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Molybdenum alkylidyne complexes that contain a 3,3′-di-*t*-butyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diolate ($[\text{Biphen}]^{2-}$) ligand

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This paper is dedicated to Prof. E.O. Fischer on the occasion of his 85th birthday

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Abstract

The reaction between K_2[Biphen] ($[\text{Biphen}]^{2-}$ = 3,3′-Di-*t*-butyl-5,5′,6,6′-tetramethyl-1,1′-Biphenyl-2,2′-diolate) and $\text{Mo(NAr}_{\text{Cl}}\text{)(CH-}t\text{-Bu)(OTf)}_2\text{(dme)}$ ($\text{Ar}_{\text{Cl}} = 2,6\text{-Cl}_2\text{C}_6\text{H}_3$) in the presence of ten equivalents of triethylamine gave $\text{Mo(NHAr}_{\text{Cl}}\text{)(C-}t\text{-Bu)}$[Biphen] (**4a**) in 40–50% yield. Addition of K_2[*S*-Biphen] to $\text{Mo(NAr}_{\text{Cl}}\text{)(CHCMe}_2\text{Ph)(OTf)}_2\text{(THF)}$ in THF led to the isolation of $\text{Mo(NHAr}_{\text{Cl}}\text{)(CCMe}_2\text{Ph)}$[*S*-Biphen] (**4b**) in ~40% yield. An X-ray crystal study of **4b** confirmed the proposed structure and also revealed that one ortho chloride approaches within 2.93 Å of the metal approximately *trans* to the alkylidyne ligand. Addition of one equivalent of H_2[Biphen] to $\text{Mo(CCH}_2\text{SiMe}_3\text{)[N(}i\text{-Pr)Ar}''\text{)]}_3$ ($\text{Ar}'' = 3,5$-dimethylphenyl) produced $\text{Mo(CCH}_2\text{SiMe}_3\text{)}$[Biphen][N(*i*-Pr)Ar″)] in situ, which when treated with one equivalent of 1-adamantanol gave a mixture of $\text{Mo(CCH}_2\text{SiMe}_3\text{)}$[Biphen](OAd) (**9**) and three equivalents of HN(*i*-Pr)Ar″, from which **9** could be isolated as a beige powder in 46% yield. An X-ray study of **9** confirmed that it is a pseudotetrahedral species in which the Mo≡C bond length is 1.707(15) Å and the Mo≡C–C angle is 168.3(11)°. Addition of ten equivalents of 2-butyne or 3-hexyne to a pale yellow solution of **9** produced the molybdacyclobutadiene complexes $\text{Mo(C}_3\text{R}_3\text{)}$[Biphen](OAd) (R = Me or Et; **10a** and **10b**, respectively) in high yield. Both **10a** and **10b** decompose slowly in solution, even in the presence of added alkyne. An X-ray structure of the decomposition product of **10a** revealed it to have the stoichiometry of **10a** plus one additional equivalent of 2-butyne. The most unusual feature of the structure of this alkyne complex is a fusion of the C_3Me_3 portion of the metallacyclobutadiene ring to carbons in position 5 and 6 in the $[\text{Biphen}]^{2-}$ backbone to create a σ allyl linkage. These results suggest that Mo biphenolate alkylidyne complexes are not likely to be stable under conditions where alkynes are metathesized.

Keywords: Molybdacyclobutadiene complexes; Metallacyclobutadiene; Pseudotetrahedral species

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1. Introduction

Molybdenum and tungsten alkylidyne complexes of the type $\text{M(C-}t\text{-Bu)(CH}_2\text{-}t\text{-Bu)}_3$ were first reported in 1978 [1]. If the neopentylidyne is viewed as a trianion (i.e. isoelectronic with a nitride) then the metal would be in the 6+ oxidation state. Like $\text{Ta(CH-}t\text{-Bu)(CH}_2\text{-}t\text{-Bu)}_3$ [2], these trineopentylneopentylidyne species melt near 70 °C and can be distilled or sublimed in a good vacuum. They each react with three equivalents of HCl in ether in the presence of dimethoxyethane to yield the trichloride complexes, $\text{M(C-}t\text{-Bu)Cl}_3\text{(dme)}$ (M = Mo or W), which in turn can be treated with lithium or sodium salts of sterically demanding alkoxides or phenoxides to yield $\text{M(C-}t\text{-Bu)(OR)}_3$ complexes [3]. Trialkoxyneopentylidyne complexes, especially those of tungsten, were studied extensively and shown to be efficient catalysts for the metathesis of alkynes. When electron withdrawing alkoxides are present, metallacyclobutadiene complexes, e.g., $\text{W(C}_3\text{Et}_3\text{)[O-2,6-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{]}_3$ [4], can be isolated and have been characterized crystallographically [3]. These tungstacyclobutadiene complexes were shown also to be active catalysts for the metathesis of

