Reaction of Neopentylidene Complexes of the Type M(CH-*t*-Bu)(*N*-2,6-C_6H_3-*i*-Pr_2)$(OR)_2$ (M = W, Mo) with Methyl Acrylate and *N*,*N*-Dimethylacrylamide To Give Metallacyclobutane Complexes

Jerald Feldman, John S. Murdzek, William M. Davis, and Richard R. Schrock*

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

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W(CH-*t*-Bu)(NAr)$[OCMe_2(CF_3)]_2$ (Ar = 2,6-C_6H_3-*i*-Pr_2) reacts with methyl acrylate to give the metallacyclobutane complex W$[CH(t\text{-Bu})CH_2CH(CO_2Me)](NAr)[OCMe_2(CF_3)]_2$ (1). 1 belongs to the space group $P2_1/c$ with a = 17.323 (3) Å, b = 10.408 (3) Å, c = 18.758 (3) Å, V = 3337 (2) Å^3, M_r = 769.52, ρ(calcd) = 1.531 g cm^{-3}, Z = 4, and μ = 37.33 cm^{-1} (R = 0.043, R_w = 0.043). The complex has an approximately square-pyramidal core geometry with the carbonyl oxygen atom bound weakly trans to the apical imido ligand. The four basal sites are occupied by the two alkoxide oxygen atoms and the two α-carbon atoms of the metallacyclobutane ligand. Similar reactions may be carried out between M(CH-*t*-Bu)(NAr)-$[OCMe_2(CF_3)]_2$ or M(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and *N*,*N*-dimethylacrylamide to give metallacyclobutane complexes of the type M$[CH(t\text{-Bu})CH_2CH(CONMe_2)](NAr)(OR)_2$ (OR = $OCMe_2(CF_3)$, O-*t*-Bu; M = W, Mo). 1 reacts with trimethylphosphine to give W(CH-*t*-Bu)(NAr)$[OCMe_2(CF_3)]_2(PMe_3)$, but complexes of the type W$[CH(t\text{-Bu})CH_2CH(CONMe_2)](NAr)(OR)_2$ (OR = $OCMe_2(CF_3)$, O-*t*-Bu) do not react readily with trimethylphosphine. Differences in reactivity of the methyl acrylate and the dimethylacrylamide tungsten complexes with ethylene are analogous. In contrast, Mo$[CH(t\text{-Bu})CH_2CH(CONMe_2)](NAr)(O\text{-}t\text{-Bu})_2$ is in equilibrium with Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and free *N*,*N*-dimethylacrylamide in solution.

Introduction

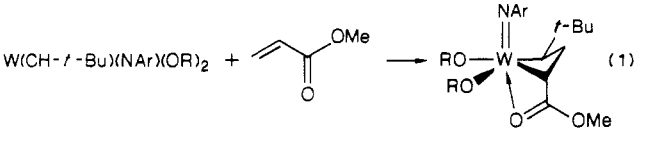
Metathesis of functionalized olefins with classical catalysts has been relatively unsuccessful, especially if the functionality is directly attached to an olefinic carbon atom.[1] Catalysts of the type M(CHR')(NAr)$(OR)_2$ (M = W, Mo; Ar = 2,6-C_6H_3-*i*-Pr_2)[2] are fully active for the metathesis of ordinary olefins when the OR group is electron-withdrawing (e.g., $OCMe(CF_3)_2$), the crucial step being attack of the olefin by the electrophilic metal center. Since these catalysts are well-characterized, are isolable, and do not require Lewis acid cocatalysts,[3] it may now be possible to determine what some of the problems with functionalized olefin metathesis might be. In this paper we report several metallacyclobutane complexes prepared by adding methyl acrylate or *N*,*N*-dimethylacrylamide to M(CH-*t*-Bu)(NAr)$(OR)_2$ complexes. Those that contain molybdenum are the first examples of stable d^0 molybdenacyclobutane complexes.

Results

W$[CH(t\text{-Bu})CH_2CH(CO_2Me)](NAr)[OCMe_2(CF_3)]_2$. The reaction between W(CH-*t*-Bu)(NAr)$[OCMe_2(CF_3)]_2$ and methyl acrylate proceeds rapidly to give W$[CH(t\text{-Bu})CH_2CH(CO_2Me)](NAr)[OCMe_2(CF_3)]_2$ (1) in high yield as a yellow-orange, crystalline solid (eq 1). Two views of the structure of 1 are shown in Figure 1, and important bond distances and angles are listed in Table I.

Table I. Selected Bond Distances (Å) and Angles (deg) in W$[CH(t\text{-Bu})CH_2CH(CO_2Me)](N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCMe_2(CF_3)]_2$[a]

W–N(1)	1.725 (6)	W–O(411)	2.372 (6)
W–O(2)	1.929 (5)	C(42)–C(43)	1.53 (1)
W–O(3)	1.889 (5)	C(41)–C(42)	1.54 (1)
W–C(41)	2.221 (8)	C(48)–O(411)	1.25 (1)
W–C(43)	2.205 (8)	C(41)–C(48)	1.42 (1)
N(1)–W–C(43)	96.4 (3)	O(2)–W–C(43)	146.3 (3)
N(1)–W–C(41)	104.3 (3)	O(2)–W–C(41)	84.4 (3)
N(1)–W–O(3)	108.2 (3)	O(2)–W–C(411)	76.3 (2)
N(1)–W–O(2)	105.0 (3)	W–O(3)–C(31)	144.2 (6)
N(1)–W–O(411)	163.8 (2)	W–O(2)–C(21)	143.3 (6)
C(41)–W–C(43)	65.1 (3)	W–C(41)–C(42)	93.1 (5)
O(2)–W–O(3)	101.2 (2)	W–C(43)–C(42)	94.2 (5)
O(3)–W–C(43)	96.3 (3)	C(41)–C(42)–C(43)	101.7 (7)
O(3)–W–C(41)	144.2 (3)	W–N(1)–C(11)	175.8 (6)
O(3)–W–C(411)	87.0 (2)		



(1)

1

OR = $OCMe_2(CF_3)$

The structure of 1 can be described as approximately a square pyramid in which the carbonyl oxygen atom binds weakly (W–O(411) = 2.372 (6) Å) trans to the nitrogen atom of the apical imido ligand (N(1)–W–O(411) = 163.8 (2)°). The four basal sites are occupied by the two alkoxide oxygen atoms and the two α-carbon atoms of the metallacyclobutane ligand, and the W atom resides 0.50 Å above the least-squares plane defined by O(1), O(2), C(41), and C(43). The angles between adjacent ligands in the basal plane vary greatly with the C(41)–W–C(43) angle (65.1 (3)°) being the smallest and the O(2)–W–O(3) angle (101.2 (2)°) being the largest. The plane of the phenyl ring of

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(2) (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) Murdzek, J. S.; Schrock, R. R. *Organometallics* **1987**, *6*, 1373. (c) Schrock, R. R.; Feldman, J.; Grubbs, R. H.; Cannizzo, L. *Macromolecules* **1987**, *20*, 1169.

