Monoadducts of Imido Alkylidene Complexes, Syn and Anti Rotamers, and Alkylidene Ligand Rotation

Richard R. Schrock,* William E. Crowe, Guillermo C. Bazan, Marcello DiMare, Marie B. O'Regan, and Mark H. Schofield

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

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Complexes of the type M(CH-*t*-Bu)(NAr)$(OR)_2$ (M = Mo, W; Ar = 2,6-C_6H_3-*i*-Pr_2; OR = $OCMe(CF_3)_2$, $OCMe_2(CF_3)$) form five-coordinate adducts upon addition of PMe_3 or quinuclidine. PMe_3 attacks the C/N/O face of the pseudotetrahedral complexes to give chiral TBP species in which the phosphine is bound in an axial position and the imido and alkylidene ligands lie in the equatorial plane. Two isomers containing syn and anti rotamers of the alkylidene ligand are observed. The syn rotamer forms first; the anti rotamer is the final product. PMe_3 binds weakly when OR = O-*t*-Bu and is lost readily in vacuo. Quinuclidine adds to either the C/O/O face or N/O/O face to give an achiral syn isomer and to the C/N/O face to give an anti chiral TBP species analogous to that formed for the PMe_3 adduct. An equilibrium mixture of syn and anti forms is observed with time. An X-ray structure of *syn*-Mo(CH-*t*-Bu)(NAr)$[OCMe(CF_3)_2]_2(PMe_3)$ shows that the *t*-Bu group points toward the imido ligand and the phenyl ring of the imido ligand lies approximately in the equatorial plane in a relatively crowded coordination environment (a = 10.979 (4) Å, b = 17.945 (7) Å, c = 18.375 (8) Å, β = 106.34 (3)°, Z = 4, V = 3474 (4) Å^3, ρ = 1.490 g/cm^3, R = 0.037, R_w = 0.045). Pyridine adducts of Mo complexes containing the 2,6-dichlorophenoxide ligand also have been characterized. Three isomers of five-coordinate molybdenum or tungsten complexes containing a *cis*- or *trans*-2-butenylidene ligand and quinuclidine are found at equilibrium, syn and anti rotamers of the chiral core previously described and a syn rotamer with an achiral core. An X-ray structure of *anti*-W(*trans*-CHCH=CHMe)(NAr)$[OCMe(CF_3)_2]_2$(quin) showed the expected trigonal-bipyramidal core with alkylidene and imido ligands occupying equatorial sites and $OCMe(CF_3)_2$ ligands occupying one axial and one equatorial site (a = 12.972 (9) Å, b = 18.049 (7) Å, c = 15.038 (9) Å, β = 92.07 (3)°, Z = 4, V = 3518 (6) Å^3, ρ = 1.673 g/cm^3, R_1 = 0.038, R_w = 0.040). The only significant difference between the structure of this anti adduct and the syn adduct described above is that the anti adduct is markedly less crowded in the equatorial plane. Syn and anti rotamers in five-coordinate adducts have been shown to interconvert after losing the base in several cases. The barrier to rotation of the alkylidene ligand has been measured in several four-coordinate species and shown to lie in the range ΔG^*_{298} = 15–18 kcal mol^{-1}. These findings are discussed in relation to the proposed mechanism of olefin metathesis by pseudotetrahedral complexes of the type M(CHR')(NAr)$(OR)_2$.

Introduction

Four-coordinate complexes of the type M(CHR')(NAr)$(OR)_2$ (M = W, Mo; Ar = 2,6-C_6H_3-*i*-Pr_2; R' = CMe_2Ph, *t*-Bu) are now readily accessible for a wide variety of OR groups.[1,2] They are active catalysts for the metathesis of ordinary olefins when OR is relatively electron-withdrawing (e.g., $OCMe(CF_3)_2$)[3] but are useful only for strained olefins such as norbornenes and norbornadienes when OR is *tert*-butoxide.[4] The rate of metathesis also depends dramatically on the size of R' in these sterically congested molecules, the difference between R' = *t*-Bu and R' = Et being perhaps 2 orders of magnitude. X-ray studies of W(CH-*t*-Bu)(NAr)$(O\text{-}t\text{-}Bu)_2$[1] and W(CHPh)(NAr)$[OCMe(CF_3)_2]_2$[3a] show them to be pseudotetrahedral complexes in which the alkylidene substituent lies in the N/W/C plane and points toward the imido nitrogen atom (syn rotamer). W$[CH(Me_3Si)CHCH_2]$(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-bipyramidal (TBP) tungstacyclobutane complexes in which the WC_3 ring is located in the equatorial plane.[3a] Square-pyramidal (SP) tungstacyclobutane complexes are a second important type;[5] only square-pyramidal metallacycles are observable for the least active catalysts (OR = O-*t*-Bu).[6] It has been suggested that syn and anti rotamers are both accessible (anti referring to the rotamer in which the alkylidene substituent points away from the imido nitrogen atom) and in some cases have been observed to interconvert with an activation barrier of ~15 kcal.[1,2]

An important question is how an olefin attacks an alkylidene complex of the type M(CHR')(NAr)$(OR)_2$. It has been proposed that the olefin adds to the metal by approaching the C/N/O face trans to one OR ligand to give an initial "axial/equatorial" metallacyclobutane complex[1] and that this initial complex then undergoes several "pseudorotations" to yield a new metallacycle of the same type in order to lose the metathesis product. Only TBP metallacycles (equatorial ring) or SP metallacycles (basal ring) have been observed, not the proposed initial TBP

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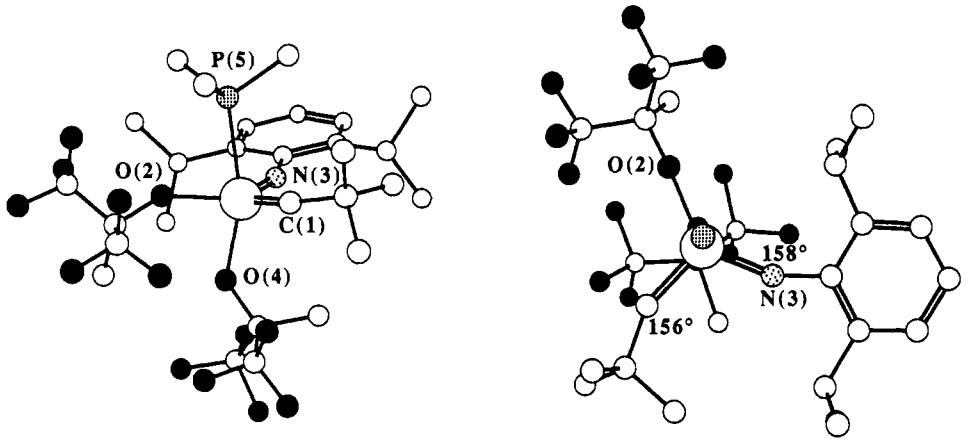


Figure 1. Two views of the structure of *syn*-Mo(CH-*t*-Bu)(NAr)[OCMe$(CF_3)_2]_2$(PMe_3). Methyl groups on PMe_3 have been omitted in the view on the right.

metallacycle in which the ring spans axial and equatorial positions. It seems unlikely that an olefin/alkylidene "intermediate" ever can be observed, since the olefin probably is only weakly bound through primarily a dative σ interaction, and such species therefore either form a metallacyclobutane complex or revert to an alkylidene complex. A study of base adducts would be valuable, since they are models for the unobservable olefin/alkylidene intermediate or transition state. It also should be noted that living polymerization of acetylene requires the presence of quinuclidine, possibly because quinuclidine slows the rate of propagation relative to initiation by coordinating to the metal in the sterically more accessible vinylalkylidene intermediates.[7] Finally, coordinating solvents also play an important role in ring-opening metathesis polymerization (ROMP), either decreasing the reactivity of the more active catalysts[3b] or allowing some functionalities such as the cyano group in 5-cyanonorbornene to be tolerated.[4g] Some base adducts such as W(CHSiMe_3)(NAr)[OCMe$(CF_3)_2]_2$(PMe_3) and W(CH_2)-(NAr)[OCMe$(CF_3)_2]_2$(PMe_3) already have been reported,[3a] but they have not been studied in detail. In this paper we present and discuss significant new findings concerning the formation of adducts of syn and anti rotamers, including vinylalkylidene complexes, species that are relevant to the polymerization of acetylene.

Results

Adducts of Molybdenum Alkylidene Complexes. Mo(CH-*t*-Bu)(NAr)[OCMe$(CF_3)_2]_2$ reacts with PMe_3 to yield Mo(CH-*t*-Bu)(NAr)[OCMe$(CF_3)_2]_2$(PMe_3) quantitatively. The PMe_3 ligand seems to be strongly bound to the metal, since coupling to phosphorus is maintained on the NMR time scale at 25 °C ($\delta(H_\alpha)$ = 11.90 ppm, $^3J_{HP}$ = 5.4 Hz; $\delta(C_\alpha)$ = 293.2 ppm, J_{CH} = 110 Hz, $^2J_{CP}$ = 26 Hz). The alkoxide ligands are inequivalent. With time this initial isomer is converted irreversibly and completely into another isomer with no symmetry ($\delta(H_\alpha)$ = 13.25 ppm, $^3J_{HP}$ = 7.8 Hz; $\delta(C_\alpha)$ = 313.9 ppm, J_{CH} = 138 Hz, $^2J_{CP}$ = 18 Hz). Note the dramatically higher J_{CH} for this second (thermodynamic) isomer. The rate of conversion of the kinetic into the thermodynamic isomer is accelerated dramatically upon addition of a few percent of Mo(CH-*t*-Bu)(NAr)-[OCMe$(CF_3)_2]_2$.

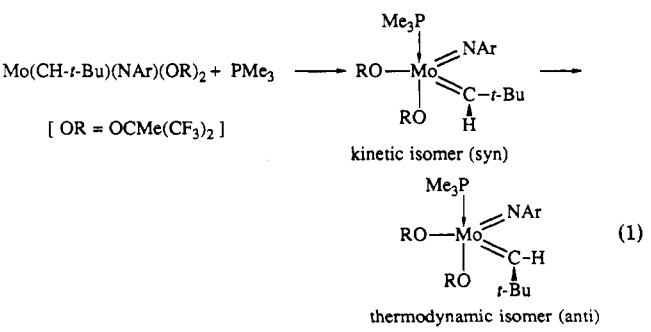
An X-ray study of the kinetic isomer showed it to be the distorted-trigonal-bipyramidal species shown in eq 1 and Figure 1, in which the *t*-Bu group is syn to the nitrogen atom of the imido ligand. (Relevant distances and angles are listed in Table I.) Trimethylphosphine appears to have added to the C/N/O face of *syn*-Mo(CH-*t*-Bu)-(NAr)[OCMe$(CF_3)_2]_2$ to give a trigonal bipyramid in which the trimethylphosphine ligand occupies an axial position. The structure of Mo(CH-*t*-Bu)(NAr)[OCMe$(CF_3)_2]_2$ in solution is likely to be syn, as the alkylidene ligands in W(CHPh)(NAr)[OCMe$(CF_3)_2]_2$,[3a] W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$,[1] Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$,[2] and the "first in-

Table I. Selected Bond Lengths (Å) and Angles (deg) in *syn*-Mo(CH-*t*-Bu)(NAr)[OCMe$(CF_3)_2]_2$(PMe_3)

Mo–N(3)	1.767 (6)	Mo–O(4)	2.038 (7)
Mo–C(1)	1.878 (9)	Mo–P(5)	2.520 (3)
Mo–O(2)	2.014 (5)		
Mo–O(4)–C(4)	134.2 (6)	N(3)–Mo–P(5)	87.4 (2)
Mo–O(2)–C(2)	146.8 (6)	O(2)–Mo–C(1)	112.2 (4)
Mo–N(3)–C(31)	158.2 (6)	O(4)–Mo–C(1)	103.0 (4)
Mo–C(1)–C(11)	156.3 (8)	C(1)–Mo–P(5)	88.0 (3)
N(3)–Mo–C(1)	110.6 (4)	O(4)–Mo–O(2)	85.3 (2)
N(3)–Mo–O(2)	133.7 (3)	O(2)–Mo–P(5)	77.3 (2)
N(3)–Mo–O(4)	101.6 (3)	O(4)–Mo–P(5)	162.1 (2)

Table II. Selected Bond Lengths (Å) and Angles (deg) in *anti*-W(*trans*-CHCH=CHMe)(NAr)[OCMe$(CF_3)_2]_2$(quin)

W–N(1)	1.737 (5)	W–N(2)	2.273 (5)
W–C(1)	1.942 (6)	C(3)–C(4)	1.49 (1)
W–O(3)	1.961 (4)	C(1)–C(2)	1.420 (9)
W–O(4)	1.985 (4)	C(2)–C(3)	1.307 (8)
O(3)–W–N(2)	80.2 (2)	C(1)–W–N(2)	89.7 (2)
O(4)–W–N(2)	163.9 (2)	O(3)–W–O(4)	83.9 (2)
N(1)–W–C(1)	100.7 (2)	W–C(1)–C(2)	126.3 (5)
N(1)–W–O(3)	138.3 (2)	C(1)–C(2)–C(3)	126.7 (6)
N(1)–W–O(4)	100.7 (2)	C(2)–C(3)–C(4)	128.3 (7)
N(1)–W–N(2)	89.7 (2)	W–O(3)–C(31)	148.5 (4)
C(1)–W–O(3)	119.5 (2)	W–O(4)–C(41)	135.7 (4)
C(1)–W–O(4)	100.2 (2)	W–N(1)–C(11)	168.0 (4)



