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Investigations of Reactions between Chiral Molybdenum Imido Alkylidene Complexes and Ethylene: Observation of Unsolvated Base-Free Methylene Complexes, Metalacyclobutane and Metalacyclopentane Complexes, and Molybdenum(IV) Olefin Complexes

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In this paper we explore reactions between $^{13}CH_2{=}^{13}CH_2$ and the imido alkylidene complexes, Mo(NAr)(CHCMe$_2$Ph)[(*S*)-Biphen] (**3a**; NAr = N-2,6-i-Pr$_2$C$_6$H$_3$), Mo(NAr$_{Cl}$)(CHCMe$_3$)[(*S*)-Biphen] (**3b**; NAr$_{Cl}$ = N-2,6-Cl$_2$C$_6$H$_3$), Mo(NAd)(CHCMe$_2$Ph)[(*S*)-Biphen] (**3c**; NAd = N-1-adamantyl), Mo(NAr)(CHCMe$_2$Ph)[(*R*)-Benz$_2$Bitet] (**3d**), and Mo(NAr$_{Cl}$)(CHCMe$_2$Ph)[(*R*)-Benz$_2$Bitet] (**3e**). (See text for a description of Biphen and Benz$_2$Bitet.) Under a variety of conditions and for various combinations of imido, alkylidene, and diolate ligands, we have observed α-substituted molybdacyclobutanes Mo(NR)(*CH$_2$*CH$_2$CHCMe$_2$Ph)[diolate] (*C = ^{13}C), unsubstituted molybdacyclobutanes Mo(NR)(*CH$_2$*CH$_2$*CH$_2$)[diolate], olefin complexes Mo(NR)(*CH$_2$=CHR)[diolate] (R = H or CMe$_2$Ph), molybdacyclopentane complexes Mo(NR)(*CH$_2$*CH$_2$*CH$_2$*CH$_2$)[diolate], and base-free methylene complexes Mo(NR)(*CH$_2$)[diolate]. We also have crystallographically characterized a molybdenum ethylene complex derived from a biphenolate complex, Mo(N-2,6-Cl$_2$C$_6$H$_3$)(CH$_2$=CH$_2$)[*rac*-Biphen](Et$_2$O).

Introduction

In the last several years we have been interested in asymmetric olefin metathesis reactions[1] catalyzed by imido alkylidene complexes of molybdenum,[2−15] or more recently of tungsten,[16] that contain an enantiomerically pure biphenolate or binaphtholate ligand. Often at least one of the olefins in a metathesis reaction is a terminal olefin, in which case ethylene usually is generated during the reaction. During our studies we have found that the course and extent of some asymmetric metathesis reactions depend on the precise reaction conditions, namely whether ethylene is allowed to accumulate in the reaction vessel, or is allowed to escape. To understand what species are formed in the presence of ethylene, how they decompose, and whether a pathway back to an alkylidene can be devised, we have turned to studies that involve the addition of ^{13}C-labeled ethylene to neopentylidene or neophylidene complexes of the type Mo(NR)(CHR′)[diolate], where the diolate is a chiral binaphtholate or biphenolate.

The first investigations involved complexes **1a**−**c**.[6] Upon reaction with ethylene these systems quickly yielded unsubstituted trigonal bipyramidal molybdacyclobutane complexes through the reaction of unobserved intermediate methylene complexes with ethylene (cf. Scheme 1). These molybdacyclobutane species decomposed over time to yield some propylene through β-hydride rearrangement of unsubstituted molybdacyclobutane complexes. A deficiency of ethylene led to more rapid decomposition of molybdacyclobutane complexes as a consequence of bimolecular decomposition of

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(1) Schrock, R. R.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4592.

(2) Aeilts, S. L.; Cefalo, D. R.; Bonitatebus, P. J., Jr.; Houser, J. H.; Hoveyda, A. H.; Schrock, R. R. *Angew. Chem., Int. Ed.* **2001**, *40*, 1452.

(3) Hoveyda, A. H.; Schrock, R. R. *Chem. Eur. J.* **2001**, *7*, 945.

(4) Cefalo, D. R.; Kiely, A. F.; Wuchrer, M.; Jamieson, J. Y.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2001**, *123*, 3139.

(5) La, D. S.; Sattely, E. S.; Ford, J. G.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2001**, *123*, 7767.

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

(7) Hultzsch, K. C.; Bonitatebus, P. J., Jr.; Jernelius, J.; Schrock, R. R.; Hoveyda, A. H. *Organometallics* **2001**, *20*, 4705.

(8) Schrock, R. R.; Jamieson, J. Y.; Dolman, S. J.; Miller, S. A.; Bonitatebus, P. J., Jr.; Hoveyda, A. H. *Organometallics* **2002**, *21*, 409.

(9) Dolman, S. J.; Sattely, E. S.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **2002**, *124*, 6991.

(10) Kiely, A. F.; Jernelius, J. A.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 2868.

(11) Hultzsch, K. C.; Jernelius, J. A.; Hoveyda, A. H.; Schrock, R. R. *Angew. Chem., Int. Ed.* **2002**, 589.

(12) Tsang, W. C. P.; Jernelius, J. A.; Cortez, G. A.; Weatherhead, G. S.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 2591.

(13) Zhu, S. S.; Cefalo, D. R.; La, D. S.; Jamieson, J. Y.; Davis, W. M.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 8251.

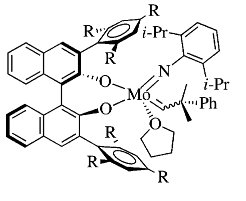
(14) Alexander, J. B.; La, D. S.; Cefalo, D. R.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1998**, *120*, 4041.

(15) Alexander, J. B.; Schrock, R. R.; Davis, W. M.; Hultzsch, K. C.; Hoveyda, A. H.; Houser, J. H. *Organometallics* **2000**, *19*, 3700.

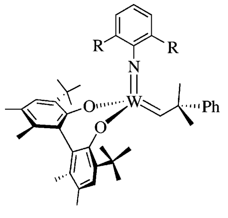
(16) Tsang, W. C. P.; Hultzsch, K. C.; Alexander, J. B.; Bonitatebus, P. J.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 2652.

10.1021/om030636+ CCC: $27.50

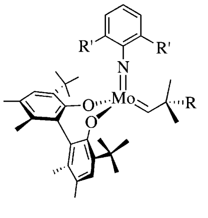
methylene complexes. But β-hydride rearrangement of the molybdacyclobutane also seemed to be *promoted* by ethylene. Therefore it appeared that too little *or* too much ethylene could lead to more rapid catalyst decomposition to Mo(IV) species.



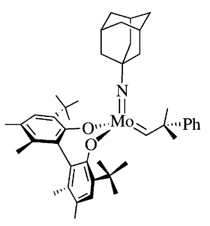
1a R = *i*-Pr
1b R = Me
1c R = H



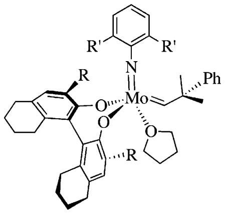
2a R = *i*-Pr
2b R = Me



3a R = Ph R' = *i*-Pr
3b R = Me R' = Cl



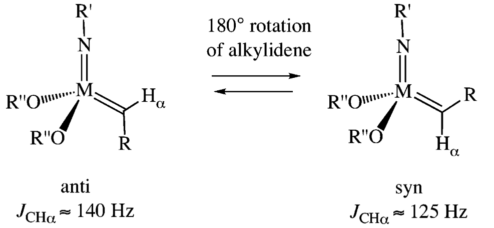
3c



3d R = $CHPh_2$ R' = *i*-Pr
3e R = $CHPh_2$ R' = Cl

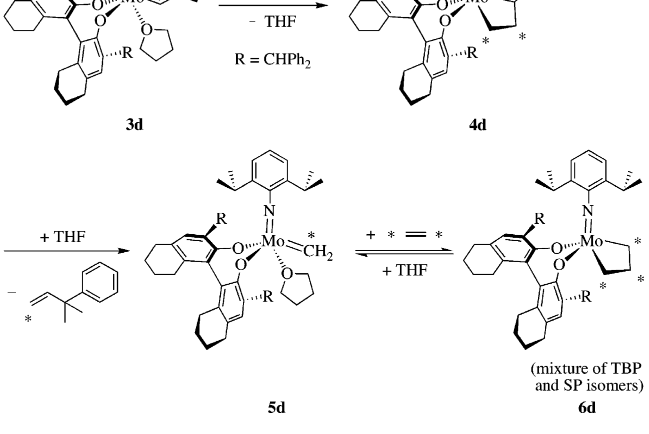
The second investigation involved complexes **2a** and **2b**.[16] Here reactions involving ^{13}C-labeled ethylene allowed observation of an unsubstituted tungstacyclobutane complex, an ethylene complex, an unsubstituted tungstacyclopentane complex, and a dimeric form of a methylene complex. This was the first time that a methylene species had been observed that did not contain a stabilizing base in systems of this general type, although the methylene ligand itself could be said to be a base, as the dimer contained asymmetrically bridging methylenes coupled to two tungsten centers.