(3) Over the past several years another class of tungsten-based metathesis catalysts have been discovered that require Lewis acid cocatalysts in order to generate a reactive, cationic, four-coordinate alkylidene complex and from them five-coordinate cationic metallacyclobutane complexes. (a) Kress, J.; Wesolek, M.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1982**, 514. (b) Kress, J.; Osborn, J. A. *J. Am. Chem. Soc.* **1983**, 105, 6346. (c) Kress, J.; Aguero, A.; Osborn, J. A. *J. Mol. Catal.* **1986**, *36*, 1. (d) Kress, J.; Osborn, J. A.; Amir-Ebrahimi, V.; Ivin, K. J.; Rooney, J. J. *J. Chem. Soc., Chem. Commun.* 1988, 1164.

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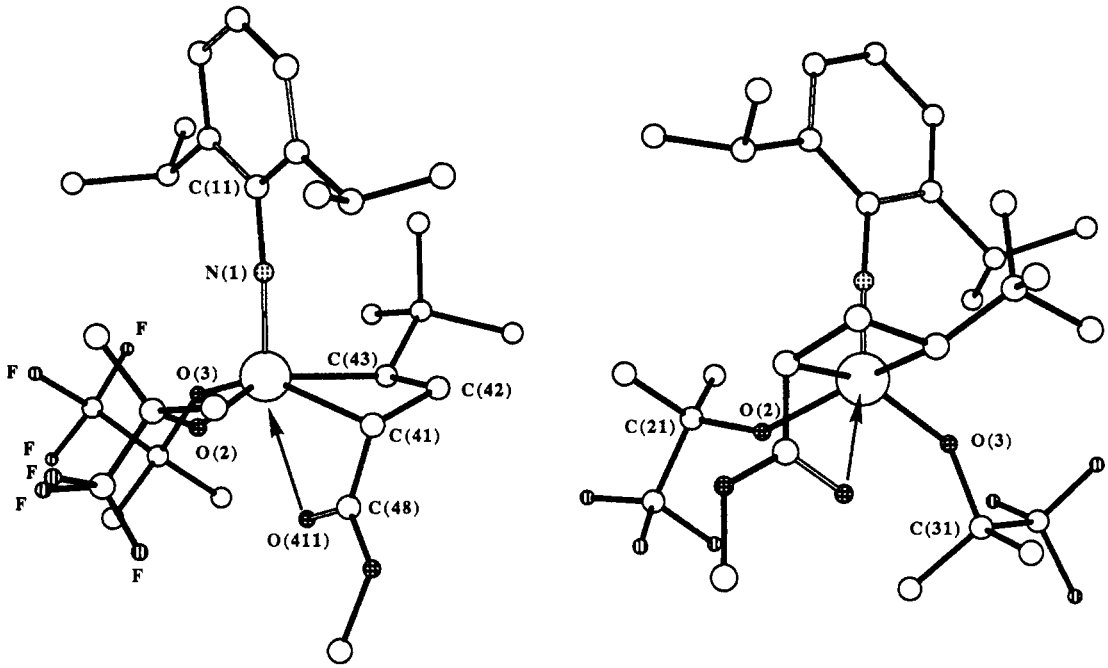


Figure 1. Two views of W[CH(*t*-Bu)CH_2CH(CO_2Me)](N-2,6-C_6H_3-*i*-Pr_2)[$OCMe_2(CF_3)$]$_2$.

the virtually linear imido ligand is oriented along the C(41)–W–O(3) axis, probably in order to minimize steric interactions between the pseudoequatorial α-*t*-Bu group on C(43) and the isopropyl groups of the imido ligand. Note that the $CMe_2(CF_3)$ group of the alkoxide ligand containing O(3) is turned away from one of the isopropyl groups of the imido ligand and O(3) is pushed slightly further away from N(1) (N(1)–W–O(3) = 108.2 (3)° vs N(1)–W–O(2) = 105.5 (3)°). The W–O–C angles (143–144°) and the W–O bond lengths in the two alkoxide ligands (1.89–1.93 Å) are virtually identical.

The metallacyclobutane ring in 1 is puckered, with the dihedral angle between the planes defined by C(41), W, C(43) and that by C(41), C(42), C(43) being 25°. The carbomethoxy ligand occupies a pseudoaxial position on C(41), most likely in order that the carbonyl oxygen atom can bind to W. Consequently the α-*t*-Bu group is forced to be in a pseudoequatorial position on C(43), and the entire ring system is twisted so that C(41) is pulled down slightly relative to C(43) (N(1)–W–C(41) = 104.3 (3)°; N(1)–W–C(43) = 96.4 (3)°).

Bond lengths and distances within the WC_3 ring are shown in Figure 2 (see also Table I). The angle at the metal (65.1 (3)°), the angle at C(42) (101.7 (7)°), and the W···C_β distance (2.772 Å) are similar to those found for square-pyramidal W[CH_2CH(*t*-Bu)CH_2](NAr)[$OCMe_2(CF_3)$]$_2$[4] but are strikingly different from what has been found for tungstacyclobutane complexes that are overall approximately trigonal bipyramids with the ring carbon atoms bound in equatorial positions.[2a] We must assume on the basis of these results that the distances and angles shown in Figure 2 are characteristic of square-pyramidal metallacycles, whether or not a ring substituent coordinates to the metal. Differences between square-pyramidal and trigonal-bipyramidal metallacycles are discussed in detail later.

In the room-temperature ^{1}H NMR spectrum of 1, the resonances associated with the 2,6-C_6H_3-*i*-Pr_2 ligand are broadened, although all other resonances are sharp. If a toluene-d_8 solution of 1 is cooled to −20 °C, then the imido

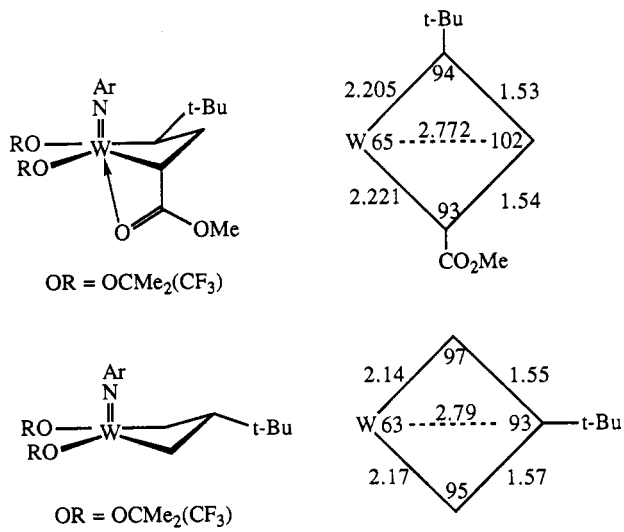


Figure 2. Comparison of bond lengths and distances in the WC_3 rings in W[CH(*t*-Bu)CH_2CH(CO_2Me)](N-2,6-C_6H_3-*i*-Pr_2)-[$OCMe_2(CF_3)$]$_2$ (above) and W[CH_2CH(*t*-Bu)CH_2](N-2,6-C_6H_3-*i*-Pr_2) [$OCMe_2(CF_3)$]$_2$ as viewed down the N–W bond.