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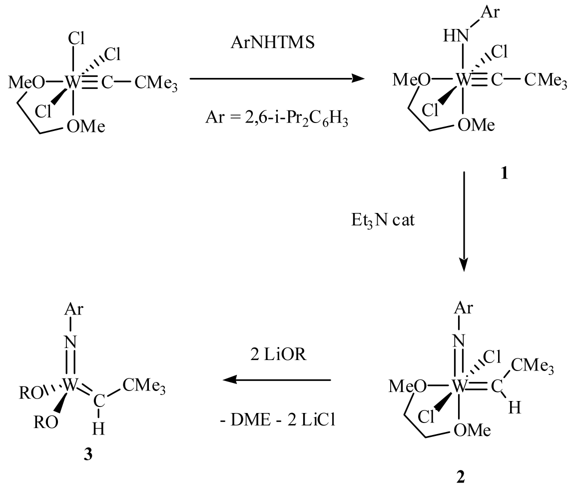
alkynes [4,5]. Recently alkyne metathesis has been applied in organic synthesis, either with isolated complexes such as W(C-*t*-Bu)(O-*t*-Bu)$_3$ as the catalyst, or with less well-defined molybdenum species that are generated in situ [6–25]. Almost certainly the Mo catalysts that are generated in situ are Mo(6+) species [23].

The W(C-*t*-Bu)Cl$_3$(dme) complex played a crucial role in the development of imido alkylidene complexes of the type W(NAr)(CH-*t*-Bu)(OR′)$_2$ (Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$ and OR′ = OCMe(CF$_3$)$_2$, for example), which were the first well-defined catalysts for the metathesis of olefins to be isolated and studied [26]. The first synthesis of imido alkylidene complexes relied on the preparation of an amido neopentylidyne complex such as tungsten species **1** shown in Scheme 1 [27]. Addition of a catalytic amount of triethylamine transforms **1** into **2**. Replacement of the chlorides in **2** with sterically demanding alkoxides then yields imido neopentylidene complexes **3** shown in Scheme 1, where OR = OCMe(CF$_3$)$_2$ or O-*t*-Bu, for example. More practical routes to imido neopentylidene and neophylidene complexes were developed over the next several years, especially a route to molybdenum catalysts that involves the three step synthesis of bis(triflate) species such as Mo(NAr)(CHCMe$_2$R′)(OTf)$_2$(dme) (R′ = Me or Ph) [28]. Treatment of Mo(NAr)(CHCMe$_2$R′)(OTf)$_2$(dme) with alkoxide salts produces the desired Mo(NAr)(CHCMe$_2$R′)(OR)$_2$ catalysts.

Recently we have been involved in the preparation of Mo imido alkylidene catalysts that contain an enantiomerically pure biphenolate or binaphtholate ligand, and the use of them as catalysts for asymmetric olefin metathesis reactions [29,30]. An example is M(NAr)(CHCMe$_2$Ph)[Biphen] ([Biphen]$^{2-}$ = [3,3′-Di-*t*-butyl-5,5′,6,6′-tetramethyl-1,1′-Biphenyl-2,2′-diolate]$^{2-}$, either racemic or, for asymmetric reactions, *S*) [31]. A complication arose during the synthesis of an analogous species that contains a *N*-*o*-CF$_3$C$_6$H$_4$ ligand in place of the NAr ligand. An alkylidyne complex was a significant impurity in the sample of Mo(*N*-*o*-CF$_3$C$_6$H$_4$)(CHCMe$_2$Ph)[Biphen]; it was proposed to be Mo(NH-*o*-CF$_3$C$_6$H$_4$)(CCMe$_2$Ph)[Biphen]. A resonance at 11.7 ppm in the proton NMR spectrum varied in intensity from sample to sample, as did a singlet resonance at 315.7 ppm in the carbon NMR spectrum. It was proposed that the resonance near 11.7 ppm is the NH proton in Mo(NH-*o*-CF$_3$C$_6$H$_4$) (CCMe$_2$Ph)[Biphen], while the resonance at 315.7 ppm is the alkylidyne carbon atom resonance [3]. Once a mixture of Mo(NH-*o*-CF$_3$C$_6$H$_4$)(CCMe$_2$Ph)[Biphen] and Mo(*N*-*o*-CF$_3$C$_6$H$_4$)(CHCMe$_2$Ph)[Biphen] was formed, the two compounds could not be interconverted cleanly using NEt$_3$ or K$_2$Biphen as a catalyst. The alkylidyne species could not be prepared and isolated in pure form.



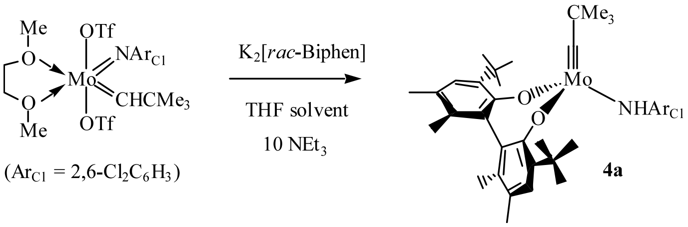
Scheme 1. Synthesis of W imido alkylidene complexes from an amido alkylidyne complex (OR = OCMe$_3$ or CMe(CF$_3$)$_2$, for example).

