by crystallization from aqueous acetonitrile. After prolonged storage at room temperature, the surface of the crystals turned brown, though NMR spectroscopy showed no perceptible decomposition. The same product **4a** was obtained when allyl bromide was used instead of allyl chloride.

Preparation of 4b. After $Mo(CO)_6$ (1 g, 3.78 mmol) was refluxed with 2-methallyl chloride (1 mL) in acetonitrile (15 mL) for 5 h, the ligand **1** (1.3 g, 3.9 mmol) in acetonitrile (5 mL) was added to the hot solution. The yellow crystalline product **4b** was isolated (0.77 g, 44%) as described for **4a**.

Preparation of 4c. The procedure is the same as that described for **4a**. From $Mo(CO)_6$ (1 g, 3.78 mmol), 2-phenyl-3-bromo-1-propene (0.75 mL), and ligand **1** (1.3 g, 3.9 mmol), there was obtained 0.436 g (23%) of **4c** as a yellow solid.

Attempted Preparation of 4c from 2. The complex **2** (0.25 g, 0.49 mmol) was refluxed with allyl bromide (1 mL) in acetonitrile (20 mL) containing THF (3 mL) for 4 h. No change was observed by TLC. When the mixture was cooled, the complex **2** (0.2 g) was recovered.

X-ray Crystal Structure Determination of 4c. An X-ray-grade crystal of **4c** was grown in toluene–hexane. Diffraction data were collected for a crystal of size 0.275 × 0.45 × 0.5 mm on an Enraf-Nonius CAD-4 diffractometer. Unit cell dimensions were determined with use of 25 well-centered reflections located in the region $17° < \theta < 41°$. An orthorhombic cell was indicated with cell constants as listed in Table IV. Reflections were measured with an index range $h = 0$–11, $k = 0$–15, and $l = 0$–17 with use of the $\omega/2\theta$ scan mode and an average scan speed of 1° min^{-1}. Three standard reflections monitored every 3000 s of X-ray time showed negligible variation in intensity.

From the systematically absent reflections in the data set, the space group $P2_12_12_1$ was inferred. The structure was solved with use of Patterson and Fourier techniques. Refinement of the structure with use of SHELX-76[22] converged to $R = 0.0817$ for 1842 observed reflections. A weighting scheme was not applied. Non-hydrogen atoms were treated with anisotropic temperature factors. Hydrogens that could be geometrically fixed were held constant during the last few cycles of refinement.

Acknowledgment. We thank Dr. S. Rajappa (FNA) for his encouragement and support and the DST, New Delhi, India, for financial assistance in the form of a Young Scientist Project. We are grateful to Dr. S. Krishnan and Dr. R. Vetrivel for their help with computation and Mr. A. G. Samuel and Dr. P. R. Rajmohanan for the NMR spectra.

Supplementary Material Available: Tables of bond lengths and bond angles and atomic coordinates and a crystal packing diagram for **4c** (5 pages); a table of structure factor amplitudes for **4c** (11 pages). Ordering information is given on any current masthead page.

(22) Sheldrick, G. M. Program for Crystal Structure Determination and Refinement; University of Cambridge: Cambridge, England, 1976.

Reduction of Molybdenum Imido–Alkylidene Complexes in the Presence of Olefins To Give Molybdenum(IV) Complexes

Jennifer Robbins, Guillermo C. Bazan, John S. Murdzek, Marie B. O'Regan, and Richard R. Schrock*

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

Received February 25, 1991

$Mo(CH\text{-}t\text{-}Bu)(NAr)[OCMe(CF_3)_2]_2$ (**1a**) (Ar = 2,6-diisopropylphenyl) reacts with excess vinyltrimethylsilane to give $Mo(NAr)[OCMe(CF_3)_2]_2(CH_2{=}CHSiMe_3)$ (**2**). Complex **2** reacts with trimethylphosphine, 2-butyne, and excess ethylene to give $Mo(NAr)[OCMe(CF_3)_2]_2(PMe_3)_2$ (**3**), $Mo(NAr)[OCMe(CF_3)_2]_2(MeC{\equiv}CMe)$ (**4**), or $Mo(NAr)[OCMe(CF_3)_2]_2(C_4H_8)$ (**8**), respectively. Complex **4** reacts with PMe_3 to give $Mo(NAr)[OCMe(CF_3)_2]_2(MeC{\equiv}CMe)(PMe_3)$ (**5**), and **8** reacts with PMe_3 to give $Mo(NAr)[OCMe(CF_3)_2]_2(CH_2{=}CH_2)(PMe_3)$ (**9**). Metallacycle $Mo(CH_2CH_2CH_2)(NAr)[OCMe(CF_3)_2]_2$ (**6**) decomposes in the presence of excess ethylene to form **8** and reacts with trimethylphosphine to give $Mo(CH_2)(NAr)[OCMe(CF_3)_2]_2(PMe_3)$ (**7**). $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ (**1b**) reacts with excess ethylene to give $Mo(CH_2CH_2CH_2)(NAr)(O\text{-}t\text{-}Bu)_2$ (**10**), which reacts with trimethylphosphine to give $Mo(CH_2)(NAr)(O\text{-}t\text{-}Bu)_2(PMe_3)$ (**11**). **10** decomposes to $[Mo(NAr)(O\text{-}t\text{-}Bu)_2]_2$ (**12**; $C2/c$, $a = 14.772$ (6) Å, $b = 15.470$ (4) Å, $c = 10.625$ (8) Å, $\beta = 104.62$ (3)°, $Z = 4$, $M_r = 834.88$, $\rho = 1.276$ g/cm^3, $\mu = 5.99$ cm^{-1}, $R_1 = 0.035$, $R_2 = 0.047$). **12** is an imido-bridged dimer that is believed to form upon coupling of methylene ligands in two $Mo(NAr)(CH_2)(O\text{-}t\text{-}Bu)_2$ complexes.

Introduction

Complexes of the type $M(CH\text{-}t\text{-}Bu)(NAr)(OR)_2$ (M = Mo,[1] W;[2] Ar = 2,6-diisopropylphenyl; R = alkyl, aryl, fluoroalkyl) have proven to be useful olefin metathesis catalysts. When R is relatively electron withdrawing (i.e., R = $CMe(CF_3)_2$), they will metathesize acyclic olefins. When R is relatively electron donating (i.e., R = *t*-Bu), they do not react readily with acyclic olefins but do react rapidly with strained cyclic olefins, especially norbornenes and norbornadienes.[3] Molybdenum complexes appear to be more tolerant of functionalities than tungsten complexes,[4] but they also appear to be less stable than their tungsten analogues.[1] In particular, molybdenum olefin metathesis catalysts appear to decompose more readily by pathways that yield reduced (Mo(IV)) complexes.[1] In this paper we attempt to clarify these decomposition pathways and the

(1) Schrock, R. R.; Murdzek, J. S.; Bazan, G.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

(2) (a) Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L. Y.; DiMare, M.; Schofield, M. H.; Anhaus, J. T.; Walborsky, E.; Evitt, E.; Kruger, E.; Betz, P. *Organometallics* **1990**, *9*, 2262. (b) Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423.