ligand resonances sharpen, and two doublets are observed for the H_{meta} protons, two septets for the isopropyl methine protons, and four doublets for the inequivalent isopropyl methyl groups. We attribute this fluxional behavior to slow rotation of the phenyl ring about the N–C bond at 25 °C; i.e., at low temperature the phenyl ring is largely oriented as found in the solid state with one isopropyl group above C(41) and the other above O(3). Circumstantial evidence (vide infra) suggests that the carbomethoxy carbonyl oxygen dissociates to give a five-coordinate intermediate before the N–C bond can rotate rapidly on the NMR time scale.

The chemical shifts and coupling constants for the metallacyclobutane ring protons and carbon atoms in 1 are listed in Table II. Homonuclear decoupling experiments confirmed that the proton that gives rise to the resonance at 2.71 ppm (ddd) is coupled to the three other ring protons, the protons that give rise to the resonances at 4.00 (dd) and 1.98 ppm (dd) are coupled to each other (and to

(4) Feldman, J.; Davis, W. M.; Schrock, R. R. *Organometallics*, following paper in this issue.

Table II. ^1H and ^{13}C NMR Data for the Metallacyclobutane Ligands in Complexes of the Type M[CH(*t*-Bu)CH_2CH(COX)](N-2,6-C_6H_3-*i*-Pr_2)$(OR)_2$ (M = W, Mo; X = OMe, NMe_2; OR = O-*t*-Bu, $OCMe_2(CF_3)$)[a]

compound	δ(H)	J_{HH}	δ(C_α)[b]	J_{CH}	J_{CW}
W[CH(*t*-Bu)CH_2CH(CO_2Me)](NAr)[$OCMe_2(CF_3)]_2$ (1)	4.00	8, 11	67.1	121	52
	2.71	9, 13, 13	39.9	149	39
	2.39	8			
	1.98	10, 12			
W[CH(*t*-Bu)CH_2CH($CONMe_2$)](NAr)[$OCMe_2(CF_3)]_2$ (**2a**)[c]	3.88	9, 11	66.4	119	53
	2.79	8, 12, 12	34.8	145	35
	2.04	8			
	1.87	9, 12			
W[CH(*t*-Bu)CH_2CH($CONMe_2$)](NAr)(O-*t*-Bu)$_2$ (**2b**)[c]	4.13	9, 11	63.7	125	53
	2.89	8, 13, 13			
	2.12	8			
	1.85	9, 12			
Mo[CH(*t*-Bu)CH_2CH($CONMe_2$)](NAr)[$OCMe_2(CF_3)]_2$ (**3a**)	3.40	8, 12	61.2	126	
	3.01	9, 12, 12			
	2.06	8, 12			
	2.03	8			
Mo[CH(*t*-Bu)CH_2CH($CONMe_2$)](NAr)(O-*t*-Bu)$_2$ (**3b**)	3.55	8, 12	59.1	125	
	3.04	8, 12, 13			
	2.14	8			
	2.08	8, 13			

[a] Spectra were recorded in C_6D_6 unless otherwise noted. Coupling constants are estimated to an accuracy of 0.5 Hz and rounded to the nearest Hz. [b] Only C_α ring resonances could be assigned and not both in every case. [c] ^{13}C NMR spectrum recorded in CD_2Cl_2.

the proton whose resonance is at 2.71 ppm), and the proton whose resonance is at 2.39 ppm (d) is coupled only to the proton whose resonance is at 2.71 ppm. Since the β protons of square-pyramidal W($CH_2CH_2CH_2$)(NAr)[$OCMe_2$-$(CF_3)]_2$ are found at 4.30 and 2.78 ppm,[4] we assign the 4.00 and 2.71 ppm resonances to the β protons in 1. In W-[CH_2CH(*t*-Bu)CH_2](NAr)[$OCMe_2(CF_3)]_2$ (in which the *t*-Bu group is in a pseudoequatorial position) the α proton resonances are found at 2.36 and 1.12 ppm, while the (pseudoaxial) β proton resonance is found at 2.62 ppm.[4] These data suggest that chemical shifts of 2.39 and 1.98 ppm are reasonable to expect for the α protons in 1 and that the 4.00 ppm resonance in 1 may be ascribed to the equatorial β proton (H_b in Figure 3). If so, then the resonance at 2.71 ppm can be assigned to H_c. The question then is which of the two α protons ("axial" H_d or "equatorial" H_a) gives rise to the doublet resonance at 2.39 ppm? A toluene-d_8 solution of 1 was cooled to −20 °C, at which temperature rotation about the N–C bond is slow (vide supra). Irradiation of the resonance at 2.39 ppm resulted in selective NOE enhancement of one of the N-2,6-C_6H_3-*i*-Pr_2 ligand's C*H*Me_2 resonances at 3.9 ppm. Enhancement was also observed for the H_b and H_c resonances but not for the resonance at 1.98 ppm. These data clearly indicate that the resonance at 2.39 ppm should be assigned to H_a, since one $CHMe_2$ group overhangs H_a and is oriented such that its methine proton is pointed directly at H_a.

Spectroscopic data for 1 clearly indicate coordination of the carbomethoxy carbonyl oxygen to tungsten. In the ^{13}C NMR spectrum of 1, the chemical shift of the carbonyl carbon atom is 187.9 ppm, about 15–18 ppm further downfield than typically observed for organic esters[5] and consistent with withdrawal of electron density from the C=O bond. In the infrared spectrum of 1 the C=O stretching frequency is found at 1585 cm^{-1}, significantly shifted to lower energy relative to a typical ester carbonyl stretching frequency[5] of 1750–1735 cm^{-1} and clearly attributable to coordination of the carbonyl oxygen to tungsten.