In this paper we broaden our studies of this general type to nonbinaphtholate complexes of molybdenum through an exploration of reactions that involve the racemic or [(*S*)-Biphen]$^{2-}$ complexes **3a**, **3b**, and **3c**, and the [(*R*)-Benz$_2$Bitet]$^{2-}$ complexes **3d** and **3e**. Complex **3a** was the first asymmetric catalyst of this general type to be prepared,[14,15] while **3b** is a relatively recent addition to the collection of complexes in this class.[8] Complex **3c** is the only example of a metathesis catalyst in this family of imido alkylidene complexes that contains an alkylimido ligand.[12] The adamantylimido catalyst offers reactivity and selectivity profiles in asymmetric olefin metathesis that have not been observed with any previous arylimido catalyst. The unique reactivity of **3c** is believed to be the result of reactions proceeding exclusively through the syn isomer, in which the alkylidene substituent points toward the imido group, as opposed to the anti isomer, in which the alkylidene substituent points away from the imido group, as shown for a generic complex in eq 1. When the alkoxides are biphenolates or binaphtholates these isomers interconvert relatively rapidly (~100 s^{-1}) at room temperature.[15,17] Complexes **3d** and **3e** are two members of yet a third category of useful catalysts that contain hydrogenated binaphtholate-based ligands.[2] We report here that the biphenolate compounds **3a**–**e** react with $^{13}CH_2{=}^{13}CH_2$ to give observable metalacyclobutane complexes, base-free molybdenum methylene complexes, olefin complexes, and molybdacyclopentane complexes. We also report isolation of the first ethylene complex of a bis(alkoxide)molybdenum imido complex and an X-ray study of it.



(1)

Scheme 1. Formation of the Initial Molybdacyclobutane 4d and Its Transformation into Methylene Complex 5d and Unsubstituted Molybdacyclobutane 6d (*C = ^{13}C)



Results

Reactions of 3d or 3e with ^{13}C-Labeled Ethylene. Experiments typically consisted of addition of one, two, several, or many equivalents of ^{13}C-labeled ethylene to an alkylidene complex in toluene-d_8 and following the reaction progress by ^{13}C NMR over time. Addition of 2 equiv of $^{13}C_2H_4$ to Mo(NAr)(CHCMe$_2$Ph)[Benz$_2$Bitet] (**3d**, Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$, as a THF adduct) led to formation of the first metathesis product ($^{13}CH_2{=}CHCMe_2Ph$), and a mixture of three molybdenum complexes (Schemes 1 and 2), according to the ^{13}C NMR spectra of reaction mixtures. (For convenience the configuration of the ligand in each enantiomerically pure complex will not be stated explicitly in formulas in the text.) The first of these that we discuss is the unsubstituted molybdacyclobutane complex **6d** (Scheme 1). For **6d** two very broad resonances are observed at ~96 and ~4 ppm at 20 °C (Figure 1). Upon cooling the sample from 20 to −40 °C, the downfield resonance sharpened into two doublets at 98.68 ppm ($^1J_{CC} = 14.8$ Hz, $^1J_{CH} = 158.6$ Hz) and 96.44 ppm ($^1J_{CC} = 13.8$ Hz, $^1J_{CH} = 156.3$ Hz), while the upfield resonance sharpened into a pseudotriplet at 0.45 ppm ($^1J_{CC} = 14.8, 13.8$ Hz, $^1J_{CH} = 153.4$ Hz). On the basis of chemical shift and coupling values in analogous binaphtholate molybdacyclobutane complexes[6] and other tungsten-based meta-

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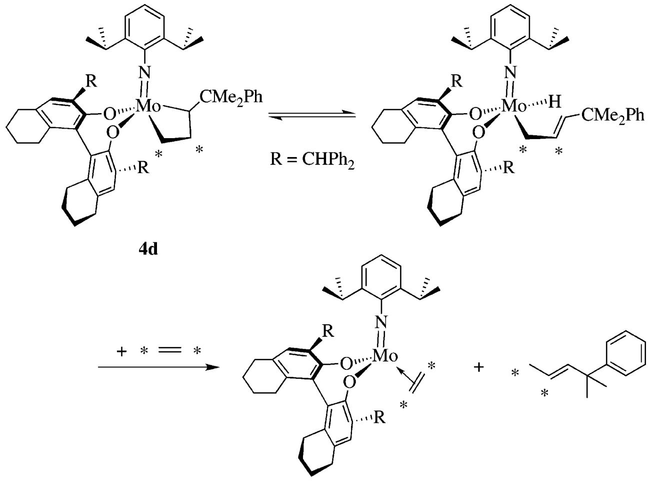
[17] Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1.

Table 1. Chemical Shift and Coupling Values for Unsubstituted Molybdenum Metalacyclobutane Complexes[a]

	^{13}C δ (ppm)	^{1}H δ (ppm)	$^{1}J_{CC}$ (Hz)	$^{1}J_{CH}$ (Hz)
Mo(NAr)($^{13}C_3H_6$)[Benz$_2$Bitet]	98.68 (98.55[c])	4.80,[c] 4.12[c]	14.83	158.6
(**6d**, TBP)[b]	96.44 (96.41[c])	4.40,[c] 4.40[c]	13.82	156.3
	0.45 (0.63[c])	0.22,[c] −0.31[c]	14.83, 13.82	153.4
Mo(NAr$_{Cl}$)($^{13}C_3H_6$)[Benz$_2$Bitet]	100.59 (100.05[c])	4.50,[c] 4.20[c]	14.68	160.9
(**6e**, TBP)[b]	98.90 (98.93[c])	4.52,[c] 4.11[c]	13.39	160.0
	0.40 (0.53[c])	0.17,[c] −0.25[c]	14.68, 13.39	153.7
Mo(NAd)($^{13}C_3H_6$)[Biphen]	42.38 (42.16[d])	2.75, 1.19	31.1[d]	125.6
(**6c**, SP)	37.72 (35.80[d])	2.62, 1.03	33.5[d]	138.0
	29.75 (31.23[d])	3.55, 2.77	32.1[d,e]	129.7

[a] All values are reported at 20 °C in toluene-d_8 unless otherwise stated; Ar = 2,6-i-$Pr_2C_6H_3$, Ar$_{Cl}$ = 2,6-$Cl_2C_6H_3$, Ad = 1-adamantyl. [b] Data are reported at −40 °C. [c] Data are reported at −20 °C. [d] Data are reported at −80 °C. [e] The average $^{1}J_{CC}$ value was reported due to the breadth of the triplet resonance.

Scheme 2. Rearrangement of Complex 4d by β-Hydride Elimination (*C = ^{13}C)



lacyclobutane complexes,[16,17] and extensive multidimensional NMR connectivity information, we assign the two downfield resonances to the α-carbons, and the upfield resonance to the β-carbon of an unsubstituted trigonal-bipyramidal molybdacyclobutane complex, Mo(NAr)($^{13}CH_2{}^{13}CH_2{}^{13}CH_2$)[Benz$_2$Bitet] (TBP-**6d**, Scheme 1 and Figure 1; NMR data are summarized in Table 1). At −40 °C, complex **6d** is entirely in its trigonal-bipyramidal (TBP) form. As the sample is warmed we propose that two things happen: the amount of a square-pyramidal form (SP-**6d**) increases and SP-**6d** and TBP-**6d** begin to interconvert before any significant amount of SP-**6d**, which we would expect to exhibit α- and β-carbon resonances in the range of 20−50 ppm,[17] is formed. Interconversion of SP-**6d** and TBP-**6d** takes place without loss of ethylene on the basis of the fact that the resonance for free ethylene (at 123 ppm) remains sharp between −40 and 20 °C. At 20 °C enough SP-**6d** is present to lead to broadening of the TBP-**6d** resonances and some shifting of them toward the 20−50 ppm region where both α- and β-carbon resonances would be found for SP-**6d**. These observations are similar to those observed in a tungsten biphenolate system,[16] although interconversion of fluxional isomers begins at much lower temperatures (−60 °C) in the tungsten system; consequently three relatively sharp weighted average resonances (for two α-carbons and one β-carbon) could be observed at 20 °C. Again ethylene loss is not part of the equilibration process.

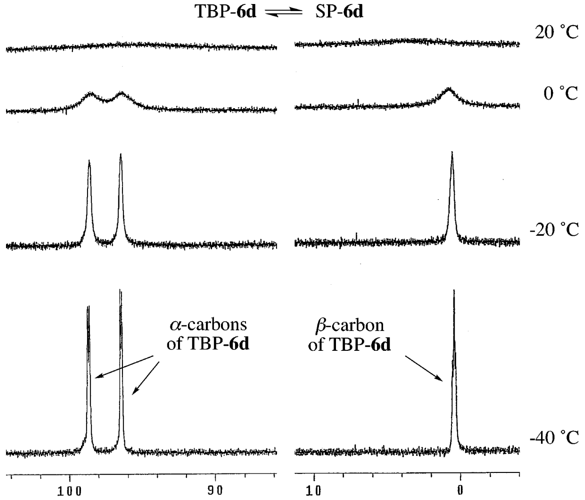


Figure 1. Variable-temperature ^{13}C NMR (125 MHz) spectra of Mo(NAr)($^{13}CH_2{}^{13}CH_2{}^{13}CH_2$) [Benz$_2$Bitet] (**6d**) in toluene-d_8. (Units are ppm; all temperatures are °C; TBP = trigonal bipyramidal; SP = square pyramidal.)

A second species that can be identified after addition of 2 equiv of $^{13}C_2H_4$ to **3d** is the initial molybdacyclobutane complex, **4d** (Scheme 1). Compound **4d** is characterized by two sets of sharp doublets at 48.4 and 44.2 ppm (Scheme 1 and Figure 2; see Table 2 for NMR details). The chemical shift values of the α- and β-carbon atoms in **4d** are more characteristic of a SP molybdacyclobutane than a TBP isomer.[17]

Complex **4d** disappears over a period of 36 h to give a third complex with sharp doublets at 66.4 and 58.6 ppm (Figure 2). On the basis of the chemical shift and coupling values,[18−20] and by comparison with other ethylene complexes to be described later, including a crystallographically characterized species, we propose that the third complex is a molybdenum(IV) ethylene adduct, **7d** (Scheme 2; see Table 3 for all NMR data). Since no propylene was observed **7d** did not form by rearrangement of **6d** to give a propylene complex followed by exchange of propylene for ethylene. On the other hand, the set of doublets at 121.5 ppm ($^{1}J_{CC}$ = 43.5 Hz, $^{1}J_{CH}$ = 149.4 Hz) and 18.5 ppm ($^{1}J_{CC}$ = 43.5 Hz, $^{1}J_{CH}$ = 125.6 Hz) suggested that *trans*-$^{13}CH_3{}^{13}CH$=CHCMe$_2$Ph (Scheme 2) had formed. (The correlated

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(18) Cameron, T. M.; Ortiz, C. G.; Ghiviriga, I.; Abboud, K. A.; Boncella, J. M. *Organometallics* **2001**, *20*, 2032.