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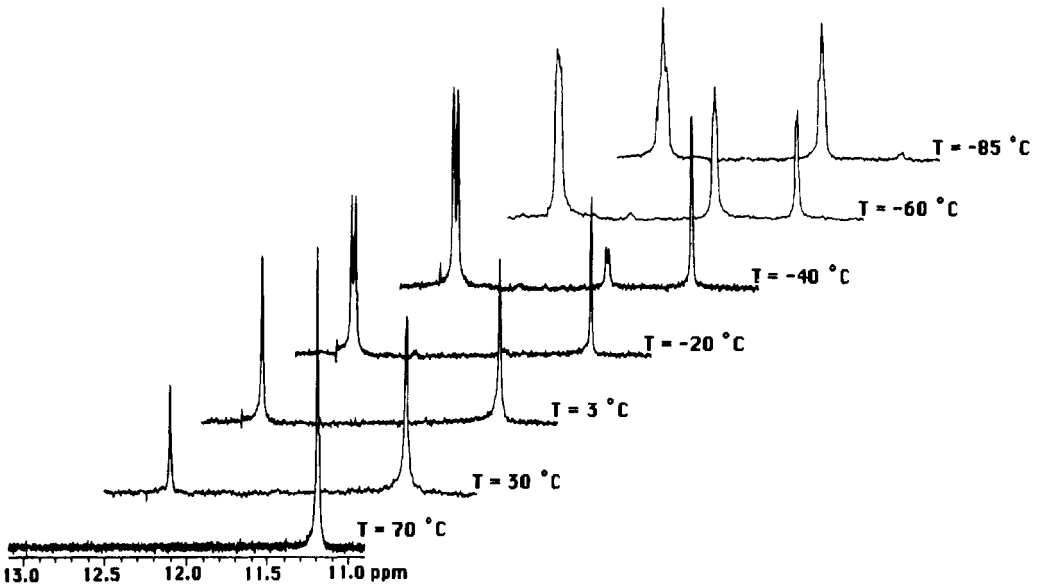

Figure 2. NMR study of the binding of PMe_3 to Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (in toluene-d_8).

sertion product" made by adding 7-isopropylidene-2,3-dicarbomethoxynorbornadiene to Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$[4f] are all syn. The *tert*-butyl group of the neopentylidene ligand in the kinetic product therefore still points toward the imido nitrogen atom. The largest angle between equatorial ligands (133.7 (3)°) is that between the imido and a hexafluoro-*tert*-butoxide ligand. The Mo–C_α–C_β angle in the neopentylidene ligand (156.3 (8)°) is relatively large compared to the W–C_α–C_β angles of 144–145° in W(CHPh)(NAr)[OCMe(CF$_3$)$_2$]$_2$[3a] and W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$,[1] 141° in trigonal-bipyramidal W(O)(CH-*t*-Bu)Cl$_2$(PEt$_3$),[8] and 140° in the first insertion product mentioned above. Note that the Mo–N–C angle is not much larger than the Mo–C_α–C_β angle, since the phenyl ring is forced to lie in the equatorial plane in order to avoid steric interaction between the isopropyl groups and the axial ligands, but the phenyl ring then must bend away from the *tert*-butyl group of the neopentylidene ligand. The imido and alkylidene ligands are tipped away from the axial alkoxide (102, 103°) toward the smaller axial PMe_3 ligand (87, 88°). The P–Mo–O_{ax} angle is only 162°, with O(4) and P(5) pointing toward O_{eq} (85° and 77°, respectively). The Mo=C, Mo=N, and Mo—P bond lengths are all normal.

An X-ray study of the thermodynamic isomer showed it to be a related trigonal-bipyramidal species in which the neopentylidene ligand is in the anti conformation. Unfortunately, this structure could not be solved completely because of a disorder problem involving one hexafluoro-*tert*-butoxide ligand, but there is no doubt that the core geometry is basically the same as that of the kinetic isomer except for the orientation of the neopentylidene ligand. It is proposed that the thermodynamic product arises when PMe_3 adds to the C/N/O face in *anti*-Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$. The structure of a related adduct that contains an anti alkylidene ligand is discussed later in this paper.

Addition of PMe_3 to W(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ yields first what we propose to be *syn*-W(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$(PMe$_3$), in which $\delta(H_\alpha)$ = 9.51, $\delta(C_\alpha)$ = 270, J_{CH} = 105 Hz, and J_{CW} = 186 Hz. Although *syn*-W(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$(PMe$_3$) is stable for 7 h in solution at 25 °C, it is converted into what we propose is *anti*-W(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$(PMe$_3$) ($\delta(H_\alpha)$ = 11.53, $\delta(C_\alpha)$ = 287, J_{CH} = 136 Hz, J_{CW} = 158 Hz) upon addition of a few percent of W(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$. The increase in J_{CH} that takes place upon formation of the anti alkylidene rotamer is accompanied by a decrease in J_{CW}. Both changes in coupling constant correspond to a decreased interaction of the alkylidene CH bond with the tungsten center, leading to weaker CW bonding and stronger CH bonding. This bonding difference also is evidenced in proton NMR spectra, where tungsten satellites are observed for the syn rotamer (J_{HW} = 14 Hz) but not for the anti rotamer (J_{HW} < ~5 Hz). Assignment of the anti conformation is supported by NOE experiments; irradiation of the alkylidene α-proton yields an 18% enhancement of the downfield isopropyl methine resonance. The same NOE experiment on *syn*-W(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$(PMe$_3$) produced no enhancement of the isopropyl methine resonance.

Other PMe_3 complexes of Mo and W neopentylidene complexes can be formed or observed whose stabilities correlate directly with the electrophilic character of the alkoxide ligands (Table III). For example, syn (J_{CH} = 106 Hz) and anti (J_{CH} = 138 Hz) isomers of W(CH-*t*-Bu)(NAr)[OCMe$_2$(CF$_3$)]$_2$(PMe$_3$) can be isolated, but reactions between W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and PMe_3 can be reversed in vacuo in the solid state. The ^{1}H NMR spectrum in toluene-d_8 of a mixture containing Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and ~0.5 equiv of PMe_3 shows two alkylidene α-proton resonances, one a sharp singlet at 12.73 ppm accounting for 40–45% of the total that we ascribe to Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$(PMe$_3$) and the second at 11.26 ppm for Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (Figure 2). The 12.73 ppm resonance is not a doublet in this case, since the PMe_3 ligand is exchanging relatively rapidly with free PMe_3. However, as the sample is cooled the rate of exchange of PMe_3 slows to the point where coupling of H_α to phosphorus can be observed. As the sample is cooled further, a second doublet upfield of the first (11.80 ppm at −25 °C) beings to grow in until at −85 °C the two alkylidene proton resonances are about equally intense. Carbon NMR spectra of low-temperature mixtures suggest that the compound that gives rise to the lower field proton resonance has a relatively high value for J_{CH} (136 Hz)

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Table III. NMR Data for Adducts of Neopentylidene and Neophylidene Complexes[a]

compd		$\delta(H_\alpha)$	$\delta(C_\alpha)$	J_{CH}	J_{CW}
Mo(CH-*t*-Bu)(NAr)[OCMe-$(CF_3)_2]_2(PMe_3)$	syn	11.90	293.2	110	
	anti	13.25	313.9	138	
W(CH-*t*-Bu)(NAr)[$OCMe(CF_3)_2]_2$-(PMe_3)	syn	9.51	270.1	105	186
	anti	11.53	286.9	136	158
W(CH-*t*-Bu)(NAr)[$OCMe_2(CF_3)]_2$-(PMe_3)	syn	9.26	264.7	106	
	anti	11.13	277.8	138	
Mo(CH-*t*-Bu)(NAr)(O-*t*-$Bu)_2$-(PMe_3)[b]	syn	11.80	281.1	110	
	anti	12.73	293.4	136	
W(CH-*t*-Bu)(NAr)(O-*t*-$Bu)_2$-(PMe_3)[b]	anti	10.87			
Mo($CHSiMe_3$)(NAr)[$OCMe_2$-$(CF_3)]_2(PMe_3)$	c	14.13	289.3	129	
Mo(CH-*t*-Bu)(NAr)[OCMe-$(CF_3)_2]_2$(quin)	syn	12.51	296.4	121	
	anti	13.16	311.1	140	
W(CH-*t*-Bu)(NAr)[$OCMe(CF_3)_2]_2$-(quin)	syn	9.24	273.5	109	189
	anti	10.77	279.3	137	175
Mo(CH-*t*-Bu)(NAr)[$OCMe_2$-$(CF_3)]_2$(quin)	syn	11.81			
	anti	12.87			
W(CH-*t*-Bu)(NAr)[$OCMe_2(CF_3)]_2$-(quin)	syn	8.61			
	anti	10.46			
Mo($CHCMe_2Ph$)(NAr)(O-2,6-$C_6H_3Cl_2)_2$(py)	syn	14.46	305.1	125	
	anti	14.31	320.2	142	

[a] In C_6D_6 at ~22 °C unless otherwise noted; δ values are in ppm and J values in hertz. [b] In toluene-d_8 at −20 °C. [c] Conformation unknown.

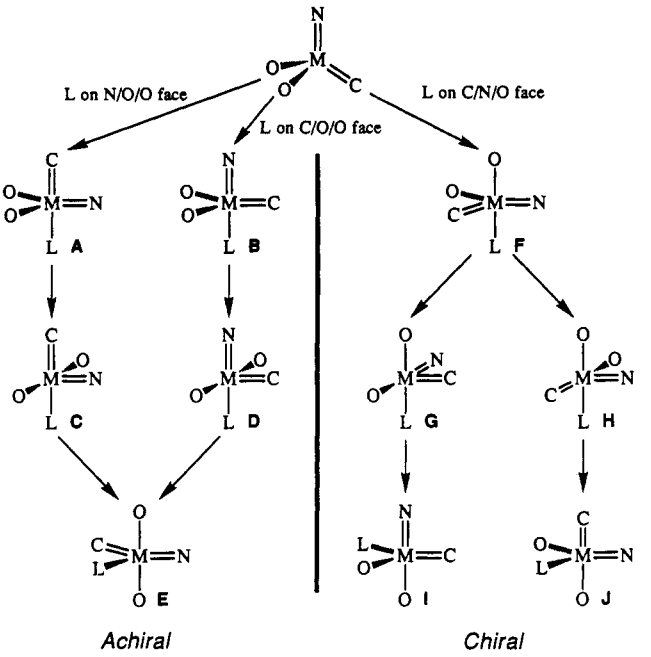
compared to that which gives rise to the higher field proton resonance (J_{CH} = 110 Hz), consistent with their being anti and syn forms, respectively. Only the thermodynamically more stable anti isomer (in which PMe_3 is exchanging rapidly) can be observed at room temperature.

$Mo(CHSiMe_3)(NAr)[OCMe_2(CF_3)]_2$ reacts with excess PMe_3 to give only one isomer of $Mo(CHSiMe_3)(NAr)$-$[OCMe_2(CF_3)]_2(PMe_3)$ in which J_{CH} = 129 Hz. We propose that $Mo(CHSiMe_3)(NAr)[OCMe_2(CF_3)]_2(PMe_3)$ is structurally analogous to Mo(CH-*t*-Bu)(NAr)$[OCMe(CF_3)_2]_2$-(PMe_3), but J_{CH} is not distinctive enough to allow us to state whether this species is syn or anti. PMe_3 now is again relatively strongly bound (the H_α resonance is a doublet), consistent with the relatively electrophilic character of the metal compared to that of *tert*-butoxide complexes.

The ^{13}C NMR spectrum of $W(CH_2)(NAr)[OC(CF_3)_2$-$(CF_2CF_2CF_3)]_2(PMe_3)$[3a] reveals that the alkylidene carbon resonance is split by phosphorus (J_{CP} = 16 Hz) and by two inequivalent protons (J_{CH} = 135 and 162 Hz). No other isomer was observed. We proposed at the time that the structure of $W(CH_2)(NAr)[OC(CF_3)_2(CF_2CF_2CF_3)]_2(PMe_3)$ was a trigonal bipyramid with equatorial methylene and imido ligands and an axial phosphine ligand. That proposal would now appear to be correct. Presumably the lower value of J_{CH} is associated with the proton that points away from the imido ligand, analogous to that in a *syn*-CHR complex.

Quinuclidine Adducts. Quinuclidine (quin) adducts of the type M(CH-*t*-Bu)(NAr)$(OR)_2$(quin) (M = Mo, W; OR = $OCMe_2(CF_3)$, $OCMe(CF_3)_2$) can be prepared straightforwardly. In each case an initial adduct is formed ($J_{CH} \approx$ 110 Hz) that slowly is converted into a second adduct ($J_{CH} \approx$ 135 Hz). The final result is a *mixture* of the two with the *initial* adduct predominating (e.g., 8:1). On the basis of J_{CH} values we believe the two species to be syn and anti rotamers, respectively. NOE studies were consistent with this assignment; irradiation of the alkylidene α-proton in the second adduct produced a 15% enhancement of the downfield isopropyl methine resonance, while an analogous experiment on the initial adduct yielded no enhancement of the isopropyl methine resonance. However, there is a significant difference between

Scheme I



the syn quinuclidine adducts and the syn PMe_3 adducts; the syn quinuclidine adducts contain equivalent alkoxides, isopropyl methines, and isopropyl methyl groups down to −80 °C. Below −80 °C isopropyl methyl groups and quinuclidine H_α resonances begin to become inequivalent, characteristic of restricted rotation of these ligands. One explanation is that the initial adduct has the same basic structure as that observed for the PMe_3 adducts (axial quinuclidine, axial and equatorial alkoxide ligands; F, Scheme I), but the structure is so distorted that alkoxides still interconvert readily at −80 °C. The other possibility is that the structure of the initial adduct is different from that of the kinetic isomer of the PMe_3 adduct; i.e., it has a plane of symmetry that contains the alkylidene, imido, and base ligands. The two groups of five TBP or SP complexes shown in Scheme I are plausible products of attack on an N/O/O face, C/O/O face, or C/N/O face of the pseudotetrahedral species. At this stage we can only say with certainty that the initial syn quinuclidine adduct appears to be achiral, although it seems most reasonable to propose that, if it is a distinct species, it results from initial attack by the base on a N/O/O or C/O/O face of the pseudotetrahedral catalyst, i.e., that it is either A or B. The proposal that an adduct other than F is formed is supported by the fact that three types of quinuclidine adducts of vinylalkylidene complexes are observed (see below). Unfortunately, although the initial adduct in which M = Mo and OR = $OCMe(CF_3)_2$ could be obtained pure in crystalline form, no crystals could be obtained that were suitable for X-ray studies.