W[CH(*t*-Bu)CH_2CH($CONMe_2$)](NAr)$(OR)_2$ [OR = $OCMe_2(CF_3)$ or O-*t*-Bu]. W(CH-*t*-Bu)(NAr)[$OCMe_2$-

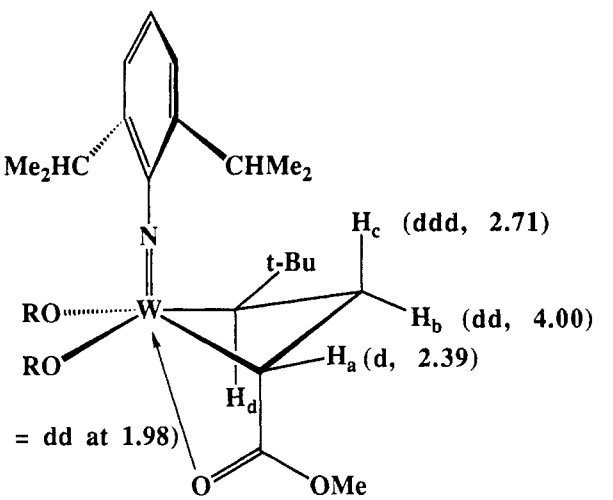
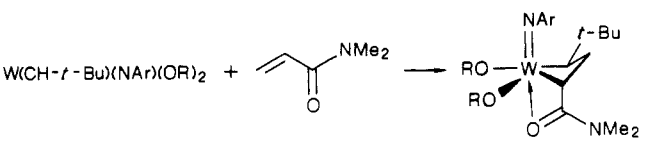


Figure 3. Labeling of the ring protons in compound 1 and possible ^1H NMR assignments (see text).

$(CF_3)]_2$ and W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ react with *N*,*N*-dimethylacrylamide to give what appear to be (by NMR) metallacyclobutane complexes analogous to 1 (**2a** and **2b**, respectively, eq 2) (Table II). These complexes are much



2a : OR = $OCMe_2(CF_3)$
b : OR = O-*t*-Bu

(2)

less soluble in hydrocarbons than 1 and can be isolated as bright yellow microcrystalline solids. Since chemical shifts and multiplicities for the ring protons in **2a** and **2b** are virtually the same as those in 1, we assume all have similar structures. One important difference between the NMR spectra of **2a** and **2b** and that of 1 is that the phenyl ring in **2a** and **2b** does not rotate as readily about the N–C bond; at 25 °C resonances for the phenyl imido ligand are all sharp and two doublets are observed for the H_{meta} protons, two septets for the isopropyl methine protons, and four doublets for the inequivalent isopropyl methyl groups. Since *N*,*N*-dimethylacrylamide is not as readily displaced

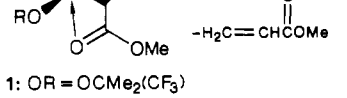
(5) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; Wiley: New York, 1981.

from **2a** or **2b** as methyl acrylate is from **1** (see below), we suspect that the carbonyl group in **2** does not dissociate as readily as that in **1** and that therefore rotation about the N–C bond is not as facile in six-coordinate species as in less crowded five-coordinate species.

^{13}C NMR and IR data for **2a** and **2b** indicate that the carbonyl oxygen of the dimethylcarbamide group is coordinated to tungsten (**2a**, $\delta(CO)$ = 186.5 and ν_{CO} = 1580 cm^{-1}; **2b**, $\delta(CO)$ = 185.3 and ν_{CO} = 1575 cm^{-1}). (In amides $\delta(CO) \approx 170$ and $\nu_{CO} \approx 1680–1630$ cm^{-1}.[5]) Note that these data do not indicate that the carbonyl oxygen is more tightly bound in **2a** than in **2b** even though the tungsten atom in **2a** should be more acidic than it is in **2b**.

Reactions of other neopentylidene complexes to give products analogous to **1** and **2** were relatively unsuccessful. The reaction of complexes containing O-2,6-C_6H_3-*i*-Pr_2 or $OCMe(CF_3)_2$ ligands with methyl acrylate or *N,N*-dimethylacrylamide leads to the formation of complex mixtures of products. Similarly, the reaction of methyl methacrylate with W(CH-*t*-Bu)(NAr)[$OCMe_2(CF_3)$]$_2$ leads initially to what appears to be W[CH(*t*-Bu)CH_2C(Me)-(CO_2Me)](NAr)[$OCMe_2(CF_3)$]$_2$ (on the basis of its ^1H NMR spectrum), but this compound readily decomposes in solution to unidentified product(s). Reaction of methyl acrylate with W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ leads to the formation of W(CH(*t*-Bu)CH_2CH(CO_2Me)](NAr)(O-*t*-Bu)$_2$ (on the basis on its ^1H NMR spectrum), but we have not yet been able to isolate this compound in pure form due to its extreme solubility. Addition of methyl vinyl ketone to W(CH-*t*-Bu)(NAr)[$OCMe_2(CF_3)$]$_2$ resulted in complete decomposition to apparently several products.

Reactions of 1 and 2 with Trimethylphosphine and Ethylene. The reaction between **1** (0.026 M in C_6D_6) and excess PMe_3 (6 equiv) yields W(CH-*t*-Bu)(NAr)[$OCMe_2$-(CF_3)]$_2$(PMe_3) and methyl acrylate (eq 3). (This compound can also be prepared simply by adding PMe_3 to W(CH-*t*-Bu)(NAr)[$OCMe_2(CF_3)$]$_2$.) According to ^1H NMR studies, the reaction is complete after approximately 1 h at room temperature. No neohexene is formed, and we see no evidence for formation of as yet unknown W[CH-(CO_2Me)](NAr)[$OCMe_2(CF_3)$]$_2$(PMe_3). **2a** and **2b** do not react with PMe_3 after 3 h at 25 °C. We attribute the stability of **2** to the greater basicity of the amide carbonyl oxygen than that of the ester. Formation of a five-coordinate intermediate by dissociation of the carbonyl oxygen atom is a plausible and necessary step that precedes attack by phosphine and/or loss of the derivatized olefin from the ring.

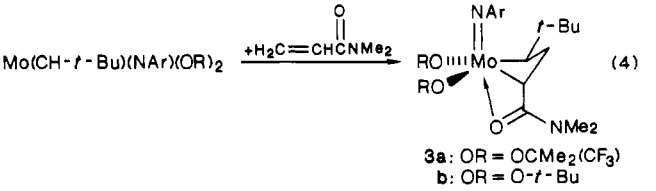


1: OR = $OCMe_2(CF_3)$

W(CH-*t*-Bu)(NAr)[$OCMe_2(CF_3)$]$_2$(PMe_3) (3)

The reaction between **1** (0.026 M in C_6D_6) and ethylene (5 equiv) at 25 °C also requires approximately 1 h at room temperature and gives a complex mixture of products that include methyl acrylate and neohexene. In contrast, **2a** and **2b** do not react with 5 equiv of ethylene at 25 °C.