A similar problem arose more recently during the attempted synthesis of Mo(NAr$_{Cl}$)(CHCMe$_2$R)[Biphen] (NAr$_{Cl}$ = *N*-2,6-Cl$_2$C$_6$H$_3$) through the addition of K$_2$Biphen to Mo(NAr$_{Cl}$)(CHCMe$_2$R)(OTf)$_2$(dme) (R = Me or Ph) [32,33]. A significant impurity in several preparations appeared to be Mo(NHAr$_{Cl}$)(CCMe$_2$R)[Biphen], according to NMR spectra of crude reaction mixtures. However, conditions could not be found where Mo(NHAr$_{Cl}$)(CCMe$_2$R)[Biphen] was the sole product. We have now found conditions that yield Mo(NHAr$_{Cl}$)(C-*t*-Bu)[Biphen] reproducibly in moderate yield. We also have explored the possibility of preparing Mo alkylidyne complexes for alkyne metathesis that contain a [Biphen]$^{2-}$ ligand using a route recently developed by Cummins [13]. Finally, we have found, much to our surprise, that [Biphen]$^{2-}$ ligands are not stable under conditions where alkyne metathesis would be expected.

2. Results and discussion

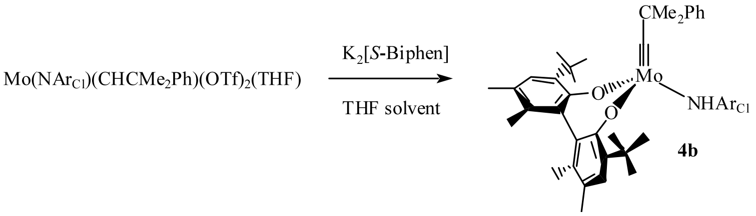
2.1. Synthesis of molybdenum 2,6-dichlorophenylamido alkylidyne [biphen]$^{2-}$ complexes

The reaction between K$_2$[Biphen] and Mo(NAr$_{Cl}$)(CH-*t*-Bu)(OTf)$_2$(dme) (the [Biphen]$^{2-}$ may be either racemic or (*S*)—it is racemic unless noted otherwise) is the reported method of synthesizing Mo(NAr$_{Cl}$)(CH-*t*-Bu)[Biphen] (as a THF adduct) [32]. Sporadically, however, the reaction yields mixtures of Mo(NAr$_{Cl}$)(CH-*t*-Bu)[Biphen] and what was postulated to be Mo(NHAr$_{Cl}$)(C-*t*-Bu)[Biphen]. In one instance a small amount of Mo(NHAr$_{Cl}$)(C-*t*-Bu)[Biphen] could be isolated in low yield (17%) as a yellow powder. We have now found that if ten equivalents of triethylamine are added to Mo(NAr$_{Cl}$)(CH-*t*-Bu)(OTf)$_2$(dme) before addition of the K$_2$[Biphen], then Mo(NHAr$_{Cl}$)(C-*t*-Bu)[Biphen] (**4a**) may be prepared in 40% yield reproducibly Eq. (1) [34]. Addition of ten equivalents of triethylamine to Mo(NHAr_{Cl})(C-*t*-Bu)[Biphen] or Mo(NAr_{Cl})(CH-*t*-Bu)[Biphen] in C_6D_6 does not lead to conversion of one into the other, i.e., the proton cannot be moved by triethylamine once the $[Biphen]^{2-}$ ligand is present.



(1)

The ^{1}H-NMR spectrum (500 MHz, C_6D_6) of **4a** shows a singlet resonance at 11.73 ppm that is assigned to the N*H* proton. This is the region where one would expect to find the α hydrogen resonance for an alkylidene in an imido alkylidene complex [26]. In the ^{13}C-NMR spectrum a resonance is found at 327.7 ppm for a carbon that has no proton attached to it. Since the resonance is in the region characteristic of an alkylidyne carbon resonance [3,35], we assign it to the alkylidyne α carbon resonance in Mo(NHAr_{Cl})(C-*t*-Bu)[Biphen]. The *meta* protons on the arylimido ligand appear as a doublet resonance at 6.69 ppm, indicating that the rate of rotation about the C_{ipso}–N bond is fast on the NMR time scale at room temperature.



(2)