Variations. Yellow, crystalline Mo$(CHCMe_2Ph)$-$(NAr)(DCP)_2$(py) (DCP = 2,6-dichlorophenoxide) could be prepared by adding 2 equiv of LiDCP to Mo(NAr)-$(CHCMe_2Ph)(OSO_2CF_3)_2$(DME) (DME = 1,2-dimethoxyethane) in the presence of pyridine. In the absence of pyridine the expected Mo$(CHCMe_2Ph)(NAr)(DCP)_2$ was not observed. When a crystalline sample of Mo-$(CHCMe_2Ph)(NAr)(DCP)_2$(py) is dissolved in CD_2Cl_2 and a proton NMR spectrum is acquired quickly, a single compound is observed with an alkylidene resonance at 14.46 ppm ($\delta(C_\alpha)$ = 305.1 ppm, J_{CH} = 122 Hz). If this sample is allowed to stand at 25 °C for 1.5 h, the ^1H NMR spectrum shows a 3:1 mixture consisting of the afore-

mentioned species and a new species possessing an alkylidene resonance at 14.32 ppm ($\delta(C_\alpha)$ = 320.2 ppm, J_{CH} = 142 Hz). All data are consistent with the initial species being a syn rotamer and the final species being an anti rotamer of the type found for PMe_3 adducts, i.e., having structure F. Irradiation of the neophylidene methyl groups of the major isomer (H_α at 14.46 ppm) gave a large NOE enhancement of the imido methine protons, consistent with a syn orientation of the alkylidene ligand, while irradiation of the alkylidene H_α proton of the minor isomer (H_α at 14.32 ppm) led to NOE enhancement of the imido methine protons, consistent with an anti orientation of the alkylidene ligand. Note that the chemical shift of the alkylidene α-proton in the syn rotamer is downfield slightly of that in the anti rotamer, opposite to what was observed in the PMe_3 adducts.

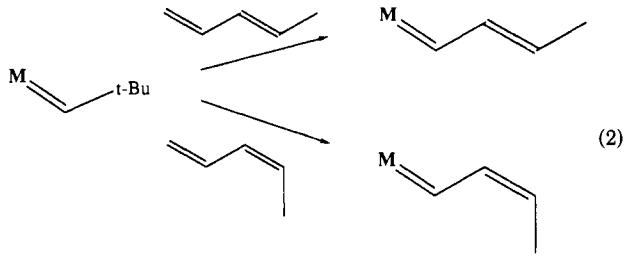
Careful examination of the proton NMR spectrum of $Mo(CHCMe_2Ph)(NAr)(DCP)_2(py)$ (CD_2Cl_2, 20 °C) revealed a very broad resonance at 12.48 ppm that constituted 9% of the total alkylidene resonance. The 12.48 ppm resonance disappeared upon cooling the sample to −20 °C but increased to 14% of the total alkylidene resonance upon warming the sample to +40 °C. Addition of 4 equiv of pyridine to the ^1H NMR sample eliminated the 12.48 ppm resonance. On the basis of these qualitative experiments we ascribe the 12.48 ppm resonance to the alkylidene proton in a small amount of $Mo(CHCMe_2Ph)(NAr)(DCP)_2$. The chemical shift is typical of a four-coordinate complex that contains electron-withdrawing alkoxides, and H_α resonances typically shift by ~2 ppm upon addition of a base to form a five-coordinate species.

A small sample of essentially pure *syn*-$Mo(CHCMe_2Ph)(NAr)(DCP)_2(py)$ could be obtained by fractional crystallization, and isomerization of it to the equilibrium mixture of syn and anti rotamers was therefore examined in more detail. In the presence of 10 equiv of added pyridine the syn → anti conversion was found to be first order with $k = 1.5 \times 10^{-5}$ s^{-1} in CD_2Cl_2 at 22 °C; in the absence of added pyridine the syn → anti conversion was found to be first order with $k = 1.8 \times 10^{-4}$ s^{-1}. The fact that pyridine significantly retards the rate of isomerization is consistent with the proposal that the alkylidene ligand rotates in $Mo(CHCMe_2Ph)(NAr)(DCP)_2$, not $Mo(CHCMe_2Ph)(NAr)(DCP)_2(py)$. Although we cannot exclude the possibility that alkylidene rotation is facile in some unobservable adduct that is present in higher concentration in the presence of excess pyridine, we know that rotation is relatively facile in other four-coordinate species (see later) and therefore prefer the explanation that alkylidene ligands rotate more readily in general in pseudotetrahedral complexes.

Addition of 11 equiv of *cis*-2-pentene to a CD_2Cl_2 solution containing *syn*-$Mo(CHCMe_2Ph)(NAr)(DCP)_2(py)$ gave (according to proton NMR spectra) two isomeric ethylidene base adducts (H_α quartets at 13.79 and 13.56 ppm in a ratio of ~1:1) and two isomeric propylidene base adducts (H_α doublet of doublets at 13.71 and 13.37 ppm) after 2 h. These species could not be isolated, and dichloromethane solutions of propylidene complexes prepared by treating *syn*-$Mo(CHCMe_2Ph)(NAr)(DCP)_2(py)$ with a mixture of *cis*- and *trans*-3-hexene were observed to have decomposed to the extent of ~25% after 96 h at 22 °C. We believe the isomers to be syn and anti rotamers analogous to those described above.

Vinylalkylidene Complexes. Base adducts of vinylalkylidene complexes are proposed intermediates in reactions in which acetylene is polymerized,[7] and what are believed to be base-free vinylalkylidene complexes have been observed in reactions involving ring-opening metathesis polymerization of 7,8-bis(trifluoromethyl)tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene.[9] In view of the relevance of base adducts of vinylalkylidene complexes to polyene chemistry, we synthesized and studied several examples.[10,11]

The quinuclidine base adducts M(CH-*t*-Bu)(NAr)$(OR)_2$(quin) (M = Mo, W; OR = $OCMe(CF_3)_2$, $OCMe_2(CF_3)$) reacts with either *cis*- or *trans*-1,3-pentadiene to give products in which the neopentylidene ligand has been replaced by the *cis*- or *trans*-CHCH=CHMe ligand (eq 2). *Three* isomers were observed for each of the eight



(2)

products in this class, two syn rotamers and one anti rotamer. Assignments were based on $^1J_{CH}$ coupling constants, NOE measurements, and symmetry inferred from chemical equivalence or inequivalence of key protons. One of the syn rotamers and the anti rotamer have chiral configurations that are believed to be analogous to that found for the PMe_3 adducts, i.e., structure F in Scheme I. The structure of the second syn rotamer is postulated to be the same as that for the achiral syn rotamer of the quinuclidine adducts of the neopentylidene complexes (see previous section), e.g., A or B (Scheme I). The ratio of isomers that is obtained differs from one experiment to another. The achiral syn rotamer is often the minor component of the product mixture. Three anti complexes could be selectively crystallized from the three-component mixture; they are *anti*-W(*trans*-CHCHCHMe)(NAr)$[OCMe(CF_3)_2]_2$(quin), *anti*-Mo(*trans*-CHCHCHMe)(NAr)$[OCMe(CF_3)_2]_2$(quin), and *anti*-Mo(*trans*-CHCHCHMe)(NAr)$[OCMe_2(CF_3)]_2$(quin). In each case irradiation of the H_α alkylidene proton produced strong NOE enhancements of the downfield isopropyl methine and H_γ resonances, consistent with the proposed structure.

Selected NMR data for the three isomers of the eight compounds are listed in Table IV. In each isomer the vinylalkylidene H_α proton resonance appears as a downfield doublet (>10 ppm for W complexes, >12 ppm for Mo complexes), the H_β proton appears as a doublet of doublet of quartets between 7.9 and 8.3 ppm, and the H_γ proton appears as a doublet of quartets between 4.1 and 4.7 ppm. Allylic methyl protons appear as a doublet of doublets between 2.1 and 2.6 for W complexes and between 1.6 and 2.0 ppm for Mo complexes. Assignments were aided by an extensive series of decoupling and NOE experiments for each product mixture. Within each series of complexes, the chemical shifts for H_α in the achiral base adducts are furthest upfield. In any complex with a chiral metal configuration the H_α resonances for the syn rotamer lie furthest upfield. Changing the vinylalkylidene geometry

(9) Knoll, K.; Schrock, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 7989.
(10) Ta(V) vinylalkylidene complexes having a substituents on the α- and β-carbon atoms are known: (a) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210. (b) Wallace, K. C.; Liu, A. H.; Davis, W. M.; Schrock, R. R. *Organometallics* **1989**, *8*, 644.
(11) Ti(IV) complexes containing an unsubstituted vinylalkylidene ligand have been observed: Binger, P.; Müller, P.; Benn, R.; Mynott, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 610.

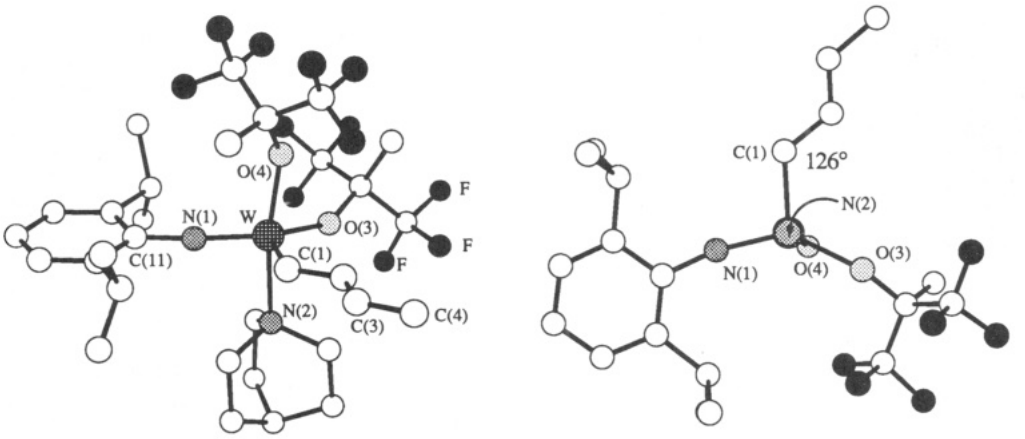


Figure 3. Two views of the structure of *anti*-W(*trans*-CHCH=CHMe)(NAr)[OCMe$(CF_3)_2$]$_2$(quin).

Table IV. NMR Data for Complexes of the Type M(CHR)(OR′)$_2$(NAr)(quinuclidine)[a]

M	OR′	CHR	isomer	$\delta(H_\alpha)$ ($J_{\alpha,\beta}$)	$\delta(C_\alpha)$	J_{CH}
W	F_6	trans	anti	11.35 (14.1)	263.3	147
			syn	10.65 (10.8)	256.8	120
			syn (achiral)	9.80	not detected	
W	F_6	cis	anti	11.87 (14.8)	256.5	144
			syn	11.06 (11.1)	249.5	122
			syn (achiral)	10.42	254.0	125
Mo	F_6	trans	anti	13.03	288.5	148
			syn	12.90	280.9	127
			syn (achiral)	12.55	286.7	127
Mo	F_6	cis	anti	13.63	281.2	153
			syn	13.36	272.8	126
			syn (achiral)	13.21	278.3	126
W	F_3	trans	anti	11.71	254.7	145
			syn	10.34	250.2	120
			syn (achiral)	9.54	not detected	
W	F_3	cis	anti	11.63	248.2	145
			syn	10.74	243.6	120
			syn (achiral)	10.06	not detected	
Mo	F_3	trans	anti	12.85	279.1	148
			syn	12.57	273.4	128
			syn (achiral)	12.21	274.5	125
Mo	F_3	cis	anti	13.41	272.4	147
			syn	13.04	266.3	126
			syn (achiral)	12.79	266.8	124

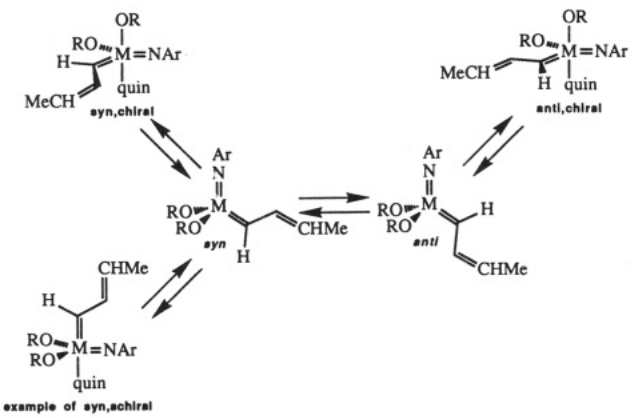
[a] CHCH=CHMe = CHR, solvent = C_6D_6, and T = 25 °C, unless otherwise noted; δ values are in ppm and J values in hertz. [b] F_6 = OCMe$(CF_3)_2$; F_3 = OCMe$_2(CF_3)$.

from trans to cis produces a downfield shift of 0.4–0.6 ppm for H_α.

The structure of *anti*-W(*trans*-CHCH=CHMe)(NAr)[OCMe$(CF_3)_2$]$_2$(quin) was confirmed by an X-ray study (Figure 3). (Relevant bond distances and angles are listed in Table II.) The molecule consists of a central tungsten atom that has a distorted-trigonal-bipyramidal coordination geometry in which the alkylidene and imido ligands occupy equatorial sites and the OCMe$(CF_3)_2$ ligands occupy one axial and one equatorial site. The W–N(1)–C(11) bond angle (168.0 (4)°) and W–N(1) bond length (1.737 (5) Å) are typical.[12] The W=C(1) bond length (1.942 (6) Å) likewise is unexceptional. Note that the W–C(1)–C(2) angle is only 126°, the N(1)–W–C(1) bond angle is only 100.7 (2)°, and the axial alkoxide ligand is bent toward the equatorial alkoxide ligand (O(3)–W–O(4) = 83.9 (2)°). Bending the axial ligand away from the equatorial π-bonding ligands leads to hybridization of the π-bonding d_{xz} and d_{yz} orbitals toward the π-bonding ligands. Such a "bending back" of axial ligands from two cis π-bonded ligands is common.[12]

(12) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988; pp 157–158, and references cited therein.