Mo[CH(*t*-Bu)CH_2CH($CONMe_2$)](NAr)(OR)$_2$ [OR = $OCMe_2(CF_3)$ or O-*t*-Bu]. When yellow Mo(CH-*t*-Bu)-(NAr)[$OCMe_2(CF_3)$]$_2$ or Mo(CH-*t*-Bu)(NAr)(O-t-Bu)$_2$ is treated in pentane at −30 °C with 1 equiv of *N,N*-dimethylacrylamide, the yellow solutions darken and red solids precipitate. All NMR data (Table II) are consistent with these products being pseudooctahedral complexes analogous to **2a** and **2b** (eq 4). ^{13}C NMR and IR data for



(4)

3a: OR = $OCMe_2(CF_3)$
b: OR = O-*t*-Bu

3a and **3b** are also entirely consistent with this conclusion (**3a**, $\delta(CO)$ = 182.9 ppm and ν_{CO} = 1580 cm^{-1}; **3b**, $\delta(CO)$ = 183.6 ppm and ν_{CO} = 1570 cm^{-1}).

Complex **3a** is somewhat unstable in solution. After 7 hours at room temperature, ~10–15% of **3a** (~20 mg in 0.70 mL of C_6D_6) decomposes to give (inter alia) Mo(CH-*t*-Bu)(NAr)[$OCMe_2(CF_3)$]$_2$ ($\delta(H_\alpha)$ = 11.61 ppm) and *N,N*-dimethylacrylamide. Heating this sample to 353 K in the NMR probe accelerates the decomposition and increases the intensity of the peaks corresponding to Mo(CH-*t*-Bu)(NAr)[$OCMe_2(CF_3)$]$_2$ and *N,N*-dimethylacrylamide. At 353 K, however, there is also a small singlet at ~11.15 ppm which *may* be due to the alkylidene α proton of Mo[CHC(O)NMe_2](NAr)[$OCMe_2(CF_3)$]$_2$. These changes are irreversible.

3b is even less stable in solution than **3a**. When **3b** is dissolved in C_6D_6 or toluene-d_8, the room-temperature ^1H NMR spectrum shows resonances characteristic of **3b** (dd at 3.55 ppm, ddd at 3.04 ppm, d at 2.14 ppm, dd at 2.08 ppm) in addition to resonances for Mo(CH-*t*-Bu)(NAr)-(O-*t*-Bu)$_2$ and an equal molar amount of *N,N*-dimethylacrylamide. When this sample is heated in the NMR probe, the intensity of the signals for the neopentylidene complex and the free olefin increases. Cooling the sample back to 298 K reverses these changes. At 353 K, however, **3b** decomposes to unidentifiable products. There is no evidence in this NMR spectrum for formation of Mo-[CHC(O)NMe_2](NAr)(O-*t*-Bu)$_2$. Since the system is stable up to 333 K, the equilibrium constant for dissociation of Mo[CH(*t*-Bu)CH_2CH($CONMe_2$)](NAr)(O-*t*-Bu)$_2$ into Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and *N,N*-dimethylacrylamide could be determined: K_{eq} = 2.61 × 10^{-3} M at 293 K, 1.22 × 10^{-2} M at 313 K, and 5.35 × 10^{-2} M at 333 K ($\Delta H°$ = 15.3 ± 1.9 kcal mol^{-1} and $\Delta S°$ = 40 ± 5 eu).

Analogous reactions between Mo(CH-*t*-Bu)(NAr)-[$OCMe_2(CF_3)$]$_2$ or Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and methyl acrylate did not appear to give stable products analogous to **1**.

Discussion

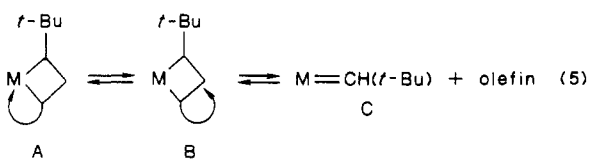
We have observed that both square-pyramidal (SP) and trigonal-bipyramidal (TBP) metallacyclobutane complexes are present when olefins are metathesized by W(CHR')-(NAr)(OR)$_2$ complexes.[4] Examples of both forms have now been characterized crystallographically. In SP W-[CH_2CH(*t*-Bu)CH_2](NAr)[$OCMe_2(CF_3)$]$_2$[4] and **1**, the apical position is occupied by the imido ligand. In two TBP forms,[2a] the axial positions are occupied by the imido ligand and one of the alkoxide ligands. There are important differences between the metallacyclobutane ligands in the two forms. For example, in TBP W(CH_2CH_2C-H_2)(NAr)[$OC(CF_3)_2(CF_2CF_2CF_3)$]$_2$ and W[CH($SiMe_3$)CH-($SiMe_3$)CH_2](NAr)[$OCMe(CF_3)_2$]$_2$ the W···C_β distance is 2.3–2.4 Å, but in SP W[CH_2CH(*t*-Bu)CH_2](NAr)-[$OCMe_2(CF_3)$]$_2$ the distance is ~2.8 Å.

The metallacyclobutane complexes described here are closely related to true square-pyramidal forms. If the bond between W and the carbonyl oxygen in **1** is ignored, the core geometry of **1** is close to that observed in square-pyramidal W[CH_2CH(*t*-Bu)CH_2](NAr)[$OCMe_2(CF_3)$]$_2$.[4] For

example, N–W–C angles are 98° and 99° in W[CH_2CH-(t-Bu)CH_2](NAr)[$OCMe_2(CF_3)$]$_2$ and 96° and 104° in **1**, while N–W–O angles are 111° and 114° in W[CH_2CH(t-Bu)CH_2](NAr)[$OCMe_2(CF_3)$]$_2$ and 105° and 108° in **1**. The 2–6° smaller (apical ligand)–W–(basal ligand) angles in **1** can be ascribed to coordination of the carbonyl oxygen in the sixth position. The geometries of the metallacyclobutane ligands in **1** and W[CH_2CH(t-Bu)CH_2]-(NAr)[$OCMe_2(CF_3)$]$_2$ also are similar (figure 2). If we ignore the slightly different angles of bending of the two rings (25° in **1**, 33° in W[CH_2CH(t-Bu)CH_2](NAr)-[$OCMe_2(CF_3)$]$_2$), then we can compare the two WC_3 rings directly. The primary differnce is longer W–C bonds in **1**. (The C–C bonds in **1** appear to be slightly shorter, but the difference is not statistically significant.) W–O and W–N bond lengths are the same in both compounds. The W–C bond lengths appear to be the only feature of the ring system that is especially sensitive to coordination geometry.

The stability of the metallacyclobutane complexes described in this study can be ascribed to a significant degree to the tridentate nature of the metallacyclobutane ligand. α-*tert*-Butyl-substituted metallacycles have been observed in the tungsten system, but they are unstable. For example, ethylene adds to W(CH-t-Bu)(NAr)[$OCMe_2(CF_3)$]$_2$ to give square-pyramidal W[CH(t-Bu)CH_2CH_2](NAr)-[$OCMe_2(CF_3)$]$_2$.[4] Above −30 °C [CH(t-Bu)CH_2CH_2]-(NAr)[$OCMe_2(CF_3)$]$_2$ decomposes in the presence of excess ethylene to give W($CH_2CH_2CH_2$)(NAr)[$OCMe_2(CF_3)$]$_2$. Molybdenacyclobutane complexes are much less stable than tungstacyclobutane complexes. Even Mo-($CH_2CH_2CH_2$)(NAr)[$OCMe(CF_3)_2$]$_2$, which can be observed at low temperature upon addition of ethylene to Mo(CH-t-Bu)(NAr)[$OCMe(CF_3)_2$]$_2$,[6] decomposes readily at 25 °C, probably by first losing ethylene to give intermediate Mo(CH_2)(NAr)[$OCMe(CF_3)_2$]$_2$. Therefore, coordination of the functionality in **1**, **2**, and **3** probably is a major factor in stabilizing these metallacycles toward loss of methyl acrylate or *N*,*N*-dimethylacrylamide.

