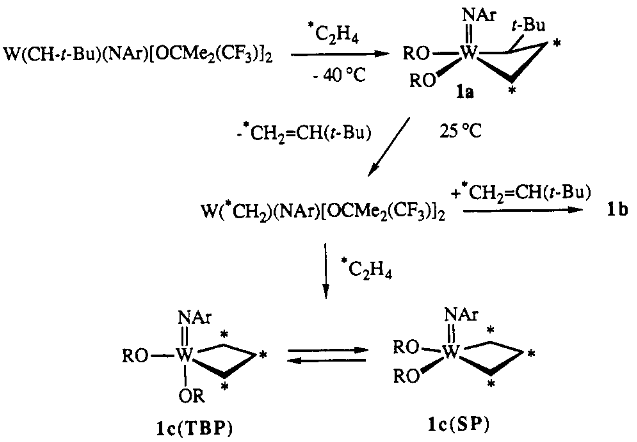
1a

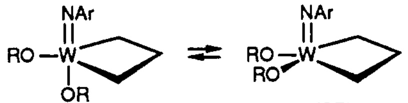
W(CH$_2$CH$_2$CH$_2$)(NAr)[OCMe$_2$(CF$_3$)]$_2$ (3)

1c

The room-temperature ^1H NMR spectrum of **1c** in the presence of excess ethylenes shows no resonances attributable to the ring protons of a metallacyclobutane ligand. However, resonances for ethylene and *tert*-butylethylene are sharp, implying that olefins are not exchanging in and out of the WC$_3$ rings rapidly on the NMR time scale. When a toluene-d_8 solution of **1c** is cooled to −40 °C, several new resonances appear. One set of multiplets can be assigned to a trigonal-bipyramidal metallacyclobutane complex analogous to those observed previously[1] [δ 4.63 (2, H$_\alpha$), 4.40 (2, H$_\alpha$′), −0.73 (1, H$_\beta$), and −1.21 (1, H$_\beta$′)]. The other set of multiplets is observed at δ 4.30, 2.78, and 2.29 (1:1:2 ratio) and is analogous to those observed in **1a** and **1b**. Therefore, one of the isomers of **1c** must be a trigonal bipyramid and the other a square pyramid, and they must interconvert readily at room temperature without losing ethylene.

Scheme I





1c(TBP) **1c(SP)**

The course of the reaction between W(CH-*t*-Bu)(NAr)[OCMe$_2$(CF$_3$)]$_2$ and ethylene is clearest when $^{13}C_2H_4$ is employed and the reaction is followed by $^{13}C\{^1H\}$ NMR spectroscopy (Scheme I). When a toluene-d_8 solution of W(CH-*t*-Bu)(NAr)[OCMe$_2$(CF$_3$)]$_2$ is treated with $^{13}C_2H_4$ at −40 °C, **1a** is formed initially. It is characterized by two doublets at 48.2 and 24.1 ppm (J_{CC} = 32 Hz), that at 48.2 ppm being assignable as C$_\alpha$ on the basis of coupling to ^{183}W (J_{CW} = 53 Hz; Figure 3). In addition, two doublets of low

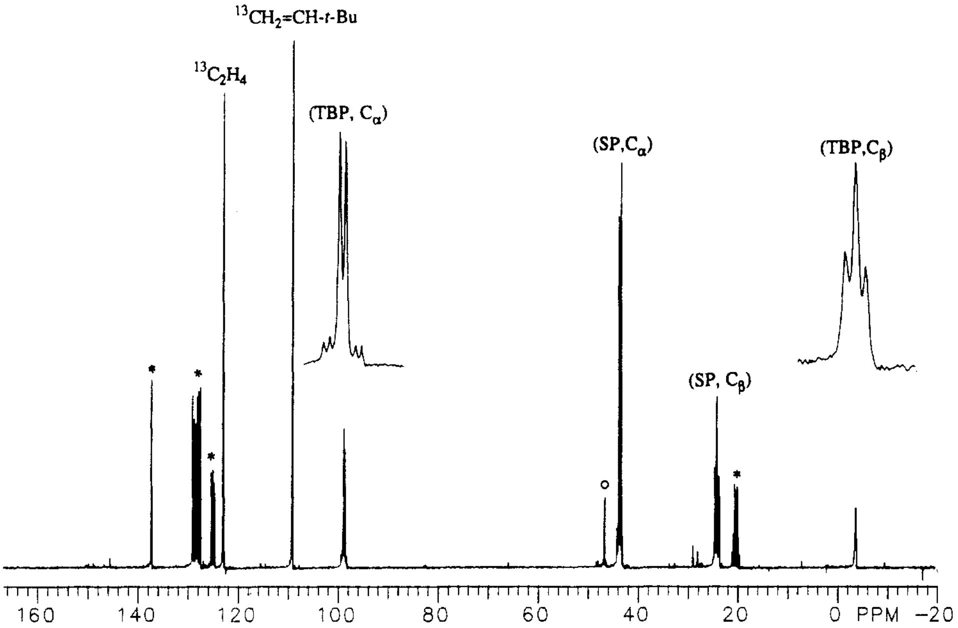
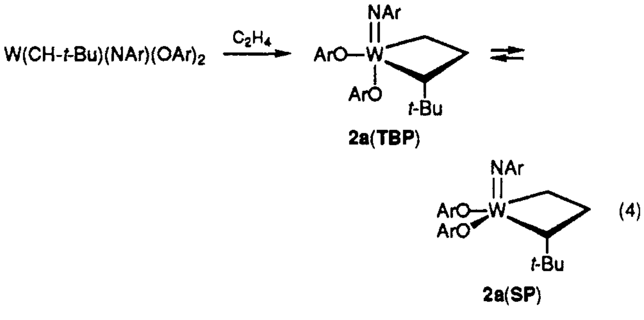


Figure 4. $^{13}C\{^1H\}$ NMR spectrum (toluene-d_8, -40 °C) of $W(^{13}CH_2{}^{13}CH_2{}^{13}CH_2)(NAr)[OCMe_2(CF_3)]_2$ (**1c**) showing trigonal-bipyramidal and square-pyramidal isomers. Resonances due to solvent are indicated by asterisks, and that due to **1b** is indicated an open circle.

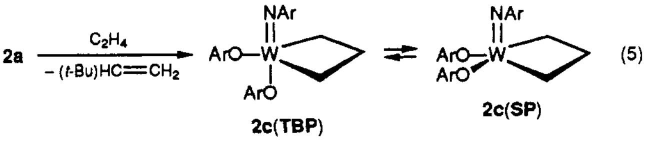
intensity are observed at 97.2 ppm (C_α) and -0.61 ppm (C_β) that may be assigned to a TBP form of **1a**. However, the TBP form is present in only trace quantities and therefore is not included in Scheme I and further discussions concerning **1a**. When the toluene-d_8 solution is warmed to room temperature, $^{13}CH_2$=CH(*t*-Bu) is produced and two broad resonances are observed at 44.0 and 24.0 ppm. When the solution is cooled to -40 °C, again two sets of resonances are observed (Figure 4). One set consists of a doublet at 98.8 ppm (J_{CW} = 68 Hz) and a triplet at 3.6 ppm (J_{CC} = 13 Hz) assigned to C_α and C_β, respectively, of **1c(TBP)**. A singlet of relatively low intensity with ^{183}W satellites is observed at 47.1 ppm, which can be assigned to the C_α resonance in **1b**. (The *tert*-butyl-substituted carbon atom is not labeled.) Most likely **1b** is formed when (*t*-Bu)CH=*CH$_2$ back-reacts with the intermediate methylene complex that is formed when (*t*-Bu)CH=*CH$_2$ is lost from **1a**, but under these conditions (*t*-Bu)CH=*CH$_2$ does not compete effectively with *C$_2$H$_4$ for that intermediate. We have seen no evidence in these ^{13}C NMR spectra for any intermediate methylene complex.

It has not proven possible to isolate **1c** cleanly. When solvents are removed from hydrocarbon solutions of **1c** and *tert*-butylethylene in vacuo, the crude product is approximately a 50:50 mixture of **1c** and **1b**. We propose that **1b** and **1c** are each in equilibrium with a small amount of a methylene complex, and when ethylene is removed from the system, *tert*-butylethylene is left behind and the equilibrium is driven toward **1b**. Although **1b** can be crystallized from such reaction mixtures, the yield is low (~20%). The yield of **1b** greatly improves (~75% after recrystallization from pentane) if a large excess of *tert*-butylethylene is added to the reaction mixture. These are the conditions under which **1b** may be isolated (eq 1).

In the reaction between W(CH-*t*-Bu)(NAr)(OAr)$_2$ and ethylene at -60 °C, an intermediate α-*tert*-butyl-substituted metallacycle (**2a**) is also formed. Two broad resonances at -0.6 and -0.8 ppm in the ^1H NMR spectrum can be assigned on the basis of their high-field chemical shift to the β-protons of a trigonal-bipyramidal form of the metallacyclobutane complex (**2a(TBP)**). When the same reaction is done with $^{13}C_2H_4$, two very broad resonances are observed at 95.5 and 1.9 ppm at low temperature in the $^{13}C\{^1H\}$ NMR spectrum, which may be assigned to the α- and β-carbon atoms, respectively, of **2a(TBP)**. In addition, an extremely broad resonance is observed in the region 20-30 ppm, which we propose belongs to **2a(SP)**. When the sample is warmed, resonances in the proton and carbon NMR spectra disappear into the base line and $^{13}CH_2$=CH(*t*-Bu) is produced. These data suggest that **2a(TBP)** and **2a(SP)** interconvert readily on the NMR time scale at 25 °C (eq 4). This situation is somewhat different from what was observed in the OCMe$_2$(CF$_3$) system, where only a trace amount of **1a(TBP)** (<5%) could be detected over the temperature range in which it was stable.



When the above solution of **2a** and C$_2$H$_4$ is warmed to room temperature, *tert*-butylethylene is produced and four broad resonances are observed in the ^1H NMR spectrum at 3.12, 2.76, 2.43, and 2.1 ppm in a 2:1:2:1 ratio. When the solution is cooled, these resonances broaden and collapse, and at -70 °C the trigonal-bipyramidal and square-pyramidal isomers of W(CH$_2$CH$_2$CH$_2$)(NAr)(OAr)$_2$ (**2c**) are observed (eq 5). The trigonal-bipyramidal isomer has ring proton resonances at 4.88 (H_α), 4.75 (H_α'), -0.58 (H_β), and -0.94 (H_β') ppm. The square-pyramidal isomer has ring proton resonances at 4.43 (H_β), 3.02 (H_β'), and 2.35 (H_α) ppm (the H_α' resonance is obscured by other resonances in the aliphatic region). In a reaction between



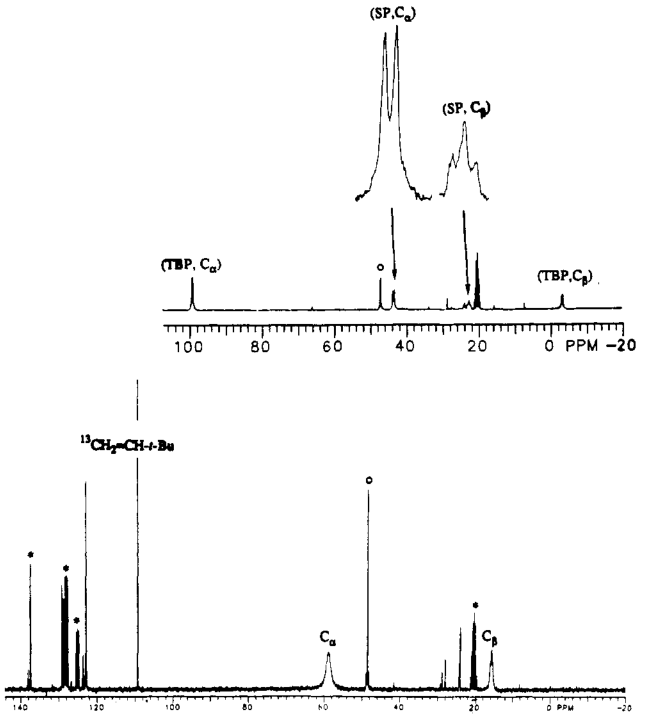
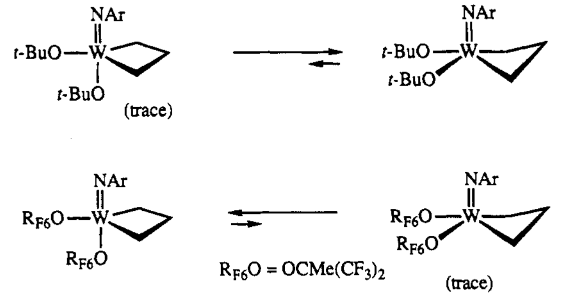


Figure 5. $^{13}C\{^1H\}$ NMR spectrum (toluene-d_8) of W($^{13}CH_2{}^{13}CH_2{}^{13}CH_2$)(NAr)(OAr)$_2$ (**2c**): (bottom) at 25 °C; (top) at −90 °C. Resonances due to solvent are indicated by asterisks, and that due to W[$^{13}CH_2CH$(*t*-Bu)$^{13}CH_2$](NAr)(OAr)$_2$ (**2b**) is indicated by an open circle.