(3) (a) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158. (b) Bazan, G.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378.

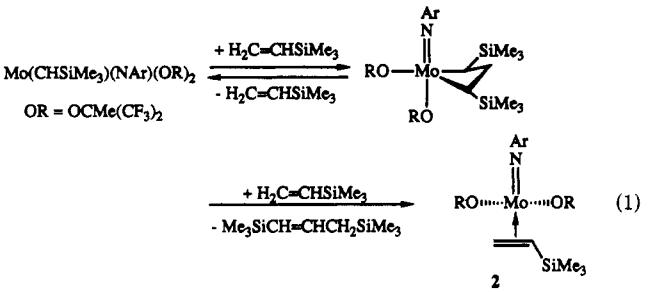
(4) Bazan, G. C.; Schrock, R. R.; Cho, H.-N.; Gibson, V. C. *Macromolecules*, in press.

0276-7333/91/2310-2902$02.50/0 © 1991 American Chemical Society

molybdenum(IV) products that are formed.

Results

Derivatives of Mo(NAr)[OCMe(CF$_3$)$_2$]$_2$(CH$_2$=CHSiMe$_3$). Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (**1a**) has been shown to react with a slight excess of vinyltrimethylsilane in pentane at −30 °C to yield Mo(CHSiMe$_3$)(NAr)[OCMe(CF$_3$)$_2$]$_2$ and neohexene.[1] Mo(CHSiMe$_3$)(NAr)[OCMe(CF$_3$)$_2$]$_2$ could not be isolated, however, because it reacts with an additional 2 equiv of vinyltrimethylsilane to give 1,3-bis(trimethylsilyl)propene, presumably via β-hydride rearrangement of an unobservable α,α'-disubstituted metallacycle (eq 1) and an unstable



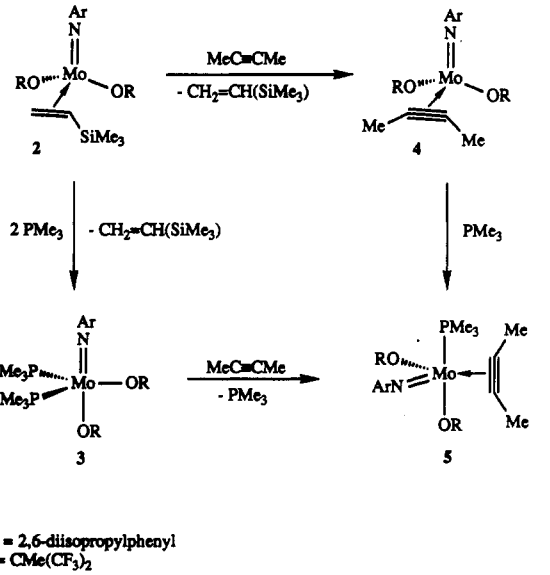
(1)

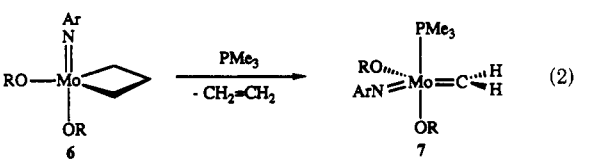
complex with the formula Mo(NAr)[OCMe(CF$_3$)$_2$]$_2$(CH$_2$=CHSiMe$_3$) (**2**), which could be characterized only in solution by NMR methods.[1] The ^{13}C NMR spectrum of **2** shows an olefin CH resonance at δ 67.4 (J_{CH} = 129 Hz) and an olefin CH$_2$ resonance at δ 63.6 (J_{CH} = 157 Hz); the alkoxide ligands are inequivalent. The structure of Mo(NAr)[OCMe(CF$_3$)$_2$]$_2$(CH$_2$=CHSiMe$_3$) is proposed to be that in which the C=C axis is oriented perpendicular to the N/Mo/(olefin center) plane in its lowest energy conformation, since in this circumstance π bonding to the olefin would be maximized. Note that **2** is relatively stable toward bimolecular decomposition reactions and toward formation of a metallacyclopentane complex by reaction with more vinyltrimethylsilane, perhaps for steric reasons. These results should be compared with those made in the system involving ethylene, which is discussed later.

Crystalline, well-characterized relatives of **2** have now been prepared (Scheme I). We propose that purple Mo(NAr)[OCMe(CF$_3$)$_2$]$_2$(PMe$_3$)$_2$ (**3**) is a trigonal bipyramid with equatorial phosphine and equatorial and axial alkoxide ligands, since it exhibits two resonances for the alkoxide ligands and one resonance for equivalent phosphines in its NMR spectra (^{1}H, ^{19}F, ^{13}C, and ^{31}P). **2** reacts with 2-butyne to yield red-orange Mo(NAr)[OCMe(CF$_3$)$_2$]$_2$(MeC≡CMe) (**4**). Proton and carbon NMR spectra of **4** indicate that the alkoxide ligands are equivalent, as are the 2-butyne methyl groups and acetylene carbon atoms (δ 170.6), consistent with a pseudotetrahedral structure analogous to the structure proposed for **2**. The reaction between **4** and trimethylphosphine gives Mo(NAr)[OCMe(CF$_3$)$_2$]$_2$(MeC≡CMe)(PMe$_3$) (**5**), which also can be formed by adding 2-butyne to **3**. Unlike **3** and **4**, **5** has no symmetry. We believe **5** is most likely to be a pseudotrigonal bipyramid in which the 2-butyne ligand occupies an equatorial position and is oriented along the O–Mo–P axis perpendicular to the equatorial plane, since in this circumstance π back-bonding to the acetylene ligand would be maximized. An analogous square-pyramidal complex cannot be ruled out. The trimethylphosphine ligand in **5** does not exchange with free phosphine on the NMR time scale, and **5** is stable to loss of PMe$_3$ in vacuo for short periods of time.

Reactions Between Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ and Ethylene. We reported that Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ reacts with excess ethylene to give trigonal-bipyramidal Mo(CH$_2$CH$_2$CH$_2$)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (**6**) in high yield, but that **6** is unstable.[1] We now find that **6** decomposes in solution in the presence of trimethylphosphine to form Mo(CH$_2$)(NAr)[OCMe(CF$_3$)$_2$]$_2$(PMe$_3$) (**7**, eq 2) in high yield. In the proton NMR

Scheme I

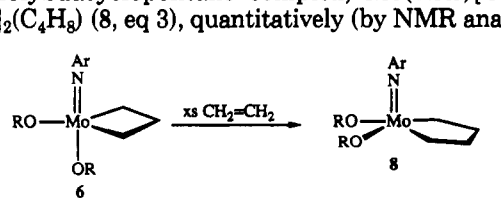




(2)

spectrum of **7** in toluene-d_8, the methylidene protons appear as two doublets of doublets at δ 12.62 (J_{HH} = J_{PH} = 6 Hz) and 12.95 (J_{HH} = 6 Hz, J_{PH} = 9 Hz). The ^{13}C NMR spectrum shows an eight-line resonance for the methylidene carbon at δ 278.7 (J_{CH} = 137 and 159 Hz, J_{CP} = 24 Hz). These data are similar to those for the analogous tungsten methylidene phosphine complexes[2b,5] and structurally characterized molybdenum and tungsten alkylidene complexes.[6] In such complexes the proton that points away from the imido ligand is that which has the lower value for J_{CH}, since it appears to be involved in an agostic interaction with the metal.[1,2a] **7** is only marginally stable; it decomposes quickly in solution, and attempts to isolate it in the solid state have failed. We believe that **6** most likely loses ethylene to give unstable Mo(CH$_2$)(NAr)[OCMe(CF$_3$)$_2$]$_2$, although attack by PMe$_3$ followed by loss of ethylene is a possibility that cannot be ruled out.