(19) Ortiz, C. G.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1999**, *18*, 4253.

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

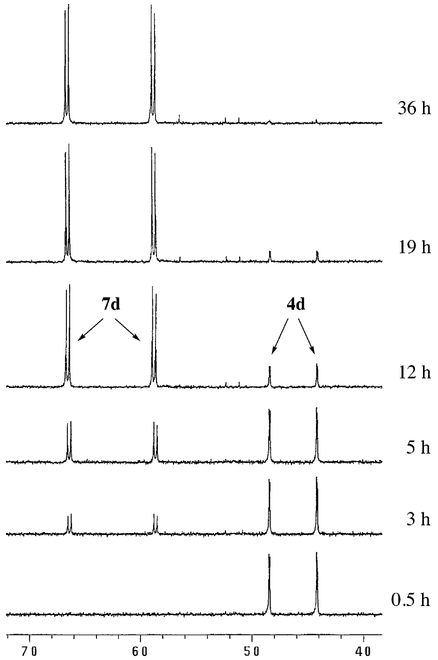


Figure 2. Expanded ^{13}C NMR (125 MHz) spectra of a sample that contains the initial molybdacyclobutane **4d** and the ethylene adduct **7d**. (Units are ppm.)

Table 2. Chemical Shift and Coupling Values for Initial Molybdacyclobutane Complexes[a]

	^{13}C δ (ppm)	^{1}H δ (ppm)	$^{1}J_{CC}$ (Hz)	$^{1}J_{CH}$ (Hz)
Mo(NAr)($^{13}CH_2{}^{13}CH_2CHR$)-	48.4	3.08, 1.14	10.94	137
[Benz$_2$Bitet] (**4d**)	44.2	2.66, 0.89	10.94	140
Mo(NAr)($^{13}CH_2{}^{13}CH_2CHR$)-	48.9	2.93, 0.74	11.66	138
[Biphen] (**4a**)	45.0	2.78, 0.82	11.66	138
Mo(NAd) ($^{13}CH_2{}^{13}CH_2CHR$)-	45.0	2.74, 0.89	11.67	138
[Biphen] (**4c**)	40.8	2.74, 0.73	11.67	140

[a] All values are reported at 20 °C in C_6D_6; Ar = 2,6-i-$Pr_2C_6H_3$, Ad = 1-adamantyl, R = CMe_2Ph.

Table 3. Chemical Shift and Coupling Values for Molybdenum Ethylene Complexes[a]

	^{13}C δ (ppm)	^{1}H δ (ppm)	$^{1}J_{CC}$ (Hz)	$^{1}J_{CH}$ (Hz)
Mo(NAr)($^{13}CH_2{=}^{13}CH_2$)-	66.4	3.11, 2.07	38.6	158.1
[Benz$_2$Bitet] (**7d**)	58.6	2.72, 0.93	38.6	154.4
Mo(NAr$_{Cl}$)($^{13}CH_2{=}^{13}CH_2$)-	66.9	3.47, 2.14	38.8	159.3
[Benz$_2$Bitet] (**7e**)	60.0	3.12, 1.12	38.8	155.4
Mo(NAr)($^{13}CH_2{=}^{13}CH_2$)-	61.2	3.15, 2.30	37.1	156.0
[Biphen] (**7a**)	60.9	3.28, 2.30	37.1	156.1
Mo(NAr$_{Cl}$)($^{13}CH_2{=}^{13}CH_2$)-	65.0	3.82, 3.03	39.7	158.2
[Biphen](THF) (**7b-THF**)	61.4	3.52, 2.85	39.7	155.8
Mo(NAd)($^{13}CH_2{=}^{13}CH_2$)-	61.5	3.33, 2.41	37.4	154.8
[Biphen] (**7c**)[b]	59.2	3.33, 2.41	37.4	154.3

[a] All values are reported at 20 °C in C_6D_6 unless otherwise stated; Ar = 2,6-i-$Pr_2C_6H_3$, Ar$_{Cl}$ = 2,6-$Cl_2C_6H_3$, Ad = 1-adamantyl. [b] Solvent is toluene-d_8.

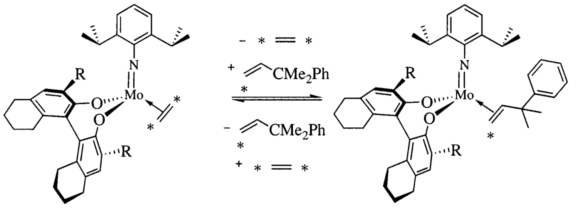
Table 4. Chemical Shift and Coupling Values for Substituted Olefin Complexes[a]

	^{13}C δ (ppm)	^{1}H δ (ppm)	$^{1}J_{CH}$ (Hz)
Mo(NAr)($^{13}CH_2{=}CHR$)-	58.2	3.20, 2.06	158, 148
[Biphen] (**8a**)			
Mo(NAd)($^{13}CH_2{=}CHR$)-	58.2	3.31, 2.26	157, 148
[Biphen] (**8c**)	55.4	2.76, 2.33	155, 152
Mo(NAr)($^{13}CH_2{=}CHR$)-	65.4 (65.2[b])	3.36, 2.46	159,[b] 153[b]
[Benz$_2$Bitet] (**8d**)	59.1	2.86, 2.38	161, 152
	56.5	3.22, 1.71	159, 146
Mo(NAr$_{Cl}$)($^{13}CH_2{=}CHCMe_3$)	64.1	3.06, 2.57	155
[Benz$_2$Bitet] (**8e**)	55.6	2.49, 2.19	154
	54.9	3.60, 1.99	159, 146

[a] All values are reported at 20 °C in C_6D_6 unless otherwise stated; Ar = 2,6-i-$Pr_2C_6H_3$, Ar$_{Cl}$ = 2,6-Cl $_2C_6H_3$, Ad = 1-adamantyl, R = CMe_2Ph. [b] Data are reported at 5 °C in C_6D_6.

proton for the carbon at 121.5 ppm was located at 5.4 ppm, suggesting that the olefin was internal as opposed to terminal. The other possible rearrangement product from **4d**, $^{13}CH_2{=}^{13}CHCH_2CMe_2Ph$, was not observed.) Quantitative analyses, via GLC/FID and GLC/MS, of the vacuum transferred organic fractions suggested that the ratio of the first metathesis product ($^{13}CH_2{=}CHCMe_2Ph$, Scheme 1) to *trans*-$^{13}CH_3{}^{13}CH{=}CHCMe_2Ph$ (Scheme 2) was 8.7:1. Therefore only ~10% of **4d** decomposes to give **7d** and *trans*-$^{13}CH_3{}^{13}CH{=}CHCMe_2Ph$, presumably via a β-hydride rearrangement process, one possible version of which is shown in Scheme 2. Approximately 90% of **4d** decomposes to give $^{13}CH_2{=}CHCMe_2Ph$ and **5d** (Scheme 1); **5d** can be observed under some conditions, as explained in a later section. Compound **5d** then either is captured by ethylene to give **6d** or decomposes bimolecularly to give **7d** and possibly other unidentified products.

Addition of only one equivalent of $^{13}C_2H_4$ to **3d** led to formation of the initial molybdacyclobutane **4d**, the ethylene adduct **7d**, and three diastereomers of the substituted olefin adduct, Mo(NAr)($^{13}CH_2{=}CHCMe_2Ph$)-[Benz$_2$Bitet] (**8d**, eq 2; see Table 4 for NMR data). Three diastereomers of **8d** out of the four possible give rise to three singlets at 65.4, 59.1, and 56.5 ppm in the ^{13}C NMR spectrum. Coupling values in **8d** are similar to those observed in ethylene complexes (Table 3). Under these conditions (1 equiv of ethylene) some of the **4d** that is formed decomposes to give either $^{13}CH_2{=}CHCMe_2$-Ph and **5d** (Scheme 1) or $^{13}CH_3{}^{13}CH{=}CHCMe_2Ph$ (Scheme 2). Since $^{13}CH_2{=}CHCMe_2Ph$ remains in solution and the system is starved for ethylene, $^{13}CH_2{=}CHCMe_2Ph$, the next most strongly binding olefin present, eventually replaces ethylene (eq 2). Propylene, the product of rearrangement of **6d**, was not observed in this experiment. In view of the observation of unsubstituted molybdacyclopentane complexes (to be described later), compounds **7d** and **8d** almost certainly interconvert in reactions that are bimolecular in Mo and olefin, and that may or may not involve molybdacyclopentane complexes as intermediates.