W(CH-*t*-Bu)(NAr)(OAr)$_2$ and $^{13}C_2H_4$ at room temperature, $^{13}CH_2$=CH(*t*-Bu) and ^{13}C-labeled **2c** are rapidly formed. Coalesced ring carbon resonances are observed at 59.0 and 25.9 ppm at 25 °C (Figure 5, bottom); at approximately −60 °C, both isomers of **2c** may be observed (Figure 5, top). The resonance with tungsten satellites observed at 48.5 ppm can be assigned to W[CH$_2$CH(*t*-Bu)CH$_2$](NAr)(OAr)$_2$ (**2b**; vide infra).

W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ reacts with ethylene within minutes at −40 °C to give square-pyramidal W[CH(*t*-Bu)CH$_2$CH$_2$](NAr)(O-*t*-Bu)$_2$ (**3a**). The NMR parameters for **3a** are almost identical with those observed for **1a(SP)** (Table II), but **3a** is far more stable, *persisting for more than 10 h at 25 °C* before decomposing to form *tert*-butylethylene and W(CH$_2$CH$_2$CH$_2$)(NAr)(O-*t*-Bu)$_2$ (**3c**) in the presence of ethylene. In contrast to the cases for fluxional **1c** and **2c**, the room-temperature ^{13}C NMR resonances for **3c** ($\delta(C_\alpha)$ = 41.9, $\delta(C_\beta)$ = 24.5) are sharp. However, the resonances for the ring protons of **3c** (Table II) are *broadened slightly* at 25 °C. At −20 °C, the ring proton resonances sharpen, but no resonances indicative of a trigonal-bipyramidal form of **3c** can be observed. We propose that **3c(TBP)** is present in concentrations large enough so that the ^{1}H NMR spectrum of **3c(SP)** is broadened by interconversion of **3c(SP)** and **3c(TBP)** at 25 °C, but not large enough to see in the proton NMR spectra at low temperatures or the carbon NMR spectra at 25 °C. (The equilibrium may shift further toward **3c-(SP)** at low temperatures, making it more difficult to observe **3c(TBP)**.) This result should be compared to that observed for W(CH$_2$CH$_2$CH$_2$)(NAr)[OCMe(CF$_3$)$_2$]$_2$,[1] which has a ^{1}H NMR spectrum consistent with a trigonal-bipyramidal geometry,[1] but the ring proton and alkoxide resonances are broadened at 25 °C. Therefore, it was proposed that trigonal-bipyramidal W(CH$_2$CH$_2$CH$_2$)(NAr)-[OCMe(CF$_3$)$_2$]$_2$ interconverts with a small, undetectable amount of a square-pyramidal complex. The two extremes are contrasted in Scheme II. Intermediate behavior is observed for **1c** and **2c**, and both TBP and SP forms are observable at low temperature. The trend is clearly toward a square-pyramidal form when more basic alkoxides are present and a trigonal-bipyramidal form when more electron-withdrawing alkoxides are present. In all cases the two forms interconvert readily on the NMR time scale at 25 °C.

Scheme II



R$_{F6}$O = OCMe(CF$_3$)$_2$

It is interesting to note that although the reaction between W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and 5 equiv of ethylene to give W[CH(*t*-Bu)CH$_2$CH$_2$](NAr)(O-*t*-Bu)$_2$ (**3a**) is fast, NMR spectra of the reaction mixture show trace amounts of residual W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$. Apparently an equilibrium between ethylene and W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ is established; i.e., **3a** loses *ethylene* more readily than *tert*-butylethylene. If *tert*-butylethylene were lost from **3a**, then **3c** would appear.

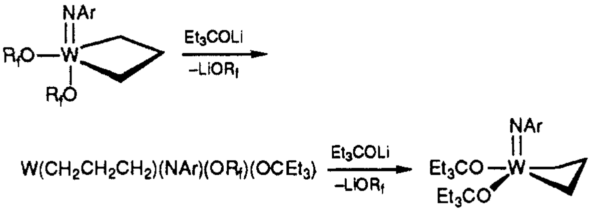
It has not proven possible to isolate W(CH$_2$CH$_2$CH$_2$)-(NAr)(O-*t*-Bu)$_2$ (**3c**) or W(CH$_2$CH$_2$CH$_2$)(NAr)(OAr)$_2$ (**2c**) as pure, crystalline solids. They appear to decompose slowly in the absence of excess ethylene. However, it is possible to isolate W[CH$_2$CH(*t*-Bu)CH$_2$](NAr)(O-*t*-Bu)$_2$ (**3b**) and W[CH$_2$CH(*t*-Bu)CH$_2$](NAr)(OAr)$_2$ (**2b**) with use of a procedure analogous to that used to prepare **1b** (eq 1). Either *tert*-butylethylene is lost less rapidly from **2b** and **3b** than ethylene is lost from **2c** and **3c** or **2b** and **3b** are more stable because of the relatively low rate of loss of *tert*-butylethylene relative to that of ethylene from solution. Like **1b**, compounds **2b** and **3b** appear to have square-pyramidal geometries and show *no* evidence of fluxionality in their room-temperature ^{1}H or ^{13}C NMR spectra (Table II).

The procedure used to prepare W[CH$_2$CH(*t*-Bu)-CH$_2$](NAr)(O-*t*-Bu)$_2$ (**3b**) differs from that used to prepare **1b** and **2b** in that relatively long reaction times are required (typically about 1 day; see Experimental Section). On one occasion, when the reaction was allowed to run for only 3 h at 25 °C, largely W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ was recovered. This result can be attributed to the relatively long lifetime of the α-*t*-Bu-substituted metallacyclobutane complex at room temperature and to its preferential loss of ethylene (vide supra). The reaction to form W-[CH$_2$CH(*t*-Bu)CH$_2$](NAr)(O-*t*-Bu)$_2$ (**3b**) is not as clean as those to give **1b** and **2b**, and it is exceedingly difficult to crystallize **3b** from the crude reaction mixture. Therefore, isolated yields are only fair (30–50% after recrystallization).

In general, the procedure used to prepare the β-*t*-Bu-substituted metallacyclobutane complexes consists of adding ethylene to a solution of the neopentylidene complex in the presence of a large excess of *tert*-butylethylene. This order of addition is not necessary, however. For example, **2b** was formed quantitatively in an experiment in which ethylene was added to a pentane solution of W(CH-*t*-Bu)(NAr)(OAr)$_2$ first, followed by *tert*-butylethylene, i.e., *tert*-butylethylene can react with W(CH$_2$CH$_2$CH$_2$)(NAr)(OAr)$_2$ to give W[CH$_2$CH(*t*-Bu)CH$_2$]-

$(NAr)(OAr)_2$. In contrast, unsubstituted metallacyclobutane complexes containing the $OCMe(CF_3)_2$ and $OC(CF_3)_2(CF_2CF_2CF_3)$ (OR_f) ligands react with *tert*-butylethylene more slowly than those that contain $OCMe_2(CF_3)$, OAr, or O-*t*-Bu ligands. $W(CH_2CH_2CH_2)(NAr)(OR_f)_2$ can be recovered virtually quantitatively from neat *tert*-butylethylene after 24 h. $W(CH_2CH_2CH_2)(NAr)[OCMe(CF_3)_2]_2$ is somewhat more reactive than $W(CH_2CH_2CH_2)(NAr)(OR_f)_2$. After 3 h in neat *tert*-butylethylene $W(CH_2CH_2CH_2)(NAr)[OCMe(CF_3)_2]_2$ was recovered, although some resonances are observed in the solid residue that can be attributed to the square-pyramidal β-*t*-Bu-substituted metallacyclobutane complex. Other products were formed that could not be identified. When 1.5 equiv of ethylene was added to a solution of $W(CH\text{-}t\text{-}Bu)(NAr)[OCMe(CF_3)_2]_2$ in the presence of 25 equiv of *tert*-butylethylene, a ^1H NMR analysis of the crude mixture after 30 min showed it to consist of $W(CH_2CH_2CH_2(NAr)[OCMe(CF_3)_2]_2$ and what we tentatively assign as square-pyramidal $W[CH_2CH(t\text{-}Bu)CH_2](NAr)[OCMe(CF_3)_2]_2$ in an approximately 2:1 ratio. The latter compound is characterized by resonances at 2.58 (1 H) and 2.42 (2 H) ppm that have the same multiplicity as analogous resonances in the fully characterized square-pyramidal complexes **1b**, **2b**, and **3b**.

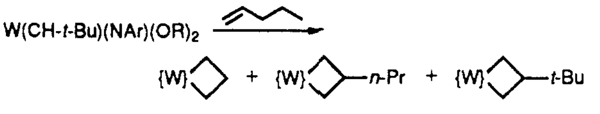
Reaction of Trigonal-Bipyramidal $W(CH_2CH_2CH_2)(NAr)(OR_f)_2$ with Et_3COLi To Give Square-Pyramidal $W(CH_2CH_2CH_2)(NAr)(OCEt_3)_2$. The reaction between $W(CH_2CH_2CH_2)(NAr)(OR_f)_2$[1] and 2 equiv of Et_3COLi requires 1–2 days at room temperature to reach completion. The ^1H NMR spectrum of the reaction mixture after 20 min at 25 °C showed mostly starting material. In addition, however, two sets of broad resonances are observed at 4.7 and 4.4 ppm and another pair of broad resonances at −0.4 and −1.1 ppm that we attribute to the α- and β-protons, respectively, of intermediate TBP $W(CH_2CH_2CH_2)(NAr)(OR_f)(OCEt_3)$. Broadening of resonances suggests that it is in equilibrium with a small amount of the square-pyramidal isomer. The resonances for $W(CH_2CH_2CH_2(NAr)(OR_f)(OCEt_3)$ gradually disappear, and resonances for a new complex grow in at 4.52 (1, H_β), 2.95 (1, H_β), and 2.35 (2, H_α) ppm. These chemical shifts are close to those observed in $W(CH_2CH_2CH_2)(NAr)(O\text{-}t\text{-}Bu)_2$ (Table II). (Other H_α resonances could not be observed.) Therefore, we believe the final complex is square-pyramidal $W(CH_2CH_2CH_2)(NAr)(OCEt_3)_2$ (eq 6) with β-proton resonances at 4.52 and 2.95 ppm and one α-proton resonance at 2.35 ppm. If TBP complexes are formed simply when the alkoxides are very bulky (e.g., OR_f), then $W(CH_2CH_2CH_2)(NAr)(OCEt_3)_2$ should not be a square-pyramidal species. If SP complexes are preferred when very bulky alkoxides are present, then $W(CH_2CH_2CH_2)(NAr)(OR_f)_2$ should not be a trigonal bipyramid. Therefore, the electronic nature of the alkoxide, not its size, must play a more important role in determining the basic geometry of the metallacyclobutane complex.



(6)

$R_fO = (CF_3CF_2CF_2)(CF_3)_2CO$

Reactions of Neopentylidene Complexes Containing $OCMe_2(CF_3)$ and OAr Ligands with 1-Pentene. The reaction of neopentylidene complexes containing the $OCMe_2(CF_3)$ and OAr ligands with 1-pentene gives mixtures of unsubstituted and β-Pr- and β-*t*-Bu-substituted metallacyclobutane complexes (eq 7). When 5 equiv of 1-pentene is added to $W(CH\text{-}t\text{-}Bu)(NAr)[OCMe_2(CF_3)]_2$ (0.029 M in C_6D_6), the ^1H NMR spectrum after 20 min at room temperature shows resonances attributable to *tert*-butylethylene, ethylene, and 4-octene. Resonances corresponding to the β-*t*-Bu-substituted metallacyclobutane complex **1b** are also observed. In addition, signals are observed at 2.56 and 2.69 ppm that have the same multiplicity as the H_α and H_β resonances, respectively, in **1b**. We tentatively assign these resonances to H_α and H_β in a square-pyramidal, β-Pr-substituted metallacyclobutane complex. Under these conditions, the ratio of β-Pr- to β-*t*-Bu-substituted metallacycles is ~1:1. Some unsubstituted metallacyclobutane complex may also be present in the reaction mixture, but the amount is difficult to quantify since resonances characteristic of this species are broad at 25 °C. Attempts to isolate $W[CH_2CH(Pr)CH_2](NAr)[OCMe_2(CF_3)]_2$ on a scale of 100–200 mg of starting material failed. $W(CH\text{-}t\text{-}Bu)(NAr)[OCMe_2(CF_3)]_2$ is a poor catalyst for 1-pentene metathesis, only a few turnovers per hour being observed at room temperature.