Scheme II



A sample of *anti*-W(*trans*-CHCH=CHMe)(NAr)[OCMe$(CF_3)_2$]$_2$(quin) was dissolved in toluene-d_8 at 0 °C. With time it was converted into a mixture of *anti*-W(*trans*-CHCH=CHMe)(NAr)[OCMe$(CF_3)_2$]$_2$(quin) and primarily chiral *syn*-W(*trans*-CHCH=CHMe)(NAr)[OCMe$(CF_3)_2$]$_2$(quin) in a ratio of ~1:3, only a trace of the achiral syn isomer is observed in this case. Selective crystallization of *anti*-W(*trans*-CHCH=CHMe)(NAr)[OCMe$(CF_3)_2$]$_2$(quin), the minor isomer at equilibrium, might be ascribed to its greater rate of crystallization under the conditions that were chosen, although it is also plausible that the syn rotamer converts to anti over the time period required for crystallization.

In any given mixture the syn rotamers interconvert rapidly and an equilibrium ratio of chiral and achiral stereoisomers is established quickly, consistent with the proposal that both are primary adducts, F and A or B (Scheme I). The two syn rotamers interconvert with the anti rotamer more slowly, as expected if (slow) rotation about the M=C bond takes place in the base-free complex. However, no base-free four-coordinate vinylalkylidene complexes could be detected. These proposals are summarized in Scheme II.

When the reactions shown in eq 2 were carried out in the absence of a Lewis base, deep red colors formed rapidly. However, no vinylalkylidene complexes could be detected by NMR methods. Similar results were observed when the reactions were carried out in the presence of bulky, weakly binding Lewis bases such as PPh_3 and $PEtPh_2$. Conversely, when relatively small tightly binding Lewis bases such as PMe_3 were added before the diene,

Table V. Activation Parameters for the Alkylidene-Interchange Process of M(CHR)(NAr)(OR')$_2$ Compounds[a]

compd	$\Delta G_{298}^{\ddagger}$ [b]	$\Delta H^{\ddagger}$ [b]	$\Delta S^{\ddagger}$ [b]
Mo(CHSiMe$_3$)(NAr)(OAr)$_2$[c]	16.3 (1)	16.4 (6)	+0.4 (2.1)
W(CHSiMe$_3$)(NAr)(OAr)$_2$[d]	15.0 (1)	12.7 (3)	−7.6 (9)
W(CHCMe$_3$)(NAr)(OAr)$_2$	16.2 (1)	18.2 (4)	+6.5 (1.2)
Mo(CHCMe$_2$Ph)(NAr)(OAr)$_2$	17.5 (1)	17.8 (1.0)	+1.0 (2.7)
Mo(CHCMe$_2$Ph)(NAr)(OTB)$_2$	18.3 (1)	22.8 (2.1)	+15 (6)
Mo(CHSiMe$_3$)(NAr)(OTB)$_2$	17.1 (1)	18.0 (1.2)	+3.0 (3.8)

[a] Activation parameters correspond to the overall rate, i.e., the sum of $k_{syn\rightarrow anti}$ and $k_{anti\rightarrow syn}$. Typical concentrations were 13–15 mg of compound in 600 μL of toluene-d_8. OAr = 2,6-diisopropylphenoxide; OTB = 2-*tert*-butylphenoxide; Ar = 2,6-diisopropylphenyl. [b] Values in kcal mol^{-1} for $\Delta G_{298}^{\ddagger}$ and $\Delta H^{\ddagger}$ and eu for $\Delta S^{\ddagger}$. [c] Previously reported values were $\Delta H^{\ddagger}$ = 16.5 kcal mol^{-1}, $\Delta S^{\ddagger}$ = 1.5 eu, and $\Delta G_{298}^{\ddagger}$ = 16.0 kcal mol^{-1}.[2] [d] See ref 1.

transalkylidenation was impractically slow at room temperature, presumably because the small base binds tightly to the neopentylidene complex and therefore blocks the diene's access to the metal.

Interconversion of Rotamers in Base-Free Complexes. Since we now have good evidence that rotamers exist and that they interconvert most readily in four-coordinate species, it is important to determine the rate of isomerization where possible and probe the dependency of that rate on solvent, temperature, metal, and ligands. Unfortunately, base-free rotamers are less often observable in tetrahedral species than in five-coordinate base adducts, and therefore the number experiments that can be done is limited.

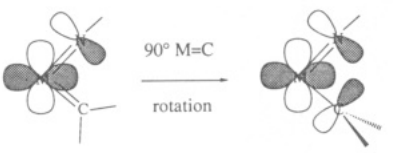
Rotamers of compounds of the type M(CHSiMe$_3$)(NAr)(OAr)$_2$ (M = Mo,[2] W[1]) were suspected on the basis of the J_{CH} values (117 and 145 Hz for M = Mo and 110 and 135 Hz for M = W). However, difference NOE experiments were inconclusive. A close examination of W(CH-*t*-Bu)(NAr)(OAr)$_2$ and Mo(CHCMe$_2$Ph)(NAr)(OAr)$_2$ revealed that rotamers were present in these cases also, but only to an extent of ~5% and 8%, respectively. (Only the rotamer with $\delta(H_\alpha)$ = 8.41 ppm had been reported for W(CH-*t*-Bu)(NAr)(OAr)$_2$.[1] Rotamers had been observed for Mo(CHCMe$_2$Ph)(NAr)(OAr)$_2$, but their interconversion was not studied.[2]) Difference NOE experiments demonstrated the major isomer to be syn in each case, but the low abundance of the minor component precluded NOE experiments that should have confirmed its anti orientation. Mo(CHCMe$_2$Ph)(NAr)(OTB)$_2$ (OTB = 2-*tert*-butylphenoxide) was reported to consist of a mixture of rotamers (94:6).[2] Finally, Mo(CHSiMe$_3$)(NAr)(OTB)$_2$ was prepared as an orange oil by treating a pentane solution of Mo(CHCMe$_2$Ph)(NAr)(OTB)$_2$ with vinyltrimethylsilane and was shown by proton NMR spectroscopy to be a 3:1 mixture of rotamers.[13] Barriers to interconversion of rotamers were determined by complete band-shape analysis[14] of the alkylidene resonances observed in variable-temperature spectra. Activation parameters are listed in Table V. The values for Mo(CHSiMe$_3$)(NAr)(OAr)$_2$ differs slightly from those reported earlier[2] with a preliminary set of data. Variable-temperature spectra of Mo(CHCMe$_2$Ph)(NAr)(OTB)$_2$ over a 5-fold range in concentration were identical.

Several observations can be made. First, $\Delta S^{\ddagger}$ values are not all close to zero, as one might expect for a unimolecular process. Second, the range in $\Delta G_{298}^{\ddagger}$ values among the six compounds is 3.3 kcal mol^{-1}, with a typical rate constant being on the order of 1 s^{-1}. Comparison of data for analogous tungsten and molybdenum complexes reveals a $\Delta\Delta G_{298}^{\ddagger}$ value of 1.3 kcal mol^{-1}, with lower barriers being associated with tungsten. Third, trimethylsilyl-substituted alkylidenes have a lower isomerization barrier than alkyl-substituted alkylidenes, $\Delta\Delta G_{298}^{\ddagger}$ being 1.2 kcal mol^{-1}. Fourth, experiments carried out on Mo(CHSiMe$_3$)(NAr)(OAr)$_2$ and Mo(CHCMe$_2$Ph)(NAr)(OAr)$_2$ in bromobenzene-d_5 (μ = 1.70 D, polarizability 17.4 × 10^{-24} cm^3) instead of toluene-d_8 (μ = 0.36 D, polarizability 12.3 × 10^{-24} cm^3) showed that the activation parameters for Mo(CHCMe$_2$Ph)(NAr)(OAr)$_2$ were unchanged while those for Mo(CHSiMe$_3$)(NAr)(OAr)$_2$ were changed negligibly ($\Delta\Delta G^{\ddagger}$ = 0.1 kcal/mol; $\Delta\Delta H^{\ddagger}$ = 1.8 kcal/mol; $\Delta\Delta S^{\ddagger}$ = 6 eu). Therefore, the transition state for alkylidene rotation does not appear to be highly polar.

We noted previously that tungsten complexes containing the CHSi(OMe)$_3$ ligand consisted of only one isomer by NMR spectroscopy[1] and that J_{CH} was unusually high (160 Hz). At that time we proposed that the rotameric form of the alkylidene ligand was anti. We now have further evidence on that point. Treatment of Mo(CHCMe$_2$Ph)(NAr)(OTB)$_2$[1] with vinylethoxydimethylsilane yields Mo[CHSi(OEt)Me$_2$](NAr)(OTB)$_2$, a carbon NMR spectrum of which showed J_{CH_α} to be 156 Hz. Irradiation of the arylimido isopropyl methyl resonance led to NOE enhancement of the alkylidene H_α resonance, good evidence that the alkylidene proton points toward the imido ligand, even though the ring in that imido ligand in the solid state is likely to be oriented perpendicular to the N–Mo–C plane. One could argue that the ethoxydimethylsilyl group is smaller than a trimethylsilyl group and that both rotamers should be observed. As this is not the case, we believe that coordination of the oxygen atom of the alkoxy group to the metal most likely stabilizes the anti isomer. There is one example of coordination of a functionality in an alkylidene complex in this class,[15] and there are examples of metallacyclobutane complexes stabilized by pendant ester or amide functionalities.[5a] It also should be noted that −80 °C NMR experiments on related CHSi(OMe)$_3$ complexes revealed no evidence for preferential coordination of one oxygen atom to the metal on that time scale.[16]

Discussion

Rotamers are a consequence of the fact that of the two orbitals that could be used to form a π bond between the metal and carbon, that which is perpendicular to the N–M–C plane (δ in relation to the imido nitrogen atom) is the most accessible; the d orbital that lies in the N–M–C plane probably is used primarily to form a second ("dative") π bond between the metal and the imido ligand. However, an alkylidene ligand that is rotated by 90° can be stabilized by the d orbital that lies in the N–M–C plane, viz.



A similar argument could be put forth to explain rotation of an alkylidene ligand that lies initially in the equatorial

(13) DiMare, M. Unpublished results.
(14) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982.
(15) Johnson, L. K.; Virgil, S. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 5384.
(16) Feldman, J. Ph.D. Thesis, Massachusetts Institute of Technology, 1989.

Table VI. Previously Documented Alkylidene Isomerization Barriers[a]

complex	T_c, K	$\Delta G_{T_c}^{\ddagger}$, kcal mol^{-1}
$Cp_2Ta(CHPh)(CH_2Ph)$[b]	391	19.3 (1)
$Cp_2Ta(CHCMe_3)(Cl)$[b]	323	16.8 (1)
$Cp(CpMe)Ta(CH_3)(CH_2)$[b]	>413	≥21.4
$Cp^*W(CH_3)_3(CH_2)$[c]	233	9.7 (2)
$(NpO)_3W(CHCMe_3)X$[d]	242–277	12.3–14.3
$(NpO)_4W(CHCMe_3)$[d]	<160	<8

[a] Cp = C_5H_5; Cp* = C_5Me_5; Np = CH_2CMe_3. [b] Schrock, R. R.; Messerle, L. W.; Wood, C. D.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 3793. [c] See ref 19. [d] Kress, J.; Osborn, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 3953.

plane of (e.g.) a chiral TBP monoadduct of type F (Scheme I). However, in this case the d orbital in the M/N/C plane also is likely to be involved in σ bonding to the equatorial alkoxide ligand and, therefore, should not stabilize the rotated alkylidene ligand in the transition state to as significant a degree. Rotation of the alkylidene ligand in a TBP species also would not be as favorable for steric reasons as in a tetrahedron, since in the transition state the alkylidene's substituents would have to lie in the same plane as the M–L_{axial} bonds. Since the energy differences between syn and anti rotamers and between the two basic types of cores in adducts that we have seen here (chiral and achiral) are small, it does not seem appropriate at this stage to attempt to rationalize when a give rotamer is likely to be observed. The importance and extent of stabilization by a functionality, such as the oxygen atom in alkoxysilyl derivatives, also is not known at this stage. Previously reported barriers to rotation of an alkylidene ligand about the M=C bond listed in Table VI have been rationalized on the basis of related electronic and steric arguments. Significant differences between these values and those listed in Table V are to be expected, since the barrier is likely to be sensitive to the availability of a π orbital 90° to the first and to whether the C–H bond of the alkylidenes is interacting with the metal or not.

The difference in values for J_{CH} in syn and anti rotamers, especially in five-coordinate adducts, often is significant and could be viewed as resulting from interaction of a C–H bond with the metal. Such "distortions" of alkylidene ligands in high-oxidation-state complexes (larger than expected M–C–R angles) have been observed for some time,[17] especially in "reduced" alkylidene complexes where an alkylidyne/hydride complex actually could be formed[18] but even in what could be viewed as a d^0 methylene complex, $WCp^*Me_3(CH_2)$.[19] Activation of the alkylidene C–H_α bond should involve the lowest energy orbital in the M/N/C plane (i.e. the plane containing the C–H_α bond). In-plane nonbonding orbitals for tetrahedral and TBP complexes are crudely depicted as

tetrahedral TBP

In each case the orbital available for C–H_α activation is oriented away from the imido ligand, a circumstance that would lead to increased C–H_α activation in the syn rotamer. An increase in the M–C–R angle, and consequently greater C–H_α activation trans to N, might be expected in adducts of type F (Scheme I), in which the phenyl ring of the imido ligand lies in the M/N/C plane with one of the isopropyl groups pointing toward R (Figure 1). Such a steric contribution would help explain why differences in values for J_{CH} in syn and anti rotamers are exaggerated in five-coordinate species relative to pseudotetrahedral species. Similar arguments could be constructed for isomers A and B.

The observations made here suggest that a base most likely will attack the C/N/O face of a four-coordinate imido alkylidene complex. However, observation of an achiral syn adduct when the base is quinuclidine leaves open the possibility of attack on the C/O/O or N/O/O face by an especially bulky base. It is interesting to note that disubstituted acetylenes have been observed to add most easily to the C/N/O face in Re(C-*t*-Bu)(NAr)-$[OCMe(CF_3)_2]_2$ to give rhenacyclobutadiene complexes that are relatively stable toward loss of acetylene from the ring, but when the acetylene contains relatively bulky substituents, then it is believed to add to the C/O/O face to give rhenacycles that readily lose acetylene.[20] Therefore, only acetylenes that contain relatively bulky substitutents can be metathesized catalytically by Re(C-*t*-Bu)(NAr)-$[OCMe(CF_3)_2]_2$. The issue is confused even further by the recent finding[21] that alkylidene ligands in some pseudooctahedral rhenium alkylidene imido complexes exert the strongest trans effect; i.e., isomer A should be preferred over B if this principle holds for five-coordinate species.