7d (*C = ^{13}C; R = $CHPh_2$) **8d**

(2)

Addition of 5 equiv of $^{13}C_2H_4$ to **3d** immediately led to a mixture of **6d** and **7d**. Propylene and what appears to be cyclopropane (^{13}C δ −2.4, ^{1}H δ 0.14, $^{1}J_{CH}$ = 161 Hz)[21,22] were both observed and quantitated by ^{1}H NMR integration. Propylene was observed in ~16% yield, while cyclopropane amounted to <1%. The unsubstituted molybdacyclopentane complex Mo(NAr)($^{13}CH_2$-$^{13}CH_2{}^{13}CH_2{}^{13}CH_2$)[Benz$_2$Bitet] (**9d**) was observed in 30% yield after 36 h. A small amount of 1-butene (~8%) was

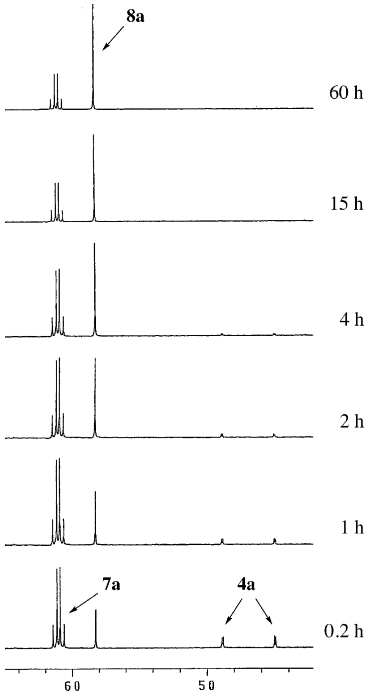


Figure 3. Expanded ^{13}C NMR (125 MHz) spectra of the initial molybdacyclobutane **4a**, the ethylene adduct **7a**, and the olefin complex **8a**. (Units are ppm.)

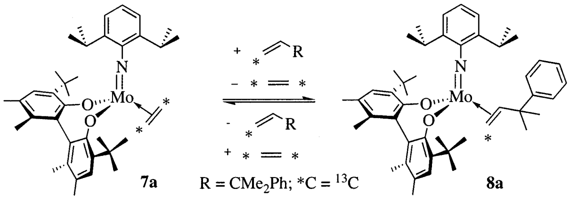
also observed. Complex **9d** was quantitatively converted to **7d** upon removing ethylene from solution in vacuo. Molybdacyclopentane complexes will be described in more detail in a later section.

An initial molybdacyclobutane complex (analogous to **4d**) was not observed when 2 equiv of $^{13}C_2H_4$ were added to complex **3e**. Broad resonances characteristic of the unsubstituted molybdacyclobutane complex, Mo(NAr$_{Cl}$)($^{13}CH_2{}^{13}CH_2{}^{13}CH_2$)[Benz$_2$Bitet] (**6e**), and sharp doublets characteristic of the ethylene adduct, Mo(NAr$_{Cl}$)($^{13}CH_2$═$^{13}CH_2$)[Benz$_2$Bitet] (**7e**), were observed. The broad resonances for **6e** sharpen at −40 °C to give a pattern analogous to that shown in Figure 1 characteristic of a TBP complex. Only the first metathesis product ($^{13}CH_2$═CHCMe$_2$Ph) was detected; no traces of *trans*-$^{13}CH_3{}^{13}CH$═CHCMe$_2$Ph or propylene were found. The chemical shift and coupling values of **6e** and **7e** are similar to those of **6d** and **7d**, respectively; all NMR data are summarized in Tables 1 and 3.

When 6 equiv of $^{13}C_2H_4$ were added to **3e**, propylene was observed in ∼5% yield; no cyclopropane was detected. The major product was the ethylene adduct **7e**, with the unsubstituted molybdacyclopentane complex Mo(NAr$_{Cl}$)($^{13}CH_2{}^{13}CH_2{}^{13}CH_2{}^{13}CH_2$)[Benz$_2$Bitet] (**9e**) amounting to <2%. Higher concentrations of ethylene promoted the formation of more **9e**. Molybdacyclopentane complexes will be described in more detail in a later section.

Three diastereomers of Mo(NAr$_{Cl}$)($^{13}CH_2$═CHCMe$_3$)[Benz$_2$Bitet] (**8e**) were observed along with ethylene adduct **7e** when 1 equiv of $^{13}C_2H_4$ was added to **3e**. Propylene was not observed in this experiment. Formation of almost exclusively **7e** in the presence of 6 equiv of ethylene is consistent with replacement of the olefin in **8e** with ethylene in the presence of sufficient ethylene.

Reactions of 3a, 3b, or 3c with ^{13}C-Labeled Ethylene. When a stoichiometric amount of $^{13}C_2H_4$ was added to **3a**, two doublets were observed at 48.9 and 45.0 ppm in the ^{13}C NMR spectrum (Figure 3). These doublets were ascribed to the initial molybdacyclobutane complex, Mo(NAr)($^{13}CH_2{}^{13}CH_2$CHCMe$_2$Ph)[Biphen] (**4a**), on the basis of the similarity of chemical shift and coupling values with those for **4d** (Table 2). Complex **4a** disappeared over a period of 2 h to give a mixture of the ethylene adduct, Mo(NAr)($^{13}CH_2$═$^{13}CH_2$)[Biphen] (**7a**), and one diastereomer of olefin complex, Mo(NAr)($^{13}CH_2$═CHCMe$_2$Ph)[Biphen] (**8a**; Figure 3); unreacted **3a** (16%) was still observed by ^1H NMR integration. The singlet at 58.2 ($^1J_{CH}$ = 158, 148 Hz) ppm in the ^{13}C NMR spectrum was attributed to **8a**, and a set of overlapping doublets at 61.2 and 60.9 ppm to Mo(NAr)($^{13}CH_2$═$^{13}CH_2$)[Biphen] (**7a**, eq 3). The ethylene resonance for **7a** is an AB quartet in this case since the resonances for the two carbons are relatively close to one another. The intensity of the singlet for **8a** gradually increased over 60 h at the expense of **7a** and **4a**. Olefin complex **8a** was formed in 40% yield eventually, leaving 60% of **7a**. No trace of an unsubstituted molybdacyclobutane complex or propylene was observed.



(3)

Addition of 2 equiv of $^{13}C_2H_4$ to **3a** yielded only **7a**. Traces of propylene (^{13}C δ 134, 116, and 20 ppm) were observed. A similar experiment was performed with unlabeled ethylene in the presence of an internal standard, 1,4-dimethoxybenzene. On the basis of ^1H NMR integration, we conclude that **7a** was formed quantitatively (>99%) and propylene was formed in <2% yield. All attempts to isolate **7a** failed, in part because the ethylene ligand is replaced by the first metathesis product ($^{13}CH_2$═CHCMe$_2$Ph) upon concentration of the mixture in vacuo, resulting in an equilibrium mixture of **7a** and **8a** (eq 3). Similar behavior was observed for **7d** and **8d**, as noted above (eq 2).

Addition of 2 equiv of $^{13}C_2H_4$ to **3b**-THF yielded only Mo(NAr$_{Cl}$)($^{13}CH_2$═$^{13}CH_2$)[Biphen](THF) (**7b**-THF). Compound **7b**-THF was formed quantitatively (according to ^1H NMR integration) in all cases. Compound **7b**-THF is relatively stable in both the presence or absence of excess ethylene. No substituted olefin complex analogous to **8a** or **8d** was observed. Well-separated doublets for the ethylene ligand were observed initially at 60.9 and 64.6 ppm (Figure 4a). After removing all volatile components and dissolving the sample in fresh benzene-d_6, the doublets shifted downfield in the ^{13}C NMR spectrum (Figure 4b). The doublets shifted further downfield when the process was repeated (Figure 4c), but no further shift was observed when the process was repeated a third time. We propose that the ethylene

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(21) Aitken, R. A.; Hodgson, P. K. G.; Morrison, J. J.; Oyewale, A. O. *J. Chem. Soc., Perkin Trans.* **2002**, 402.

(22) Rol, N. C.; Clague, A. D. H. *Org. Magn. Reson.* **1981**, *16*, 187.

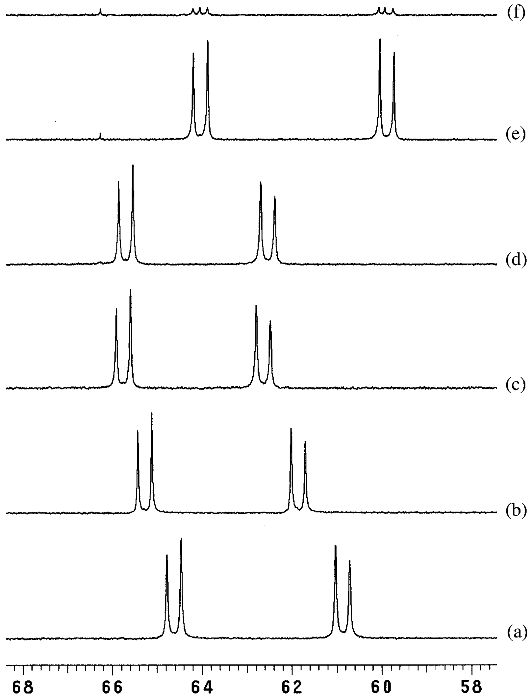

Figure 4. Effect of solvent coordination and ethylene exchange on the ^{13}C NMR spectrum of **7b**-THF. (Units are ppm.) (a) Addition of 3 equiv of $^{13}CH_2{=}^{13}CH_2$; (b) all volatiles removed (first cycle); (c) all volatiles removed (second cycle); (d) addition of 3.5 equiv of diethyl ether; (e) addition of 4.2 equiv of THF; (f) exposed to 1 atm of $^{12}CH_2{=}^{12}CH_2$.

adduct is free of THF at that point. Addition of 3.5 equiv of diethyl ether to the sample resulted in only a slight upfield shift (Figure 4d), whereas addition of 4.2 equiv of THF shifted the doublets upfield to 64.03 and 59.88 ppm (Figure 4e). The labeled ethylene largely disappeared upon exposure of the sample to unlabeled ethylene (Figure 4f). These results are consistent with a facile equilibrium between **7b**-THF and **7b**, and ready replacement of labeled ethylene with unlabeled ethylene, as we would expect on the basis of what was observed as shown in eqs 2 and 3, and molybdacyclopentane formation to be described in detail below.