When **6** is allowed to decompose in the presence of excess ethylene, it yields an unstable species that we propose is a molybdacyclopentane complex, Mo(NAr)[OCMe(CF$_3$)$_2$]$_2$(C$_4$H$_8$) (**8**, eq 3), quantitatively (by NMR analysis).



(3)

8 also can be prepared quantitatively by adding excess

(5) Feldman, J.; Davis, W. M.; Thomas, J. K.; Schrock, R. R. *Organometallics* **1990**, *9*, 2535.
(6) Schrock, R. R.; Crowe, W. E.; Bazan, G. C.; DiMare, M.; O'Regan, M. B.; Schofield, M. H. *Organometallics* **1991**, *10*, 1832.

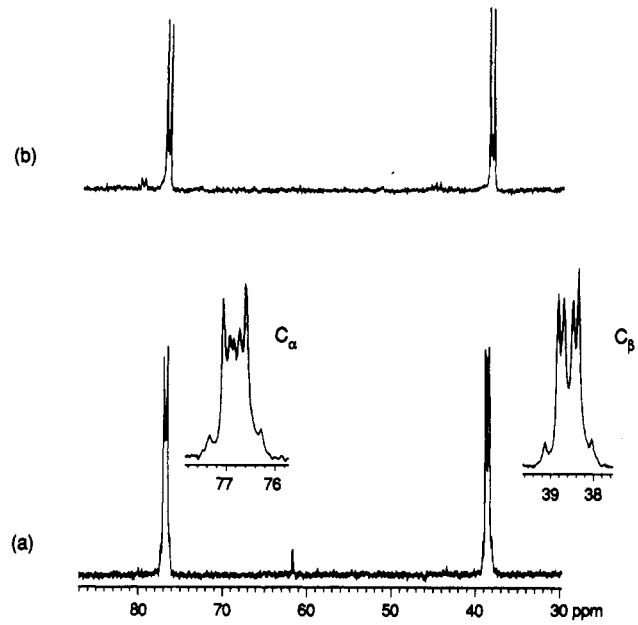


Figure 1. (a) $^{13}C\{^1H\}$ NMR spectrum (75.4 MHz, toluene-d_8, −40 °C) of Mo(NAr)[OCMe$(CF_3)_2]_2(^{13}C_4H_8)$ (8-$^{13}C_4$). (b) $^{13}C\{^1H\}$ NMR spectrum (same conditions) of 8 made by using $^{13}C_2H_4$ and $^{12}C_2H_4$ in a 1:3 ratio.

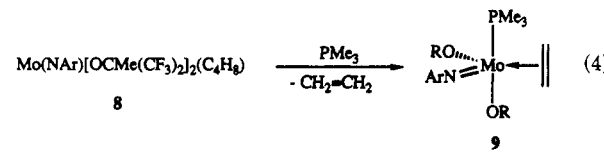
ethylene to Mo(NAr)[OCMe$(CF_3)_2]_2(CH_2$=CHSiMe$_3)$ (**2**). Since the most stable type of metallacyclo*butane* complex in this class of complexes is a square pyramid,[5] we believe **8** most likely is a square pyramid. Decomposition of **6** in the presence of propylene gives a complex mixture of unidentifiable products that are not observed in the presence of ethylene alone. Since ^{13}C labeling studies (see below) do not reveal any trace of propylene, we propose that **6** decomposes by loss of ethylene and bimolecular coupling of methylene ligands in Mo(CH_2)(NAr)[OCMe$(CF_3)_2]_2$ to give ethylene.

It has been possible to characterize **8** only by proton and carbon NMR spectroscopy. The proton NMR spectrum (300 MHz) of **8** in toluene-d_8 at −40 °C displays broad resonances for the ethylene protons at δ 3.10, 2.80, 2.60, and 2.52. One reasonance each is observed for the alkoxide methyl, isopropyl methyl, and isopropyl methine protons, consistent with the relatively high symmetry of the proposed square-pyramidal **8**. Mo(NAr)[OCMe$(CF_3)_2]_2$-$(^{13}C_4H_8)$ (8-$^{13}C_4$) can be prepared either by allowing ^{13}C-labeled **6** to decompose in solution under $^{13}C_2H_4$ or by adding $^{13}C_2H_4$ to **2**. The $^{13}C\{^1H\}$ NMR spectrum of 8-$^{13}C_4$ at −40 °C in toluene-d_8 (Figure 1a) shows two multiplets at δ 76.8 and 38.6 for the metallacycle carbons, indicative of an AA′XX′ spin system. If **8** is made with a mixture of $^{13}C_2H_4$ and $^{12}C_2H_4$ (1:3), both resonances become doublets (Figure 1b), consistent with formation of primarily a Mo$^{13}CH_2{}^{13}CH_2{}^{12}CH_2{}^{12}CH_2$ ring and consequently simplification of the NMR spectrum to a first-order pattern. The coupling constant observed from this spectrum is 32 Hz ($J_{C_\alpha C_\beta}$); $J_{C_\alpha C_{\beta'}}$ = 4 Hz and $J_{C_\beta C_{\beta'}}$ = 32 Hz subsequently can be determined from the spectrum of the fully labeled metallacycle.[7] ($J_{C_\alpha C_{\alpha'}}$ is evidently too small to be detected in this experiment.) Similar NMR spectra were observed recently for a structurally characterized tungstacyclopentane complex.[8] We assign the downfield carbon resonance to C_α and the upfield resonance to C_β on the basis of comparison with the tungstacyclopentane complex and its analogues.[8]

The singlet resonance between each branch of each doublet in Figure 1b appears with time and is consistent with the presence of mono-^{13}C-labeled metallacycles. We speculate that $^{12}CH_2$=$^{13}CH_2$ arises via metathesis that is catalyzed by a trace amount of an alkylidene complex which remains in the system as a result of the synthetic method. However, at this stage we cannot exclude the possibility that traces of unidentified alkylidene complexes are being formed through hydrolysis or decomposition reactions, nor can we exclude the (less likely) possibility that traces of an alkylidene complex are being formed through contraction of the MC_4 ring to an MC_3 ring[9] followed by loss of olefin from the MC_3 ring.