Facile attack by a base on the C/N/O face can be rationalized. The LUMO in d^0 MCp_2X_2 complexes is often the a_1 orbital that lies in the MX_2 plane and therefore is oriented perpendicular to the M[Cp(centroid)]$_2$ plane. Since the $M(NR)_2$ fragment can be regarded as isolobal with the MCp_2 fragment (if each imido ligand is considered to be a 2π, 1σ ligand),[22b,c] the LUMO is likely to be an a_1 orbital that is oriented perpendicular to the MN_2 plane. A M(NR)(CR′) fragment is isolobal with a $M(NR)_2$ fragment, which explains why an acetylene adds preferentially to the C/N/O face in Re(C-*t*-Bu)(NAr)$[OCMe(CF_3)_2]_2$. However, a M(NR)(CHR′) fragment can be regarded as a variation of the $M(NR)_2$ fragment in which one of the nitrogen p orbitals in the $M(NR)_2$ plane is replaced by a C–H bond. This will lower the energy of the d orbitals involved in in-plane π bonding but should still leave an a_1-type orbital perpendicular to the M/N/C plane as the LUMO. Therefore, addition of a base to the C/N/O face will be electronically favored, giving a TBP adduct of type F.

These findings have two important implications for metathesis of olefins by complexes of this type. First, as has been proposed elsewhere,[6] an olefin, which can be regarded as a σ base in these systems, appears to add most readily to the C/N/O face to yield an initial metallacyclobutane complex in which the ring spans axial and equatorial sites. If the alkylidene contains a chiral center, then the two C/N/O faces are diastereotopic, a circumstance that has been used to explain how stereoselectivity

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can arise in ring-opening metathesis polymerization reactions.[4f] Second, rotamers should react with olefins at different rates. Therefore, the rate at which rotamers interconvert could be an important factor in some circumstances. If initial complexes such as B lead to metallacycles and new olefins and alkylidene complexes at a rate competitive with other pathways, then any prediction of stereochemistry becomes that much more difficult.

It will be interesting in future studies to determine what mechanistic principles operate in complexes of the type $Re(CR)(CHR')(OR'')_2$, species that have been found to metathesize olefins and that are closely related to the M=NAr species discussed here.[23]

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 alumina.

NMR data are listed in parts per million downfield from tetramethylsilane for proton and carbon and relative to 85% phosphoric acid for phosphorus. 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.

In all variable-temperature studies of rotamer interconversion the alkylidene H_α resonances were observed. The temperature was determined with use of ethylene glycol[24] and is accurate to ±1 °C. T_2 was determined at the low-temperature extreme, and only spectra that were significantly affected by exchange broadening were evaluated. Theoretical band shapes were calculated with use of DNMR4 (QCPE No. 466) on a Digital VAX 11-780 computer. Rate constants were evaluated by means of visual fitting of calculated and experimental spectra. Only $\delta\nu$, relative populations, and k were varied. In systems where $\delta\nu$ and relative populations were temperature-dependent, values near and beyond coalescence were obtained by extrapolation of slow-exchange values. Activation parameters were determined by linear regression analysis of plots of log (k/T) vs $1/T$.

Preparation of Compounds. *syn*-Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$(PMe$_3$). PMe_3 (55 μL, 0.54 mmol) was added all at once to a pentane solution (20 mL) of Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (0.35 g, 0.50 mmol) stirring at −30 °C. The solution was warmed to room temperature over the next 60 min, and then solvents were removed in vacuo. The yellow-orange solid thus obtained was virtually pure by ^{1}H NMR spectroscopy. Recrystallization from a minimum amount of pentane at −40 °C yielded 0.31 g (80%) of yellow-orange crystals in two crops: ^{1}H NMR δ 11.90 (d, $^3J_{HP}$ = 5.4, 1, MoC*H*-*t*-Bu), 6.93 (m, 3, NAr), 4.56 (br, 1, C*H*Me$_2$), 3.24 (br sept, 1, C*H*Me$_2$), 2.14 (s, 3, OC*Me*(CF$_3$)$_2$), 1.53 (s, 3, OC*Me*(CF$_3$)$_2$), 1.28 (br, 6, CH*Me*$_2$), 1.20 (d, 6, CH*Me*$_2$), 1.13 (s, 9, MoCH-*t*-*Bu*), 0.88 (d, $^2J_{HP}$ = 9.4, 9, P*Me*$_3$); ^{13}C NMR δ 293.2 (dd, $^1J_{CH}$ = 110, $^2J_{CP}$ = 26, MoC*H*-*t*-Bu), 150.6 (C_{ipso}), 149.7 and 142.7 (C_o), 128.4 (C_m), 126.2, 125.7, and 125.5 (q, $^1J_{CF}$ = 290, 289, and 290, respectively, OCMe(*C*F$_3$)$_2$), 123.7 (C_p), 82.1 and 80.4 (sept, $^2J_{CF}$ = 28 for each, O*C*Me(CF$_3$)$_2$), 48.5 (MoCH*C*Me$_3$), 31.5 (MoCH*CMe*$_3$), 30.3, 27.5, 25.8, and 24.1 (br, *C*HMe$_2$ and CH*Me*$_2$), 20.0 and 17.6 (OC*Me*(CF$_3$)$_2$), 15.2 (dq, $^1J_{CP}$ = 24, $^1J_{CH}$ = 130, P*Me*$_3$); ^{19}F NMR δ −75.0, −75.6, −76.5, and −77.7 (s, 3 each, OCMe(*C*F$_3$)$_2$); ^{31}P{^{1}H} NMR δ 0.45 (*P*Me$_3$). Anal. Calcd for $MoC_{28}H_{42}F_{12}O_2NP$: C, 43.14; H, 5.43. Found: C, 43.08; H, 5.61.

***anti*-Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$(PMe$_3$).** Heating a solution of the syn isomer (15 mg) in C_6D_6 (800 μL) at 60 °C for 12 h yields 95% pure *anti*-Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$(PMe$_3$) according to its proton NMR spectrum. Alternatively, the product can be isolated by stirring a solution of the syn isomer (250 mg, 0.32 mmol) and Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (22 mg, 3×10^{-5} mol) in a mixture of pentane and toluene (7:1, ~3 mL) for 12 h. Storing the resulting solution for 48 h at −40 °C gave the anti product as yellow needles (160 mg, 64%): ^{1}H NMR δ 13.25 (d, $^3J_{HP}$ = 7.8, 1, MoC*H*-*t*-Bu), 6.90 (m, 3, NAr), 4.23 (sept, 1, C*H*Me$_2$), 3.58 (sept, 1, C*H*Me$_2$), 2.07 (s, 3, OC*Me*(CF$_3$)$_2$), 1.53 (s, 3, OC*Me*(CF$_3$)$_2$), 1.37 (d, 3, CH*Me*$_2$), 1.28 (d, 3, CH*Me*$_2$), 1.20 (s, 9, MoCH-*t*-*Bu*), 0.84 (d, J_{HP} = 9, 9, PMe$_3$); ^{13}C NMR 313.9 (dd, $^1J_{CH}$ = 138, $^2J_{CP}$ = 18, MoC*H*-*t*-Bu).

W(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$(PMe$_3$). This compound was prepared in high yield as described for the Mo analogue above. Characterization data: ^{1}H NMR (syn rotamer, toluene-d_8) δ 9.51 (d, 1, J_{HP} = 3.9 Hz, C*H*-*t*-Bu), 7.06 (d, 2, H_m), 6.92 (t, 1, H_p), 4.55 (br m, 1, C*H*Me$_2$), 3.22 (br m, 1, C*H*Me$_2$), 2.10 (s, 3, OC*Me*(CF$_3$)$_2$), 1.62 (s, 3, OC*Me*(CF$_3$)$_2$), 1.2–1.4 (br m, 6, CH*Me*$_2$), 1.26 (d, 6, CH*Me*$_2$), 1.23 (s, 9, CH-*t*-*Bu*), 1.11 (d, 9, J_{HP} = 9.2 Hz, P*Me*$_3$); ^{1}H NMR (anti rotamer, toluene-d_8) δ 11.53 (d, 1, J_{HP} = 6.6 Hz, C*H*-*t*-Bu), 7.05 (d, 2, H_m), 6.94 (t, 1, H_p), 4.25 (sept, 1, C*H*Me$_2$), 3.59 (sept, 1, C*H*Me$_2$), 2.07 (s, 3, OC*Me*(CF$_3$)$_2$), 1.61 (s, 3, OC*Me*(CF$_3$)$_2$), 1.38 (d, 3, CH*Me*$_2$), 1.33 (d, 3, CH*Me*$_2$), 1.29 (s, 9, CH-*t*-Bu), 1.27 (d, 3, CH*Me*$_2$), 1.26 (d, 3, CH*Me*$_2$), 1.11 (d, 9, J_{HP} = 9.4 Hz, P*Me*$_3$); ^{13}C NMR (syn rotamer) 270.1 (dd with W satellites, J_{CH} = 105 Hz, J_{CP} = 14 Hz, J_{CW} = 186 Hz); ^{13}C NMR (anti rotamer) 286.9 (dd with W satellites, J_{CH} = 136 Hz, J_{CP} = 14 Hz, J_{CW} = 158 Hz); NOEDS (anti rotamer) irradiation at 11.53 ppm, δ 4.25 (18% NOE). Anal. Calcd for $C_{28}H_{42}F_{12}NO_2PW$: C, 38.77; H, 4.88; N, 1.61. Found: C, 38.88; H, 4.85; N, 1.38.

W(CH-*t*-Bu)(NAr)[OCMe$_2$(CF$_3$)]$_2$(PMe$_3$). This compound was prepared as described for the analogues above. Characterization data: ^{1}H NMR (anti rotamer) δ 11.13 (d, 1, J_{HP} = 6.1 Hz, C*H*-*t*-Bu), 7.05 (d, 2, H_m), 6.92 (t, 1, H_p), 4.11 (sept, 1, C*H*Me$_2$), 3.63 (sept, 1, C*H*Me$_2$), 1.87 (s, 3, OC*Me*$_2$CF$_3$), 1.76 (s, 3, OC*Me*$_2$CF$_3$), 1.51 (s, 3, OC*Me*$_2$CF$_3$), 1.37 (d, 3, CH*Me*$_2$), 1.31 (d, 3, CH*Me*$_2$), 1.29 (d, 3, CH*Me*$_2$), 1.29 (s, 3, OC*Me*$_2$CF$_3$), 1.24 (s, 9, CH-*t*-*Bu*), 1.21 (d, 3, CH*Me*$_2$), 0.99 (d, 9, J_{HP} = 8.8 Hz, P*Me*$_3$); ^{1}H NMR (syn rotamer) δ 9.26 (d, 1, C*H*-*t*-Bu); ^{13}C NMR (syn rotamer) 264.7 (d, J_{CH} = 106 Hz); ^{13}C NMR (anti rotamer) 277.8 (d, J_{CH} = 138 Hz); NOEDS (anti rotamer) irradiation at 11.13 ppm, δ 4.11 (17% NOE), 1.24 (4.8% NOE). Anal. Calcd for $C_{28}H_{48}F_6NO_2PW$: C, 44.28; H, 6.37; N, 1.84. Found: C, 44.34; H, 6.35; N, 1.90.

Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$(PMe$_3$). Trimethylphosphine (100 μL, 1 mmol) in pentane (500 μL) was added all at once to a solution of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (150 mg, 0.3 mmol) in pentane (~1 mL). The resulting solution was stored at −40 °C overnight, from which bright orange crystals were obtained; these were quickly filtered, placed under vacuum for 5–10 min, and kept cold (−40 °C). The VT NMR spectrum of this material in toluene-d_8 is shown in Figure 2; the ratio of trimethylphosphine to alkylidene was determined to be approximately 1:1. Due to the lability of the phosphine ligand and the presence of isomers, the NMR spectrum is broad and complex; however, the alkylidene C_α signals are sufficiently removed from other resonances to be assigned: ^{1}H NMR (toluene-d_8, −25 °C) δ 12.73 (d, $^3J_{HP}$ = 7, H_α anti rotamer), 11.80 (d, $^3J_{HP}$ = 5, H_α syn rotamer); ^{13}C NMR (toluene-d_8, −25 °C) δ 293.4 ($^3J_{CP}$ = 18, J_{CH} = 136, C_α anti rotamer), 281.1 ($^3J_{CP}$ = 18, J_{CH} = 110, C_α syn rotamer); ^{31}P{^{1}H} NMR δ −6.0 (*P*Me$_3$, anti rotamer), −7.3 (*P*Me$_3$, syn rotamer).

Observation of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$(PMe$_3$): ^{1}H NMR (anti rotamer, toluene-d_8, −20 °C) δ 10.87 (d, J_{HP} = 6.5 Hz, 1, C*H*-*t*-Bu), 7.08 (d, 2, H_m), 6.91 (t, 1, H_p), 4.12 (sept, 1, C*H*Me$_2$), 3.73 (sept, 1, C*H*Me$_2$), 1.57 (s, 9, O-*t*-*Bu*), 1.47 (d, 3, CH*Me*$_2$), 1.46 (O-*t*-*Bu*), 1.40 (d, 3, CH*Me*$_2$), 1.37 (d, 3, CH*Me*$_2$), 1.36 (s, 9, CH-*t*-Bu), 1.29 (d, 3, CH*Me*$_2$), 0.97 (d, J_{HP} = 8.3 Hz, 9, P*Me*$_3$); NOEDS (anti rotamer, toluene-d_8, −40 °C) irradiation at 10.87 ppm, δ 4.12 (12% NOE).