When 1 equiv of $^{13}C_2H_4$ was condensed into a sample of **3c**, a mixture of a short-lived initial molybdacyclobutane (**4c**, $t_{1/2} \approx 30$ min), analogous to complexes **4d** and **4a**, and a complex characterized by a broad resonance at 60.4 ppm in the ^{13}C NMR spectrum was formed. As free ethylene was essentially fully consumed in the first 30 min, the broad resonance gradually separated into two sharp doublets at 61.5 and 59.2 ppm, which we can ascribe to the ethylene adduct (**7c**). Broadening of the resonances for **7c** in the presence of ethylene and sharpening of them as ethylene was consumed is consistent with dynamic exchange of the coordinated ethylene with free ethylene, again probably through an unobservable intermediate bis(ethylene) or an observable (vide infra) metalacyclopentane complex. Resonances for the substituted olefin complex, Mo(NAd)($^{13}CH_2{=}^{13}CHR$)[Biphen] (**8c**, R = CMe$_2$Ph), grew in relatively slowly over 36 h; a comparable intensity for **8a** was reached in 4 h. Only two of the four possible diastereomers of **8c** were observed, with the resonance for the major diastereomer found at 58.2 ppm in the ^{13}C NMR spectrum and the minor diastereomer at 55.4 ppm. Chemical shift and coupling values for both diastereomers are summarized (along with others) in Table 4. Propylene was not observed in this experiment.

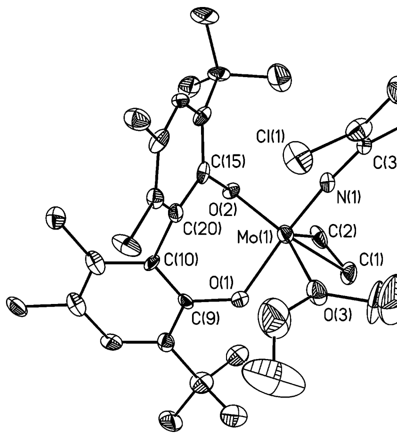

Figure 5. Thermal ellipsoid drawing of *rac*-**7b**-Et$_2$O. Thermal ellipsoids are displayed at the 50% probability level. Hydrogen atoms were omitted for clarity.

When 2 equiv of $^{13}C_2H_4$ were added to **3c**, four broad resonances were observed at 60.35, 42.38, 37.72, and 29.75 ppm in the ^{13}C NMR spectrum at 20 °C. The 60.35-ppm resonance was ascribed to Mo(NAd)($^{13}CH_2{=}^{13}CH_2$)[Biphen] (**7c**) on the basis of its chemical shift, although its identity could not be confirmed without further investigation as detailed in the section on molybdacyclopentane complexes. At −80 °C, two broad doublets and a well-defined pseudotriplet were observed at 42.16, 35.80, and 31.23 ppm, respectively. They were assigned to an SP-unsubstituted molybdacyclobutane complex, Mo(NAd)($^{13}CH_2{}^{13}CH_2{}^{13}CH_2$)[Biphen] (**6c**, Table 1). Only traces of propylene (<2%) were observed when **6c** was fully converted to **7c**, which suggests that **6c** loses ethylene to yield Mo(NAd)($^{13}CH_2$)[Biphen], which then yields **7c** upon bimolecular decomposition and coordination of additional ethylene.

X-ray Structure of Mo(NAr$_{Cl}$)($^{13}CH_2{=}^{13}CH_2$)[*rac*-Biphen](Et$_2$O) (*rac*-7b-Et$_2$O). It should be noted that **3b** is the only species discussed here that contains a neopentylidene ligand instead of a neophylidene ligand. A subtle but potentially significant difference between the outcome of reactions involving neophylidene and neopentylidene complexes and ethylene is the volatility of the initial metathesis products, CH$_2$=CHCMe$_2$Ph and CH$_2$=CHCMe$_3$, respectively. The volatility of CH$_2$=CHCMe$_3$ is perhaps a factor that allows **7b**-THF to be isolated from THF in a 60% yield on a 1.75-g scale by simply removing all volatile components in vacuo. Slow diffusion of diethyl ether into a concentrated toluene solution of *rac*-**7b**-THF at −25 °C yielded red single crystals of the diethyl ether adduct Mo(NAr$_{Cl}$)($^{13}CH_2{=}^{13}CH_2$)[*rac*-Biphen](Et$_2$O) (*rac*-**7b**-Et$_2$O). (Since only 1 equiv of THF is present an excess of ether resulted in formation and crystallization of the ether adduct instead of the THF adduct.) An X-ray study was carried out and revealed the structure shown in Figure 5. Crystal data can be found in Table 5, and selected

Table 5. Crystal Data and Structure Refinement for *rac*-7b-Et_2O[a]

empirical formula	$MoC_{36}H_{49}Cl_2NO_3$
fw	710.60
temp	183(2) K
wavelength	0.71073 Å
cryst syst	orthorhombic, *Pbca*
a	20.086(9) Å
b	17.150(7) Å
c	20.086(9) Å
$\alpha = \beta = \gamma$	90°
vol, *Z*	6919(5) Å^3, 8
density (calcd)	1.364 Mg/m^3
abs coeff	0.569 mm^{-1}
F(000)	2976
cryst size	0.15 × 0.13 × 0.08
θ range for data collection	2.03−20.00°
index ranges	$-18 \leq h \leq 19$, $-9 \leq k \leq 16$, $-19 \leq l \leq 18$
no. of reflns collected	19184
no. of independent reflns	3229 [$R_{int} = 0.0834$]
completeness to θ	99.9%
data/restraints/parameters	3229/0/395
goodness-of-fit on F^2	1.287
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0773, wR2 = 0.1384
R indices (all data)	R1 = 0.0837, wR2 = 0.1407
extinction coeff	0.0003(4)
largest diff peak and hole	0.529 and −0.894 e·Å^{-3}

[a] No absorption correction was applied, and the refinement method was full-matrix least-squares on F^2.

Table 6. Selected Bond Distances (Å) and Angles (deg) in *rac*-7b-Et_2O

Mo(1)−C(1)	2.204(9)	N(1)−Mo(1)−C(1)	95.8(4)
Mo(1)−C(2)	2.128(9)	N(1)−Mo(1)−C(2)	97.8(4)
Mo(1)−N(1)	1.723(7)	N(1)−Mo(1)−O(1)	163.7(3)
Mo(1)−O(1)	1.958(6)	N(1)−Mo(1)−O(2)	101.3(3)
Mo(1)−O(2)	2.008(6)	N(1)−Mo(1)−O(3)	87.4(4)
Mo(1)−O(3)	2.307(6)	O(1)−Mo(1)−O(2)	90.0(2)
C(1)−C(2)	1.400(13)	O(1)−Mo(1)−O(3)	77.6(3)
C(1)−C(2)−Mo(1)	74.1(6)	O(1)−Mo(1)−C(1)	89.2(3)
C(2)−C(1)−Mo(1)	68.2(5)	O(1)−Mo(1)−C(2)	95.6(3)
C(3)−N(1)−Mo(1)	169.4(7)	O(2)−Mo(1)−O(3)	154.8(2)
C(1)−Mo(1)−O(3)	84.7(3)	O(2)−Mo(1)−C(2)	80.2(3)
C(2)−Mo(1)−O(3)	122.3(3)	C(9)−C(10)−C(20)−C(15)	70.6(12)

bond distances and angles in Table 6. The complex is essentially a trigonal bipyramid with O(2), O(3), and the center of the ethylene ligand occupying equatorial positions. The similarity of the bond distances between Mo and the two ethylene carbon atoms (Mo−C(1) = 2.204(9) Å; Mo−C(2) = 2.128(9) Å) suggests that the ethylene is symmetrically bound, as expected. The C(1)−C(2) bond distance (1.400(13) Å) is similar to the value observed in a tungsten ethylene complex, W(NPh)[*o*-$(Me_3SiN)_2C_6H_4$]$(PMe_3)_2(CH_2{=}CH_2)$ (1.434(6) Å), a rare related ethylene complex of W(IV).[23] The C(9)−C(10)−C(20)−C(15) dihedral angle in the intact biphenolate backbone is 70.6(12)°. This value is considerably smaller than the dihedral angle observed in the parent complex (**3b**-THF, 80°);[8] it is also smaller than the dihedral angles typically observed in other four-coordinate imido alkylidene complexes (which range from 78° to 103° [7,8,12,15]) or that observed in Mo(NAr_{Cl})($CHCMe_3$)[Biphen](THF)[8] (80°), in which the imido and neopentylidene ligands occupy equatorial positions. Complex **7b**-Et_2O is the only crystallographically characterized ethylene complex derived from a molybdenum imido bisalkoxide alkylidene compound.

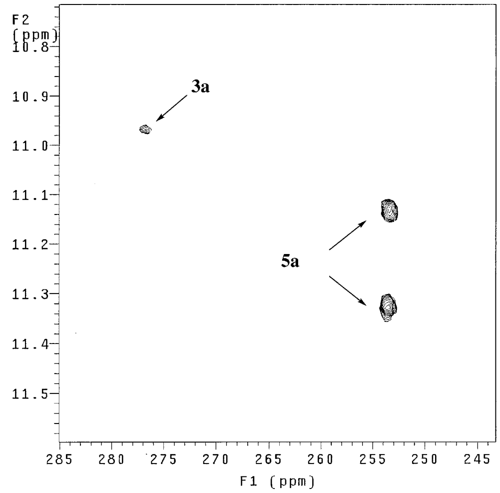

Figure 6. Expanded $^1H-^{13}C$ HMQC spectrum of **3a** and Mo(NAr)($^{13}CH_2$)[Biphen] (**5a**).