Attempts to prepare the neophylidene complex, Mo(NAr_{Cl})($CHCMe_2Ph$)$(OTf)_2$(dme), and subsequently Mo(NAr_{Cl})($CHCMe_2Ph$)[Biphen], were not successful [32]. The only species that could be isolated upon addition of three equivalents of HOTf to Mo(NAr_{Cl})$_2$(CH_2CMe_2Ph)$_2$ at −30 °C in dme was a yellow powder in 28% yield that analyzed as Mo(NAr_{Cl})($CHCMe_2Ph$)$(OTf)_2$(THF). (In THF solution NMR data suggest that two isomers of Mo(NAr_{Cl})($CHCMe_2Ph$)$(OTf)_2(THF)_2$ are present; see Section 4). Subsequent addition of K_2[*S*-Biphen] in THF to a suspension of Mo(NAr_{Cl})($CHCMe_2Ph$)$(OTf)_2$(THF) in THF (5 ml) led to Mo(NHAr_{Cl})($CCMe_2Ph$)[*S*-Biphen] (**4b**) as a yellow powder in 38% yield (Eq. (2)). Proton NMR spectra of **4b** show the amido proton resonance at 11.59 ppm and the carbon NMR spectrum shows the alkylidyne carbon resonance at 322.1 ppm (cf. 337.2 ppm in Mo(C-*t*-Bu)$(DIPP)_3$, where DIPP = O-2,6-*i*-$Pr_2C_6H_3$ [36]). Unfortunately, this synthesis of **4b** has not been reproducible, with mixtures of Mo(NAr_{Cl})($CHCMe_2Ph$)[*S*-Biphen] and Mo(NHAr_{Cl})($CCMe_2Ph$)[*S*-Biphen] usually being obtained. Mo(NAr_{Cl})($CHCMe_2Ph$)[*S*-Biphen] still has not been isolated in pure form, in contrast to Mo(NAr_{Cl})(CH-*t*-Bu)[*S*-Biphen] [32].

An X-ray crystal structure of **4b** is shown in Fig. 1. (See Table 1 for crystal data and Table 2 for selected bond lengths and angles.) The Mo≡C(1) distance (1.721(7)Å) and Mo≡C–C bond angle (170.5(5)°) are typical of a high oxidation state alkylidyne complex [3]. The Mo–N(1) bond length (1.990(6)Å) is much longer (by ~0.2 Å) than is typically found for a Mo=N pseudo triple bond (e.g. Mo=N = 1.872 Å in Mo(NAr_{Cl})(CH-*t*-Bu)[*S*-Biphen](THF) [32]) and moreover the Mo–N(1)–

Table 1
Crystallographic data, collection parameters, and refinement parameters for Mo(NH-2,6-$Cl_2C_6H_3$)($CCMe_2Ph$)[*S*-Biphen] (**4b**)

Empirical formula	$C_{40}H_{47}Cl_2MoNO_2$
Formula weight	740.63
Temperature (K)	183(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a (Å)	10.1338(8)
b (Å)	17.5044(14)
c (Å)	20.6093(17)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	3655.8(5)
Z	4
D_{calc} (Mg m^{-3})	1.346
Absorption coefficient (mm^{-1})	0.539
F(0 0 0)	1544
Theta range for data collection (°)	2.24–23.31
Index ranges	$-11 \leq h \leq 11$, $-19 \leq k \leq 13$, $-22 \leq l \leq 22$
Reflections collected	15059
Independent reflections	5275 [$R_{int} = 0.1025$]
Completeness to theta (°)	23.31(99.9%)
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5275/0/419
Goodness-of-fit on F^2	0.977
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0559$, $wR_2 = 0.0855$
R indices (all data)	$R_1 = 0.0877$, $wR_2 = 0.0932$
Absolute structure parameter	0.03(5)
Largest difference peak and hole (e Å^{-3})	0.578 and -0.359

Table 2
Selected bond lengths (Å) and angles (°) for Mo(NH-2,6-$Cl_2C_6H_3$)($CCMe_2Ph$)[*S*-Biphen] (**4b**)

Bond lengths		Bond angles	
Mo–C(1)	1.721(7)	C(1)–Mo–O(1)	107.1(3)
Mo–O(2)	1.962(4)	C(1)–Mo–O(2)	97.5(2)
Mo–O(1)	1.988(4)	C(1)–Mo–N(1)	94.8(3)
Mo–N(1)	1.990(6)	Mo–N(1)–C(11)	133.8(5)
Mo···Cl(1)	2.93	Mo–C(1)–C(2)	170.5(5)
		Mo–O(1)–C(17)	98.9(3)
		Mo–O(2)–C(28)	104.6(3)
		O(1)–Mo–O(2)	122.66(18)
		O(1)–Mo–N(1)	115.2(2)
		O(2)–Mo–N(1)	113.2(2)

C_{ipso} angle is only 133.8(5)°; both are characteristic of an amido ligand. Although the amido α proton was not located, we believe it is likely to lie in the Mo–N–C_{ipso} plane, since amido ligands have always been found to be planar when bound to high oxidation state metals. An interesting twist is that one ortho chloride (Cl(1)) is pointed toward the metal and approaches within 2.93 Å of the metal approximately *trans* to the alkylidyne ligand. Weak binding of an ortho chloride to the metal was also found in Mo(NAr_{Cl})(CH-*t*-Bu)[*S*-Biphen](THF) where one ortho chloride approaches within ~3.0 Å of the metal [32].