Mo(CHSiMe$_3$)(NAr)[OCMe$_2$(CF$_3$)]$_2$(PMe$_3$). Trimethylphosphine (250 μL, 2.46 mmol) was added to a stirred solution of yellow-orange Mo(CHSiMe$_3$)(NAr)[OCMe$_2$(CF$_3$)]$_2$ (1.50 g, 2.45 mmol) in 40 mL of pentane. After 2 h all solvents were removed in vacuo, leaving a yellow-orange solid. This solid was dissolved in a minimum amount of pentane, and the solution was cooled to −40 °C to give a yellow-orange powder (1.13 g, 67%) in two crops: ^{1}H NMR δ 14.13 (d, $^3J_{HP}$ = 7.1, 1, MoC*H*SiMe$_3$), 6.97 (m, 3, NAr), 4.45 and 3.60 (sept, 1 each, C*H*Me$_2$), 1.99 and 1.76 (s, 3 each, OC*Me*$_2$(CF$_3$)), 1.36 and 1.30 (d, 3 each, CH*Me*$_2$), 1.27 and

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1.24 (s, 3 each, $OCMe_2(CF_3)$), 1.24 and 1.18 (d, 3 each, $CHMe_2$), 0.88 (d, $^2J_{HP}$ = 9.4, PMe_3), 0.26 (s, 9, $MoCHSiMe_3$); ^{13}C NMR δ 289.3 (dd, $^1J_{CH}$ = 129, $^2J_{CP}$ = 20, $MoCHSiMe_3$), 152.0 (C_{ipso}), 147.5 and 146.0 (C_o), 129.0 and 128.9 (q, $^1J_{CF}$ = 288 for both, $OCMe_2(CF_3)$), 128.3 (C_p), 123.7 and 123.4 (C_m), 79.1 and 76.8 (q, $^2J_{CF}$ = 28 and 27, respectively, $OCMe_2(CF_3)$), 29.0 and 28.8 ($CHMe_2$), 25.8, 25.5, 24.8, 24.3, 24.1, 23.4, 23.2, and 22.9 ($OCMe_2(CF_3)$ and $CHMe_2$), 14.8 (dq, $^1J_{CP}$ = 26, $^1J_{CH}$ = 129, PMe_3), 1.4 ($MoCHSiMe_3$); ^{19}F NMR δ −80.3 and −81.9 (s, 3 each, $OCMe_2(CF_3)$); $^{31}P\{^1H\}$ NMR δ −1.21 (PMe_3). Anal. Calcd for $MoC_{27}H_{48}F_6O_2NPSi$: C, 47.16; H, 7.04. Found: C, 47.44; H, 7.10.

Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$(quin): ^1H NMR (syn rotamer) δ 12.51 (s, 1, C*H*-*t*-Bu), 6.94 (s, 3, H_m + H_p), 3.65 (sept, 2, C*H*Me_2), 2.86 (m, 6, quin H_α), 1.37 (s, 6, $OCMe(CF_3)_2$), 1.2–1.3 (obscured m, 7 H, quin H_β + H_γ), 1.20 (d, 12, $CHMe_2$), 1.07 (s, 9, CH-*t*-*Bu*); ^1H NMR (anti rotamer) δ 13.16 (s, 1, C*H*-*t*-Bu), 6.94 (s, 3, H_m + H_p), 4.56 (sept, 1, C*H*Me_2), 3.70 (sept, 1, C*H*Me_2), 3.06 (m, 6, quin H_α), 2.12 (s, 3, $OCMe(CF_3)_2$), 1.41 (s, 3, $OCMe(CF_3)_2$), 1.27 (s, 9, CH-*t*-*Bu*), 1.0–1.3 (obscured m, 7 H, quin H_β + H_γ); ^{13}C NMR (syn rotamer) δ 296.4 (d, J_{CH} = 121 Hz, vinylalkylidene C_α), 46.4 (t, quin C_α); ^{13}C NMR (anti rotamer) δ 311.1 (d, J_{CH} = 140 Hz, vinylalkylidene C_α), 52.9 (t, quin C_α); NOEDS (syn rotamer) irradiation at 12.51 ppm, δ 1.37 (6.5% NOE), 1.07 (3.5% NOE), irradiation at 2.86 ppm, δ 3.65 (2.8% NOE), 1.2–1.3 (5.6% combined NOE), irradiation at 3.65 ppm, 2.86 (1.2% NOE), 1.37 (2.5% NOE), 1.20 (11% NOE), 1.07 (1.6% NOE). Anal. Calcd for $C_{32}H_{46}F_{12}N_2O_2Mo$: C, 47.18; H, 5.69; N, 3.44. Found: C, 47.12; H, 5.61; N, 3.21.

W(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (quin). This and other quinuclidine adducts were prepared as described for a sample below. Characterization data: ^1H NMR (syn rotamer) δ 9.24 (s, 1, C*H*-*t*-Bu), 7.04 (d, 2, H_m), 6.94 (t, 1, H_p), 3.68 (sept, 2, C*H*Me_2), 2.83 (m, 6, quin H_α), 1.48 (s, 6, $OCMe(CF_3)_2$), 1.24 (d, 12, $CHMe_2$), 1.15 (s, 9, CH-*t*-*Bu*); ^1H NMR (anti rotamer) δ 10.77 (s, 1, C*H*-*t*-Bu), 7.06 (d, 2, H_m), 6.88 (t, 1, H_p), 4.51 (sept, 1, C*H*Me_2), 3.65 (sept, 1, C*H*Me_2), 3.16 (m, 6, quin H_α), 2.05 (s, 3, $OCMe(CF_3)_2$), 1.50 (s, 3, $OCMe(CF_3)_2$), 1.38 (d, 3, $CHMe_2$), 1.33 (d, 3, $CHMe_2$), 1.30 (s, 9, CH-*t*-*Bu*), 1.20 (d, 3, $CHMe_2$), 1.19 (d, 3, $CHMe_2$), 1.06 (m, 6, quin H_β); ^{13}C NMR (syn rotamer) δ 273.5 (d with W satellites, J_{CH} = 109 Hz, J_{CW} = 189 Hz, vinylalkylidene C_α), 46.6 (t, quin C_α); ^{13}C NMR (anti rotamer) δ 279.3 (d with W satellites, J_{CH} = 137 Hz, J_{CW} = 175 Hz, vinylalkylidene C_α), 53.6 (t, quin C_α); NOEDS (anti rotamer) irradiation at 10.77 ppm, δ 4.51 (15% NOE). Anal. Calcd for $C_{32}H_{46}F_{12}N_2O_2W$: C, 42.58; H, 5.14; N, 3.10. Found: C, 42.63; H, 5.09; N, 2.82.

Mo(CH-*t*-Bu)(NAr)[OCMe$_2$(CF$_3$)]$_2$(quin): ^1H NMR (syn rotamer) δ 11.81 (s, 1, C*H*-*t*-Bu), 7.00 (s, 3, H_m + H_p), 3.80 (sept, 2, C*H*Me_2), 2.85 (m, 6, quin H_α), 1.38 (s, 6, $OCMe_2CF_3$), 1.27 (s, 6, $OCMe_2CF_3$), 1.22 (d, 12, $CHMe_2$), 1.15 (s, 9, CH-*t*-*Bu*); ^1H NMR (anti rotamer) δ 12.87 (s, 1, C*H*-*t*-Bu); NOEDS (syn rotamer) irradiation at 11.81 ppm, δ 1.38 (4.2% NOE), 1.27 (4.2% NOE), 1.15 (6.9% NOE). Anal. Calcd for $C_{32}H_{52}F_6N_2O_2Mo$: C, 54.39; H, 7.42; N, 3.96. Found: C, 54.44; H, 7.29; N, 3.87.

W(CH-*t*-Bu)(NAr)[OCMe$_2$(CF$_3$)]$_2$(quin): ^1H NMR (syn rotamer) δ 8.61 (s, 1, C*H*-*t*-Bu), 7.10 (m, 2, H_m), 7.00 (t, 1, H_p), 3.81 (sept, 2, C*H*Me_2), 2.83 (m, 6, quin H_α), 1.39 (s, 6, $OCMe_2CF_3$), 1.31 (s, 6, $OCMe_2CF_3$), 1.25 (d, 12, $CHMe_2$), 1.21 (s, 9, CH-*t*-*Bu*); ^1H NMR (anti rotamer) δ 10.46 (s, 1, C*H*-*t*-Bu), 7.07 (d, 2, H_m), 6.89 (t, 1, H_p), 4.50 (sept, 1, C*H*Me_2), 3.74 (sept, 1, C*H*Me_2), 3.17 (m, 6, quin H_α), 1.89 (s, 3, $OCMe_2CF_3$), 1.45 (s, 3, $OCMe_2CF_3$), 1.37 (s, 3, $OCMe(CF_3)_2$), 1.33 (s, 9, CH-*t*-*Bu*), 1.17 (d, 3, $CHMe_2$); NOEDS (anti rotamer) irradiation at 10.46 ppm, δ 4.50 (11% NOE), 3.74 (9% NOE), 1.33 (9%). Anal. Calcd for $C_{32}H_{52}F_6N_2O_2W$: C, 48.37; H, 6.60; N, 3.53. Found: C, 48.67; H, 6.59; N, 3.46.

Mo(CHCMe$_2$Ph)(NAr)(O-2,6-C$_6$H$_3$Cl$_2$)$_2$(py). A cold (−30 °C) solution of $Mo(CHCMe_2Ph)(NAr)(OSO_2CF_3)_2(DME)$ (500 mg, 0.632 mmol) in 20 mL of diethyl ether and 10 mL of tetrahydrofuran was treated with one portion of solid lithium 2,6-dichlorophenoxide (213 mg, 1.263 mmol). The initially yellow solution darkened to red as it was warmed to room temperature. After 1 h, the reaction mixture was concentrated, and the resulting solids were extracted with pentane. The pentane extracts were filtered into 5 mL of pentane containing pyridine (61.3 μL, 0.758 mmol) to give a cloudy solution. The solvents were removed in vacuo to give a dark yellow solid, which was dissolved in a minimal volume of diethyl ether. This solution was cooled to −40 °C to yield 298 mg (58%) of product as yellow crystals: ^1H NMR (CD_2Cl_2, syn rotamer) δ 14.46 (s, 1, C*H*CMe_2Ph), 8.86 (dd, 2, py), 7.79 (tt, 1, py), 7.30–6.40 (m, 16, aromatic), 3.78 (sept, 2, C*H*Me_2), 1.67 (s, 3, $CHCMe_2Ph$), 1.57 (s, 3, $CHCMe_2Ph$), 0.97 (6, $CHMe_2$), 0.88 (6, $CHMe_2$); ^1H NMR (CD_2Cl_2, anti rotamer) δ 14.31 (s, 1, C*H*CMe_2Ph), 8.12 (dd, 2, py), 7.55 (tt, 1, py), 7.30–6.40 (m, 16, aromatic), 4.05 (sept, 2, C*H*Me_2), 2.20 (s, 3, $CHCMe_2Ph$), 1.32 (s, 3, $CHCMe_2Ph$), 1.23 (6, $CHMe_2$), 1.09 (6, $CHMe_2$); ^{13}C NMR (CD_2Cl_2) δ 320.2 (minor C_α), 305.1 (d, J_{CH} = 125, major C_α), 160.8, 157.3, 153.2, 151.9, 151.3, 149.5, 148.7, 147.5, 147.3, 139.4, 138.7, 128.7, 128.5, 128.4, 128.2, 128.0, 127.8, 127.5, 126.4, 126.3, 126.2, 126.1, 125.6, 125.4, 124.8, 123.8, 118.4, 117.9, 117.7, 117.4, 66.1, 55.0, 53.3, 32.7, 32.0, 29.2, 28.6, 28.5, 27.5, 25.6, 24.7, 24.3, 24.1, 15.5. This compound could not be analyzed, since it loses pyridine readily, and the four-coordinate complex that is formed when it does is thermally unstable in the solid state.

Mo(*trans*-CHCHCHMe)(NAr)[OCMe(CF$_3$)$_2$]$_2$(quin): ^1H NMR (syn rotamer) δ 12.90 (d, J = 10.7 Hz, 1, vinylalkylidene H_α), 8.15 (ddq, 1, vinylalkylidene H_β), 4.60 (dq, 1, vinylalkylidene H_γ), 1.82 (dd, 3, allylic C*H*Me); ^1H NMR (anti rotamer) δ 13.04 (d, J = 13.4 Hz, 1, vinylalkylidene H_α), 8.15 (br t, 1, vinylalkylidene H_β), 6.94 (m, 3, H_m + H_p), 4.62 (dq, 1, vinylalkylidene H_γ), 4.52 (sept, 1, C*H*Me_2), 3.63 (sept, 1, C*H*Me_2), 3.03 (m, 6, quin H_α), 2.16 (s, 3, $OCMe(CF_3)_2$), 1.94 (br d, 3, allylic C*H*Me), 1.38 (d, 3, $CHMe_2$), 1.38 (s, 3, $OCMe(CF_3)_2$), 1.33 (d, 3, $CHMe_2$), 1.32 (d, 3, $CHMe_2$), 1.25 (d, 3, $CHMe_2$), 1.10 (m, 1, quin H_γ), 0.99 (m, 6, quin H_β); ^{13}C NMR (syn rotamer) δ 280.2 (J_{CH} = 127 Hz, vinylalkylidene C_α), 151.4 (C_{ipso}), 148.8 (C_o), 143.8 (C_o), 139.0 (d, J_{CH} = 158 Hz, vinylalkylidene C_β or C_γ), 134.9 (d, J_{CH} = 150 Hz, vinylalkylidene C_γ or C_β); ^{13}C NMR (syn rotamer) δ 280.2 (d, J_{CH} = 127 Hz, vinylalkylidene C_α); ^{13}C NMR (anti rotamer) δ 287.8 (d, J_{CH} = 148 Hz, vinylalkylidene C_α), 151.4 (C_{ipso}), 148.3 (C_o), 144.3 (C_o), 139.0 (d, J_{CH} = 158 Hz, vinylalkylidene C_β or C_γ), 134.9 (d, J_{CH} = 150 Hz, vinylalkylidene C_γ or C_β), 124.2, 123.7, 121.5 (C_m + C_p), 82.0 (m, $OCMe(CF_3)_2$), 52.5 (t, J_{CH} = 141 Hz, quin H_α), 25.8 (quin H_β), 30.3, 28.8, 24.7, 24.6, 24.4, 24.3, 19.9, 18.8, 17.3, 17.2 ($CHMe_2$, $OCMe(CF_3)_2$, allylic Me, quin H_γ); NOEDS (anti rotamer) irradiation at 13.04 ppm, δ 4.62 (20% NOE), 4.52 (15% NOE). Anal. Calcd for $C_{31}H_{42}F_{12}N_2O_2Mo$: C, 46.62; H, 5.30; N, 3.51. Found: C, 46.63; H, 5.24; N, 3.39.