Table 7. Chemical Shift and Coupling Values for Molybdenum Methylene Complexes[a]

	^{13}C δ (ppm)	^1H δ (ppm)	$^1J_{CH}$ (Hz)
Mo(NAr)($^{13}CH_2$)[Biphen] (**5a**)	253.5	11.33	134
		11.13	163
Mo(NAd)($^{13}CH_2$)[Biphen] (**5c**)	253.7	11.27	137
		11.13	157
Mo(NAr)($^{13}CH_2$)[$Benz_2Bitet$](THF) (**5d**)	275.3	12.48	140
		12.22	161

[a] All values are reported at 20 °C in C_6D_6; Ar = 2,6-*i*-$Pr_2C_6H_3$, Ad = 1-adamantyl.

Observation of Molybdenum Methylene Complexes. Investigations involving $^1H-^{13}C$ HMQC experiments on complexes **7a**, **8a**, and **4a** revealed a species with a strong ^{13}C signal at 253.5 ppm, a chemical shift that is typical for an alkylidene carbon in complexes of this type.[17,24,25] Two protons at 11.33 ($^1J_{CH}$ = 134 Hz) and 11.13 ($^1J_{CH}$ = 163 Hz) ppm were found to be through-bond coupled to the carbon giving rise to the resonance at 253.5 ppm (Figure 6); the only other alkylidene species observed in these experiments was the unreacted neophylidene complex (**3a**). We propose that the new species is an unsolvated molybdenum methylene complex, Mo(NAr)($^{13}CH_2$)[Biphen] (**5a**). The $^1J_{CH}$ coupling values (see Table 7 for NMR data) are comparable to previously observed base adducts of imido methylene complexes of molybdenum or tungsten.[20,26−28] Unlike base adducts of tungsten methylene complexes, which are relatively stable, **5a** is short-lived and highly reactive; only a trace amount (~0.6%) was present according to ^1H NMR integration. The ^{13}C resonance of **5a** can be detected only in $^1H-^{13}C$ HMQC experiments, with an acquisition time of 9 ms per scan, in the first 2 h immediately after the addition of a stoichiometric amount of $^{13}C_2H_4$ to *rac*- or (*S*)-**3a**.[29] Although the

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(23) Wang, S. S.; VanderLende, D. D.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1998**, *17*, 2628.

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

(25) Oskam, J. H.; Fox, H. H.; Yap, K. B.; McConville, D. H.; O'Dell, R.; Lichtenstein, B. J.; Schrock, R. R. *J. Organomet. Chem.* **1993**, *459*, 185.

(26) Schrock, R. R.; DePue, R.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423.

(27) Fox, H. H.; Lee, J.-K.; Park, L. Y.; Schrock, R. R. *Organometallics* **1993**, *12*, 759.

(28) Feldman, J.; Davis, W. M.; Thomas, J. K.; Schrock, R. R. *Organometallics* **1990**, *9*, 2535.

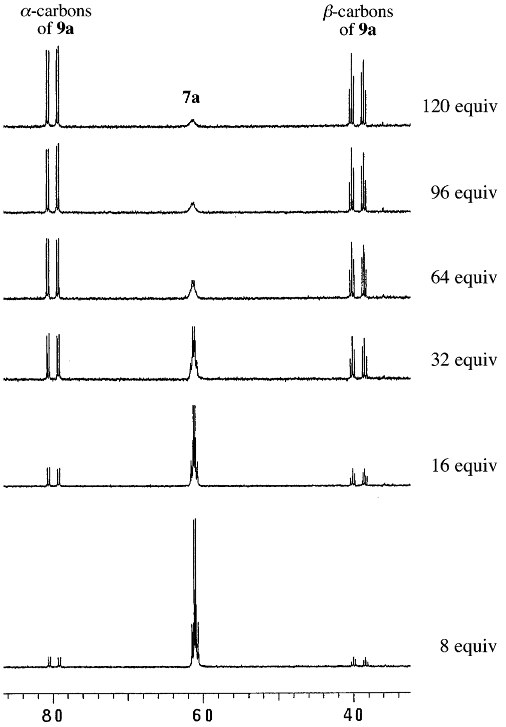


Figure 7. Conversion of ethylene adduct **7a** to unsubstituted molybdacyclopentane **9a** in the presence of increasing amounts of ethylene. (Units are ppm.)

concentration of **5a** was only ~0.04 times that of unreacted **3a** (16%), the intensity of the HMQC signals for **5a** were significantly stronger than those of unreacted **3a** at 277 ppm, clearly showing that the methylene carbon in **5a** is ^{13}C-labeled (Figure 6). The low concentration of **5a** is in part a consequence of its rapid bimolecular decomposition to yield the ethylene adduct **7a**. To the best of our knowledge complex **5a** is the first solvent- and base-free molybdenum methylene complex in the family of imido alkylidene bisalkoxide complexes to be observed.

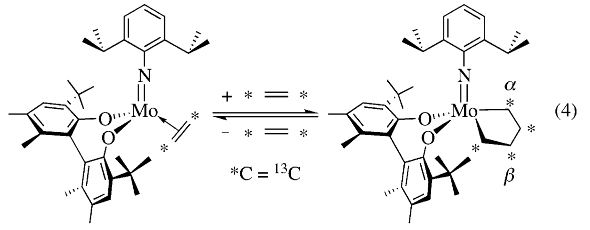
Addition of a stoichiometric amount of $^{13}C_2H_4$ to *rac*- or (*S*)-**3c** allowed a second base-free molybdenum-methylene complex, Mo(NAd)($^{13}CH_2$)[Biphen] (**5c**), to be observed within the first hour. Chemical shift and coupling values of complex **5c** were very similar to those of **5a** (Table 7).

When a sample of **3d** was exposed to 1 equiv of $^{13}C_2H_4$, a third molybdenum methylene complex, Mo(NAr)($^{13}CH_2$)[Benz$_2$Bitet](THF) (**5d**), was observed. The molybdenum methylene carbon was located at 275.3 ppm, and its through-bond coupled protons were observed at 12.48 and 12.22 ppm. The proton resonances were approximately 1 ppm downfield from those observed in **5a** or **5c**, consistent with the effect of THF coordination in many previously observed imido alkylidene complexes.[1,17,30] Complex **5d** was slightly longer lived than base-free methylene complexes; it was still observable after 3 h with its intensity being strongly dependent on the initial concentration of **3d**.

No methylene complexes were observed when 1 equiv, or a substoichiometric amount, of $^{13}C_2H_4$ was added to **3b**-THF or **3e**.

Observation of Unsubstituted Molybdacyclopentane Complexes. In previous sections we alluded several times to the formation of molybdacyclopentane complexes upon reaction of ethylene complexes with ethylene. This type of behavior has been observed when ethylene is added to the tungsten species **2a** or **2b**.[16] Tungsten also was found to be a catalyst for the slow catalytic formation of 1-butene from ethylene, with tungstacyclopentane complexes being observed during this reaction. In this section we elaborate on the formation of molybdacyclopentane complexes from ethylene complexes and ethylene.

As noted earlier, ethylene complex **7a** is formed quantitatively when 2−4 equiv of ethylene are added to **3a**. Addition of 8 equiv of $^{13}C_2H_4$ to **3a** produced a mixture of **7a** and a complex characterized by two sets of doublets at 80.5 ppm ($^1J_{CC}$ = 35.4 Hz, $^1J_{CH}$ = 129.5 Hz) and 79.1 ppm ($^1J_{CC}$ = 35.0 Hz, $^1J_{CH}$ = 129.8 Hz), and two sets of triplets at 40.0 ppm ($^1J_{CC}$ = 35.0, 33.9 Hz, $^1J_{CH}$ = 125.5 Hz) and 38.4 ppm ($^1J_{CC}$ = 35.4, 33.9 Hz, $^1J_{CH}$ = 125.6 Hz), in the ^{13}C NMR spectrum (Figure 7). The doublets were assigned to the α-carbons, and the triplets to the *β*-carbons, in the unsubstituted molybdacyclopentane complex Mo(NAr)($^{13}CH_2{}^{13}CH_2{}^{13}CH_2{}^{13}CH_2$)[Biphen] (**9a**, eq 4). These assignments are consistent with connectivity information obtained from multidimensional NMR spectroscopy experiments. Propylene and cyclopropane were both observed in ~15% yield by ^{1}H NMR integration. A higher concentration of ethylene promoted further conversion of **7a** to **9a**. For example, only 6% of **9a** was observed when 8 equiv of ethylene were added to **3a** (Figure 7). In the presence of 120 equiv of ethylene, complex **9a** was obtained in 61% yield and the resonances for ethylene adduct **7a** were significantly broadened in both ^{1}H and ^{13}C NMR spectra. We attribute the broadening of the resonances for **7a** to an ethylene dependent exchange between free and coordinated ethylene. However, since ethylene is in large excess, no significant broadening of the ethylene resonance was observed. Conversion of **7a** to **9a** was fully reversible. Compound **7a** was recovered quantitatively upon degassing any mixture of **7a** and **9a**. Dimerization of ethylene to 1-butene via **9a** was not observed even in the presence of 120 equiv of ethylene. In summary, the main points are that (i) the ethylene complex (**7a**) readily adds ethylene reversibly to give a molybdacyclopentane complex (**9a**); (ii) since the resonances for **9a** are not broadened in the presence of a large excess of ethylene, the intermediate in the relatively rapid ethylene dependent exchange between free and coordinated ethylene is not the molybdacyclopentane complex; and (iii) 1-butene is not formed readily by a *β*-hydride rearrangement of the molybdacyclopentane complex. Whether **9a** is a square-pyramidal or a



(4)

7a **9a**

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

(30) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145.