At higher temperatures (0–50 °C) reversible changes in the NMR spectra of **8** in the presence of ethylene are complex. At least one new species is present in addition to **8**; this new compound displays resonances for the alkoxide and imido ligands (see Experimental Section) but no new resonances for bound ethylene. A broad resonance that is found at ~5.2 ppm in the presence of excess ethylene, the approximate chemical shift of the protons in free ethylene, suggests that ethylene is involved in exchange processes. The ^{13}C NMR spectrum of 8-$^{13}C_4$ shows no evidence for the presence of a monoethylene adduct; the metallacycle carbon resonances decrease in intensity and the resonance at 123 ppm for free ethylene broadens as the temperature is increased. Although extensive studies of equilibria between tantallacyclopentane complexes and Ta(III) olefin complexes might suggest that ethylene is lost from **8** to give a monoethylene complex analogous to **2**,[9] there is no evidence that could be used to support the proposal that a Mo(IV) monoethylene complex is present in this system.

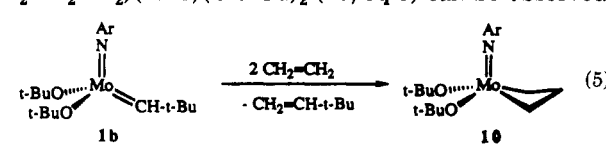
The reaction between **8** and trimethylphosphine produces Mo(NAr)[OCMe$(CF_3)_2]_2(CH_2$=$CH_2)$(PMe$_3)$ (**9**, eq 4) quantitatively (by proton NMR analysis). **9** also is



(4)

formed when Mo(NAr)[OCMe$(CF_3)_2]_2$(PMe$_3)_2$ is treated with excess ethylene. Proton and carbon NMR studies show that **9** is structurally similar to Mo(NAr)$(OR)_2$-(MeC≡CMe)(PMe$_3)$ (**5**). We think that **9** most likely is a trigonal bipyramid in which the ethylene is bound in an equatorial position and the C–C axis lies parallel to the P–Mo–O axis, although again a square-pyramidal version cannot be excluded. The reaction between **9** and 2-butyne gives **5** quantitatively. Attempts to isolate **8** and **9**, even at low temperatures, failed.

Reactions of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ with Ethylene. When an NMR sample of Mo(CH-*t*-Bu)-(NAr)(O-*t*-Bu)$_2$ (**1b**) is allowed to react with 4 equiv of ethylene for 5 h at room temperature in toluene-d_8, Mo-$(CH_2CH_2CH_2)$(NAr)(O-*t*-Bu)$_2$ (**10**, eq 5) can be observed



(5)

by NMR spectroscopy. Complex **10** is formed in low yield

(7) Raman, A. *Nuclear Magnetic Resonance, Basic Principles*; Springer-Verlag: New York, 1986; p 62.
(8) Chisholm, M. H.; Huffman, J. C.; Hampden-Smith, M. J. *J. Am. Chem. Soc.* **1990**, *111*, 5284.
(9) McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 5610.

Table I. Selected Bond Lengths (Å) and Angles (deg) in $[Mo(NAr)(O\text{-}t\text{-}Bu)_2]_2$ (12)

Mo(1)-Mo(2)	2.654 (1)	Mo(1)-N(1)	1.955 (4)
Mo(1)-O(3)	1.887 (3)	Mo(2)-N(1)	1.952 (4)
Mo(2)-O(4)	1.892 (3)		
Mo(1)-N(1)-Mo(2)	85.6 (2)	O(3)-Mo(1)-N(1)	118.2 (1)
O(4)-Mo(2)-O(4)'	111.6 (2)	Mo(1)-N(1)-C(11)	137.4 (3)
O(3)-Mo(2)-O(3)'	111.1 (2)	Mo(2)-N(1)-C(11)	137.0 (3)
O(4)-Mo(2)-N(1)	117.4 (1)		

(~25%), but the only other complex observed by NMR spectroscopy is **1b**. Resonances for the metallacycle protons appear as three broad unresolved resonances at room temperature (δ 3.8, 3.0, 2.3) in a 1:1:2 ratio. At −40 °C, the resonance at δ 3.8 appears as a broad virtual quartet and the resonance at δ 2.3 as a broad virtual triplet. By comparison with a variety of square-pyramidal tungstacyclobutane complexes[5] the resonances at δ 3.8 and 3.0 can be assigned to the two β-protons, and that at δ 2.3 to two of the four α-protons. (The other two α-proton resonances apparently are obscured, as is often the case in analogous tungsten systems.[5]) In the carbon NMR spectrum of **10** made with ^{13}C-labeled ethylene, the α-carbon resonance appears as a doublet at δ 34.9 and the β-carbon resonance at δ 29.1 (J_{CC} = 32 Hz; cf. C_α at δ 41.9 and C_β at δ 24.5, J_{CC} = 30 Hz, in the tungsten analogue[5]). The reaction between **10** and PMe_3 yields $Mo(CH_2)(NAr)(O\text{-}t\text{-}Bu)_2(PMe_3)$ (**11**). The yield of **11** is low (~10% based on **1b**) because ethylene competes with PMe_3 to reform **10**. In contrast, note that **7** forms irreversibly in the presence of ethylene, presumably because the metal is considerably more electrophilic. The proton NMR spectrum of **11** displays two doublets of equal intensity at room temperature at δ 12.32 and 11.94 (J_{HH} = 5 Hz), consistent with a structure analogous to that of **7** (eq 2). The sample must be cooled to −40 °C in order to resolve hydrogen–phosphorus coupling (J_{HP} = 4 Hz for each), since PMe_3 is bound much less strongly in **11** than it is in **7**. (Free PMe_3 exchanges with that in **11** on the NMR time scale.) All attempts to isolate **10** and **11** have failed.

Even under ethylene, **10** decomposes to form a product with the empirical formula $Mo(NAr)(O\text{-}t\text{-}Bu)_2$ (**12**). It can be isolated in ~50% yield. An X-ray study shows **12** to be a dimer (Figure 2) that contains symmetrically bridging imido ligands (M–N = 1.955 (4), 1.952 (4) Å), a planar Mo_2N_2 ring, and a pseudotetrahedral arrangement of ligands around each metal. (See Table I for bond distances and angles.) The Mo–Mo distance (2.654 (1) Å) is shorter than most Mo–Mo single bonds, but substantially longer than the longest Mo–Mo double bond.[10] It is not necessary to postulate that there is a bond between the two molybdenum centers, since the Mo–Mo distance may be established by the Mo_2N_2 core itself.[11] **12** does not react with simple olefins or PMe_3, consistent with a relatively inert, delocalized Mo_2N_2 core.