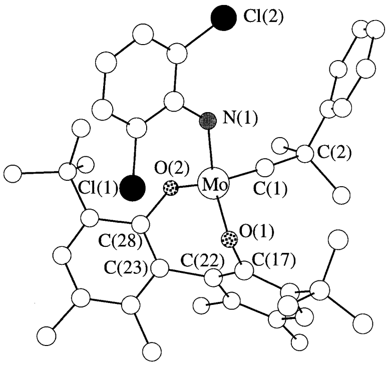
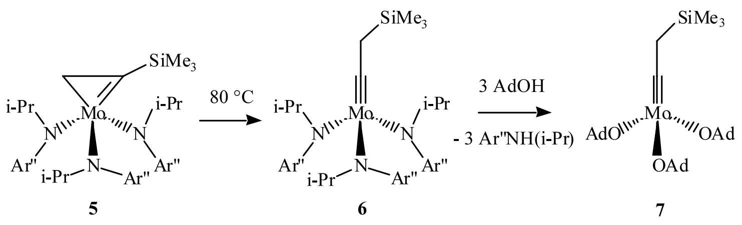


Fig. 1. Chem 3D drawing of Mo(NH–2,6-$Cl_2C_6H_3$)($CCMe_2Ph$)[*S*-Biphen] (**4b**).

Attempts to prepare three other amido alkylidyne complexes in the presence of ten to twenty equivalents of triethylamine failed. Addition of K_2[Biphen] to Mo(*N*-*o*-$CF_3C_6H_4$)($CHCMe_2Ph$)$(OTf)_2$(dme) in the presence of twenty equivalents of triethylamine yielded neither Mo(*N*-*o*-$CF_3C_6H_4$)($CHCMe_2Ph$)[Biphen] nor Mo(NH-*o*-$CF_3C_6H_4$)($CCMe_2Ph$)[Biphen]; the product or products of this reaction could not be identified. (As noted earlier, mixtures of Mo(*N*-*o*-$CF_3C_6H_4$)($CHCMe_2Ph$)-[Biphen] and Mo(NH-*o*-$CF_3C_6H_4$)($CCMe_2Ph$)[Biphen] were sometimes obtained upon the attempted synthesis of Mo(*N*-*o*-$CF_3C_6H_4$)($CHCMe_2Ph$)[Biphen] [31].) Addition of K_2[Biphen] to Mo(*N*-2,6-$R_2C_6H_3$)($CHCMe_2$-Ph)$(OTf)_2$(dme) (R = Me or *i*-Pr) led only to the known Mo(*N*-2,6-$R_2C_6H_3$)($CHCMe_2Ph$)(Biphen) species [31].

2.2. Synthesis of a molybdenum alkylidyne [Biphen]$^{2-}$ adamantoxide complex

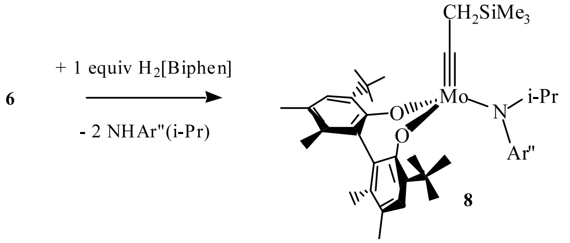
Once we had isolated and characterized Mo(N-HAr_{Cl})(C-*t*-Bu)[Biphen], we became interested in the possibility of preparing related Mo(amido)(C-*t*-Bu)[Biphen] complexes as well as complexes of the type Mo(CR)[Biphen](OR′). To this end we were attracted to the method employed by Cummins to synthesize Mo(CCH_2SiMe_3)$(OAd)_3$ (**7**), as shown in Eq. (3) (Ar″ = 3,5-dimethylphenyl). The approach relies on the rearrangement of **5** to **6** and subsequent displacement of the three amido groups in **6** upon addition of three equivalents of



(3)

1-adamantanol. Compound **7** was found to react readily with 3-hexyne or 2-butyne to yield $(AdO)_3Mo(CR)$ ($R = Et$ or Me) and was shown to metathesize $MeC\equiv CCH_2CH_2OTs$ to yield $TsOCH_2CH_2C\equiv CCH_2CH_2OTs$ and 2-butyne. Compound **7** was characterized crystallographically; the $Mo\equiv C$ bond length was found to be 1.743(4) Å. Compound **7** could be isolated in the presence of three equivalents of NHRAr″ because it is relatively insoluble.

Compound **6** was first prepared in situ by heating a solution of **5** to 80 °C in toluene. One equivalent of H_2[Biphen] was then added to give **8** and 2 additional equivalents of HN(*i*-Pr)Ar″ cleanly (Eq. (4) [34]), according to NMR spectra. Unfortunately, conditions could not be found that would allow **8** to be crystallized in the presence of HN(*i*-Pr)Ar″. Therefore one equivalent of 1-adamantanol was added to the mixture of **8** and HN(*i*-Pr)Ar″ to give a mixture of $Mo(CCH_2SiMe_3)$[Biphen](OAd) (**9**) and a total of three equivalents of HN(*i*-Pr)Ar″ (Eq. (5)). Compound **9** can be separated from HN(*i*-Pr)Ar″ by recrystallization from pentane (−30 °C). It is obtained as a beige powder in 46% yield.