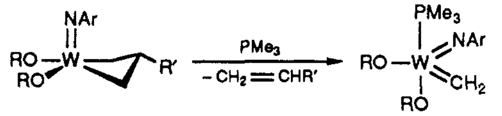
(7)

$OR = OCMe_2(CF_3)$, OAr

The reaction between $W(CH\text{-}t\text{-}Bu)(NAr)(OAr)_2$ and 1-pentene is analogous to that between $W(CH\text{-}t\text{-}Bu)(NAr)[OCMe_2(CF_3)]_2$ and 1-pentene. After 5 equiv of 1-pentene is added to a solution of $W(CH\text{-}t\text{-}Bu)(NAr)(OAr)_2$ (0.038 M, C_6D_6), the ^1H NMR spectrum of the solution shows resonances attributable to *tert*-butylethylene, ethylene, 4-octene, **2b**, and **2c**. In addition, a signal at 2.62 ppm can be tentatively assigned to one set of α-protons in a β-Pr-substituted metallacyclobutane complex. Under these conditions, the ratio of β-Pr- to β-*t*-Bu-substituted metallacycles is ~1:1. $W[CH_2CH_2(Pr)CH_2](NAr)(OAr)_2$ could not be crystallized from pentane on a scale of 120 mg.

It is interesting to compare the results of the reactions discussed here with those obtained for neopentylidene complexes containing the $OCMe(CF_3)_2$ and $OC(CF_3)_2(CF_2CF_2CF_3)$ ligands.[1] When $W(CH\text{-}t\text{-}Bu)(NAr)[OCMe(CF_3)_2]_2$ or $W(CH\text{-}t\text{-}Bu)(NAr)(OR_f)_2$ is treated with 1-pentene, a mixture of unsubstituted and β-Pr-substituted metallacyclobutane complexes that have trigonal-bipyramidal geometries is formed. Roughly the same result is observed here, except that the metallacyclobutane complexes formed have square-pyramidal geometries and a substantial quantity of the β-*t*-Bu-substituted metallacyclobutane complex is also formed.

Reactions of Metallacyclobutane Complexes with Trimethylphosphine To Give Methylene Complexes. Metallacyclobutane complexes containing the $OCMe_2(CF_3)$ or OAr ligands react with trimethylphosphine to give monoadducts that are proposed to have the structure shown in eq 8. The reaction works equally well (and virtually quantitatively) if PMe_3 is added after ethylene

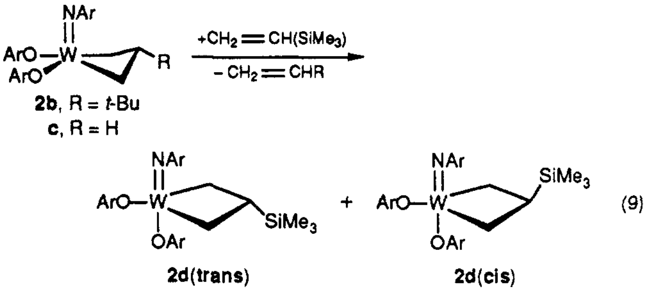


(8)

R' = H, Pr, *t*-Bu; $OR = OCMe_2(CF_3)$, OAr or 1-pentene has been added to a solution of the neopentylidene complex. If PMe_3 is added to the solution of the neopentylidene complex and ethylene then added, only the PMe_3 adduct of the neopentylidene complex can be isolated. The NMR spectra of the adducts are entirely analogous to those reported for the $OCMe(CF_3)_2$ and $OC(CF_3)_2(CF_2CF_2CF_3)$ analogues;[1] the methylene protons are inequivalent since they lie in the W/C/N/O plane. It should be noted that the two values for J_{CH} in the $OCMe_2(CF_3)$ and OAr complex, like those in the $OCMe(CF_3)_2$ and $OC(CF_3)_2(CF_2CF_2CF_3)$ complexes,[1] differ significantly; one is ~132 Hz while the other is ~154 Hz. The reasons for such different values for J_{CH} and the dynamic behavior of such compounds will be discussed in a future paper on the subject of adducts of alkylidene complexes.

Metallacyclobutane complexes containing the *tert*-butoxide ligand are surprisingly unreactive toward trimethylphosphine. In one experiment, 3 equiv of PMe_3 was added to a solution of $W[CH_2CH(t\text{-}Bu)CH_2](NAr)(O\text{-}t\text{-}Bu)_2$ (0.055 M, C_6D_6). After 3.5 h at room temperature, only a trace of what is probably $W(CH_2)(NAr)(O\text{-}t\text{-}Bu)_2(PMe_3)$ (two downfield doublets at 10.4 and 10.7 ppm) could be observed in the ^1H NMR spectrum of the reaction mixture. Most of what remained was starting material. In an analogous experiment, the reaction between $W[CH_2CH(t\text{-}Bu)CH_2](NAr)[OCMe_2(CF_3)]_2$ and PMe_3 to give $W(CH_2)(NAr)[OCMe_2(CF_3)]_2(PMe_3)$ was complete in 30 min at room temperature. These observations are consistent with first-order loss of *tert*-butylethylene followed by capture of an incipient methylene complex by PMe_3 and a variation in the rate of forming this intermediate methylene complex in the order OR = O-*t*-Bu ≪ $OCMe_2(CF_3)$ ≈ OAr.

Reactions of Square-Pyramidal Metallacyclobutane Complexes with Olefins. In general, metallacyclobutane complexes discussed here react with olefins to give new metallacyclobutane complexes. A particularly interesting reaction is shown in eq 9. Compound **2d** is formed cleanly as *a mixture of trigonal-bipyramidal isomers* (ratio ~2:1), according to characteristic proton and carbon NMR spectra. We assign the two isomers as those in which the $SiMe_3$ group is either cis or trans to the imido ligand. The formation of two isomers can be rationalized on the basis of little difference in size between the axial imido (NAr) and phenoxide (OAr) ligands. It is not known which isomer is the major isomer, but it seems reasonable to propose that since the W–N pseudo triple bond should be approximately 0.1 Å shorter than the W–O bond, the trans isomer would be slightly favored for steric reasons. **2d** also can be prepared by adding ethylene and vinyltrimethylsilane sequentially to a solution of $W(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$. These results clearly illustrate that the geometry of a metallacyclobutane complex can depend sensitively on the nature of a ring substituent.

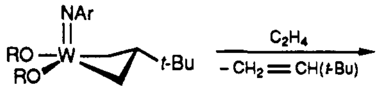


2b, R = *t*-Bu
c, R = H

2d(trans) + **2d(cis)** (9)

Attempts to prepare other β-Me_3Si-substituted metallacyclobutane complexes were only moderately successful. The addition of ethylene to $W(CH\text{-}t\text{-}Bu)(NAr)[OCMe_2(CF_3)]_2$ followed by vinyltrimethylsilane gave a 2:1 mixture of $W(CHSiMe_3)(NAr)[OCMe_2(CF_3)]_2$ and $W[CH_2CH(SiMe_3)CH_2](NAr)[OCMe_2(CF_3)]_2$. The α-proton resonances (both doublets of doublets) for the latter appear at 2.93 and 4.29 ppm; the β-proton resonance appears at −0.98 ppm. When vinyltrimethylsilane was added to $W[CH_2CH(t\text{-}Bu)CH_2](NAr)(O\text{-}t\text{-}Bu)_2$, $W(CHSiMe_3)(NAr)(O\text{-}t\text{-}Bu)_2$ was formed only slowly, and no new metallacyclobutane complexes were observed.

Reaction of β-*t*-Bu-substituted metallacyclobutane complexes **1b**, **2b**, and **3b** with ethylene gave the unsubstituted metallacyclobutane complexes and **1c**, **2c**, and **3c** (eq 10). The rate of this reaction also depends dramatically on the nature of the OR ligand. The reaction of $W[CH_2CH(t\text{-}Bu)CH_2](NAr)(O\text{-}t\text{-}Bu)_2$ (**3b**) with 10 equiv of ethylene in a sealed NMR tube was monitored by ^1H NMR spectroscopy. The extent of reaction could be followed by integrating the *t*-Bu resonance in **3b** versus that in *tert*-butylethylene. After 10 h at room temperature, mostly starting material remained, although resonances characteristic of *tert*-butylethylene and **3c** could be observed. The ratio of **3b** to *tert*-butylethylene was 4.6:1.0. After 78 h at room temperature, some **3b** still remained and the ratio of **3b** to *tert*-butylethylene was 1.0:1.8. The slow reaction between **3b** and ethylene is not surprising, since we noted above that ethylene reacts only slowly with $W[CH(t\text{-}Bu)CH_2CH_2](NAr)(O\text{-}t\text{-}Bu)_2$. In contrast, the reaction between **2b** and ethylene is much faster than that between **3b** and ethylene. When **2b** and 10 equiv of ethylene are combined in a sealed NMR tube and the reaction is monitored by ^1H NMR spectroscopy 50% of **2b** is consumed to give **2c** and *tert*-butylethylene in 30 min at room temperature. The reaction between **1b** and 10 equiv of ethylene is the fastest, all **1b** being consumed within 20 min at room temperature to give *tert*-butylethylene and **1c**. Therefore, the rate of the reaction shown in eq 10 follows the order OR = O-*t*-Bu ≪ OAr < $OCMe_2(CF_3)$.

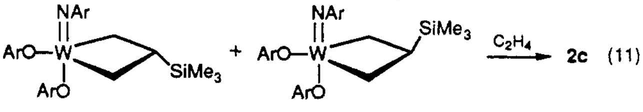


1b, 2b, 3b

$W(CH_2CH_2CH_2)(NAr)(OR)_2$ (10)
1c, 2c, 3c
OR = $OCMe_2(CF_3)$ (**a**), OAr (**b**), O-*t*-Bu (**c**)

Kinetics of the Reactions between Several Tungstacycles and Ethylene. The kinetics of the reaction of $W[CH_2CH(t\text{-}Bu)CH_2](NAr)(OAr)_2$ (**2b**) with ethylene was studied by monitoring the decrease in the β-*t*-Bu resonance in the proton NMR spectrum of **2b** as a function of time. The observed first-order rate constants over the temperature range 9–34 °C are collected in Table III. The rate of the reaction is independent of ethylene concentration, consistent with a dissociative mechanism. An Arrhenius plot of the data in Table III is shown in Figure 6. Activation parameters can be found in Table V.

The kinetics of the reaction between *cis*- and *trans*-$W[CH_2CH(SiMe_3)CH_2](NAr)(OAr)_2$ (**2d**) and ethylene to give **2c** (eq 11) were also studied. The rate of the reaction was monitored by following the decrease in the Si*Me*$_3$



2d(trans) **2d(cis)** (11)

Table III. Rates of Reaction of $W[CH_2CH(t\text{-}Bu)CH_2](NAr)(OAr)_2$ (2b) with Ethylene[a]

run no.	T, °C	$[C_2H_4]$, M	k_{obs}, s^{-1}
1	8.6	0.6	1.07×10^{-4}
2	13.6	1.3	1.98×10^{-4}
3	14.2	0.6	2.50×10^{-4}
4	23.7	0.6	7.62×10^{-4}
5	28.4	2.2	1.16×10^{-3}
6	28.6	0.6	1.26×10^{-3}
7	29.2	1.1	1.22×10^{-3}
8	33.2	1.0	2.07×10^{-3}
9	34.0	2.1	2.29×10^{-3}

[a] The error in T is estimated to be ±0.5 °C; thus, runs 5–7 are essentially the same temperature. The error in k_{obs} is therefore ±5% at best.

Table IV. Rates of Reaction of *cis*- and *trans*-$W[CH_2CH(SiMe_3)CH_2](NAr)(OAr)_2$ with Ethylene[a]

T, °C	$[C_2H_4]$, M	k_{obs}(trans), s^{-1}	k_{obs}(cis), s^{-1}
14.9	1.1	7.81×10^{-5}	7.94×10^{-5}
24.1	1.2	3.18×10^{-4}	3.93×10^{-4}
24.1	0.5	3.42×10^{-4}	3.06×10^{-4}
32.5	0.5	1.11×10^{-3}	1.04×10^{-3}
32.7	1.2	1.05×10^{-3}	1.21×10^{-3}

[a] The error in T is ±0.5 °C and in k_{obs} ±5% at best.

Table V. Comparison of Kinetic Parameters for Reactions between Tungstacycles and Ethylene[a]

tungstacycle	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}_{298}$, kcal mol^{-1}
$W[CH_2CH(t\text{-}Bu)CH_2](NAr)(OAr)_2$ (SP)	19.7 (0.4)	−6 (1)	22.2
$W[CH_2CH(Me_3Si)CH_2](NAr)(OAr)_2$ (TBP, cis)	26.0 (1.7)	11 (4)	22.7
$W[CH_2CH(Me_3Si)CH_2](NAr)(OAr)_2$ (TBP, trans)	25.3 (0.5)	11 (2)	22.0
$W[CH_2CH(Me_3Si)CH_2](NAr)[OCMe(CF_3)_2]_2$ (TBP)	26.6 (1.0)	13 (3)	22.7
$W[CH_2CH(Me_3Si)CH_2](NAr)(OR_f)_2$ (TBP)	31.9 (0.8)	23 (2)	25.0

[a] The error in $\Delta G^{\ddagger}_{298}$ is estimated to be ±0.5 kcal mol^{-1} at best.

resonances in **2d** as a function of time. The observed first-order rate constants for the reaction are collected in Table IV and values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in Table V. Note that the entropies of activation are positive and, at any given temperature, **2d(cis)** and **2d(trans)** react at the same rate within experimental error. Therefore, we cannot exclude the possibility that **2d(trans)** and **2d(cis)** interconvert rapidly relative to the rate at which olefin is lost, although it also would not be surprising if they did not interconvert readily and yet lost olefin at approximately the same rate.[7] Note that **2d** reacts at approximately the same rate as **2b** at room temperature.