Table 8. Chemical Shift and Coupling Values for Unsubstituted Molybdenum Metalacyclopentane Complexes[a]

	^{13}C δ (ppm)	^{1}H δ (ppm)	$^{1}J_{CC}$ (Hz)	$^{1}J_{CH}$ (Hz)
Mo(NAr)($^{13}C_4H_8$)-[Biphen] (**9a**)	80.5	4.08, 3.10	35.4	129.5
	79.1	3.62, 2.86	35.0	129.8
	40.0	2.66, 2.66	35.0, 33.9	125.5
	38.4	2.82, 2.57	35.4, 33.9	125.6
Mo(NAd)($^{13}C_4H_8$)-[Biphen] (**9c**)	81.8	3.60, 3.27	36.0	129.5
	69.9	3.48, 3.03	35.4	132.8
	41.7	2.85, 2.85	36.0, 34.7	125.0
	38.4	2.73, 2.53	35.4, 34.7	125.2
Mo(NAr)($^{13}C_4H_8$)-[Benz$_2$Bitet] (**9d**)	84.3	3.49, 3.38	36.0	127.6
	73.5	3.49, 2.85	35.4	131.9
	40.8	2.86, 2.48	36.0, 33.7	127.0
	37.3	2.63, 2.34	35.4, 33.7	127.0
Mo(NAr$_{Cl}$)($^{13}C_4H_8$)-[Benz$_2$Bitet] (**9e**)	94.5	3.41, 3.12	36.3	128.9
	76.0	3.83, 2.91	35.4	133.8
	41.9	2.97, 2.40	36.3, 34.6	128.2
	38.0	2.82, 2.19	35.4, 34.6	126.8

[a] All values are reported at 20 °C in C_6D_6; Ar = 2,6-i-$Pr_2C_6H_3$, Ar$_{Cl}$ = 2,6-$Cl_2C_6H_3$, Ad = 1-adamantyl.

trigonal-bipyramidal species cannot be determined on the basis of the data in hand. We also have no information about the structure of the nonmetalacyclic intermediate, “Mo(NAr)(C_2H_4)$_2$[Biphen]”, in the ethylene exchange process.

No molybdacyclopentane complex was detected when a huge excess of ethylene was added to complex **7b**-THF, presumably because THF is a much better donor than ethylene, thus preventing coordination of a second ethylene ligand. Addition of 8 equiv of $^{13}C_2H_4$ to complex **3c** led to a mixture of propylene (28%), cyclopropane (8%), ethylene adduct **7c** (75%), and an unsubstituted molybdacyclopentane complex, Mo(NAd)($^{13}CH_2{}^{13}CH_2{}^{13}CH_2{}^{13}CH_2$)[Biphen] (**9c**, 24% yield). Chemical shift and coupling values of complex **9c** are similar to those of **9a** (Table 8). Conversion of **7c** to **9c** was reversible. No 1-butene was observed.

As mentioned in an earlier section addition of 5 equiv of $^{13}C_2H_4$ to **3d** immediately led to a mixture of **6d**, **7d**, and the unsubstituted molybdacyclopentane complex Mo(NAr)($^{13}CH_2{}^{13}CH_2{}^{13}CH_2{}^{13}CH_2$)[Benz$_2$Bitet] (**9d**) in 30% yield after 36 h. A small amount of 1-butene (~8%) was also observed. Complex **9d** was quantitatively converted to **7d** upon removing ethylene from solution in vacuo. Similarly, complex **7e** was fully converted to **9e** in the presence of 125 equiv of ethylene; no 1-butene was detected. Complex **7e** was recovered quantitatively upon degassing a solution of **9e**. Chemical shifts and coupling constants for **9d** and **9e** are similar to those of **9a** and **9c** (Table 8).

Discussion

The studies presented here outline reactions that can take place between molybdenum imido alkylidene complexes that contain biphenolate ligands and ethylene. The results overall are similar to those found in the molybdenum hexafluoro-*tert*-butoxide system in 1991,[20] and what has been found for molybdenum binaphtholate[6] and tungsten biphenolate complexes,[16] although there are some important differences. In the presence of ethylene the end result in the case of Mo biphenolate complexes seems to be the generation of a complex of Mo(IV) (plus unidentified products that do not contain a ^{13}C label) that contains either ethylene or the relatively nonvolatile primary metathesis product, *CH_2=$CHCMe_2Ph$, if the reaction began with a Mo=$CHCMe_2Ph$ complex. In contrast, no ethylene or molybdacyclopentane complexes have been observed in binaphtholate systems **1a**−**c**. Perhaps binaphtholate complexes are simply less stable toward irreversible bimolecular decomposition reactions that ultimately yield species that contain bridging imido ligands (and no ^{13}C label).[20]

Methylene complexes have always been pivotal intermediates in any reaction in which ethylene can be generated. They are of course much more reactive than any monosubstituted alkylidene complex, and therefore were found in only barely detectable concentrations. Methylene complexes can be sequestered through a reaction with ethylene to form a molybdacyclobutane complex, although decomposition of methylene complexes bimolecularly to give ethylene or ethylene complexes and unidentified Mo decomposition products still appears to be rapid and competitive. Molybdenum methylene complexes have been observed previously only as adducts that contain PMe_3 and DME,[20,26−28] which are relatively stable toward bimolecular decomposition. It should be noted that dimers of these Mo methylene complexes are not observed, according to chemical shifts for the methylene protons and carbons, as was the case for racemic W methylene complexes of this general type.[16] It should be noted that enantiomerically pure or racemic Mo complexes yield the same result, but no dimeric W methylene complex was observed in an analogous enantiomerically pure system. It was proposed that the dimeric tungsten methylene complex formed in an enantiomerically pure system decomposed too readily to be observed, and that the dimer formed in a racemic system was composed of enantiomeric halves.

It has been proposed previously that unsubstituted molybdacyclobutane complexes more readily lose ethylene than do unsubstituted tungstacyclobutane complexes.[17] That is still thought to be the case, as judged qualitatively by the ready decomposition of several of the molybdacyclobutane complexes reported here to yield ethylene complexes. Unfortunately, it is difficult at this stage to quantitate such conversions and to compare their rates with analogous decomposition reactions of tungstacyclobutane complexes. However, it does appear that the rate of forming an ethylene complex increases dramatically upon changing from a N-2,6-i-$Pr_2C_6H_3$ to a N-2,6-$Cl_2C_6H_3$ group. Rearrangement of molybdacyclobutanes to propylene also seems to be less common with complexes that contain the N-2,6-$Cl_2C_6H_3$ group.

It has now been demonstrated clearly that even initial molybdacyclobutane complexes can be observed if the initial ethylene concentration is low. These species appear to have square-pyramidal structures, in contrast to the TBP structures observed for most unsubstituted molybdacyclobutanes, the exception being adamantylimido molybdacyclobutane complexes. In tungsten systems, it has been found that more electron-withdrawing alkoxides stabilize TBP tungstacycles, while more electron-donating alkoxides stabilize SP tungstacycles.[17]

Square-pyramidal tungstacycles also appear to be more stable with respect to olefin loss than TBP tungstacycles.[17]

Rearrangement of molybdacyclobutane complexes does not appear to be a significant mode of their decomposition, although small amounts of rearrangement products of both the initial molybdacyclobutane and unsubstituted molybdacyclobutane complexes have been observed in several systems reported here. Products of rearrangement of molybdacyclobutanes have been observed in other molybdenum systems that contain species of this general type.[20] Formation of what appears to be cyclopropane has never been observed before in systems of this type, or any high oxidation state alkylidene system to the best of our knowledge. Cyclopropane would seem to be formed most likely through reductive elimination in an unsubstituted molybdacyclobutane complex. The fact that the amount of cyclopropane that is formed is small is consistent with the predominant form of metalacyclobutane decomposition being either rearrangement or metathesis. In general, formation of cyclopropanes in reactions between carbene complexes and olefins predominates as metals become more electron rich. For example, Casey showed that $(CO)_5W{=}CPh_2$ would react with olefins to yield both cyclopropanes and metathesis products in substoichiometric quantities[31] and that $(CO)_5W{=}CHPh$ would react with olefins at −78 °C to yield cyclopropanes exclusively.[32] Carbenoid complexes of later transition metals such as copper yield only cyclopropanes upon reaction with olefins.[33]

In the molybdenum systems explored here it appears that unsubstituted molybdacyclopentane complexes lose ethylene more readily than tungstacyclopentane complexes, i.e., the equilibrium between ethylene and metalacyclopentane complexes lies more toward ethylene complexes when the metal is molybdenum. Catalytic dimerization of ethylene to 1-butene also appears to be relatively slow in the molybdenum systems explored here, either because metalacyclopentane complexes are less easily formed, or because they rearrange more slowly, or (most likely) both. In contrast, slow dimerization of ethylene to 1-butene was found in two related tungsten systems.[16] Tungsten systems appear to be less prone to lose ethylene from a tungstacyclopentane to give an ethylene complex and more prone toward rearrangement by a β-hydride rearrangement-based process. The tendency of W ethylene complexes to react with ethylene to form tungstacyclopentanes is one reason tungsten ethylene complexes have not been isolated. The lower tendency for molybdenum ethylene complexes to form molybdacyclopentanes allows a molybdenum ethylene complex to be isolated in one instance. It should be noted that rearrangement of tantalacyclopentane complexes to olefins involves a contraction of the TaC_4 ring to a TaC_3 ring, the so-called “ring contraction” mechanism.[34−38] Ring contraction has also been noted in a rhenium-based system.[39] It is not known at this time whether ring contraction is a feature of the mechanism of rearrangement of molybdacyclopentane or tungstacyclopentane rings, although that would now seem to be a more likely possibility than simple β-hydride elimination/reductive elimination (as in Scheme 2).