(4)

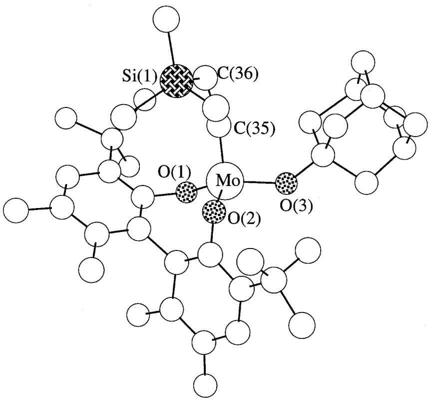
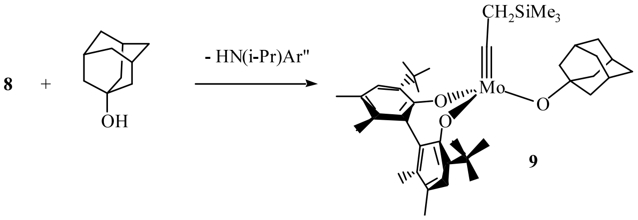


Fig. 2. Chem 3D drawing of $Mo(CCH_2SiMe_3)$[Biphen](OAdamantyl) (**9**).



(5)

An X-ray crystallographic study of pale yellow crystals of **9** grown from a concentrated ether and pentane solution at −30 °C revealed the structure shown in Fig. 2. Crystallographic data, collection

Table 3
Crystallographic data, collection parameters, and refinement parameters for $Mo(CCH_2SiMe_3)$[Biphen](OAd) (**9**)

Empirical formula	$MoC_{39}H_{58}O_3Si$
Formula weight	698.88
Temperature (K)	183(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	10.2512(6)
b (Å)	13.0936(8)
c (Å)	15.9276(10)
α (°)	78.5090(10)
β (°)	76.2910(10)
γ (°)	85.9270(10)
V (Å^3)	2034.7(2)
Z	2
D_{calc} (Mg m^{-3})	1.141
Absorption coefficient (mm^{-1})	0.383
F(0 0 0)	744
Theta range for data collection (°)	2.51–23.28
Limiting indices	$-11 \le h \le 11$, $-9 \le k \le 14$, $-13 \le l \le 17$
Reflections collected/unique	8181/6715 [$R_{int} = 0.0445$]
Completeness to theta (°)	23.29(97.7%)
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6715/3/821
Goodness-of-fit on F^2	1.085
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0663$, $wR_2 = 0.1990$
R indices (all data)	$R_1 = 0.0696$, $wR_2 = 0.2071$
Absolute structure parameter	0.31(9)
Largest different peak and hole (e A^{-3})	3.494 and −0.594

Table 4
Selected bond lengths (Å) and angles (°) for $Mo(CCH_2SiMe_3)$[Biphen](OAd) (**9**)

Bond lengths		Bond angles	
Mo–C(35)	1.707(15)	C(35)–Mo–O(3)	101.5(5)
Mo–O(1)	2.026(10)	C(35)–Mo–O(2)	101.7(5)
Mo–O(2)	1.949(9)	C(35)–Mo–O(1)	108.0(5)
Mo–O(3)	1.858(10)	Mo–C(35)–C(36)	168.3(11)
		Mo–O(1)–C(11)	100.4(8)
		Mo–O(2)–C(17)	101.4(7)
		Mo–O(3)–C(1)	140.2(9)
		O(3)–Mo–O(2)	110.3(4)
		O(3)–Mo–O(1)	110.6(4)
		O(2)–Mo–O(1)	122.4(4)
		C(35)–C(36)–Si(1)	114.0(11)

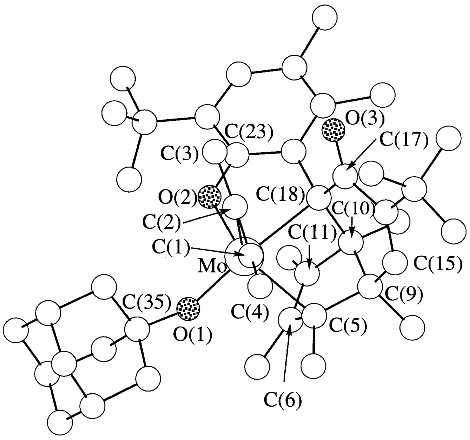


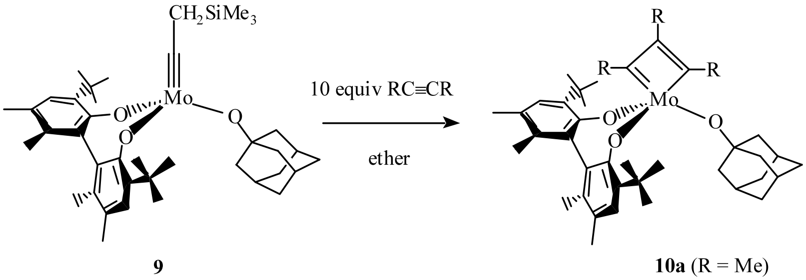
Fig. 3. Chem 3D drawing of **11a**.

parameters and refinement parameters are given in Table 3 while selected bond lengths and angles are given in Table 4. Both the *R*- and [*S*-Biphen]$^{2-}$ complexes were present in the unit cell. (The [*S*-Biphen]$^{2-}$ complex is shown in Fig. 2.) The alkylidyne bond length is 1.707(15) Å (cf. 1.743(4) Å in $Mo(CCH_2SiMe_3)(OAd)_3$ [13]) and the Mo≡C–C angle is 168.3(11)°. The adamantoxide group is bent away from the [Biphen]$^{2-}$ ligand while the trimethylsilyl group on the alkylidyne is bent away from the adamantoxide group, most likely for steric reasons. Note that the O(1)–Mo–O(2) angle (122.4(4)°) is virtually the same as it is in **4b** (122.66(18°). Other bond lengths and angles are not unusual.