A curious side reaction was observed during the course of the kinetic study of the reaction shown in eq 11. After a given kinetic run was completed, a trace amount of 1-butene usually could be observed (identified by NMR comparison with an authentic sample). The total amount present was so small (less than 5% of the concentration of ethylene) that its effect on the reaction kinetics was negligible. However, when a sample was allowed to stand for several days at 25 °C, the amount of 1-butene in the sample increased. Addition of ethylene to $W[CH_2CH(t\text{-}Bu)CH_2](NAr)[OCMe_2(CF_3)]_2$ also yielded trace amounts of 1-butene. Because of the sporadic and irreproducible nature of 1-butene formation, we speculate that some trace decomposition product is the catalyst, perhaps a W(IV) species that could dimerize ethylene via metallacyclopentane intermediates.[8] There is now good evidence that Mo(VI)[9] and Re(VII)[10] metallacycles rearrange to olefins when the metal is relatively electron-poor, so a relatively slow reduction of W(VI) to W(IV) under similar circumstances is plausible.

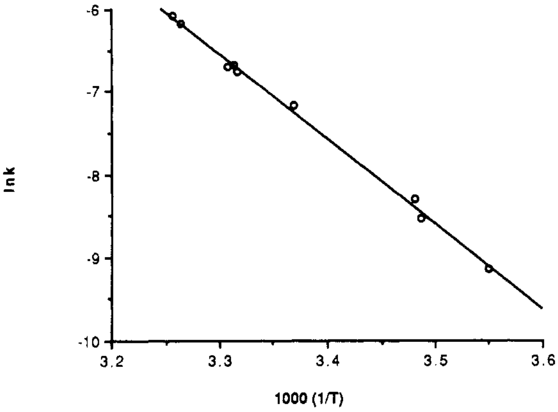


Figure 6. Arrhenius plot for the reaction of $W[CH_2CH(t\text{-}Bu)CH_2](NAr)(OAr)_2$ (**2b**) with ethylene.

The reaction of two other $W[CH_2CH(SiMe_3)CH_2](NAr)(OR)_2$ complexes with ethylene were examined in order to compare the results with those obtained for **2d**. The trigonal-bipyramidal complex in which OR = $OCMe(CF_3)_2$ was reported previously.[1] An analogous complex in which OR = $OC(CF_3)_2(CF_2CF_2CF_3)$ was prepared by treating $W(CH_2CH_2CH_2)(NAr)(OR_f)_2$[1] with $Me_3SiCH{=}CH_2$. It is also a trigonal-bipyramidal species, according to its proton NMR spectra, presumably analogous to structurally characterized $W(CH_2CH_2CH_2)(NAr)(OR_f)_2$.[1] The details of the kinetic analyses can be found in the Experimental Section, and the kinetic parameters for the reactions can be found in Table IV. The enthalpy of activation for loss of $Me_3SiCH{=}CH_2$ from the ring in the OR_f complex is significantly greater than in the $OCMe(CF_3)_2$ complex, and at 298 K the rate of loss of $Me_3SiCH{=}CH_2$ from the ring is approximately 50 times faster in the $OCMe(CF_3)_2$ complex than in the OR_f complex.

Discussion

Resonances for β-protons and β-carbons in metallacyclobutane rings are found well upfield of those for α-protons and α-carbons in d^0 metallocene complexes containing titanium, zirconium, and hafnium[11-13] and in trigonal-bipyramidal complexes containing tantalum,[14]

---

[7] (a) Grubbs found that *cis*- and *trans*-$(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)Ti[CH_2CH(t\text{-}Bu)CH_2]$ react with diphenylacetylene at the same rate.[7b] The same is also true for *cis*- and *trans*-$(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_2Me_3)Ti[CH_2CH(t\text{-}Bu)CH_2]$. In this case isomers equilibrate by loss of olefin, so isomer equilibration is not responsible for the observed equal rates. (b) Finch, W. C.; Anslyn, E. V.; Grubbs, R. H. *Organometallics* **1988**, *8*, 2406.

[8] (a) McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 1315. (b) Grubbs, R. H.; Miyashita, A.; Liu, M.; Burk, P. *J. Am. Chem. Soc.* **1978**, *100*, 2418.

[9] Schrock, R. R.; Murdzek, J. S.; Bazan, G.; Robbins, J.; DiMare, M.; O'Regan, M.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

[10] Toreki, R.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2448.

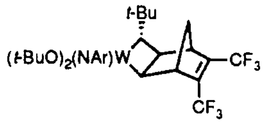
[11] (a) Howard, T. R.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 6876. (b) Lee, J. B.; Gajda, G. J.; Schaefer, W. P.; Howard, T. R.; Ikariya, T.; Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 7358. (c) Straus, D. A.; Grubbs, R. H. *J. Mol. Catal.* **1985**, *28*, 9.

[12] (a) Seetz, J. W. F. L.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 248. (b) Seetz, J. W. F. L.; van de Heisteeg, B. J.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *J. Mol. Catal.* **1985**, *28*, 71.

[13] Erker, G.; Czisch, P.; Krüger, C.; Wallis, J. M. *Organometallics* **1985**, *4*, 2059.

[14] (a) Wallace, K. C.; Liu, A. H.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 4964. (b) Wallace, K. C.; Schrock, R. R. *Organometallics* **1986**, *5*, 2162.

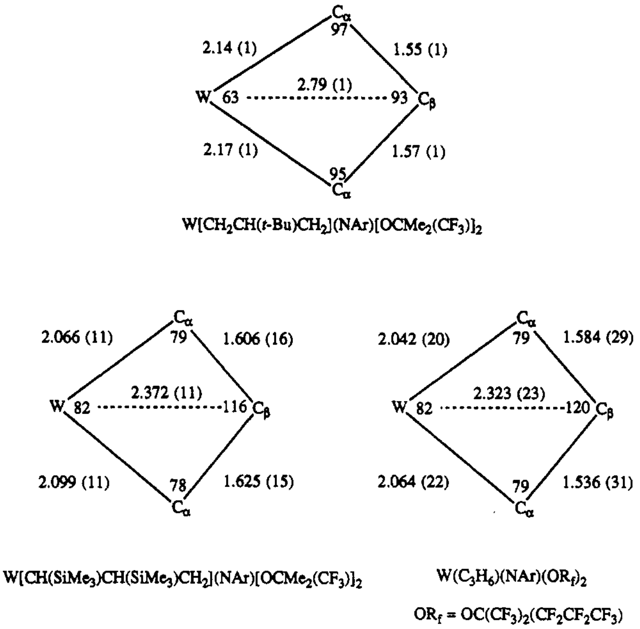
Table VI. Structural Data for Square-Pyramidal Tantalum and Tungsten Metallacyclobutane Complexes[a]

compd	M---C_α	M---C_β	C_α–M–C_α	M–C_α–C_β	C_α–C_β–C_α	ref
Ta[CH(Ph)CH(*t*-Bu)CH_2](DIPP)$_3$	2.188 (24) 2.168 (24)	2.782 (24)	64.4 (9)	94.2 (1.4) 97.0 (1.5)	98.4 (18)	14
W[CHCH(*t*-Bu)CH_2](NAr)[$OCMe_2(CF_3)$]$_2$	2.14 (1) 2.17 (1)	2.79 (1)	63.4 (4)	95.4 (6) 97.1 (6)	92.9 (8)	this work
	2.25 (1) 2.19 (1)		64.6 (5)	94.1 (8) 97.5 (9)	104 (1)	16
W[CH(*t*-Bu)$CH_2CH(CO_2Me)$](NAr)[$OCMe_2(CF_3)$]$_2$	2.221 (8) 2.205 (8)		65.1 (3)	93.1 (5) 94.2 (5)	101.7 (7)	6

[a] Distances are in angstroms and angles in degrees.

molybdenum,[9] and tungsten.[1,15] This effect has been attributed to the β-carbon being "shielded" by the metal. In structurally characterized titanacyclobutane complexes, a typical Ti---C_β distance is 2.5–2.6 Å, $\delta(H_\alpha) - \delta(H_\beta) \approx 3$ ppm, and $\delta(C_\alpha) - \delta(C_\beta) \approx 60$ ppm. In structurally characterized trigonal-bipyramidal tungstacyclobutane complexes,[1] a typical W---C_β distance is 2.3–2.4 Å, $\delta(H_\alpha) - \delta(H_\beta) \approx 5$ ppm, and $\delta(C_\alpha) - \delta(C_\beta) \approx 100$ ppm. Ta[CH(C_5H_8)CHCH(*t*-Bu)](OAr)$_3$ has a trigonal-bipyramidal geometry with axial phenoxide ligands and a Ta---C_β distance of 2.382 (16) Å.[14a] NMR chemical shifts in this tantalacycle are not as clear as in the analogous O-2,6-$C_6H_3Me_2$ species, for which $\delta(H_\alpha) = 5.21$ and 3.72 ppm, $\delta(H_\beta) = 0.84$ ppm, $\delta(C_\alpha) = 132.5$ and 135.0 ppm, and $\delta(C_\beta) = 29.0$ ppm. Therefore, there appears to be a direct correlation between $\delta(C_\alpha) - \delta(C_\beta)$ and the M---C_β distance in a variety of compounds, the largest $\delta(C_\alpha) - \delta(C_\beta)$ value (100 ppm) being associated with the smallest M---C_β distance (2.3–2.4 Å). Since the shortest M–C_α bonds are also found when $\delta(C_\alpha) - \delta(C_\beta)$ is maximized, a reasonable rationalization of the low-field α-carbon and α-proton chemical shifts is that the α-CR_2 group is an incipient alkylidene. The high-field chemical shifts for β-carbons and β-protons are directly proportional to the extent to which that is the case, but it is not as clear why, since β-proton and -carbon shifts in "ordinary" high-oxidation-state alkylidene complexes are not unusual.

Three square-pyramidal metallacycles have been structurally characterized in addition to the one reported here, Ta[$CH_2CH(Ph)CH$(*t*-Bu)](OAr)$_3$,[14] the metallacycle that results from addition of 2,3-bis(trifluoromethyl)norbornadiene to W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$,[16] and W[CH(*t*-Bu)$CH_2CH(CO_2Me)$](NAr)(O-*t*-Bu)$_2$.[6] Structural data for these species are similar to those for W[CH_2CH(*t*-Bu)CH_2](NAr)[$OCMe_2(CF_3)$]$_2$ (Table VI). In square-pyramidal metallacyclobutane complexes the relatively long M---C_β distance and approximately single M–C_α bonds give rise to smaller C_α–M–C_α and C_α–C_β–C_α angles and larger M–C_α–C_β angles (Figure 7). Since there is not as much multiple-bond character to the M–C_α bonds and the M---C_β distance is well outside what could be called a M–C_β bonding distance, NMR data for square-pyramidal metallacycles are substantially different from those for trigonal-bipyramidal metallacycles (Table II); i.e., chemical shifts for H_α and H_β are comparable, and $\delta(C_\alpha) - \delta(C_\beta)$ is ~20 ppm for similarly substituted carbon atoms. (In Ta[CH(Ph)CH(*t*-Bu)CH_2](DIPP)$_3$ $\delta(C_\alpha) - \delta(C_\beta)$ is 39 ppm for CHPh and 21 ppm for CH_2.[14]) Therefore, the correlation between $\delta(C_\alpha) - \delta(C_\beta)$ and M---C_β appears to continue in the square pyramids, $\delta(C_\alpha) - \delta(C_\beta)$ being only ~20 ppm when M---C_β is the largest observed so far (~2.8 Å). Chemical shifts for α-carbons and α-protons and J_{CH} values (~130 Hz) in SP metallacycles appear to be significantly more "aliphatic" compared to the "olefinic" values in TBP species.



W[CH_2CH(*t*-Bu)CH_2](NAr)[$OCMe_2(CF_3)$]$_2$

W[$CH(SiMe_3)CH(SiMe_3)CH_2$](NAr)[$OCMe_2(CF_3)$]$_2$

W(C_3H_6)(NAr)(OR_f)$_2$

$OR_f = OC(CF_3)_2(CF_2CF_2CF_3)$

Figure 7. Bond lengths and distances in the metallacyclobutane ligands of W[CH_2CH(*t*-Bu)CH_2](NAr)[$OCMe_2(CF_3)$]$_2$ (**1b**), W[$CH_2CH(SiMe_3)CH(SiMe_3)$](NAr)[$OCMe(CF_3)_2$]$_2$, and W($CH_2CH_2CH_2$)(NAr)[$OC(CF_3)_2(CF_2CF_2CF_3)$]$_2$.

In the types of complexes presented here, it appears that highly electron-withdrawing alkoxide ligands stabilize a trigonal-bipyramidal geometry, whereas relatively electron-donating alkoxide ligands stabilize a square-pyramidal geometry. This is seen most clearly in the series of unsubstituted metallacyclobutane complexes W($CH_2CH_2CH_2$)(NAr)(OR)$_2$. When OR is highly electron-withdrawing ($OC(CF_3)_2(CF_2CF_2CF_3)$ or $OCMe(CF_3)_2$), the complex has a trigonal-bipyramidal geometry. If OR is relatively electron-donating (O-*t*-Bu or $OCEt_3$), the complex has a square-pyramidal geometry. If OR is intermediate in electron-withdrawing ability ($OCMe_2(CF_3)$ or OAr), then both metallacyclobutane complexes are present.