Discussion

The two most common modes of decomposition of high oxidation state ("d^0") alkylidene complexes in the presence of olefins are rearrangement of metallacyclobutane complexes by a β-hydride mechanism and bimolecular coupling of alkylidene ligands, especially methylenes.[12] Rearrangement of an alkylidene ligand to an olefin is a third

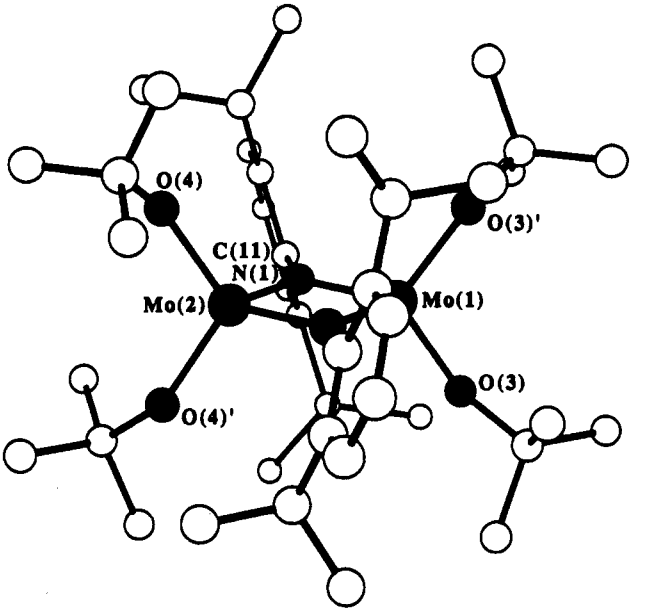


Figure 2. Drawing of the structure of $[Mo(NAr)(O\text{-}t\text{-}Bu)_2]_2$ (**12**).

decomposition mode that has been observed[13] but one that does not appear to be as common as the first two. Although the instability of many of the most important compounds discussed here has prevented a full documentation of alkylidene decomposition pathways, all that we have observed here suggests that they are analogous to the two most commonly observed. One important difference in the chemistry of molybdenum complexes observed here versus their tungsten counterparts is that molybdenum complexes are less stable toward what can be regarded as reductive processes, consistent with what one might predict on the basis of periodic trends. It has been shown recently that certain rhenium alkylidene and metallacyclobutane complexes that contain the $Re(C\text{-}t\text{-}Bu)(OR)_2$ core are even more susceptible to reductive decomposition pathways,[14] again consistent with periodic trends.

Propylene, the product of rearrangement of the unsubstituted molybdacyclobutane ring in **6**, is not observed. Therefore the faster reaction is likely to be loss of ethylene to give an intermediate methylene complex, which then decomposes bimolecularly to give ethylene. Details of the coupling reaction are obscure at this stage, but there is abundant evidence that methylene complexes decompose via formation of bis(μ-methylene) species initially followed by coupling of the two methylene ligands to give 0.5 equiv of an ethylene complex.[12a] Cleavage of a bis(μ-methylene) intermediate in this system would give "$Mo(NAr)(OR)_2$". It is interesting to note that a d^2 trigonal-planar tungsten species of this type has been isolated, in which OR is the relatively bulky silox ligand.[15]

Almost certainly **12** is formed also when $Mo(CH_2)(NAr)(O\text{-}t\text{-}Bu)_2$ decomposes bimolecularly. A lower electrophilicity of the Mo center in *tert*-butoxide complexes versus $OCMe(CF_3)_2$ complexes would account for decomposition to give **12** even in the presence of ethylene. Since the isolated yield of **12** is only ~50%, other as yet unidentified decomposition pathways probably are accessible.

(10) Chisholm, M. H. *Polyhedron* **1983**, *2*, 681.
(11) (a) A similar situation is found in $[Ru(NAr)(\eta^6\text{-}C_6H_6)]_2$.[9b] (b) Kee, T. P.; Park, L. Y.; Robbins, J.; Schrock, R. R. *J. Chem. Soc., Chem. Commun.* **1991**, 121.
(12) (a) Schrock, R. R. In *Reactions of Coordinated Ligands*; Braterman, P. R., Ed.; Plenum: New York, 1986; p 221. (b) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.*, in press.
(13) Rocklage, S. M.; Fellmann, J. D.; Rupprecht, G. A.; Messerle, L. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 1440.
(14) (a) Toreki, R.; Schrock, R. R.; Vale, M. G. *J. Am. Chem. Soc.* **1991**, *113*, 3610. (b) Toreki, R.; Schrock, R. R. Unpublished results.
(15) Eppley, D. F.; Wolczanski, P. T. Presented at the 199th National Meeting of the American Chemical Society, Boston, MA, April 1990; INOR 137.

These proposals are consistent with the fact that **12** was first observed as a side product of the reaction between Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and vinylferrocene to give Mo(CHFc)(NAr)(O-*t*-Bu)$_2$ (Fc = ferrocenyl).[16] Since Mo(CHFc)(NAr)(O-*t*-Bu)$_2$ is relatively stable in the absence of vinylferrocene, it was proposed that **12** formed via decomposition of Mo(CH$_2$)(NAr)(O-*t*-Bu)$_2$, an unobservable intermediate formed via metathesis.

To our knowledge **8** is the only example of a metallacyclopentane complex of a d^0 metal in group 6. In view of the fact that related metallacyclobutane complexes are well-known,[5] it is not surprising to find that such a species can be observed. However, it is somewhat surprising to find that it is not more stable toward loss of ethylene or that it does not decompose via a β-hydride rearrangement to give 1-butene. On the other hand a metallacyclopentane complex does not form from **2** and vinyltrimethylsilane. All of these characteristics would appear to limit the potential utility of metallacyclopentane complexes of this type as catalysts for the selective dimerization of terminal olefins, reactions which tantallacyclopentane complexes containing the TaCp*Cl$_2$ core carry out relatively efficiently.[17]

Mo(CHR)(NAr)(OR)$_2$ complexes, **2**, and **4**, all could be regarded as members of the same class of pseudotetrahedral complexes of the type Mo(NAr)(OR)$_2$(π-ligand), and adducts of **5** and **9** appear to be analogous to structurally characterized trigonal-bipyramidal Mo(CHR)(NAr)(OR)$_2$(PR$_3$).[6] The ready formation and interconversion of four- and five-coordinate species suggests that the chemistry of Mo and W complexes containing the d^2 M(NAr)(OR)$_2$ core could be relatively extensive, although a greater resistance to bimolecular decomposition processes through the use of even bulkier ligands would be highly desirable. Under some circumstances even the M(NR')(OR)$_2$ core itself is stable, forming a trigonal-planar molecule[15] analogous to recently characterized trigonal-planar d^2 Os(NAr)$_3$.[18]

Experimental Section

General Procedures. All preparative-scale experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by using standard Schlenk techniques, unless otherwise noted. All NMR-scale experiments were carried out in NMR tubes adapted with high-vacuum valves made by Brunfeldt Co., unless otherwise noted. Reagent grade 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. Deuterated NMR solvents were passed through a column of activated alumina.

Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$, Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$, and Mo(NAr)[OCMe(CF$_3$)$_2$]$_2$(CH$_2$=CHSiMe$_3$) were prepared as described in the literature.[1] $^{13}C_2H_4$ (99%) was purchased from MSD Isotopes and was used as received. 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 downfield from CCl$_3$F (0 ppm) for fluorine. ^{31}P NMR spectra were referenced to P(OMe$_3$) (141.0 ppm relative to 85% H$_3$PO$_4$). Coupling constants are quoted in hertz. Obvious multiplicities and routine coupling constants usually are not listed. Spectra were obtained in benzene-d_6 at 25 °C unless otherwise noted. Compounds **7**–**11** were not isolable and were therefore characterized only by NMR methods.