2.3. Reaction of $Mo(CCH_2SiMe_3)$[biphen](OAd) with alkynes

Since $Mo(CCH_2SiMe_3)(OAd)_3$ reacts with 2-butyne to give $Mo(CCH_3)(OAd)_3$ quantitatively [13], we expected $Mo(CCH_2SiMe_3)$[Biphen](OAd) to react with ten equivalents of 2-butyne to give $Mo(CCH_3)$[Biphen](OAd). However, a pale yellow solution of **9** immediately turned dark red upon addition of 2-butyne and what is proposed to be a metallacyclobutadiene complex, $Mo(C_3Me_3)$[Biphen](OAd) (**10a**) precipitated as a rosy red powder in 78% yield (Eq. (6)). The proton and carbon NMR spectra of **10a** are characteristic of a metallacyclobutadiene complex [3]. Two resonances characteristic of methyl groups attached to the ring's α-carbons appear at 2.89 and 2.74 ppm with the resonance for the methyl group attached to the β-carbon appearing at 1.90 ppm. In the ^{13}C-NMR spectrum the three resonances corresponding to metallacyclobutadiene ring carbons were found at 254.24, 218.03 and 192.79 ppm. Typically ^{13}C-NMR resonances for C_α carbons in tungstacyclobutadiene complexes are found between 200 and 260 ppm, while C_β resonances are found between 170 and 220 ppm [3]. Only one molybdacyclobutadiene complex, $Mo(C_3Et_3)(DIPP)_3$ (DIPP = O-2,6-*i*-$Pr_2C_6H_3$), is known, but no ^{13}C-NMR spectrum was recorded [36].

The analogous ethyl-substituted molybdacyclobutadiene complex (**10b** in Eq. (6)) was isolated in 59% yield. Complex **10b** revealed three distinct ethyl resonances in the proton NMR spectrum, with the resonances for the four $C_\alpha CH_2$ protons appearing as multiplets at 3.55, 3.04, 2.66 and 1.98 ppm and the resonance for the two $C_\beta CH_2$ protons appearing as a multiplet at 2.94 ppm. The triplet resonances corresponding to the two $C_\alpha CH_2CH_3$ groups and the $C_\beta CH_2CH_3$ group appeared at 0.64, 0.77 and 1.31 ppm, respectively. It was not possible to obtain a clean ^{13}C-NMR spectrum of **10b** because it was only sparingly soluble and because it decomposed more readily in solution than **10a**. For comparison the proton NMR spectrum of $Mo(C_3Et_3)(DIPP)_3$ at 233 K in toluene showed methyl-



9

10a (R = Me)
10b (R = Et)

(6)

Table 5
Crystallographic data, collection parameters, and refinement parameters for **11a**

Empirical formula	$MoC_{44}H_{62}O_3$
Formula weight	734.88
Temperature (K)	183(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	8.9508(11)
b (Å)	9.9851(12)
c (Å)	22.656(3)
α (°)	78.997(2)
β (°)	80.498(2)
γ (°)	88.923(2)
V (Å^3)	1960.2(4)
Z	2
D_{calc} (Mg m^{-3})	1.245
Absorption coefficient	0.372 mm^{-1}
F(0 0 0)	784
Theta range for data collection	2.31–23.28°
Index ranges	$-9 \le h \le 9$, $-6 \le k \le 11$, $-25 \le l \le 25$
Reflections collected	8002
Independent reflections	5534 [$R_{int} = 0.0604$]
Completeness to theta (°)	23.28(98.3%)
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5534/0/449
Goodness-of-fit on F^2	1.059
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0565$, $wR_2 = 0.1240$
R indices (all data)	$R_1 = 0.0690$, $wR_2 = 0.1300$
Extinction coefficient	0.0000(5)
Largest different peak and hole (e A^{-3})	0.532 and −0.721

This structure was solved by the Patterson method.

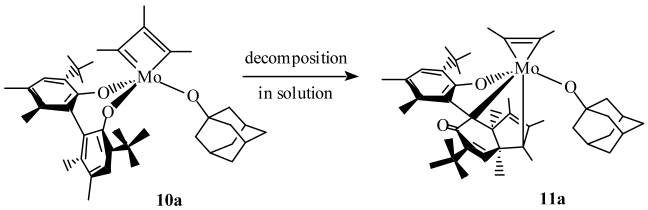
Table 6
Selected bond lengths (Å) and angles (°) for **11a**