Many of the findings reported here are similar to those observed in molybdenum and tungsten imido alkylidene systems that contain the $[o\text{-}(Me_3SiN)_2C_6H_4]^{2-}$ supporting ligand.[18,19,23] Both tungsten(VI)[23] and molybdenum(VI)[18,19] phenylimido dineopentyl and neopentylidene complexes (as PMe_3 adducts) were prepared. The tungsten dineopentyl complex will react slowly with ethylene at temperatures above 70 °C to give neopentane (from the initial α-hydrogen abstraction reaction), *tert*-butylethylene (from the reaction of the intermediate neopentylidene complex with ethylene), and a structurally characterized (distorted square pyramidal) tungstacyclopentane complex. In reactions between $W(NPh)[o\text{-}(Me_3SiN)_2C_6H_4](CH\text{-}t\text{-}Bu)(PMe_3)$ and ethylene the initial α *tert*-butyl-substituted tungstacyclobutane complex was observed in solution, as were the unsubstituted tungstacyclobutane and ethylene complexes. All were converted into the tungstacyclopentane complex with time in the presence of ethylene. In $[o\text{-}(Me_3SiN)_2C_6H_4]W$ complexes, the tungstacyclobutane did not appear to rearrange to propylene and the tungstacyclopentane complex did not appear to rearrange to 1-butene.

We conclude that reactions between ethylene and enantiomerically pure biphenolate and binaphtholate complexes proceed through intermediates that have been proposed in other high oxidation state alkylidene systems, although these intermediates cannot be isolated and the precise outcome depends on many factors. Unfortunately, however, precisely how actual metathesis reactions in which ethylene is formed can alter the outcome of those reactions still cannot be predicted at this time. Nevertheless, it is clear that the end result in the presence of ethylene is reduction of the metal to Mo(IV), either as a simple ethylene complex, or in the form of some other as yet unidentified species such as a dimer that contains bridging imido ligands.[20] In cases where the yield of the ethylene complex is high we are interested in exploring ways of regenerating a molybdenum alkylidene complex, e.g., by transferring an alkylidene fragment from an ylide.[40−42]

Experimental Section

General. All reactions were conducted in oven or flame-dried glassware under an inert atmosphere of nitrogen or argon. Commercially available chemicals were obtained from Aldrich Co. or Lancaster Synthesis. Liquid reagents were distilled from CaH_2 under nitrogen and stored over molecular sieves (4 Å) before use. Ether, pentane, toluene, benzene, and

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(31) Casey, C. P.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 7808.

(32) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282.

(33) Kirmse, W. *Angew. Chem., Int. Ed.* **2003**, *42*, 1088.

(34) McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 1315.

(35) McLain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 4558.

(36) McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5451.

(37) Schrock, R. R.; McLain, S. J.; Sancho, J. *Pure Appl. Chem.* **1980**, *52*, 729.

(38) Smith, S.; McLain, S. J.; Schrock, R. R. *J. Organomet. Chem.* **1980**, *202*, 269.

(39) Yang, G. K.; Bergman, R. G. *Organometallics* **1985**, *4*, 129.

(40) Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43.

(41) Johnson, L. K.; Frey, M.; Ulibarri, T. A.; Virgil, S. C.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 8167.

(42) Johnson, L. K.; Virgil, S. C.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 5384.

THF were dried with columns of activated alumina. Dimethoxyethane (DME) was distilled from a purple solution of sodium benzophenone ketyl. Dichloromethane was distilled from calcium hydride. Benzene-d_6 and toluene-d_8 were vacuum transferred from calcium hydride or sodium benzophenone ketyl prior to use. All NMR spectra were collected on a Varian Inova 500 spectrometer unless otherwise stated. Microanalyses were performed by Kolbe Microanalytical Laboratories (Mülheim an der Ruhr, Germany). Mo(NAr)(CHCMe$_2$Ph)[(*S*)-Biphen] (**3a**),[15] Mo(NAr$_{Cl}$)(CHCMe$_3$)[(*S*)-Biphen] (**3b**),[8] Mo(NAd)(CHCMe$_2$Ph)[(*S*)-Biphen] (**3c**),[12] Mo(NAr)(CHCMe$_2$Ph)[(*R*)-Benz$_2$Bitet] (**3d**),[8] and Mo(NAr$_{Cl}$)(CHCMe$_2$Ph)[(*R*)-Benz$_2$Bitet] (**3e**)[8] were prepared as described in the literature.

Representative Procedure for Reactions Involving Ethylene. A benzene-d_6 solution (0.6 mL) of Mo(NAr)(CHCMe$_2$Ph)[Benz$_2$Bitet](THF) (20 mg) was loaded in a J-Young tube, which was then sealed and attached to a gas transfer setup equipped with a 760-Torr gauge. The volume of the setup was calibrated immediately before the experiment (23.73 mL). The sample was degassed by freeze−pump−thaw and re-sealed with the J-Young cap. Ethylene (70 Torr, 5 equiv) was passed into the setup by slowly opening the regulator attached to the ethylene tank. All the ethylene in the setup was condensed into the frozen sample (with liquid nitrogen) by opening the J-Young seal. The sample was then brought to the spectroscopy facility under liquid nitrogen before it was thawed and immediately inserted into the NMR probe. Subsequent removal of excess ethylene was achieved by freeze−pump−thaw using a heavily salted ice bath.

Attempt to Isolate Mo(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(CH$_2$═CH$_2$)[Biphen] (7a). A benzene-d_6 solution (0.5 mL) of Mo(NAr)(CHCMe$_2$Ph)[Biphen] (50 mg, 0.66 mmol) was degassed by freeze−pump−thaw and exposed to 1 atm of ethylene for 1 h. A deep red solution was obtained that was shown by integration versus an internal standard to contain a virtually quantitative yield of **7a**. All volatiles were removed in vacuo and the oily residue was redissolved in C$_6$D$_6$ (0.5 mL). Attempts to isolate the complex, even on gram scales, have not been successful: ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 7.27 (s, 1, Aryl), 7.24 (s, 1, Aryl), 6.9 (m, 3, Aryl), 3.28 (m, 1, CH$_2$), 3.15 (m, 1, CH$_2$), 3.12 (sept, 2, CHMe$_2$), 2.30 (m, 2, CH$_2$), 2.07 (s, 3, ArCH$_3$), 1.99 (s, 3, ArCH$_3$), 1.78 (s, 3, ArCH$_3$), 1.66 (s, 9, C(CH$_3$)$_3$), 1.63 (s, 3, ArCH$_3$), 1.47 (s, 9, C(CH$_3$)$_3$), 1.17 (d, 6, CH(C*H*$_3$)$_2$), 0.97 (d, 6, CH(C*H*$_3$)$_2$); ^{13}C NMR (100 MHz, C$_6$D$_6$) δ 156.5, 154.2, 150.0, 145.3, 141.7, 138.5, 135.9, 133.8, 131.6, 131.5, 126.9, 126.6, 124.9, 122.8, 61.2, 60.9, 35.4, 35.3, 30.7, 29.8, 29.1, 24.0, 23.6, 20.6, 20.2, 16.8, 16.7.

Mo(N-2,6-Cl$_2$C$_6$H$_3$)(CH$_2$═CH$_2$)[*rac*-Biphen](Solvent) (*rac*-7b-Solvent, Solvent = THF or Ether). To a 1-L Teflon-sealed bomb was added Mo(N-2,6-Cl$_2$C$_6$H$_3$)(CHCMe$_3$)[*rac*-Biphen] (2.85 g, 3.80 mmol) and toluene (50 mL). The solution was degassed three times by freeze−pump−thaw and refilled with ethylene (1 atm). The container was sealed and the mixture was stirred for 1 h. The toluene solution was concentrated in vacuo to approximately 25 mL and a dark orange powder was filtered through a fine frit. The isolated powder was recrystallized from THF to give bright orange Mo(N-2,6-Cl$_2$C$_6$H$_3$)(CH$_2$═CH$_2$)[*rac*-Biphen](THF) in a yield of 1.76 g (59%): ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 7.29 (s, 1, Aryl), 7.20 (s, 1, Aryl), 6.65 (d, 2, Aryl), 6.07 (t, 1, Aryl), 3.82 (m, 1, CH$_2$CH$_2$), 3.65 (m, 4, OCH$_2$), 3.52 (m, 1, CH$_2$CH$_2$), 3.03 (m, 1, CH$_2$CH$_2$), 2.85 (m, 1, CH$_2$CH$_2$), 2.12 (s, 3, ArCH$_3$), 2.02 (s, 3, ArCH$_3$), 1.90 (s, 3, ArCH$_3$), 1.57 (s, 9, C(CH$_3$)$_3$), 1.55 (s, 9, C(CH$_3$)$_3$), 1.50 (s, 3, ArCH$_3$), 1.34 (m, 4, OCH$_2$C*H*$_2$); ^{13}C NMR (125 MHz, CD$_2$Cl$_2$) δ 162.66, 152.74, 149.58, 141.18, 137.16, 134.31, 133.75, 133.32, 132.10, 131.24, 129.27, 128.08, 127.69, 127.10, 126.48, 125.30, 72.19, 63.70, 60.77, 35.80, 34.54, 30.68, 30.23, 29.85, 26.11, 20.43, 20.15, 17.06, 16.48. Anal. Calcd for MoC$_{32}$H$_{39}$NO$_2$Cl$_2$: C, 60.38; H, 6.18; N, 2.20; Cl, 11.14. Found: C, 60.26; H, 6.25; N, 2.04; Cl, 11.22.

Single crystals of *rac*-**7b**-Et$_2$O suitable for X-ray diffraction were obtained by layering diethyl ether over a concentrated toluene solution of *rac*-**7b**-THF.

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Supporting Information Available: Fully labeled thermal ellipsoid drawing, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **7b**-Et$_2$O, and selected multidimensional spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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