Preparation of Compounds. Mo(NAr)[OCMe(CF$_3$)$_2$]$_2$(PMe$_3$)$_2$ (3). Excess PMe$_3$ (100 μL, 0.98 mmol) was added to a chilled (−30 °C) solution of Mo(NAr)[OCMe(CF$_3$)$_2$]$_2$(CH$_2$=CHSiMe$_3$) (0.20 g, 0.27 mmol) in a minimum of pentane (>0.5 mL). A green microcrystalline solid immediately precipitated. This solid was filtered off and washed with cold pentane. The filtrate was taken to dryness, and the residue was recrystallized from a mixture of pentane and ether to give purple crystals. The green microcrystals produce a purple solution when dissolved in pentane or ether, and cooling of such solutions subsequently gives purple crystals. The green and purple materials give identical solution NMR spectra and elemental analytical data: ^{1}H NMR δ 6.92 (m, 3 H, Ar), 3.52 (sept, 2 H, C*H*Me$_2$), 2.04 (s, 3 H, OC*Me*(CF$_3$)$_2$), 1.43 (s, 3 H, OC*Me*(CF$_3$)$_2$), 1.25 (d, 6 H, CH*Me*$_2$), 1.06 (d, $^2J_{PH}$ = 9, 18 H, PMe$_3$), 1.07 (d, 6 H, CH*Me*$_2$); ^{13}C NMR (100.6 MHz) δ 152.6 (C$_{ipso}$), 143.7 (C$_o$) 126.5 (q, $^1J_{CF}$ = 293, OCMe(*C*F$_3$)$_2$), 125.7 (C$_p$), 125.6 (q, $^1J_{CF}$ = 289, OCMe(*C*F$_3$)$_2$), 123.8 (C$_m$), 81.5 (sept, $^2J_{CF}$ = 28, O*C*Me(CF$_3$)$_2$), 21.0 (OC*Me*(CF$_3$)$_2$), 18.9 (OC*Me*(CF$_3$)$_2$), 18.9 (d, $^1J_{CP}$ = 24, PMe$_3$); ^{19}F NMR δ −75.8 and −76.8 (OCMe(CF$_3$)$_2$); ^{31}P NMR δ 25.3 (PMe$_3$). Anal. Calcd for C$_{26}$H$_{41}$F$_{12}$NO$_2$P$_2$Mo: C, 39.76; H, 5.26; N, 1.78. Found: C, 39.50; H, 5.07; N, 1.73.

Mo(NAr)[OCMe(CF$_3$)$_2$]$_2$(MeC≡CMe) (4). 2-Butyne (29 μL, 0.36 mmol) was added all at once to a solution of Mo(NAr)[OCMe(CF$_3$)$_2$]$_2$(CH$_2$=CHSiMe$_3$) (0.25 g, 0.34 mmol) in pentane (25 mL). The solution slowly turned red-orange. After 2 h the solution was filtered to remove a small amount of white precipitate. The filtrate was taken to dryness to give **4** as a red-orange powder (0.22 g, 0.32 mmol, 94% yield) which is >95% pure by NMR spectroscopy. Recrystallization from pentane yields analytically pure red-orange needles: ^{1}H NMR δ 6.89 (m, 3 H, Ar), 3.59 (sept, 2 H, C*H*Me$_2$), 2.29 (s, 6 H, *Me*C≡C*Me*), 1.42 (s, 6 H0, OC*Me*(CF$_3$)$_2$), 1.15, (d, 12 H, CH*Me*$_2$); ^{13}C NMR δ 170.6 (MeC≡CMe), 153.5 (C$_{ipso}$), 145.8 (C$_o$), 127.9 (C$_p$), 124.2 (q, CF$_3$, $^1J_{CF}$ = 289), 123.0 (C$_m$), 81.8 (sept, OCMe(CF$_3$)$_2$, $^2J_{CF}$ = 29), 28.2 (*C*HMe$_2$), 23.3 (CH*Me*$_2$), 18.9 (OC*Me*(CF$_3$)$_2$), 15.4 (*Me*C≡C*Me*). Anal. Calcd for C$_{24}$H$_{29}$F$_{12}$NO$_2$Mo: C, 41.93; H, 4.25; N, 2.04. Found: C, 41.99; H, 4.33; N, 1.90.

Mo(NAr)[OCMe(CF$_3$)$_2$]$_2$(MeC≡CMe)(PMe$_3$) (5). Excess PMe$_3$ (20 μL, 0.19 mmol) was added all at once to a solution of Mo(NAr)[OCMe(CF$_3$)$_2$]$_2$(MeC≡CMe) (70 mg, 0.10 mmol) in pentane (1 mL). The solution immediately turned dark yellow. Solvents were removed in vacuo to give the yellow crystalline product quantitatively: ^{1}H NMR δ 6.79 (m, 3 H, Ar), 3.85 (sept, 1 H, C*H*Me$_2$), 2.64 (s, 3 H, *Me*C≡CMe), 2.59 (sept, 1 H, C*H*Me$_2$), 2.21 (s, 3 H, MeC≡C*Me*), 1.89 (s, 3 H, OC*Me*(CF$_3$)$_2$), 1.48 (s, 3 H, OC*Me*(CF$_3$)$_2$), 1.25 (d, 3 H, CH*Me*$_2$), 1.08 (d, 9 H, PMe$_3$), 1.01 (d, 3 H, CH*Me*$_2$), 0.86 (d, 3 H, CH*Me*$_2$), 0.63 (d, 3 H, CH*Me*$_2$); ^{13}C NMR (toluene-d_8) δ 156.7 (C$_{ipso}$, J_{PC} = 7), 152.1 (C$_o$), 151.0 (MeC≡CMe, J_{PC} = 32), 150.8 (MeC≡CMe, J_{PC} = 7), 145.8 (C$_o$), 129.0 (C$_p$), 124.4 (C$_m$), 123.0 (C$_m$), 83.1 (sept, OCMe(CF$_3$)$_2$, $^2J_{CF}$ = 28), 81.3 (sept, O*C*Me(CF$_3$)$_2$, $^2J_{CF}$ = 28), 27.7, 26.4, 25.8, 25.1, 19.9, 17.3, 16.2, 13.7, 13.4, 13.2. The CF$_3$ carbon resonances could not be assigned unambiguously. Anal. Calcd for C$_{27}$H$_{38}$F$_{12}$NO$_2$PMo: C, 42.48; H, 5.02; N, 1.83. Found: C, 42.47; H, 5.34; N, 1.93.

Mo(CH$_2$)(NAr)[OCMe(CF$_3$)$_2$]$_2$(PMe$_3$) (7). PMe$_3$ (5.0 μL, 0.057 mmol) was added to a solution of Mo(CH$_2$CH$_2$CH$_2$)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (**6**) (0.021 mmol) in toluene-d_8 and the sample was examined immediately by proton NMR spectroscopy.