---

(15) (a) Kress, J.; Osborn, J. A.; Greene, R. M. E.; Ivin, K. J.; Rooney, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 899. (b) Kress, J.; Osborn, J. A.; Amir-Ebrahimi, V.; Ivin, K. J.; Rooney, J. J. *J. Chem. Soc., Chem. Commun.* **1988**, 1164. (c) Ivin, K. J.; Kress, J.; Osborn, J. A.; Rooney, J. J. In *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer: Dordrecht, The Netherlands, 1989. (d) Kress, J.; Osborn, J. A.; Ivin, K. J.; Rooney, J. J. In *Recent Advances in Mechanistic and Synthetic Aspects of Polymerization*; Guyot, A., Fontanille, M., Eds.; Reidel: Dordrecht, The Netherlands, 1987; p 363. (e) Kress, J., Osborn, J. A.; Ivin, K. J. *J. Am. Chem. Soc., Chem. Commun.* **1989**, 1234.

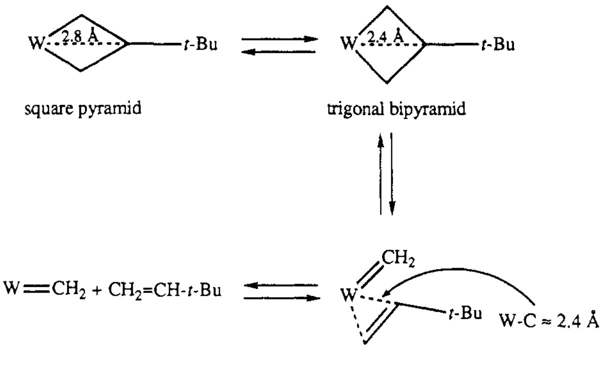
(16) Bazan, G. C.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J.; Davis, W. M. *J. Am. Chem. Soc.*, in press.

Evidence suggests that all complexes are fluxional on the NMR time scale at 25 °C, although that process is fully observable only when a significant amount of each geometry is present, and therefore little is known about the relative rates for different alkoxide complexes at this stage. We can think of two possible explanations of various metallacycle core geometries. First, the trigonal-bipyramidal geometry is disfavored when relatively strong electron-donating alkoxides are present because the axial imido and alkoxide ligands must compete as π-donors for the same set of empty d orbitals. Second, electron-withdrawing alkoxides should increase the electrophilicity of the metal and therefore its tendency to form shorter M–C bonds of higher order, as found in TBP species. The size of the alkoxide ligand seems to be relatively unimportant in determining the geometry, as evidenced by the fact that both $W(CH_2CH_2CH_2)(NAr)(O\text{-}t\text{-}Bu)_2$ and $W(CH_2CH_2CH_2)(NAr)(OCEt_3)_2$ are square pyramids.

The nature of the metallacycle's substituents is also a factor in determining structure. For example, β-*t*-Bu-substituted metallacycles are square pyramidal (OR = $OCMe_2(CF_3)$, OAr, O-*t*-Bu) while β-$SiMe_3$-substituted metallacycles are trigonal bipyramidal (OR = OR_f, $OCMe(CF_3)_2$, OAr); note that for OR = OAr both types are known. That β-*t*-Bu-substituted metallacycles are square pyramidal can perhaps be rationalized on the basis of sterics; i.e., the bulky *tert*-butyl group is furthest away from the metal in a square pyramid. However, subtle electronic factors must also be important. For example, on might expect $W[CH_2CH(SiMe_3)CH_2](NAr)(OAr)_2$ to be either square pyramidal or a mixture of TBP and SP forms, since the corresponding unsubstituted metallacyclobutane complex exists as a mixture of TBP and SP forms, while the β-*t*-Bu-substituted metallacycle is a square pyramid. In fact, **2b** is a mixture of cis and trans TBP isomers. Perhaps it is the ability of a trimethylsilyl group to stabilize an adjacent carbanion that causes the TBP form to be favored. (C_β is relatively close to the metal in the TBP species and therefore should be relatively carbanionic in these high-oxidation-state complexes.)

In a previous paper[1a] we suggested that trigonal-bipyramidal metallacycles that contain electron-withdrawing alkoxides lose olefin less readily. This proposal makes some sense since the rate of loss of olefins from an "olefin/alkylidene" transition state should slow as the alkoxide becomes more electron-withdrawing; i.e., re-formation of the metallacycle becomes more competitive. We now have some kinetic evidence which supports that suggestion. $\Delta G^{\ddagger}_{298}$ (25.0 kcal mol^{-1}) for loss of vinyltrimethylsilane from $W[CH_2CH(Me_3Si)CH_2](NAr)(OR_f)_2$ versus $\Delta G^{\ddagger}_{298}$ (22.7 kcal mol^{-1}) for loss of vinyltrimethylsilane from $W[CH_2CH(Me_3Si)CH_2](NAr)[OCMe(CF_3)_2]_2$ translates into a rate difference of ~50 (Table V). Unfortunately these data are tainted by the fact that OR_f and $OCMe(CF_3)_2$ are not the same size. Therefore, one also could propose that it is simply more difficult to lose an olefin from $W[CH_2CH(Me_3Si)CH_2](NAr)(OR_f)_2$ because OR_f is larger than $OCMe(CF_3)_2$ and it seems likely that *an olefin must migrate toward the metal and possibly even* twist by up to 90° before being lost (see discussion below). Under those circumstances bulkier substituents (or ligands) should slow the rate of loss of the olefin. There is some evidence that supports this view. In titanium systems an olefin is lost more slowly when bulkier substituents are present on the MC_3 ring,[17] and tantalacycles[14] and tungstacycles[15] appear to ring-open more slowly in the presence of bulky substituents. The fact $\Delta S^{\ddagger}$ values for opening titanacyclobutane[7b,18,19] and tantalacyclobutane[14] rings are only slightly smaller than those found here is evidence that the rate-limiting step is similar in all such metallacycle systems. In the titanium systems it was concluded that an "alkylidene/olefin" complex was a transition state in a reaction in which an olefin was lost from a TiC_3 ring.[7b] It is interesting to note in this context that ethylene, not *tert*-butylethylene, appears to be lost most readily from the α-*tert*-butyl-substituted metallacycles observed here. This fact would be consistent with formation of an "ethylene/neopentylidene" transition state more easily for steric reasons than a "*tert*-butylethylene/methylene" transition state. This suggestion is still speculative, since we still know little about what could conceivably be a greater inherent stability of neopentylidene complexes relative to that of methylene complexes. However, the suggestion that electron-withdrawing alkoxides slow the rate of loss of an olefin from a WC_3 ring for electronic reasons alone at least should not be accepted without qualification.

Scheme III



It is difficult to ignore the evidence for a stronger *opposite* trend, i.e., that *electron-donating* alkoxides stabilize metallacycles (square pyramids) toward loss of an olefin. For example, $W[CH_2CH(t\text{-}Bu)CH_2](NAr)[OCMe_2(CF_3)]_2$ reacts with ethylene (10 equiv, 25 °C) to give $W[CH_2CH_2CH_2](NAr)[OCMe_2(CF_3)]_2$ quantitatively within 20 min, while the analogous reaction between $W[CH_2CH(t\text{-}Bu)CH_2](NAr)(O\text{-}t\text{-}Bu)_2$ and ethylene requires days to reach completion. That rate difference could easily be a factor of 500. The reaction between $W[CH(t\text{-}Bu)CH_2CH_2](NAr)(OR)_2$ and ethylene also is much slower when OR = O-*t*-Bu than when OR = $OCMe_2(CF_3)$ or OAr. This proposal would be consistent with bindings in titanacyclobutane chemistry, where an electron-donating substituent on a Cp ring slowed loss of an olefin from the TiC_3 ring.[7b]

The profoundly different geometries of the two kinds of WC_3 rings suggest why the rate-limiting step for loss of olefin from the two types of rings could be significantly different. An "alkylidene/olefin" transition state should be more accessible from the trigonal-bipyramidal metallacycle since the β-carbon atom is already within bonding distance of the metal and there is already a significant amount of M–C_α π bonding, i.e., an alkylidene ligand is beginning to form (Scheme III). On the other hand, in order for what appears to be a much more aliphatic square-pyramidal metallacycle to reach an alkylidene/olefin transition state, the β-carbon atom (and also an α-carbon atom) would have to be pulled closer to the metal,

---

(17) Straus, D. A.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1658.

(18) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733.

(19) Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 4880.

a process that may be significantly easier when electron-withdrawing alkoxides are present. There are some data in the literature that also suggest a connection between metallacycle geometry and transition-state accessibility. The metallacyclobu*tene* complex $Cp_2Ti[C(SiMe_3)C(SiMe_3)CH_2]$, in which the Ti---$C_\beta$ distance is 2.348 Å, can be substituted by acetylenes readily, while $Cp_2Ti(CPhCPhCH_2)$, in which the Ti---C_β distance is 2.533 Å, is relatively inert to substitution. The enhanced reactivity of $Cp_2Ti[C(SiMe_3)C(SiMe_3)CH_2]$ was attributed to the fact that it was distorted significantly toward a "carbene/acetylene adduct".[20]

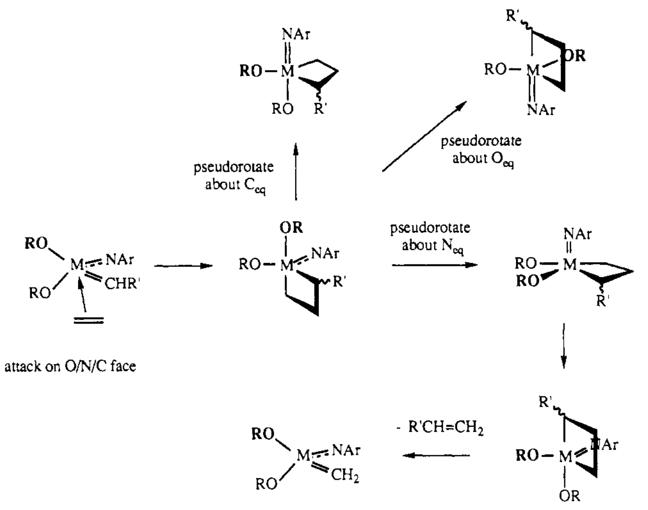
Data that could be used as evidence against the proposal that an olefin is lost less readily from a square pyramid is that the rate of loss of (*t*-Bu)CH=CH_2 from square-pyramidal $W[CH_2CH(t\text{-}Bu)CH_2](NAr)(OAr)_2$ is virtually the same at 298 K as the rate of loss of $(Me_3Si)CH{=}CH_2$ from trigonal-bipyramidal $W[CH_2CH(Me_3Si)CH_2](NAr)(OAr)_2$. However, the difference between $(Me_3Si)CH{=}CH_2$ and (*t*-Bu)CH=CH_2 as leaving groups is probably significant enough in these delicately balanced systems to invalidate even a comparison of what are superficially closely related TBP and SP species. Other uncertainties include the role played by other core geometries (see below). In short, we cannot conclude on the basis of these data alone that a given olefin would *not* be lost more slowly from a square-pyramidal complex than from a trigonal-bipyramidal complex.

Since trigonal-bipyramidal complexes are accessible at rates on the order of the NMR time scale, one could go one step further by proposing that a square-pyramidal metallacyclobutane complex *must rearrange* to form a trigonal-bipyramidal metallacycle of the type observed here before an olefin can be lost (Scheme III). This proposal would explain why square-pyramidal metallacycles that contain *tert*-butoxide ligands do not lose an olefin readily; little of the required trigonal-bipyramidal species is present. The TBP species also may not form as rapidly or lose an olefin as readily as when a more electron-withdrawing alkoxide is present, but the low concentration of the TBP species alone would account for a significantly slower rate of olefin loss.

There are few other kinetic data in the literature for tungstacycles with which to compare the data obtained here. A square-pyramidal tungstacycle prepared by adding 2,3-bis(trifluoromethyl)norbornadiene to W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ has been shown to open with $\Delta H^{\ddagger} = 22$ kcal mol^{-1} and $\Delta S^{\ddagger} = -3$ eu;[16] note that $\Delta S^{\ddagger}$ is similar to that for $W[CH_2CH(t\text{-}Bu)CH_2](NAr)(OAr)_2$ (−6 eu, Table V). A tungstacycle prepared by adding *endo*,*endo*-5,6-dimethylnorbornene to "$[W(CH\text{-}t\text{-}Bu)(OCH_2\text{-}t\text{-}Bu)_2Br]^+$" opens with $\Delta S^{\ddagger} = -6$ eu.[15b] Its structure has not been determined, but NMR data ($\delta(H_\alpha) = 4.89$ and 7.14 ppm and $\delta(H_\beta) = 0.82$ ppm) suggest that it is a trigonal bipyramid. $\Delta S^{\ddagger} = -6$ eu is not consistent with the positive values for $\Delta S^{\ddagger}$ for loss of olefin in several TBP complexes studied here (Table V), but not enough is known at this stage to state that such a difference is significant.