Mo(*cis*-CHCHCHMe)(NAr)[OCMe(CF$_3$)$_2$]$_2$(quin): ^1H NMR (syn rotamer) δ 13.36 (d, J = 11.8 Hz, 1, vinylalkylidene H_α), 8.20 (ddq, 1, vinylalkylidene H_β); ^1H NMR (anti rotamer) δ 13.63 (d, J = 13.4 Hz, 1, vinylalkylidene H_α), 8.20 (ddq, 1, vinylalkylidene H_β); ^{13}C NMR (syn rotamer) δ 272.8 (d, J_{CH} = 126 Hz, vinylalkylidene C_α); ^{13}C NMR (anti rotamer) δ 278.3 (d, J_{CH} = 153 Hz, vinylalkylidene C_α). Anal. Calcd for $C_{31}H_{42}F_{12}N_2O_2Mo$: C, 46.62; H, 5.30; N, 3.51. Found: C, 46.35; H, 5.35; N, 3.35.

Mo(*trans*-CHCHCHMe)(NAr)[OCMe$_2$(CF$_3$)]$_2$(quin): ^1H NMR (syn rotamer) δ 12.57 (d, J = 11.4 Hz, 1, vinylalkylidene H_α), 8.25 (br dd, 1, vinylalkylidene H_β), 4.63 (sept, 1, C*H*Me_2), 4.53 (dq, 1, vinylalkylidene H_γ), 3.62 (sept, 1, C*H*Me_2); ^1H NMR (anti rotamer) δ 12.85 (d, J = 13.4 Hz, 1, vinylalkylidene H_α), 8.04 (tq, 1, vinylalkylidene H_β), 6.98 (d, 2, H_m), 6.92 (t, 1, H_p), 4.65 (dq, 1, vinylalkylidene H_γ), 4.53 (sept, 1, C*H*Me_2), 3.73 (sept, 1, C*H*Me_2), 3.06 (m, 6, quin H_α), 2.03 (s, 3, $OCMe(CF_3)_2$), 1.90 (br d, 3, allylic C*H*Me), 1.89 (s, 3, $OCMe(CF_3)_2$), 1.38 (d, 3, $CHMe_2$), 1.36 (d, 3, $CHMe_2$), 1.32 (s, 3, $OCMe(CF_3)_2$), 1.25 (d, 3, $CHMe_2$), 1.22 (d, 3, $CHMe_2$), 1.17 (s, 3, $OCMe(CF_3)_2$), 1.13 (m, 1, quin H_γ), 1.07 (m, 6, quin H_β); ^{13}C NMR (syn rotamer) δ 273.4 (d, J_{CH} = 128 Hz, vinylalkylidene C_α); ^{13}C NMR (anti rotamer) δ 279.1 (d, J_{CH} = 148 Hz, vinylalkylidene C_α); NOEDS (anti rotamer) irradiation at 12.85 ppm, δ 4.65 (12% NOE), 4.53 (7% NOE). Anal. Calcd for $C_{31}H_{48}F_6N_2O_2Mo$: C, 53.91; H, 7.00; N, 4.06. Found: C, 53.88; H, 6.87; N, 3.95.

Mo(*cis*-CHCHCHMe)(NAr)[OCMe$_2$(CF$_3$)]$_2$(quin): ^1H NMR (syn rotamer) δ 13.04 (d, J = 11.6 Hz, 1, vinylalkylidene H_α), 8.32 (br t, 1, vinylalkylidene H_β), 7.01 (m, 2, H_m), 6.92 (t, 1, H_p), 4.63 (sept, 1, C*H*Me_2), 4.53 (dq, 1, vinylalkylidene H_γ), 3.62 (sept, 1, C*H*Me_2), 1.64 (br d, allylic Me); ^1H NMR (anti rotamer) δ 13.41 (d, J = 14.1 Hz, 1, vinylalkylidene H_α), 8.16 (ddq, 1, vinylalkylidene H_β), 7.01 (m, 2, H_m), 6.92 (t, 1, H_p), 4.60 (sept, 1, C*H*Me_2), 4.41 (dq, 1, vinylalkylidene H_γ), 3.75 (sept, 1, C*H*Me_2), 3.04 (m, 6, quin H_α), 1.73 (dd, 1, allylic Me); ^{13}C NMR (syn

rotamer) δ 266.3 (d, J_{CH} = 126 Hz, vinylalkylidene C_α); ^{13}C NMR (anti rotamer) δ 272.4 (d, J_{CH} = 147 Hz, vinylalkylidene C_α); NOEDS (anti rotamer) irradiation at 13.41 ppm, δ 4.60 (7% NOE), 3.75 (6% NOE), 1.73 (12% NOE). Anal. Calcd for $C_{31}H_{48}F_6N_2O_2Mo$: C, 53.91; H, 7.00; N, 4.06. Found: C, 53.83; H, 6.92; N, 3.74.

W(*trans*-CHCHCHMe)(NAr)[OCMe(CF$_3$)$_2$]$_2$(quin): ^1H NMR (syn rotamer) δ 10.65 (d, 1, J = 10.8 Hz, vinylalkylidene H_α), 8.10 (ddq, 1, vinylalkylidene H_β), 7.07 (m, 2, H_m), 6.89 (t, 1, H_p), 4.67 (sept, 1, C*H*Me$_2$), 4.32 (dq, 1, vinylalkylidene H_γ), 3.48 (sept, 1, C*H*Me$_2$), 3.00 (m, 6, quin H_α), 2.38 (dd, 3, allylic CH*Me*), 2.11 (s, 3, OC*Me*(CF$_3$)$_2$), 1.47 (s, 3, OC*Me*(CF$_3$)$_2$), 1.37 (d, 3, CH*Me*$_2$), 1.36 (d, 3, CH*Me*$_2$), 1.33 (d, 3, CH*Me*$_2$), 1.24 (d, 3, CH*Me*$_2$), 1.04 (m, 1, quin H_γ), 0.95 (m, 6, quin H_β); ^1H NMR (anti rotamer) δ 11.35 (d, J = 13.5 Hz, 1, vinylalkylidene H_α), 8.00 (br t, 1, vinylalkylidene H_β), 7.06 (d, 1, H_m), 7.05 (d, 1, H_m), 6.88 (t, 1, H_p), 4.48 (sept, 1, C*H*Me$_2$), 4.25 (dq, 1, vinylalkylidene H_γ), 3.60 (sept, 1, C*H*Me$_2$), 3.08 (m, 6, quin H_α), 2.56 (br d, 3, allylic CH*Me*), 2.11 (s, 3, OC*Me*(CF$_3$)$_2$), 1.48 (s, 3, OC*Me*(CF$_3$)$_2$), 1.36 (d, 3, CH*Me*$_2$), 1.34 (d, 3, CH*Me*$_2$), 1.33 (d, 3, CH*Me*$_2$), 1.24 (d, 3, CH*Me*$_2$), 1.04 (m, 1, quin H_γ), 0.95 (m, 6, quin H_β); ^{13}C NMR (syn rotamer) δ 256.8 (d, J_{CH} = 120 Hz, vinylalkylidene C_α), 52.6 (t, quin C_α); ^{13}C NMR (anti rotamer) δ 263.3 (d, J_{CH} = 147 Hz, vinylalkylidene (C_α), 52.6 (t, quin C_α); NOEDS (anti rotamer) irradiation at 11.35 ppm, δ 4.48 (18% NOE), 4.25 (19% NOE), quin H_α (10% NOE), 2.56 (4.6% NOE). Anal. Calcd for $C_{31}H_{42}F_{12}N_2O_2W$: C, 42.00; H, 4.78; N, 3.16. Found: C, 42.02; H, 4.76; N, 3.13.

W(*cis*-CHCHCHMe)(NAr)[OCMe(CF$_3$)$_2$]$_2$(quin). A solution of W(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$(quin) (504 mg, 0.558 mmol) in pentane (25 mL) was treated with *cis*-1,3-pentadiene (600 μL in 5 mL of pentane containing 10 mg of quinuclidine). The mixture was stirred for 1 h; then volatiles were removed in vacuo to give a yellow-orange solid. This solid was extracted with pentane, filtered through Celite, and recrystallized at −40 °C to afford a yellow-orange microcrystalline solid (424 mg, 86% in two crops): ^1H NMR (syn rotamer) δ 11.05 (d, J = 11.0 Hz, 1, vinylalkylidene H_α), 8.19 (tq, 1, vinylalkylidene H_β), 7.07 (m, 2, H_m), 6.88 (t, 1, H_p), 4.63 (sept, 1, C*H*Me$_2$), 4.16 (dq, 1, vinylalkylidene H_γ), 3.49 (sept, 1, C*H*Me$_2$), 2.9–3.1 (m, 6, quin H_α), 2.14 (dd, 3, allylic CH*Me*), 2.09 (s, 3, OC*Me*(CF$_3$)$_2$), 1.46 (s, 3, OC*Me*(CF$_3$)$_2$), 1.36 (d, 3, CH*Me*$_2$), 1.33 (d, 3, CH*Me*$_2$), 1.27 (d, 3, CH*Me*$_2$), 1.25 (d, 3, CH*Me*$_2$), 1.05 (m, 1, quin H_γ), 0.96 (m, 6, quin H_β); ^1H NMR (anti rotamer) δ 11.87 (d, J = 14.8 Hz, 1, H_α), 8.10 (ddq, 1, H_β), 7.07 (m, 2, H_m), 6.88 (t, 1, H_p), 4.60 (sept, 1, C*H*Me$_2$), 4.25 (dq, 1, H_γ), 3.62 (sept, 1, C*H*Me$_2$), 2.39 (dd, 3, allylic CH*Me*), 2.08 (s, 3, OC*Me*(CF$_3$)$_2$), 1.47 (s, 3, OC*Me*(CF$_3$)$_2$), 1.04 (m, 1, quin H_γ), 0.96 (m, 6, quin H_β); ^{13}C NMR (syn rotamer) δ 249.5 (d, J_{CH} = 122 Hz, vinylalkylidene C_α), 52.8 (t, quin C_α); ^{13}C NMR (anti rotamer) δ 256.5 (d, J_{CH} = 144 Hz, vinylalkylidene C_α), 52.8 (t, quin C_α); NOEDS (syn rotamer) irradiation at 11.05 ppm, δ 2.14 (19% NOE); NOEDS (anti rotamer) irradiation at 11.87 ppm, δ 4.60 (15% NOE), 2.39 (18% NOE). Anal. Calcd for $C_{31}H_{42}F_{12}N_2O_2W$: C, 42.00; H, 4.78; N, 3.16. Found: C, 41.89; H, 4.67; N, 3.04.

W(*trans*-CHCHCHMe)(NAr)[OCMe$_2$(CF$_3$)]$_2$(quin): ^1H NMR (syn rotamer) δ 10.34 (d, 1, J = 11.0 Hz, vinylalkylidene H_α), 8.25 (ddq, 1, vinylalkylidene H_β), 7.10 (m, 2, H_m), 6.89 (m, 1, H_p), 4.68 (sept, 1, C*H*Me$_2$), 4.38 (dq, 1, vinylalkylidene H_γ), 3.60 (sept, 1, C*H*Me$_2$), 3.0–3.2 (m, 6, quin H_α), 2.45 (d, 3, allylic CH*Me*); ^1H NMR (anti rotamer) δ 11.17 (d, J = 13.5 Hz, 1, vinylalkylidene H_α), 7.91 (tq, 1, vinylalkylidene H_β), 7.10 (d, 2, H_m), 6.89 (d, 1, H_p), 4.48 (sept, 1, C*H*Me$_2$), 4.32 (dq, 1, vinylalkylidene H_γ), 3.68 (sept, 1, C*H*Me$_2$), 3.0–3.2 (m, 6, quin H_α), 2.48 (br d, 3, allylic CH*Me*); ^{13}C NMR (syn rotamer) δ 250.2 (d, J_{CH} = 120 Hz, vinylalkylidene C_α); ^{13}C NMR (anti rotamer) δ 254.7 (d, J_{CH} = 145 Hz, vinylalkylidene C_α); NOEDS (anti rotamer) irradiation at 11.17 ppm, δ 4.48 (13% NOE), 4.32 (16% NOE). Anal. Calcd for $C_{31}H_{48}F_6N_2O_2W$: C, 47.87; H, 6.21; N, 3.60. Found: C, 47.86; H, 6.34; N, 3.59.

W(*cis*-CHCHCHMe)(NAr)[OCMe$_2$(CF$_3$)]$_2$(quin): ^1H NMR (syn rotamer) δ 10.74 (d, 1, J = 11.4 Hz, vinylalkylidene H_α), 8.31 (tq, 1, vinylalkylidene H_β), 7.12 (m, 2, H_m), 6.89 (m, 1, H_p), 4.63 (sept, 1, C*H*Me$_2$), 4.19 (dq, 1, vinylalkylidene H_γ), 3.59 (sept, 1, C*H*Me$_2$), 2.13 (dd, 3, allylic CH*Me*); ^1H NMR (anti rotamer) δ 11.63 (d, J = 14.3 Hz, 1, vinylalkylidene H_α), 8.02 (ddq, 1, vinylalkylidene H_β), 7.12 (d, 2, H_m), 6.89 (d, 1, H_p), 4.56 (sept, 1, C*H*Me$_2$), 4.12 (dq, 1, vinylalkylidene H_γ), 3.69 (sept, 1, C*H*Me$_2$), 2.24 (dd, 3, allylic CH*Me*); ^{13}C NMR (syn rotamer) δ 243.6 (d, J_{CH} = 120 Hz, vinylalkylidene C_α); ^{13}C NMR (anti rotamer) δ 248.2 (d, J_{CH} = 145 Hz, vinylalkylidene C_α); NOEDS (anti rotamer) irradiation at 11.63 ppm, δ 4.56 (14% NOE), 2.24 (9% NOE). Anal. Calcd for $C_{31}H_{48}F_6N_2O_2W$: C, 47.87; H, 6.21; N, 3.60.