The role that the functionality plays in loss of an olefin from the WC_3 ring is important, since other donors (PMe_3 or ethylene) replace an olefin in the ring whenever (it appears) the functionality can dissociate to give a five-coordinate intermediate. The question is whether the added ligand can then coordinate and actually force loss of the olefin from the ring or whether a four-coordinate alkylidene complex is formed in a straightforward metathetical reaction and the added ligand simply captures the alkylidene complex C, as shown schematically in eq 5. We favor the latter explanation at this stage, since even



(5)

B is probably a relatively crowded intermediate. Bimolecular "displacement" reactions could become competitive if there are fewer or smaller substituents on the MC_3 ring or if the added ligand is small and an excellent nucleophile. We plan to resolve these questions in future kinetic and mechanistic studies.

One point that we have not touched on yet is whether the functionality coordinates to the metal in a four-coordinate alkylidene complex before the olefin and thereby accelerates formation of the MC_3 ring. That would not appear to be the case if the mechanism for *loss* of the functionalized olefin from the ring were to involve dissociation of the functionality first, as we propose.

These results should have some more general implications as far as metathesis of certain functionalized olefins is concerned. The most straightforward explanation as to why directly functionalized olefins are not metathesized is that all relevant alkylidene complexes are destroyed in irreversible side reactions. A second possibility is that an alkylidene complex with a functionality directly attached to the α carbon atom of the alkylidene ligand would have significantly altered reactivity, and the methathesis reaction depends upon (inter alia) all alkylidene complexes and metallacycles having similar energies. Other explanations have included intramolecular coordination of the functionality in an alkylidene complex, thereby blocking reaction between that alkylidene and an olefin.[1,7] On the basis of the results reported here, intramolecular stabilization of metallacycle intermediates seems to be at least as likely as intramolecular coordination of the functionality in alkylidene complex. In this vein it should be noted again that tungsten complexes that contain trifluoro-*tert*-butoxide ligand are (qualitatively) good catalysts for the metathesis of ordinary olefins,[2a] yet **2a** does not react readily with ethylene.

The results described here suggest that coordination of functionalities can significantly alter the activity of catalysts of the type M(CHR')(NAr)$(OR)_2$, as one might suspect. It has already been observed that polymerization of cyclooctatetraene by W(CH-t-Bu)(NAr)[$OCMe(CF_3)_2$]$_2$ is slowed significantly in THF[8] and more recently that the living polymerization of acetylene itself by W(CH-t-Bu)(NAr)(O-t-Bu)$_2$ is possible in the presence of quinuclidine.[9] Studies of base effects at a fundamental level will be the focus of future investigations.

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 diethyl ether was 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. All deuterated NMR solvents were passed through a column of activated alumina.

^1H, ^{13}C, and ^{19}F NMR spectra were recorded in C_6D_6 (unless otherwise stated) on Varian XL-300 and Varian VXR-500 spectrometers. ^1H and ^{13}C NMR data are listed in parts per million downfield from TMS. Coupling constants are quoted in hertz. Obvious multiplicities and routine coupling constants usually are not listed. Elemental analyses were performed by Schwarzkopf, Inc.

W[CH(t-Bu)CH_2CH(CO_2Me)](NAr)[$OCMe_2(CF_3)$]$_2$ (1). Methyl acrylate (40 μL, 0.44 mmol) was added all at once to a pentane solution (10 mL) of W(CH-t-Bu)(NAr)[$OCMe_2(CF_3)$]$_2$ (0.300 g, 0.44 mmol). The solution was stirred for 2 h at 25 °C. The solvent was then removed in vacuo. The resulting yellow foam was dissolved in a minimal volume of pentane, and the solution was stored at −40 °C. Yellow crystals (0.27 g, 81%) were isolated by decanting the mother liquor and dried in vacuo: ^1H NMR δ 7.07 (1,H_m), 7.00 (1,H_m), 6.87 (1,H_p), 4.15 (1, C*H*Me_2), 4.00 (dd, J = 11 and 9, 1, $C_\beta H_{eq}$), 3.89 (1, C*H*Me_2), 3.43 (3, OMe), 2.71 (ddd, J = 9, 13, and 13, 1, $C_\beta H_{ax}$), 2.39 (d, J = 8, 1, C*H*(CO_2Me)), 1.85 (3, O$CMe_2(CF_3)$), 1.75 (3, O$CMe_2(CF_3)$), 1.98 (dd, J = 10 and 12, C*H*(t-Bu)), 1.42–1.26 (overlapping d's, 9, CHMe_2), 1.15 (9,

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$CHMe_2$ and $OCMe_2(CF_3)$), 1.06 (9, *t*-Bu); ^{13}C NMR δ 187.9 (CO_2Me), 150.6 (C_{ipso} or C_o), 149.0 (C_{ipso} or C_o), 146.9 (C_{ipso} or C_o), 127.6 (q, $^1J_{CF}$ = 284, CF_3), 127.4 (q, $^1J_{CF}$ = 288, CF_3), 123.4 (C_m or C_p), 123.1 (C_m or C_p), 84.2 (q, $^2J_{CF}$ = 30, $OCMe_2(CF_3)$), 81.3 (q, $^2J_{CF}$ = 28, $OCMe_2(CF_3)$), 67.1 (d, J_{CH} = 121, J_{WC} = 51, *C*H(CO_2Me)), 52.2 (OMe), 39.9 (d, J_{CH} = 149, J_{WC} = 39, *C*H(CMe_3)), 36.6, 32.0, 27.5, 27.2, 24.8, 24.6, 24.5, 24.4, 24.3 23.7, 23.4, 22.8 (C_β, CH(*C*Me_3), CH(C*Me*$_3$), O*C*$Me_2(CF_3)$, *C*HMe_2, CH*Me*$_2$, not necessarily in that order); IR (Nujol, cm^{-1}) 1585 (ν_{CO}) (s). Anal. Calcd for $WC_{29}H_{45}F_6O_4N$: C, 45.26; H, 5.89. Found: C, 45.02; H, 5.84.