Data concerning ring opening of titanacycles are extensive.[7b,18,19] Although these data cannot be compared directly with those presented here because of the relatively rigid nature of the $TiCP_2$ framework, there turn out to be many more similarities than differences between the two systems. In particular, the concept of the metallacycle as an incipient "olefin/alkylidene complex" appears to be valid for both. The fact that alkylidene complexes of Ti are relatively high-energy species (multiple M–ligand bonds are rare for group IV metals) in part explains why titanacycles do not lose an olefin nearly as readily as metallacycles that contain metals further to the right.

Scheme IV



It is worth discussing now more specifically how an olefin might add to an alkylidene complex of the type discussed here, in addition to the microsocopic reverse, how it leaves the coordination sphere of a metallacyclobutane complex. From a steric point of view it seems most reasonable that the olefin will add to one of the faces of the pseudotetrahedral catalyst to give (in an ideal situation) an initial axial/equatorial metallacycle, as shown in Scheme IV for ethylene attacking the C/N/O face of a generalized alkylidene complex (no rotamer specified). This initial complex then must rearrange so that R'CH=CH_2 can be lost from an axial position. Rearrangement by a Berry-type pseudorotation about the equatorial nitrogen atom gives an intermediate square-pyramidal species (of the type observed here) and then a new TBP species of the type required for loss of R'CH=CH_2. Pseudorotation about an equatorial carbon atom in the initial complex would generate a new TBP species (the other type of tungstacycle that has been observed here), while pseudorotation about an equatorial oxygen atom would generate a TBP species of the type that would be formed if an olefin were to attack a C/O/O face of the tetrahedron. (The third possibility, attack on the N/O/O face of the catalyst, cannot lead to a metallacycle.) Five-coordinate metallacycles will all be distorted to a signficant degree, a fact that will further decrease the energy differences between them and facilitate their interconversion. However, energy differences are still significant enough so that certain structures are preferred, and therefore it makes some sense to propose that such species interconvert by relatively well-defined pathways and that there may indeed by geometric restrictions on how a metallacycle can form, and conversely, on how it can break up. The point is that an *unobservable* (axial/equatorial) metallacyclobutane complex may actually be the one that is formed first and the one from which an olefin is lost. A point for debate, however, is whether the initial distorted axial/equatorial metallacyclobutane complex has any stability or should best be considered a transition state, from which either of the observable type of TBP or SP metallacycles can form. Under these circumstances it does not appear to be fruitful to discuss whether bonding restrictions dictate how the olefin must be oriented when it attacks the C/N/O face.

There is evidence that attack on a C/N/O face is the kinetically most favorable one. One of the first alkylidene

---

[20] McKinney, R. J.; Tulip, T. H.; Thorn, D. L.; Coolbaugh, T. S.; Tebbe, F. N. *J. Am. Chem. Soc.* 1981, *103*, 5584.

complexes of tungsten to be characterized crystallographically, W(O)(CH-*t*-Bu)Cl$_2$(PEt$_3$),[21] is a trigonal bipyramid containing equatorial oxo and neopentylidene ligands and an axial phosphine ligand. (The *tert*-butyl group of the neopentylidene ligand points toward the oxo ligand.). More recent studies have shown that trimethylphosphine reacts with Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$, which is known to have a structure in which the neopentylidene ligand is syn,[9] to give a product that is an analogous trigonal bipyramid in which a syn neopentylidene and an imido ligand are located in equatorial positions in a trigonal bipyramid and trimethylphosphine is bound in an axial position.[22] This species is slowly converted into a related species that is believed to have a structure analogous to W(CHCH=CHMe)(NAr)[OCMe(CF$_3$)$_2$]$_2$(quinuclidine), a trigonal-bipyramidal species containing an anti equatorial vinyl alkylidene and imido ligands and an axial quinuclidine ligand.[23] Less direct support consists of the fact that Re(C-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ reacts with excess 3-hexyne to yield a distorted-trigonal-bipyramidal triethyl rhenacyclobuta*diene* complex in which the ring spans axial and equatorial sites and in which the imido ligand is in an equatorial position,[24] i.e., the one that would be formed when 3-hexyne attacks the C/N/O face of incipient Re(CEt)(NAr)[OCMe(CF$_3$)$_2$]$_2$.

Conclusion

Although there are still many details to fill in, there now seem to be two main reasons an alkylidene complex that contains relatively electron-withdrawing ligands is much more active for the metathesis of ordinary olefins than a complex that contains *tert*-butoxide ligands. First, as has been proposed elsewhere,[1] the initial interaction between the metal and the olefin can be regarded as an electrophilic attack on the olefin. The rate of that reaction should be very sensitive to the nature of the alkoxide, especially if the olefin attacks a C/N/O face of the tetrahedron trans to one of the alkoxide ligands to give the initial "olefin/alkylidene" complex and then the initial metallacycle. Second, electron-withdrawing ligands create metallacyclobutane complexes that are more distorted toward "olefin/alkylidene" complexes. Therefore, the pathway for loss of the olefin from a distorted ring is significantly lower in energy than from a ring that is relatively undistorted, even though the metal is relatively electrophilic. A potential third reason some catalysts are especially active is that a variety of distorted five-coordinate metallacycles are close in energy and interconvert readily, thereby facilitating formation of the geometry that is required for rapid loss of the olefin metathesis product. Distortion of five-coordinate geometries can be attributed to a significant extent to bulky ligands.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by using standard Schlenk techniques. Reagent grade ether, tetrahydrofuran, and toluene were distilled from sodium benzophenone ketyl under nitrogen. Pentane was washed with 5% nitric acid in sulfuric acid, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was distilled from calcium hydride under nitrogen. All deuterated NMR solvents were passed through a column of activated alumin.

W(CHSiMe$_3$)(NAr)[OCMe$_2$(CF$_3$)]$_2$,[1a] W(CHSiMe$_3$)(NAr)[OCMe(CF$_3$)$_2$]$_2$,[1a] and W(CH-*t*-Bu)(NAr)(OAr)$_2$[1b] were prepared as described in the literature. All other reagents were purchased from commercial sources and purified by standard techniques.

NMR data are listed in parts per million downfield from TMS for proton and carbon and relative to 85% phosphoric acid for phosphorus. Coupling constants are quoted in hertz. Obvious multiplicities and routing coupling constants often are not listed. Spectra were obtained in benzene-d_6 at 25 °C unless otherwise noted.

Preparation of Compounds. W[CH$_2$CH(*t*-Bu)CH$_2$](NAr)[OCMe$_2$(CF$_3$)]$_2$ (1b). A 1.1-mmol amount of ethylene was added via vacuum transfer to a solution of 150 mg (0.219 mmol) of W(CH-*t*-Bu)(NAr)[OCMe$_2$(CF$_3$)]$_2$ and 424 μL (3.29 mmol) of *tert*-butylethylene in 3.0 mL of pentane. After the solution had been stirred at 25 °C for 30 min, it was concentrated to a volume of ~0.25 mL and cooled to −40 °C. **1b** (108 mg, 0.152 mmol, 69%) was isolated as a yellow, microcrystalline solid after removing the mother liquor by pipet: ^{1}H NMR δ 7.06–6.98 (mult, ^{3}H, H$_{aryl}$), 3.89 (sept, J_{HH} = 6, 2 H, C*H*Me$_2$), 2.62 (tt, J_{HH} = 6 and 3, 1 H, H$_\beta$), 2.36 (ddd, J_{HH} = 7, 5, and 3, 2 H, H$_\alpha$), 1.36 (s, 6 H, OCMe$_2$(CF$_3$)), 1.31 (s, 6 H, OCMe$_2$(CF$_3$)), 1.13 (ddd, 2 H, H$_\alpha$'), 0.918 (s, 9 H, *t*-Bu); ^{13}C NMR δ 150.4 (C$_{ipso}$), 146.1 (C$_o$), 126.9 (q, J_{CF} = 284, CF$_3$), 127.1 (C$_p$), 123.0 C$_m$), 82.7 (J_{CF} = 30, OCMe$_2$(CF$_3$)), 47.1 (J_{CH} = 125, J_{CW} = 50, C$_\alpha$), 46.0 (J_{CH} = 127, C$_\beta$), 37.2 (*C*Me$_3$), 28.2 (*C*HMe$_2$), 26.0, 24.1, 24.0 (*t*-Bu, CH*Me*$_2$, and OC*Me*$_2$(CF$_3$)). Anal. Calcd for WC$_{27}$H$_{46}$F$_6$NO$_2$: C, 45.58; H, 6.09. Found: C, 45.86; H, 6.14.

W[CH$_2$CH(*t*-Bu)CH$_2$](NAr)(O-*t*-Bu)$_2$ (3b). A 2.2-mmol amount of ethylene was added via vacuum transfer to a solution of 250 mg (0.434 mmol) of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and 0.84 mL (6.51 mmol) of *tert*-butylethylene in 3.0 mL of pentane. After the solution had been stirred at 25 °C for 23 h, it was concentrated to a volume of ~0.5 mL and cooled to −40 °C. The orange solid that precipitated was recrystallized a second time from minimal pentane at −40 °C to afford 73 mg (0.121 mmol, 28%) of **3b** as a bright yellow solid: ^{1}H NMR δ 7.11–7.00 (mult, 3 H, H$_{aryl}$), 4.06 (C*H*Me$_2$), 2.68 (tt, J_{HH} = 6 and 3, 1 H, H$_\beta$), 2.36 (ddd, J_{HH} = 9, 7, and 2, 2 H, H$_\alpha$), 1.33 (O-*t*-Bu), 1.31 (CH*Me*$_2$), 1.09 (ddd, 2 H, H$_\alpha$), 1.01 (*t*-Bu); ^{13}C NMR δ 151.1 (C$_{ipso}$), 145.1 (C$_o$), 125.7 (C$_p$), 122.9 (C$_m$), 82.1 (O-*t*-Bu), 46.8 (J_{CH} = 130, C$_\beta$), 44.9 (J_{CH} = 133, C$_\alpha$), 37.6 (*C*Me$_3$), 32.1, 28.2, 26.5 (O-*t*-Bu, *t*-Bu, and CH*Me*$_2$).

W[CH$_2$CH(*t*-Bu)CH$_2$](NAr)(OAr)$_2$ (2b). A 1.3-mmol amount of ethylene was added via vacuum transfer to a solution of 200 mg (0.255 mmol) of W(CH-*t*-Bu)(NAr)(OAr)$_2$ and 493 μL (3.83 mmol) of *tert*-butylethylene in 4.0 mL of pentane. After the solution had been stirred at 25 °C for 30 min, it was concentrated to a volume of ~0.5 mL and cooled to −40 °C. **2b** (178 mg, 0.219 mmol, 86%) was isolated as a bright yellow, microcrystalline solid after removing the mother liquor by pipet: ^{1}H NMR δ 7.11–6.94 (mult, 9 H, H$_{aryl}$), 3.80 (sept, 2 H, C*H*Me$_2$(NAr)), 3.65 (sept, 4 H, C*H*Me$_2$(OAr)), 2.71 (tt, J_{HH} = 6 and 3, 1 H, H$_\beta$), 2.39 (ddd, J_{HH} = 9, 6, and 3, 2 H, H$_\alpha$), 1.25 (d, J_{HH} = 7, 24 H, CH*Me*$_2$), 1.20 (d, J_{HH} = 7, 12 H, CH*Me*$_2$), 0.781 (*t*-Bu); ^{13}C NMR δ 157.5 (C$_o$ (NAr)), 151.2 (C$_{ipso}$ (NAr)), 145.0 (C$_{ipso}$ (OAr)), 138.5 (C$_o$ (OAr)), 128.3 (C$_p$ (NAr)), 126.9 (C$_m$ (NAr)), 123.9 (C$_m$ (OAr)), 123.0 (C$_p$ (OAr or NAr)), 48.5 (J_{CH} = 133, J_{CW} = 49, C$_\beta$), 45.1 (J_{CH} = 131, C$_\beta$), 37.2 (*C*Me$_3$), 28.9 (*C*HMe$_2$), 28.1 (*C*HMe$_2$), 25.9 (CH*Me*$_2$ or *t*-Bu), 24.2 (CH*Me*$_2$ or *t*-Bu), 24.1 (CH*Me*$_2$ or *t*-Bu). One of the C$_p$ resonances is obscured by the C$_6$D$_6$ resonance. Anal. Calcd for WC$_{43}$H$_{65}$NO$_2$: C, 63.62; H, 8.07. Found: C, 63.69; H, 8.05.