A ^{13}C-enriched NMR sample was prepared as follows: PMe$_3$ (0.050 mmol) was transferred in vacuo onto a frozen solution of Mo(NAr)(^{13}CH$_2$^{13}CH$_2$^{13}CH$_2$)[OCMe(CF$_3$)$_2$]$_2$ (0.021 mmol, made by addition of $^{13}C_2H_4$ to **1a**). The sample was warmed to room temperature and NMR spectra were acquired immediately: ^{1}H NMR (toluene-d_8) δ 12.95 (dd, 1 H, H$_O$, J_{HH} = 6, J_{PH} = 6), 12.62 (dd, 1 H, H$_N$, J_{HH} = 6, J_{PH} = 9), 4.25 (br m, 1 H, C*H*Me$_2$), 3.79 (br m, 1 H, C*H*Me$_2$), 3.6–3.2 (br overlapping, 2 H, C*H*Me$_2$), 2.11 (br s, 3 H, OC*Me*(CF$_3$)$_2$), 1.40 (br s, 3 H, OC*Me*(CF$_3$)$_2$), 1.25 (br, 12 H, CH*Me*$_2$) 0.78 (d, PMe$_3$ overlapping with free PMe$_3$, J_{PH} = 12 Hz); ^{13}C NMR (toluene-d_8, −40 °C) δ 278.7 (ddd, J_{CH_O} = 137, J_{CH_N} = 159, J_{PC} = 24).

Mo(NAr)[OCMe(CF$_3$)$_2$]$_2$(C$_4$H$_8$) (8). (a) Ethylene (3 mL, 0.12 mmol, 5.7 equiv) was added all at once via syringe to a septum-capped NMR tube containing **1a** (15 mg, 0.021 mmol) in tolu-

(16) Albagli, D.; Bazan, G. C.; Wrighton, M. S.; Schrock, R. R. Submitted for publication.
(17) McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 5610.
(18) Anhaus, J. T.; Kee, T. P.; Schofield, M.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 1642.

Table II. Non-Hydrogen Coordinates for 12

	x	y	z
Mo(1)	0.0000	0.82817 (3)	0.2500
Mo(2)	0.0000	0.65664 (3)	0.2500
O(3)	−0.0601 (2)	0.8972 (2)	0.1726 (2)
O(4)	0.0333 (2)	0.5879 (2)	0.3322 (2)
N(1)	−0.0907 (3)	0.7423 (2)	0.2639 (2)
C(11)	−0.1813 (3)	0.7418 (2)	0.2773 (2)
C(12)	−0.2601 (3)	0.7622 (3)	0.2237 (3)
C(13)	−0.3462 (3)	0.7599 (3)	0.2381 (3)
C(14)	−0.3561 (3)	0.7367 (4)	0.3032 (3)
C(15)	−0.2792 (4)	0.7172 (3)	0.3562 (3)
C(16)	−0.1904 (3)	0.7193 (3)	0.3451 (2)
C(121)	−0.2564 (3)	0.7905 (3)	0.1501 (3)
C(122)	−0.2774 (4)	0.8870 (4)	0.1414 (3)
C(123)	−0.3247 (4)	0.7393 (4)	0.0923 (3)
C(161)	−0.1105 (4)	0.6954 (3)	0.4060 (3)
C(162)	−0.1099 (5)	0.7477 (4)	0.4726 (3)
C(163)	−0.1136 (4)	0.5986 (4)	0.4217 (3)
C(311)	−0.0690 (5)	1.0385 (4)	0.1267 (4)
C(31)	−0.0287 (4)	0.9493 (3)	0.1230 (3)
C(313)	0.0772 (4)	0.9543 (4)	0.1423 (3)
C(312)	−0.0681 (5)	0.9092 (4)	0.0515 (3)
C(41)	0.1076 (4)	0.5276 (3)	0.3583 (3)
C(413)	0.1722 (4)	0.5219 (4)	0.3086 (3)
C(412)	0.1610 (5)	0.5597 (4)	0.4302 (3)
C(411)	0.0631 (4)	0.4406 (3)	0.3645 (3)

ene-d_8. Within 0.5 h, the solution had turned red-orange, indicating the formation of Mo(NAr)$(CH_2CH_2CH_2)_2[OCMe(CF_3)_2]_2$ (verified by ^{1}H NMR analysis). Within 5 h, the color had changed again to deep red, indicating the formation of **8**: ^{1}H NMR (toluene-d_8) δ 6.90 (m, 3 H, Ar), 5.24 (br, C_2H_4), 3.62 (sept, 2 H, C*H*Me$_2$), 1.40 (br s, 6 H, OC*Me*$(CF_3)_2$), 1.12 (d, 6 H, CH*Me*$_2$); ^{1}H NMR (toluene-d_8, −40 °C) 6.90 (m, 3 H, Ar), 3.81 (sept, 2 H, C*H*Me$_2$), 3.10 (br m, 2 H, C_4H_8), 2.80 (br m, 2 H, C_4H_8), 2.60 (br m, 2 H, C_4H_8), 2.52 (br m, 2 H, C_4H_8), 1.33 (br s, 6 H, OC*Me*$(CF_3)_2$), 1.19 (d, 6 H, CH*Me*$_2$).

(b) Ethylene (3 mL, 0.12 mmol, 5.7 equiv) was added all at once via syringe to a septum-capped NMR tube containing Mo(NAr)$[OCMe(CF_3)_2]_2(CH_2{=}CHSiMe_3)$ (15 mg, 0.021 mmol) in toluene-d_8. Formation of **8** was complete in 1 h.

^{13}C NMR data for the metallacycle carbons were obtained from a sample of 8-$^{13}C_4$ prepared by adding $^{13}C_2H_4$ (0.12 mmol, 5.7 equiv) to a frozen solution of either **1a** (15 mg, 0.021 mmol) or Mo(NAr)$[OCMe(CF_3)_2]_2(CH_2{=}CHSiMe_3)$ (15 mg, 0.021 mmol) in toluene-d_8 in an NMR tube fitte with a Teflon valve on a high-vacuum line. The solution was allowed to warm to room temperature, and ^{13}C NMR spectra were acquired after 5 or 1 h, respectively.

NMR spectra were simplified and various carbon–carbon coupling constants were extracted from spectra of a sample more dilute in ^{13}C. $^{13}C_2H_4$ (0.06 mmol) was condensed onto a frozen solution of **8** made from Mo(NAr)$[OCMe(CF_3)_2]_2(CH_2{=}CHSiMe_3)$ (32 mg, 0.045 mmol) and $^{12}C_2H_4$ (0.18 mmol) in toluene-d_8. The sample was kept frozen until the spectrum was taken.

^{13}C NMR (toluene-d_8, −40 °C) δ 76.8 (C_α and $C_{\alpha'}$, J_{CH} = 128), 38.6 (C_β and $C_{\beta'}$, J_{CH} = 141, $J_{C_\alpha C_\beta}$ = 32, $J_{C_\alpha C_{\beta'}}$ = 4, $J_{C_\beta C_{\beta'}}$ = 32).