W[CH(*t*-Bu)CH_2CH($CONMe_2$)](NAr)[$OCMe_2(CF_3)$]$_2$ (2a). *N,N*-Dimethylacrylamide (18 μL, 0.18 mmol) was added all at once to a pentane solution (5 mL) of W(CH-*t*-Bu)(NAr)-[$OCMe_2(CF_3)$]$_2$ (0.120 g, 0.18 mmol). The solution was stirred at 25 °C for 60 min, and the solvent was removed in vacuo. The crude yellow powder was washed with a few drops of pentane at −30 °C to afford a bright yellow powder (0.118 g, 86%): ^1H NMR δ 7.14 (1, H_m), 7.06 (1, H_m), 6.91 (1, H_p), 4.31 (1, C*H*Me_2, 4.08 (1, C*H*Me_2), 3.88 (dd, J = 9 and 11, 1, $C_\beta H_{eq}$), 2.79 (ddd, 1, $C_\beta H_{ax}$), 2.49 (3, NMe_2), 2.29 (3, NMe_2), 2.04 (d, J = 8, 1, C*H*($CONMe_2$)), 1.95 (3, O*C*$Me_2(CF_3)$), 1.87 (dd, J = 9 and 12, 1, C*H*(*t*-Bu)), 1.84 (3, O*C*$Me_2(CF_3)$), 1.48 (3, CH*Me*$_2$), 1.45 (3, CH*Me*$_2$), 1.41 (3, CH*Me*$_2$), 1.27 (3, CH*Me*$_2$), 1.22 (3, O*C*$Me_2(CF_3)$), 1.15 (9, *t*-Bu), 1.13 (3, O*C*$Me_2(CF_3)$); ^{13}C NMR (CD_2Cl_2) δ 186.5 (*C*$ONMe_2$), 151.0 (C_{ipso} or C_o), 149.4 (C_{ipso} of C_o), 147.4 (C_{ipso} or C_o), 127.9 (C_m or C_p), 127.9 (q, $^1J_{CF}$ = 284, CF_3), 127.6 (q, $^1J_{CF}$ = 289, CF_3), 123.1 (C_m or C_p), 83.2 (q, $^2J_{CF}$ = 30, $OCMe_2(CF_3)$), 80.5 (q, $^2J_{CF}$ = 30, $OCMe_2(CF_3)$), 66.4 (d, J_{CH} = 119, J_{CW} = 53, *C*H($CONMe_2$)), 34.8 (d, J_{CH} = 145, J_{CW} = 35, *C*H(CMe_3)), 36.5, 36.4, 34.0, 32.0, 31.6, 27.4, 27.3, 25.2, 25.1, 24.8, 24.5, 23.7, 23.6, 23.5, 22.9 (C_β, CH(*C*Me_3), CH(C*Me*$_3$), CH(CON*Me*$_2$), O*C*$Me_2(CF_3)$, *C*HMe_2, CH*Me*$_2$, not necessarily in that order); IR (Nujol, cm^{-1}) 1580 (ν_{CO}) (s). Anal. Calcd for $WC_{30}H_{48}F_6O_3N_2$: C, 46.05; H, 6.18; N, 3.58. Found: C, 46.29; H, 6.07; N, 3.55.

W[CH(*t*-Bu)CH_2CH($CONMe_2$)](NAr)(O-*t*-Bu)$_2$ (2b). The preparation of **2b** is analogous to that of **2a** employing 27 μL (0.26 mmol) of *N,N*-dimethylacrylamide and 0.150 g (0.26 mmol) of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (yield 0.129 g, 73%): ^1H NMR δ 7.18–7.12 (2, H_m), 6.98 (1, H_p), 4.45 (1, C*H*Me_2), 4.26 (1, C*H*Me_2), 4.13 dd, J = 9 and 11, 1, $C_\beta H_{eq}$), 2.89 (ddd, J = 8, 13, and 13, 1, $C_\beta H_{ax}$), 2.51 (3, NMe_2), 2.36 (3, N*Me*$_2$), 2.12 (d, J = 8, 1, C*H*($CONMe_2$)), 1.85 (dd, J = 9 and 12, 1, C*H*(*t*-Bu)), 1.71 (9, O-*t*-Bu or CH(*t-Bu*)), 1.49 (3, CH*Me*$_2$), 1.45 (3, CH*Me*$_2$), 1.43 (3, CH*Me*$_2$), 1.38 (3, CH*Me*$_2$), 1.23 (9, O-*t*-Bu or CH(*t-Bu*)), 1.17 (9, O-*t*-Bu or CH(*t-Bu*)); ^{13}C NMR (CD_2Cl_2) δ 185.3 (*C*$ONMe_2$), 150.2 (C_{ipso} or C_o), 149.7 (C_{ipso} or C_o), 146.2 (C_{ipso} or C_o), 126.1 (C_m or C_p), 122.6 (C_m or C_p), 82.6 (O*C*Me_3), 79.8 (O*C*Me_3), 63.7 (d, J_{CW} = 53, *C*H($CONMe_2$)), 36.5, 36.0, 33.8, 33.1, 32.1, 32.0, 31.6, 27.2, 27.1, 25.1, 24.9, 24.7, 24.2, 23.0 (C_β, *C*H(CMe_3), CH(*C*Me_3), CH(C*Me*$_3$), CH(CON*Me*$_2$), O*C*Me_3, *C*HMe_2, CH*Me*$_2$, not necessarily in that order); IR (Nujol, cm^{-1}) 1575 (ν_{CO}) (s). Anal. Calcd for $WC_{30}H_{54}O_3N_2$: C, 53.41; H, 8.07; N, 4.15. Found C, 53.16; H, 8.11; N, 4.24.