Observation of W[CH(*t*-Bu)CH$_2$CH$_2$](NAr)[OCMe$_2$(CF$_3$)]$_2$ (1a) and W(CH$_2$CH$_2$CH$_2$)(NAr)[OCMe$_2$(CF$_3$)]$_2$ (1c). W(CH-*t*-Bu)(NAr)[OCMe$_2$(CF$_3$)]$_2$ (20 mg, 0.0293 mmol) was dissolved in 700 μL of toluene-d_8 and the solution placed inside an NMR tube fitted with a septum cap. The solution was frozen in liquid N$_2$, and ethylene (3.6 mL, ~0.15 mmol) was injected by syringe into the NMR tube. The NMR sample was quickly thawed and lowered into a −70 °C probe. **1a** formed slowly at −70 °C. The reaction to form **1a** was complete by the time the temperature was raised to −40 °C. ^{1}H NMR assignments for the metallacycle protons are made by analogy to unsubstituted and β-*t*-Bu-substituted metallacycles: ^{1}H NMR (**1a**, toluene-d_8, −40 °C) δ

---

[21] Wengrovius, J. H.; Schrock, R. R.; Churchill, M. R.; Missert, J. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 4515.

[22] Bazan, G.; O'Regan, M.; Davis, W. M. Unpublished results.

[23] Crowe, W. E.; Davis, W. M. Unpublished results.

[24] Schrock, R. R.; Weinstock, I. A.; Horton, A. D.; Liu, A. H.; Schofield, M. H. *J. Am. Chem. Soc.* **1988**, *110*, 2686.

7.05–6.90 (H_{aryl}), 4.11 (dd, J_{HH} = 18 and 10, 1 H, H_β), 3.95 (s, C*H*Me$_2$), 2.60 (mult, 1 H, H_β'), 2.27 (dd, J_{HH} = 13 and 5, 1 H, H_α), 1.80 (overlapping multiplets, 2 H, H_α' and H_α''), 1.42–1.12 (8 lines, 33 H, CH*Me*$_2$, OC*Me*$_2$(CF$_3$), *t*-Bu) (above −30 °C *tert*-butylethylene and **1c** began to form); ^{1}H NMR (**1c**, toluene-d_8, 28 °C) δ 7.10–7.22 (H_{aryl}), 3.90 (C*H*Me$_2$), 1.42 (br singlet, OC*Me*$_2$(CF$_3$)), 1.25 (CH*Me*$_2$) (resonances for the metallacycle protons are too broad to be observed at this temperature); ^{1}H NMR (toluene-d_8, −30 °C) δ 7.15–6.70 (H_{aryl}), 4.65 (mult, H_α(TBP)), 4.40 (mult, H_α'(TBP)), 4.30 (mult, H_β(SP)), 3.86 (sept, 2 H, C*H*Me$_2$ for both isomers), 2.80 (mult, H_β'(SP)), 2.29 (mult, H_α(SP)), 1.72–0.80 (overlapping signals, CH*Me*$_2$ and OCMe$_2$(CF$_3$) for both isomers and H_α'(SP)), −0.73 (H_β(TBP)), −1.21 (H_β'(TBP)).

W(CH-*t*-Bu)(NAr)[OCMe$_2$(CF$_3$)]$_2$ (20 mg, 0.0293 mmol) was placed inside an NMR tube fitted with a 14/20 female joint and the tube attached to a calibrated gas bulb. The assembly was attached to a high-vacuum line. Toluene-d_8 (700 μL) was freeze–pump–thaw-degassed three times and vacuum-transferred to the tube. The solution was frozen in liquid N$_2$, and $^{13}C_2H_4$ (0.15 mmol assuming ideal gas) was added to the tube by vacuum transfer. The tube was then flame-sealed. The NMR solution was quickly thawed and placed inside a −40 °C probe: ^{13}C NMR (**1a(SP)**, toluene-d_8, −40 °C) δ 48.2 (d, J_{CC} = 32, J_{CH} = 138 and 127, J_{CW} = 53, $C_\alpha H_2$), 24.1 (d, J_{CC} = 31, J_{CH} = 128, $C_\beta H_2$); ^{13}C NMR (**1a(TBP)** (trace), toluene-d_8, −40 °C) δ 97.2 (d, J_{CC} = 11), −0.61 (t). The solution was warmed to 25 °C and recooled to −40 °C: ^{13} NMR (**1a(SP)**, toluene-d_8, −40 °C) δ 43.6 (d, J_{CC} = 28, J_{CH} = 134, J_{CW} = 55, $C_\alpha H_2$), 24.2 (t, J_{CC} = 28, J_{CH} = 134, $C_\beta H_2$); ^{13}C NMR (**1a(TBP)**, toluene-d_8, −40 °C) δ 98.8 (d, J_{CC} = 13, J_{CH} = 154, J_{CW} = 68), −3.59 (t, J_{CC} = 13, J_{CH} = 154, $C_\beta H_2$).

Observation of W[CH(*t*-Bu)CH$_2$CH$_2$](NAr)(O-*t*-Bu)$_2$ (3a) and W(CH$_2$CH$_2$CH$_2$)(NAr)(O-*t*-Bu)$_2$ (3c). W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (15 mg, 0.0261 mmol) was dissolved in 700 μL of C$_6$D$_6$ and the solution placed inside an NMR tube fitted with a septum cap. Ethylene (3.0 mL, ~0.13 mmol) was injected by syringe. After 20 min the ^{1}H NMR spectrum of **3a** was recorded: ^{1}H NMR δ 7.08 (H_m), 6.97 (H_p), 4.29 (mult, 1 H, H_β), 4.11 (C*H*Me$_2$), 2.71 (mult, 1 H, H_β), 2.35 (mult, 1 H, H_α), 1.53 (mult, 1 H, H_α), 1.38 (s, O-*t*-Bu or C_αH(*t*-Bu)), 1.35 (d, CH*Me*$_2$), 1.31 (d, CH*Me*$_2$), 1.24 (s, O-*t*-Bu or C_αH(*t*-Bu)), 1.18 (s, O-*t*-Bu or C_αH(*t*-Bu)). One of the α-proton resonances is obscured. After 30 h an NMR spectrum of **3c** was obtained at −20 °C: ^{1}H NMR (toluene-d_8, −20 °C) δ 7.10–7.00 (H_{aryl}), 4.51 (dd, J_{HH} = 19 and 8, 1 H, H_β), 4.03 (C*H*Me$_2$), 2.88 (mult, 1 H, H_β'), 2.35 (mult, 2 H, H_α), 1.29 (overlapping resonances for *t*-Bu and CH*Me*$_2$). The H_α' resonance could not be identified unambiguously.

A ^{13}C NMR sample was obtained by vacuum-transferring 700 μL of toluene-d_8 and $^{13}C_2H_4$ (0.17 mmol) onto W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (20 mg, 0.0348 mmol). The solution was allowed to stand for 1.75 h at 25 °C and the ^{13}C NMR spectrum then recorded. The ratio of **3a** to **3d** was 2:1 at this time: ^{13}C NMR (**3a**, toluene-d_8, 25 °C) δ 45.4 (d, J_{CC} = 33, J_{CH} = 131 and 125, J_{CW} = 54, $C_\alpha H_2$), 24.9 (d, J_{CC} = 33, J_{CH} = 132, $C_\beta H_2$). After several hours, resonances for **3a** disappeared and were replaced by those for **3c** and ^{13}CH$_2$═CH(*t*-Bu): ^{13}C NMR (**3c**, toluene-d_8, 25 °C) δ 41.9 (d, J_{CC} = 30, J_{WC} = 52, $C_\alpha H_2$), 24.5 (t, J_{CC} = 29, $C_\beta H_2$).

Observation of W[CH(*t*-Bu)CH$_2$CH$_2$](NAr)(OAr)$_2$ (2a) and W(CH$_2$CH$_2$CH$_2$)(NAr)(OAr)$_2$ (2c). Ethylene (3.1 mL, ~0.13 mmol) was added by syringe to an NMR tube containing a frozen solution of W(CH-*t*-Bu)(NAr)(OAr)$_2$ (20 mg, 0.0255 mmol) in 600 μL of toluene-d_8. The solution was quickly thawed and placed inside the −60 °C probe: ^{1}H NMR (**2a**, toluene-d_8, −60 °C) δ 7.2–6.7 (v br, H_{aryl}), 6.0 (v br, H_α for a TBP metallacycle), 5.0 (v br, H_α' for a TBP metallacycle), 4.3 (v br, H_α'' for a TBP metallacycle or H_β for an SP metallacycle), 3.9–3.4 (3 broad lumps, C*H*Me$_2$ for OAr and NAr), 1.6–0.5 (several v br resonances, CH*Me*$_2$, *t*-Bu), −0.6 (v br, H_β for a TBP metallacycle), −0.8 (v brm, H_β' for a TBP metallacycle). Warming the sample to 25 °C yielded **2c**: ^{1}H NMR (**2c**, toluene-d_8, 25 °C) δ 7.06–6.95 (H_{aryl}), 3.71 (sept, 2 H, C*H*Me$_2$(NAr)), 3.61 (sept, 4 H, C*H*Me$_2$(OAr)), 3.03 (br, 2 H, H_α), 2.87 (br, 1 H, H_β), 2.32 (br, 2 H, H_α'), 1.81 (br, 1 H, H_β'), 1.21 (d, J_{HH} = 7, 24 H, CH*Me*$_2$(OAr)), 1.12 (d, J_{HH} = 7, 24 H, CH*Me*$_2$(NAr)). When the solution was recooled to −90 °C, both square-pyramidal and trigonal-bipyramidal isomers of **2c** were observed in a ratio of 1:1. ^{1}H NMR (**2c** isomers, toluene-d_8, −90 °C) δ 7.2–6.6 (H_{aryl}), 4.87 (br, H_α(TBP)), 4.75 (br, H_α'(TBP)), 4.43 (br, H_β(SP)), 3.9–3.5 (br overlapping signals, C*H*Me$_2$'s of NAr and OAr in both isomers), 3.0 (br, H_β'(SP)), 2.35 (br, H_α(SP)), 1.5–0.8 (several overlapping and v br resonances, CH*Me*$_2$'s of NAr and OAr in both isomers and H_α'(SP)), −0.56 (H_β(TBP)), −0.94 (H_β'(TBP)).

Partial ^{13}C NMR spectra of **2a** and **3c** were obtained by vacuum-transferring $^{13}C_2H_4$ (0.13 mmol) onto a frozen solution of W(CH-*t*-Bu)(NAr)(OAr)$_2$ (20 mg, 0.0255 mmol) in 700 μL of toluene-d_8: ^{13}C NMR (**2a**, toluene-d_8, −50 °C) δ 95.5 (v br, C_α for a TBP metallacycle), 30–20 (extremely broad, C_α and C_β in an SP metallacycle), −1.9 (v br, C_β for a TBP metallacycle). At 25 °C, **2c** and ^{13}CH$_2$═CH(*t*-Bu) are rapidly formed, but the C_α and C_β resonances for **2c** are coalesced at this temperature: ^{13}C NMR (**2c**, toluene-d_8, −50 °C) δ 59 (br, C_α), 15.7 (br, C_β); ^{13}C NMR (**2c(TBP)**, toluene-d_8, −50 °C) δ 99.3 (br, J_{CH} = 161, C_α), −3.25 (br, J_{CH} = 156, C_β); ^{13}C NMR (**2c(SP)**, toluene-d_8, −50 °C) δ 43.5 (br d, J_{CH} = 138 J_{CC} = 29, C_α), 22.6 (br t, J_{CH} = 133, J_{CC} = 29, C_β).

W(CH$_2$)(PMe$_3$)(NAr)[OCMe$_2$(CF$_3$)]$_2$. A solution of W(CH-*t*-Bu)(NAr)[OCMe$_2$(CF$_3$)] (150 mg, 0.220 mmol) and 1-pentene (120 mL, 1.10 mmol) in 5 mL of pentane was stirred for 5 min at room temperature, and trimethylphosphine (80 μL, 0.787 mmol) was added. After 15 min the volatile components were removed in vacuo to give an orange oil that could be recrystallized from minimal pentane at −40 °C to afford 96 mg of yellow-orange, crystalline product (62%). The same compound may be prepared by using ethylene in place of 1-pentene or by adding trimethylphosphine to **1b**: ^{1}H NMR δ 10.78 (dd, J_{HH} = J_{HP} = 7, 1 H, H_α), 10.49 (dd, J_{HH}, J_{HP} = 8 and 6, 1 H, H_α'), 7.05 (H_m), 6.92 (H_p), 4.23 (br, 1 H, C*H*Me$_2$), 3.50 (br, 1 H, C*H*Me$_2$), 1.90 (s, 3 H, OCMe$_2$(CF$_3$)), 1.79 (s, 3 H, OCMe$_2$(CF$_3$)), 1.39 (s, 3 H, OCMe$_2$(CF$_3$)), 1.29 (two overlapping doublets and a singlet, 15 H, OCMe$_2$(CF$_3$) and CH*Me*$_2$), 0.94 (d, J_{HP} = 10, 9 H, PMe$_3$); ^{13}C NMR δ 243.2 (J_{CH} = 131 and 154, J_{CP} = 11, C_α), 150.7 (C_{ipso}), 145.5 (br, C_o), 144.6 (br, C_o), 128.3 (C_m or C_p), 126.1 (C_m or C_p), 123.0 (C_m or C_p), 78.9 ($^2J_{CF}$ = 25, O*C*Me$_2$(CF$_3$)), 77.1 ($^2J_{CF}$ = 27, O*C*Me$_2$(CF$_3$)), 29.3 (*C*HMe$_2$), 28.0 (*C*HMe$_2$), 24.9, 23.6, 23.1, 22.0 (OC*Me*$_2$(CF$_3$) and OCHMe$_2$), 15.3 (J_{CP} = 26, PMe$_3$). Anal. Calcd for WC$_{24}$H$_{40}$NO$_2$P: C, 40.98; H, 5.73. Found: C, 41.09; H, 5.64.