Mo(NAr)$[OCMe(CF_3)_2]_2(CH_2{=}CH_2)(PMe_3)$ (9). Ethylene (3 mL, 0.12 mmol) was added via syringe to a solution of Mo(NAr)$[OCMe(CF_3)_2]_2(PMe_3)_2$ (50 mg, 0.064 mmol) in 0.5 mL of benzene-d_6 or toluene-d_8 in a septum-capped NMR tube. The sample turned from deep purple to yellow immediately: ^{1}H NMR δ 6.74 (m, 2 H, Ar), 6.61 (m, 1 H, Ar), 3.82 (br sept, 1 H, C*H*Me$_2$), 2.63 (m, 1 H, ethylene), 2.23 (br sept, 1 H, C*H*Me$_2$), 1.91 (m, 1 H, ethylene), 1.80 (br s, 3 H, OC*Me*$(CF_3)_2$), 1.77 (m, 1 H, ethylene), 1.52 (br s, 3 H, OC*Me*$(CF_3)_2$), 1.32 (br d, 3 H, CH*Me*$_2$), 1.20 (br, 1 H, ethylene), 1.07 (br d, 3 H, CH*Me*$_2$), 0.96 (d, J_{PH} = 9, 9 H, P*Me*$_3$), 0.93 (br d, 3 H, CH*Me*$_2$), 0.76 (br d, 3 H, CH*Me*$_2$); ^{13}C NMR (toluene-d_8) δ 150.4 (C_{ipso}), 147.4 (C_o), 146.4 (C_o) 124.4, 123.8, 123.6, 123.2, 81.4 (sept, $OCMe(CF_3)_2$, $^2J_{CF}$ = 29), 44.9 ($CH_2{=}CH_2$, J_{PC} = 13), 43.7 ($CH_2{=}CH_2$), 29.5, 27.4, 25.4, 24.3, 24.3, 24.0, 23.7, 17.4, 16.4, 16.2, 13.5, 13.1.

A ^{13}C-enriched NMR sample was prepared as follows: PMe_3 (0.060 mmol) was condensed onto a frozen solution of Mo(NAr)$[OCMe(CF_3)_2]_2(^{13}C_4H_8)$ (0.021 mmol) in an NMR tube: ^{13}C NMR δ 44.9 (J_{CC} = 35, J_{CP} = 13, J_{CH} = 156), 43.7 (J_{CC} = 35, J_{CH} = 159).

Mo$(CH_2CH_2CH_2)$(NAr)(O-*t*-Bu)$_2$ (10). Ethylene (0.12 mmol, 4 equiv) was condensed onto a frozen solution of **1b** (15 mg, 0.031 mmol) in toluene-d_8 in an NMR tube via gas transfer on the high-vacuum line. The sample was allowed to stand at room temperature for 5 h, after which time the metallacycle had formed in 25% yield by NMR spectroscopy. Only resonances for some metallacycle protons could be assigned unambiguously: ^{1}H NMR (toluene-d_8, −40 °C) δ 3.7 (br m, 1 H, H_β), 3.0 (br m, 1 H, $H_{\beta'}$), 2.3 (br m, 2 H, H_α).

A partial ^{13}C NMR spectrum was obtained as follows: $^{13}C_2H_4$ (0.15 mmol, 5 equiv) was condensed onto a frozen solution of **1b** (15 mg, 0.031 mmol) in toluene-d_8 in an NMR tube via gas transfer on the high-vacuum line. The sample was warmed to room temperature and left for 5 h: ^{13}C NMR (toluene-d_8) δ 34.9 (dt, J_{CH} = 140, J_{CC} = 32, C_α), 29.1 (tt, J_{CH} = 129, J_{CC} = 32, C_β).

Mo(CH_2)(NAr)(O-*t*-Bu)$_2$(PMe$_3$) (11). Excess PMe_3 (0.12 mmol, 4 equiv) was added via gas transfer to a solution of **10** in an NMR tube prepared as described above. A proton NMR spectrum taken immediately afterwards showed that the methylidene complex (**11**) had formed in 10% yield (based on **1b**). Only resonances for the methylidene protons could be assigned unambiguously: ^{1}H NMR (toluene-d_8, −40 °C) δ 12.32 (dd, J_{HH} = 5, J_{PH} = 4), 11.94 (dd, J_{HH} = 5, J_{PH} = 4). Only one broad resonance for the phosphine methyl groups was observed.

[Mo(NAr)(O-*t*-Bu)$_2$]$_2$ (12). Ethylene (2 atm) was placed over a solution of **1b** (200 mg, 0.42 mmol) in 1 mL of toluene in a pressure vessel. After 2 days the sample was taken to dryness in vacuo, leaving behind a red-brown semisolid. This solid was washed with cold pentane, leaving behind the product as a purple-red powder, which was slightly soluble pentane (90 mg, 0.11 mmol, 52% yield): ^{1}H NMR δ 7.24 (m, 6 H, Ar), 2.25 (sept, 4 H, C*H*Me$_2$), 1.28 (overlapping s and d, 60 H, O-*t*-Bu and CH*Me*$_2$); ^{13}C NMR (125.7 MHz) δ 160.4 (C_i), 141.4 (C_o), 126.7 (C_p), 125.0 (C_m), 79.6 ($OCMe_3$), 32.6 (OC*Me*$_3$), 27.1 ($CHMe_2$), 26.3 (CH*Me*$_2$). Anal. Calcd for $C_{40}H_{70}N_2O_4Mo_2$: C, 57.55; H, 8.45; N, 3.36. Found: C, 57.68; H, 8.85; N, 3.09.

X-ray Crystal Structure of [Mo(NAr)(O-*t*-Bu)$_2$]$_2$. X-ray-quality crystals were obtained from recrystallization from pentane. Data were collected at −72 °C on a Rigaku AFC6R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) and a 12-kW rotating anode generator. A total of 4944 reflections were collected, 4646 of which were unique. Equivalent reflections were merged. The intensities of three representative reflections measured after every 150 reflections remained constant throughout data collection, indicating crystal and electronic stability. The structure was solved by direct methods.[19] Refinement was by full-matrix least squares using TEXSAN. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions (d_{C-H} = 0.95 Å). Crystal data are a = 14.772 (6) Å, b = 15.470 (4) Å, c = 19.625 (8) Å, β = 104.62 (3)°, V = 4346 (3) Å^3, space group = $C2/c$ (No. 15), Z = 4, M_r = 834.88, ρ = 1.276 g/cm^3, and μ = 5.99 cm^{-1}. Final R = 0.035 and R_w = 0.047. Important bond distances and angles can be found in Table I and final non-hydrogen positional parameters in Table II.

Acknowledgment. R.R.S. thanks the National Science Foundation for research support CHE 88-22508), G.C.B. thanks the Science and Engineering Research Council of Canada for a predoctoral fellowship, and we all thank Dr. W. M. Davis for collecting the data set for **12**.

Supplementary Material Available: A labeled ORTEP drawing and tables of final positional parameters and final thermal parameters for **12** (3 pages); a listing of final observed and calculated structure factors for **12** (17 pages). Ordering information is given on any current masthead page.

(19) (a) Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42. (b) Beurskens, P. T. Technical Report 1984/1; Crystallography Laboratory: Toernooiveld, 6525 Ed. Nijmegen, Netherlands.