Table VII. Crystal Data for Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$(PMe$_3$) and *anti*-W(*trans*-CHCH=CHMe)(NAr)[OCMe(CF$_3$)$_2$]$_2$(quin)

empirical formula	$C_{28}H_{42}NO_2F_{12}PMo$	$C_{31}H_{42}F_{12}N_2O_2W$
fw	779.54	886.52
cryst dimens, mm	0.200 × 0.150 × 0.250	0.300 × 0.250 × 0.180
cryst syst	monoclinic	monoclinic
no. of reflns used for unit cell determination (2θ range, deg)	25 (25.0–32.0)	25 (25.0–31.0)
a, Å	10.979 (4)	12.972 (9)
b, Å	17.945 (7)	18.049 (7)
c, Å	18.375 (8)	15.038 (9)
β, deg	106.34 (3)	92.07 (3)
V, Å^3	3474 (4)	3518 (6)
space group	*Cc*	$P2_1/n$
Z	4	4
ρ(calcd), g/cm^3	1.490	1.673
μ, cm^{-1}	5.00	34.43
final R_1, R_2	0.037, 0.045	0.038, 0.040

Table VIII. Final Positional Parameters for *syn*-Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$(PMe$_3$)

atom	x	y	z
Mo(1)	1.0000	0.99439 (4)	$^3/_4$
P(5)	0.8295 (2)	0.9901 (1)	0.8174 (2)
F(211)	1.187 (1)	0.8888 (5)	0.9630 (4)
F(212)	1.3185 (8)	0.8175 (5)	0.9356 (5)
F(213)	1.2942 (9)	0.9274 (5)	0.8898 (5)
F(221)	1.1232 (8)	0.7217 (3)	0.8886 (5)
F(222)	0.9628 (8)	0.7561 (4)	0.7981 (5)
F(223)	0.9910 (8)	0.8003 (4)	0.9093 (5)
F(411)	1.3372 (7)	1.0513 (5)	0.7885 (4)
F(412)	1.4268 (7)	1.0574 (6)	0.6982 (5)
F(413)	1.4112 (7)	0.9543 (5)	0.7529 (5)
F(431)	1.2730 (8)	0.8827 (4)	0.6297 (5)
F(432)	1.3263 (9)	0.9783 (5)	0.5751 (5)
F(433)	1.1317 (8)	0.9468 (5)	0.5525 (4)
O(2)	1.0448 (6)	0.9019 (3)	0.8141 (4)
O(4)	1.1453 (6)	0.9644 (3)	0.7073 (3)
N(3)	0.8792 (6)	1.0163 (3)	0.6665 (4)
C(1)	1.062 (1)	1.0813 (5)	0.8051 (6)
C(2)	1.128 (1)	0.8441 (5)	0.8370 (5)
C(4)	1.219 (1)	1.0020 (6)	0.6705 (5)
C(11)	1.067 (1)	1.1650 (6)	0.8233 (7)
C(21)	1.232 (2)	0.8703 (8)	0.9062 (8)
C(22)	1.051 (1)	0.7807 (5)	0.8584 (7)
C(23)	1.188 (1)	0.8129 (6)	0.7779 (6)
C(31)	0.7740 (7)	1.0055 (5)	0.6043 (4)
C(32)	0.713 (1)	1.0682 (5)	0.5640 (6)
C(33)	0.610 (1)	1.0566 (6)	0.5025 (6)
C(34)	0.568 (1)	0.9849 (7)	0.4782 (5)
C(35)	0.630 (1)	0.9248 (6)	0.5180 (7)
C(36)	0.733 (1)	0.9324 (5)	0.5811 (6)
C(41)	1.350 (1)	1.0163 (7)	0.7270 (7)
C(42)	1.168 (1)	1.0760 (6)	0.6357 (6)
C(43)	1.236 (1)	0.9520 (7)	0.6057 (7)
C(51)	0.891 (1)	0.9888 (5)	0.9197 (5)
C(52)	0.720 (1)	1.0662 (5)	0.7965 (6)
C(53)	0.724 (1)	0.9102 (5)	0.7972 (7)
C(111)	1.205 (1)	1.1909 (6)	0.8354 (8)
C(112)	1.029 (1)	1.1805 (5)	0.8943 (6)
C(113)	0.985 (2)	1.2099 (5)	0.7571 (8)
C(321)	0.758 (1)	1.1469 (5)	0.5898 (6)
C(322)	0.646 (1)	1.1957 (6)	0.5997 (7)
C(323)	0.820 (1)	1.1835 (6)	0.5359 (8)
C(361)	0.796 (1)	0.8626 (6)	0.6205 (7)
C(362)	0.898 (1)	0.8373 (8)	0.5836 (8)
C(363)	0.703 (2)	0.7993 (7)	0.6232 (8)

Table IX. Final Non-Hydrogen Positional Parameters for W(*trans*-CHCH=CHMe)(NAr)[OCMe(CF$_3$)$_2$]$_2$(quin)

atom	x	y	z
W(1)	0.41220 (2)	0.21880 (1)	0.13563 (2)
F(331)	0.5551 (4)	0.4438 (2)	0.1954 (4)
F(332)	0.6422 (5)	0.3966 (3)	0.0906 (3)
F(333)	0.7153 (4)	0.4234 (3)	0.2149 (4)
F(341)	0.5083 (3)	0.3586 (3)	0.3290 (3)
F(342)	0.5717 (5)	0.2474 (3)	0.3347 (3)
F(343)	0.6697 (3)	0.3427 (3)	0.3545 (3)
F(431)	0.5843 (4)	−0.0262 (2)	0.2691 (3)
F(432)	0.6307 (4)	0.0822 (3)	0.3115 (3)
F(433)	0.4727 (4)	0.0523 (3)	0.3097 (3)
F(441)	0.6269 (4)	0.0946 (3)	0.0386 (3)
F(442)	0.7224 (3)	0.0931 (3)	0.1557 (4)
F(443)	0.6616 (4)	−0.0080 (2)	0.1043 (3)
O(3)	0.5150 (3)	0.2959 (2)	0.1631 (3)
O(4)	0.5237 (3)	0.1503 (2)	0.1769 (3)
N(1)	0.3065 (4)	0.1789 (3)	0.1847 (3)
N(2)	0.3163 (4)	0.3214 (3)	0.1034 (3)
C(1)	0.3911 (5)	0.1853 (4)	0.0137 (4)
C(2)	0.4553 (5)	0.2011 (3)	−0.0584 (4)
C(3)	0.4395 (5)	0.1812 (4)	−0.1413 (4)
C(4)	0.5022 (6)	0.1994 (4)	−0.2191 (5)
C(11)	0.2292 (4)	0.1547 (3)	0.2398 (4)
C(12)	0.2323 (5)	0.1712 (3)	0.3314 (4)
C(13)	0.1538 (5)	0.1457 (4)	0.3826 (4)
C(14)	0.0713 (5)	0.1055 (4)	0.3463 (4)
C(15)	0.0694 (5)	0.0905 (4)	0.2567 (5)
C(16)	0.1450 (5)	0.1139 (3)	0.2025 (4)
C(17)	0.3185 (5)	0.2181 (4)	0.3757 (4)
C(18)	0.2765 (6)	0.2896 (4)	0.4151 (4)
C(19)	0.3771 (6)	0.1743 (4)	0.4497 (5)
C(21)	0.2097 (5)	0.3006 (4)	0.0698 (5)
C(22)	0.3048 (6)	0.3686 (4)	0.1828 (4)
C(23)	0.3630 (6)	0.3671 (4)	0.0312 (5)
C(24)	0.1455 (6)	0.3692 (4)	0.0432 (5)
C(25)	0.2366 (5)	0.4365 (4)	0.1647 (5)
C(26)	0.3044 (6)	0.4394 (4)	0.0142 (5)
C(27)	0.2061 (6)	0.4393 (4)	0.0664 (5)
C(31)	0.6055 (5)	0.3167 (4)	0.2081 (5)
C(32)	0.6977 (5)	0.2682 (4)	0.1848 (6)
C(33)	0.6285 (6)	0.3963 (5)	0.1765 (6)
C(34)	0.5881 (6)	0.3167 (5)	0.3055 (6)
C(41)	0.5422 (5)	0.0746 (4)	0.1707 (4)
C(42)	0.4557 (6)	0.0301 (4)	0.1267 (5)
C(43)	0.5595 (7)	0.0454 (4)	0.2652 (5)
C(44)	0.6394 (6)	0.0634 (4)	0.1182 (5)
C(110)	0.1390 (5)	0.0960 (4)	0.1039 (5)
C(111)	0.1500 (7)	0.0132 (5)	0.0883 (5)
C(112)	0.0367 (7)	0.1243 (6)	0.0612 (5)

Found: C, 47.48; H, 6.19; N, 3.58.

Mo[CHSi(OEt)Me$_2$](NAr)(OTB)$_2$. Vinyldimethylethoxysilane (21.2 μL, 0.128 mmol) was added to an ethereal solution (4 mL) of Mo(CHCMe$_2$Ph)(NAr)(OTB)$_2$ (75 mg, 0.107 mmol). After 1 h, the reaction mixture was concentrated in vacuo, and the resulting orange solid was recrystallized from a minimal volume of pentane at −30 °C to give 44 mg of product as a yellow crystalline solid (60%): ^{1}H NMR δ 12.79 (s, 1, C*H*Si(OEt)Me$_2$), 7.31 (dd, 2, OTB), 7.06 (ddd, 2, OTB), 6.98 (dd, 2, OTB), 6.93 (s, 3, NAr), 6.84 (ddd, 2, OTB), 3.76 (q, 2, OC*H*$_2$CH$_3$), 3.75 (sept, 2, C*H*Me$_2$), 1.60 (s, 18, C*Me*$_3$), 1.04 (d, 12, CH*Me*$_2$), 0.87 (t, 3, OCH$_2$C*H*$_3$), 0.37 (s, 6, Si*Me*$_2$); ^{13}C NMR δ 255.9 (d, J_{CH} = 156, C$_\alpha$), 162.4, 148.5, 137.7, 128.7, 127.2, 126.5, 123.0, 121.8, 120.7, 61.1, 35.3, 30.3, 28.5, 24.1, 17.6, 1.6. Anal. Calcd for MoC$_{37}$H$_{55}$NO$_3$Si: C, 64.79; H, 8.08; N, 2.04. Found: C, 64.92; H, 8.11; N, 2.01.

Mo(CHSiMe$_3$)(NAr)(OTB)$_2$. A light orange solution of Mo(CHCMe$_2$Ph)(NAr)(OTB)$_2$ (20 mg, 0.028 mmol) in 5 mL of pentane was treated with vinyltrimethylsilane (13.2 μL, 0.085 mmol). After 1 h, the reaction mixture was concentrated in vacuo to give an orange oil. Efforts to crystallize this material failed. Analysis of the ^{1}H NMR spectrum of **5** revealed a 3:1 mixture of isomers (integrals are with respect to each isomer): ^{1}H NMR (major rotamer, toluene-d_8, 298 K) δ 13.24 (s, 1, C*H*SiMe$_3$), 7.28–6.86 (m, 9, aromatic), 6.76 (dd, 2, OTB), 3.64 (sept, 2, C*H*Me$_2$), 1.60 (s, 18, CC*Me*$_3$), 1.04 (d, 12, CH*Me*$_2$), 0.30 (s, 9, Si*Me*$_3$); ^{1}H NMR (minor rotamer, toluene-d_8) δ 12.65 (s, 1, C*H*SiMe$_3$), 7.32–6.84 (m, 9, aromatic), 6.72 (dd, 2, OTB), 3.56 (h, 2, C*H*Me$_2$), 1.60 (s, 18, CC*Me*$_3$), 0.98 (d, 12, CH*Me*$_2$), 0.23 (s, 9, Si*Me*$_3$); ^{1}H NMR (coalesced, toluene-d_8, 373 K) δ 13.25 (br s, 1, C*H*SiMe$_3$), 7.24 (d, 2, aromatic), 7.07–6.95 (m, 5, aromatic), 6.80 (d, 2, aromatic), 6.72 (d, 2, aromatic), 3.63 (sept, 2, C*H*Me$_2$), 1.53 (s, 18, CC*Me*$_3$), 1.03 (d, 12, CH*Me*$_2$), 0.24 (s, 9, Si*Me*$_3$).

Structure of Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$(PMe$_3$). Data were collected at −72 (1) °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 3717 reflections were collected, 3504 of which were unique (R_{int} = 0.077). The angular range ($2\theta_{min}$–$2\theta_{max}$) was 4.0–55.1°. Equivalent reflections were merged. The intensities of three representative reflections, which were measured after every 150 reflections, remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied). An absorption correction was applied (transmission factors 0.89–1.14). The structure was solved by direct methods.[25] Refinement was by full-matrix least squares based on 2436 reflections with use of TEXSAN. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions (d_{C-H} = 0.95 Å). Crystal data may be found in Table VII.

Structure of W(*trans*-CHCH=CHMe)(NAr)[OCMe(CF$_3$)$_2$]$_2$(quin). Data were collected at −78 (1) °C on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Of the 8684 reflections that were collected, 8507 were unique (R_{int} = 0.038). The angular range ($2\theta_{min}$–$2\theta_{max}$) was 4.0–55°. Equivalent reflections were merged. The intensities of three representative reflections, which were measured after every 60 min of X-ray exposure time, remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied). An absorption correction was applied (transmission factors 0.87–1.29). The structure was solved by direct methods.[25] Refinement was by full-matrix least squares based on 5423 reflections with use of TEXSAN. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions (d_{C-H} = 0.95 Å). Crystal data may be found in Table VII.

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Supplementary Material Available: Labeled drawings and tables of final positional parameters and anisotropic thermal parameters for *syn*-Mo(CH-*t*-Bu)(NAr)[OC(CF$_3$)$_2$]$_2$(PMe$_3$) and *anti*-W(*trans*-CHCH=CHMe)(NAr)[OCMe(CF$_3$)$_2$]$_2$(quin) (11 pages); listings of final observed and calculated structure factors (73 pages). Ordering information is given on any current masthead page.

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