W(CH$_2$)(PMe$_3$)(NAr)(OAr)$_2$. Ethylene (1.6 mmol) was added by vacuum transfer to W(CH-*t*-Bu)(NAr)(OAr)$_2$ (250 mg, 0.319 mmol) dissolved in 5 mL of diethyl ether. The solution was thawed and warmed to room temperature. After 1 h trimethylphosphine (32 μL, 0.315 mmol) was added. After 30 min the yellow precipitate was filtered off and washed with pentane at −40 °C to afford 136 mg of pale yellow product. The filtrate was concentrated and an additional 32 mg filtered off (combined yield 65%). This compound also can be prepared with 1-pentene in place of ethylene: ^{1}H NMR δ 11.51 (dd, J_{HH}, J_{HP} = 5 and 8, 1 H, H_α), 11.16 (dd, J_{HH} = J_{HP} = 7, 1 H, H_α'), 7.50–6.93 (H_{aryl}), 3.88 (br sept, 3 H, C*H*Me$_2$), 3.83 (sept, 2 H, C*H*Me$_2$), 3.42 (br sept, 1 H, C*H*Me$_2$), 1.65–0.94 (several br overlapping doublets, 45 H, CH*Me*$_2$ and PMe$_3$); ^{13}C NMR (CD$_2$Cl$_2$) δ 251.3 (J_{CH} = 133 and 157, J_{CP} = 14, J_{CW} = 171, C_α), 164.7, 162.0, 158.7, 151.2, 144–146 (br), 138.0, 137.2, 135.9 (C_{ipso} and C_o for OAr and NAr), 125.9, 123.4, 123.0, 122.7, 119.5, 119.0 (C_m and C_p for OAr and NAr), 28.9, 27.5, 26.2, 24.9, 24.4, 24.2, 23.5 (*C*HMe$_2$ and CH*Me*$_2$ for OAr and NAr), 17.7 (J_{CP} = 28, PMe$_3$).

W[CH$_2$CH(SiMe$_3$)CH$_2$](NAr)(OAr)$_2$ (2d(cis), 2d(trans)). A solution of 120 mg (0.148 mmol) of W[CH$_2$CH(*t*-Bu)CH$_2$](NAr)(OAr)$_2$ and 107 μL (0.745 mmol) of vinyltrimethylsilane in 5 mL of pentane was stirred at 25 °C for 2 h. Volatiles were removed in vacuo to afford an orange foam, which was recrystallized from pentane at −40 °C to afford 82 mg (0.099 mmol, 67%) of **2d** as a yellow powder. **2d** can also be prepared by allowing ~3 equiv of ethylene to react with W(CH-*t*-Bu)(NAr)(OAr)$_2$ for 30 min at 25 °C and then adding 5 equiv of vinyltrimethylsilane. **2d** is a 2:1 mixture of isomers: ^{1}H NMR (**2d(cis)**) δ 7.14–6.69 (H_{aryl} for both isomers), 5.24 (dd, J_{HH} = 10 and 6, 2 H, H_α), 4.20 (dd, J_{HH} = 10 and 7, 2 H, H_α'), 4.00 (sept, J_{HH} = 7, 2 H, C*H*Me$_2$ (OAr)), 3.52 (sept, J_{HH} = 6, 2 H, C*H*Me$_2$ (NAr)), 1.25 (d, J_{HH} = 6, 24 H, CH*Me*$_2$ (OAr) *or* CH*Me*$_2$ (NAr) for **2d(trans)**), 1.12 (d, J_{HH} = 6, 24 H, CH*Me*$_2$ (OAr) *or* CH*Me*$_2$ (NAr) for **2d(trans)**), 1.04 (d, J_{HH} = 6, 12 H, CH*Me*$_2$ (NAr)), 0.129 (9 H, SiMe$_3$), −1.23 (mult, H_β); ^{1}H NMR (**2d(trans)**) δ 7.14–6.69 (H_{aryl} for both isomers), 4.87 (dd, J_{HH} = 11 and 7, 2 H, H_α), 4.49 (dd, J_{HH} = 8 and 7, 2

H, H_{α}'), 3.75 (sept, J_{HH} = 6, 6 H, $CHMe_2$ (OAr) and $CHMe_2$ (NAr)), 1.29 (d, J_{HH} = 7, 24 H, $CHMe_2$ (OAr)), 1.25 (d, J_{HH} = 6, 12 H, $CHMe_2$ (NAr) *or* $CHMe_2$ (OAr) for **2d(cis)**), 1.12 (d, J_{HH} = 6, 12 H, $CHMe_2$ (NAr) *or* $CHMe_2$ (OAr) for **2d(cis)**), −0.172 (9 H, $SiMe_3$), −1.13 (mult, H_{β}); ^{13}C NMR (both isomers) δ 159.9, 158.4, 148.1, 147.8, 146.6, 137.3, 137.1 (C_{ipso} and C_o for NAr and OAr in both isomers), 126.7, 126.5, 123.4, 123.2, 122.6, 121.0 (C_m and C_p for NAr and OAr in both isomers), 100.5 (t, J_{CW} = 71, J_{CH} = 152, C_{α} of **2d(trans)**), 99.6 (t, J_{CW} = 74, J_{CH} = 151, C_{α} of **2d(cis)**), 28.2, 27.8, 25.0, 24.3, 24.1 ($CHMe_2$ and $CHMe_2$ for NAr and OAr in both isomers; we assume some resonances are coincidentally equivalent), 0.28 (q, J_{CH} = 121, $SiMe_3$ of **2d(cis)**), −0.42 (q, J_{CH} = 123, $SiMe_3$ of **2d(trans)**), −0.63 (d, J_{CH} = 132, C_{β} of **2d(cis)**), −0.99 (d, J_{CH} = 136, C_{β} of **2d(trans)**). Anal. Calcd for $WC_{42}H_{65}NO_2Si$: C, 60.93; H, 7.91. Found: C, 60.75; H, 7.95.

$W[CH_2CH(SiMe_3)CH_2](NAr)[OC(CF_3)_2(CF_2CF_2CF_3)]_2$. $W(CH_2CH_2CH_2)(NAr)[OC(CF_3)_2(CF_2CF_2CF_3)]_2$ (100 mg, 0.0933 mmol) and vinyltrimethylsilane (677 μL, 4.67 mmol) were dissolved in 3 mL of pentane. The solution was stirred for 3 h at 25 °C, and then the volatile components were removed in vacuo to afford an oily, pale yellow solid. Recrystallization from minimal pentane at −40 °C afforded 73 mg of a white, crystalline solid (68%): ^1H NMR δ 6.82 (H_m), 6.64 (H_p), 5.20 (dd, 2 H, J_{HH} = 6 and 11, H_{α}), 4.48 (dd, 2 H, J_{HH} = 6 and 8, H_{α}'), 3.91 ($CHMe_2$), 1.12 ($CHMe_2$), −0.23 ($SiMe_3$), −1.21 (mult, 1 H, H_{β}). Anal. Calcd for $WC_{30}H_{31}NO_2F_{26}Si$: C, 31.51; H, 2.73. Found: C, 31.22; H, 2.93.

X-ray Structure of $W[CH_2CH(t\text{-}Bu)CH_2](NAr)[OCMe_2(CF_3)]_2$. Suitable crystals of **1b** were obtained by crystallization from pentane at −40 °C. A yellow prism having approximate dimensions 0.300 × 0.350 × 0.350 mm was mounted on a glass fiber. Data were collected at −70 °C on an Rigaku AFC6R diffractometer using monochromatic graphite Mo Kα radiation ($2\theta_{max}$ = 55.0°; $h,\pm k,l$; 15 317 total reflections; 12 889 unique reflections). Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement with the setting angles of 50 carefully centered reflections in the range $25.00 < 2\theta < 27.12°$, corresponded to a tetragonal cell with dimensions a = 25.26 (2) Å, c = 9.720 (5) Å, and V = 6.202 Å^3. For Z = 8 and M_r = 711.48 the calculated density is 1.524 g cm^{-3}. The structure was difficult to refine due to severe disorder in one of the alkoxide ligands. In the final cycles of least squares, this alkoxide ligand was refined with isotropic thermal parameters and its CF_3 group held as a rigid group with fixed thermal parameters. With the successful solution and refinement of the structure the space group was determined to be $P4_2/n$. The structure was solved by direct methods. The non-hydrogen atoms were refined either anisotropically or isotropically. Hydrogen atoms were included in the structure factor calculation in idealized positions (d_{C-H} = 0.95 Å) and were assigned isotropic thermal parameters that were 20% greater than the B_{eq} value of the atom to which they were bonded. The final cycle of full-matrix least-squares refinement was based on 6738 observed reflections ($I > 3\sigma(I)$) and 289 variable parameters and converged with agreement factors of R = 0.056 and R_w = 0.082. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.56 and −2.03 e Å^{-3}, respectively. Labeled drawings, final positional parameters, final anisotropic thermal parameters, and final observed and calculated structure factors for $W(CH_2CH(t\text{-}Bu)CH_2)(NAr)[OCMe_2(CF_3)]_2$ were supplied as supplementary material elsewhere.[3b]

Kinetic Study of the Reaction between $W[CH_2CH(t\text{-}Bu)CH_2](NAr)[OCMe_2(CF_3)]_2$ (1b) and Ethylene. A 10.0-mL stock solution was prepared by dissolving hexamethyldisiloxane (67 mg, 0.413 mmol) in toluene-d_8 in a volumetric flask. $W[CH_2CH(t\text{-}Bu)CH_2](NAr)[OCMe_2(CF_3)]_2$ (15 mg, 0.019 mmol) was dissolved in 0.50 mL of the stock solution. The solution was transferred to a medium-wall NMR tube (Wilmad, 524-PP) fitted with a 14/20 female joint. The NMR tube was then attached to a calibrated gas bulb, fitted with Teflon stopcocks on either side. The assembly was then attached to a high-vacuum line and the solution frozen in liquid N_2 and degassed. Ethylene (1–2 mmol assuming ideal gas) was added to the tube by vacuum transfer. (The amount of ethylene actually present in solution was determined by integration vs the internal standard). The tube was then flame-sealed, and the solution was kept frozen in liquid N_2 until the kinetics run commenced. The probe of a Varian XL-300 spectrometer was precooled or prewarmed to the desired temperature. The solution was quickly thawed, and the NMR tube was placed inside the probe. After 5 min the first NR spectrum was recorded. The rate of the reaction was determined by monitoring the decrease of the CMe_3 integral of **1b** vs the $(SiMe_3)_2O$ resonance. Good first-order behavior ($\rho \geq 0.998$) was observed for at least 3 half-lives.

Kinetic Study of the Reaction between $W[CH_2CH(SiMe_3)CH_2](NAr)(OAr)_2$ (Cis and Trans) and Ethylene. The method was analogous to that described above with use of mesitylene as the internal standard and with the decrease of the $SiMe_3$ integral monitored for the two isomers vs the $C_6H_3Me_3$ resonance. For the major isomer, good first-order behavior ($\rho \geq 0.998$) was observed for 2–3 half lives. For the minor isomer, slightly more scatter was observed in the first-order plots (for the worst case ρ = 0.996) over 1.7–2.7 half-lives.

Kinetic Study of the Reaction between $W[CH_2CH(SiMe_3)CH_2](NAr)[OCMe(CF_3)_2]_2$ and Ethylene. The method was analogous to that described above; the decrease in the Me_3Si resonance was followed. Individual rate constants (s^{-1}): 40.6 °C, 4.35×10^{-5} and 3.93×10^{-5}; 45.7 °C, 1.60×10^{-4}; 55.0 °C, 4.06×10^{-4}; 55.5 °C, 4.55×10^{-4}; 60.2 °C, 8.15×10^{-4}. The best straight line in the log plot had ρ = 0.987.

Kinetic Study of the Reaction between $W[CH_2CH(SiMe_3)CH_2](NAr)[OC(CF_3)_2(CF_2CF_2CF_3)]_2$ and Ethylene. The method was analogous to that described above; the decrease in Me_3Si resonance was followed. Individual rate constants (s^{-1}): 18.7 °C, 5.22×10^{-5}; 20.4 °C, 8.32×10^{-5}; 26.3 °C, 1.67×10^{-4}; 30.3 °C, 3.90×10^{-4}; 30.5 °C, 4.17×10^{-4}; 31.4 °C, 4.69×10^{-4}; 37.0 °C, 7.67×10^{-4}. The best straight line in the log plot had R = 0.990.

Acknowledgment. R.R.S. thanks the National Science Foundation for research support (Grant No. CHE 88-22508), the U.S. Department of Energy, Division of University and Industry Programs, for funds to purchase the X-ray diffractometer (Grant No. DE-FG05-86ER75292), and L. R. Sita for preparing perfluoro-2-methyl-2-pentanol. J.F. thanks the National Science Foundation for a predoctoral fellowship.