Mo[CH(*t*-Bu)CH_2CH($CONMe_2$)](NAr)[$OCMe_2(CF_3)$]$_2$ (3a). *N,N*,-Dimethylacrylamide (64 μL, 0.62 mmol) was added all at once to a yellow-orange pentane solution (20 mL) of Mo-(CH-*t*-Bu)(NAr)[$OCMe_2(CF_3)$]$_2$ (0.37 g, 0.61 mmol) at −30 °C. The solution darkened almost immediately, and a red solid precipitated as the mixture was allowed to warm to room temperature over the next 60 min. Solvents were then removed in vacuo, and the dark residue was extracted with ether/pentane (1:1). The extracts were filtered through Celite, and the filtrate was evaporated to dryness in vacuo. The red residue was dissolved in a minimum amount of ether/pentane (1:2), and the solution was stored at −40 °C. Red crystals (0.29 g, 67%) were isolated in two crops by filtration and dried in vacuo: ^1H NMR δ 7.03 (1, H_m), 7.03 (1, H_m), 6.94 (1, H_p), 4.36 (1, C*H*Me_2), 4.08 (1, C*H*Me_2), 3.40 (dd, J = 8 and 12, 1, $C_\beta H_{eq}$), 3.01 (ddd, J = 9 and 12, 1, $C_\beta H_{ax}$), 2.55 (s, 3, N*Me*$_2$), 2.35 (s, 3, N*Me*$_2$), 2.06 (dd, J = 8 and 12, 1, C*H*(*t*-Bu)), 2.03 (d, J = 8, 1, C*H*($CONMe_2$)), 2.00 (3, O*C*$Me_2(CF_3)$), 1.88 (3, O*C*$Me_2(CF_3)$), 1.45 (3, CH*Me*$_2$), 1.42 (3, CH*Me*$_2$), 1.39 (3, CH*Me*$_2$), 1.24 (3, CH*Me*$_2$), 1.23 (3, O*C*$Me_2(CF_3)$), 1.12 (3, O*C*$Me_2(CF_3)$), 1.12 (s, 9, *t*-Bu); ^{13}C NMR δ 182.9 (*C*$ONMe_2$), 151.9 (C_{ipso} or C_o), 151.5 (C_{ipso} or C_o), 146.9 (C_{ipso} or C_o), 128.9 (C_m), 127.6 (q, $^1J_{CF}$ = 287, $OCMe_2(CF_3)$), 123.9 (C_m), 123.5 (C_p), 83.1 (q, $^2J_{CF}$ = 29, $OCMe_2(CF_3)$), 80.6 (q, $^2J_{CF}$ = 28, $OCMe_2(CF_3)$), 61.2 (d, J = 126, CH($CONMe_2$)), 37.3, 35.6, 33.3, 31.4, 29.3, 27.8, 27.6, 25.0, 24.9, 24.5, 23.9, 23.6, and 23.5 (C_β, CH(CMe_3), CH(*C*Me_3), CH(C*Me*$_3$), CH(CON*Me*$_2$), O*C*$Me_2(CF_3)$, *C*HMe_2, CH*Me*$_2$, not necessarily in that order); ^{19}F NMR (282.2 MHz) δ −82.8 (s, 3, $OCMe_2(CF_3)$), −82.9 (s, 3, $OCMe_2(CF_3)$); IR (Nujol, cm^{-1}) 1580 (ν_{CO}) (s). Anal. Calcd for $MoC_{30}H_{48}F_6O_3N_2$: C, 51.87; H, 6.96; N, 4.03. Found: C, 51.85; H, 7.16; N, 3.77.

Mo[CH(*t*-Bu)CH_2CH($CONMe_2$)](NAr)(O-*t*-Bu)$_2$ (3b). *N,N*-Dimethylacrylamide (115 μL, 1.12 mmol) was added all at once to a yellow-orange pentane solution (25 mL) of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (0.52 g, 1.07 mmol) at −30 °C. The solution darkened almost immediately, and red solid precipitated as the mixture was allowed to warm to room temperature over the next 90 min. Solvents were then removed in vacuo, and the red residue was recrystallized from a minimum amount of ether/pentane (1:1) at −40 °C. Red crystals (0.45 g, 72%) were isolated in two crops by filtration and dried in vacuo. The room-temperature ^1H and ^{13}C NMR spectra showed that 10–15% of this complex was dissociated into Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and *N,N*-dimethylacrylamide: ^1H NMR δ 7.07 (1, H_m), 7.02 (1, H_m), 6.96 (1, H_p), 4.52 (1, C*H*Me_2), 4.26 (1, C*H*Me_2), 3.55 (dd, J = 8 and 12, 1, $C_\beta H_{eq}$), 3.04 (ddd, J = 8, 12, and 13, 1, $C_\beta H_{ax}$), 2.57 (3, NMe_2), 2.41 (3, NMe_2), 2.14 (d, J = 8, 1, C*H*($CONMe_2$), 2.08 (dd, J = 8 and 13, 1, C*H*(*t*-Bu)), 1.75 (9, CH(*t-Bu*)), 1.47 (3, CH*Me*$_2$), 1.41 (3, CH*Me*$_2$), 1.41 (3, CH*Me*$_2$), 1.35 (3, CH*Me*$_2$), 1.20 (9, O-*t*-Bu), 1.18 (9, O-*t*-Bu); ^{13}C NMR δ 183.6 (*C*$ONMe_2$), 152.1 (C_{ipso} or C_o), 150.4 (C_{ipso}or C_o), 145.9 (C_{ipso} or C_o), 127.5 (C_p), 123.5 (C_m), 123.3 (C_m), 82.5 (O*C*Me_3), 79.8 (O*C*Me_3), 59.1 (d, J = 125, *C*H($CONMe_2$), 36.9, 35.8, 33.4, 32.6, 32.4, 32.0, 31.9, 31.6, 29.2, 28.2, 27.9, 27.5, 27.4, 25.2, 25.0, 24.8, 24.0, and 23.2 (C_β, C_αH(CMe_3), C_αH(*C*Me_3), C_αH(C*Me*$_3$), CH(CON*Me*$_2$), O*C*Me_3, *C*HMe_2, CH*Me*$_2$, H_2C=-CHC(O)N*Me*$_2$, CH*C*Me_3, CHC*Me*$_3$, not necessarily in that order); IR (Nujol, cm^{-1}) 1570 (ν_{CO}) (s). Anal. Calcd for $MoC_{30}H_{54}O_3N_2$: C, 61.42; H, 9.28; N, 4.77. Found: C, 61.16; H, 9.35; N, 4.65.

X-ray Structure of W[CH(*t*-Bu)CH_2CH(CO_2Me)]-(NAr)[$OCMe_2(CF_3)$]$_2$ (1). Suitable crystals of 1 were obtained by crystallization from pentane at −40 °C. A yellow crystal having approximate dimensions 0.300 × 0.250 × 0.270 mm was mounted on a glass fiber in a cold stream of dinitrogen. Data were collected at −65 °C on an Enraf-Nonius CAD-4 diffractometer using monochromatic graphite Mo Kα radiation. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $25 < 2\theta < 55°$, corresponded to a monoclinic cell with dimensions a = 17.323 (3) Å, b = 10.408 (3) Å, c = 18.758 (4) Å, β = 99.36 (2)°, and V = 3337 (2) Å^3. For Z = 4 and fw = 769.52 the calculated density is 1.531 g/cm^3. With the successful solution and refinement of the structure the space group was determined to be $P2_1/c$. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealized positions (d_{C-H} = 0.95 Å) and were assigned isotropic thermal parameters which 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 4507 observed reflections ($I > 3\sigma(I)$) and 370 variable parameters and converged (largest parameter shift was 0.01 times its esd) with agreement factors of R = 0.043 and R_w = 0.043. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.92 and −0.90 e/Å^3, respectively.

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Supplementary Material Available: A completely labeled ORTEP drawing of W[CH(*t*-Bu)CH_2CH(CO_2Me)](N-2,3-C_6H_3-*i*-Pr_2)[$OCMe_2(CF_3)$]$_2$ and listings of final positional and thermal parameters (8 pages); a listing of final observed and calculated structure factors (52 pages). Ordering information is given on any current masthead page.