Bond lengths		Bond angles	
Mo–O(1)	1.873(3)	O(1)–Mo–C(18)	155.76(15)
Mo–O(2)	1.996(3)	O(1)–Mo–O(2)	96.57(14)
Mo–C(1)	2.013(5)	O(1)–Mo–C(5)	95.57(16)
Mo–C(2)	1.999(5)	O(1)–Mo–C(1)	101.21(17)
Mo–C(5)	2.226(5)	C(18)–Mo–O(2)	74.59(15)
Mo–C(6)	2.488(5)	C(18)–Mo–C(5)	77.47(17)
Mo–C(18)	2.389(4)	C(18)–Mo–C(1)	102.29(17)
C(23)–O(2)	1.347(6)	O(2)–Mo–C(1)	124.93(18)
C(17)–O(3)	1.238(6)	O(2)–Mo–C(5)	136.73(16)
C(10)–C(11)	1.542(7)	C(2)–Mo–C(5)	123.5(2)
C(6)–C(11)	1.367(7)	C(1)–C(2)–C(3)	145.4(5)
C(5)–C(6)	1.490(7)	C(2)–C(1)–C(4)	140.3(5)
C(5)–C(9)	1.539(7)		
C(1)–C(2)	1.307(7)		
Mo···C(11)	2.769		
C(1)–C(4)	1.498(7)		
C(2)–C(3)	1.475(7)		

ene resonances in the ethyl groups at 2.79 ppm (on C_α) and 2.69 ppm (on C_β), and methyl resonances in the ethyl groups at 1.61 ppm (on C_α) and 0.34 ppm (on C_β) [36].

Both **10a** and **10b** were stable for days in the solid state and could be analyzed satisfactorily. It also was shown that **10a** did not react with twenty equivalents of 3-hexyne to give **10b**, while **10a** did not behave as a metathesis catalyst for 3-heptyne over a period of 12 h at room temperature in toluene. Ultimately studies were complicated by the fact that **10a** and **10b** both decompose slowly in solution, even in the presence of added alkyne.

Attempts to obtain crystals of either **10a** or **10b** for an X-ray structural determination were unsuccessful as a consequence of their decomposition. For example, an attempted crystallization of **10a** over a period of several days from a concentrated solution in a mixture of ether and pentane at −30 °C led to pale yellow crystals, but these crystals turned out to be those of decomposition product **11a** (Eq. (7)). Typically only a low yield (< 10%) of **11a** could be isolated



10a **11a**

(7)

and the yield was found to vary from one reaction to another. An X-ray study showed that **11a** has the stoichiometry of **10a** plus one equivalent of 2-butyne. The characteristic resonances for **11a** in the complex ^{1}H-NMR spectrum are the two singlet resonances at 6.85 and 5.21 ppm for protons in what had been the 4 and 4′ positions of the [Biphen]$^{2-}$ ligand.

A Chem 3D drawing of **11a** is shown in Fig. 3. Crystallographic data, collection parameters, and refinement parameters are given in Table 5 while selected bond lengths and angles are given in Table 6. The most bizarre feature of **11a** is that half of the [Biphen]$^{2-}$ ligand has been rotated away from the metal and the C_3Me_3 portion of the metallacyclobutadiene ring in **10a** fused to carbons in position 5 (C(9)) and 6 (C(10)) in the [Biphen]$^{2-}$ backbone to create two quaternary carbon centers and a kind of allyl linkage (C(5), C(6), C(11)). The bond distances to the three carbons in this allyl ligand differ significantly, with Mo–C(5) = 2.226(5) Å, Mo–C(6) = 2.488(5) Å, and Mo–C(11) = 2.769 Å. Since the C(6)–C(11) bond is so short (1.367(7) Å) and the Mo–C(11) distance so long, this moiety probably is best viewed as a σ allyl, i.e., with Mo–C(5) being the only formal (single) bond. The Mo–C(18) distance (2.389(4) Å) could be characterized as a long single bond, and the

C(17)–O(3) distance (1.238(6) Å) as a C=O bond. Therefore the metal is in the 4+ oxidation state, counting the alkyne (C(1)–C(2)) as a neutral ligand, or a 6+ oxidation state viewing the alkyne as a dianionic ligand (part of a metallacyclopropene structure). The C(1)–C(2) distance (1.307(7) Å), C(1)–C(2)–C(3) and C(2)–C(1)–C(4) angles (145.4(5) and 140.3(5)°, respectively), and Mo–C(1) and Mo–C(2) bond distances (2.013(5) and 1.999(5) Å, respectively), are typical of what is found in Mo and W alkyne complexes [37].

No information concerning the mechanism of decomposition of **10a** could be obtained. Clearly the second equivalent of 2-butyne must come from another molecule of **10a**. It is peculiar that the yield of **11a** did not seem to increase significantly when **10a** was allowed to decompose in the presence of several equivalents of 2-butyne. However, decomposition of **10a** in neat 2-butyne was not attempted.

Decomposition of **10b** in solution also produced a product (**11b**) that is analogous to **11a** on the basis of the appearance in the ^{1}H-NMR spectrum of a resonance at 5.16 ppm. This resonance is believed to be characteristic of a proton attached to C(15) in the drawing shown in Fig. 3 (cf., 5.21 ppm in **11a**).

3. Discussion and conclusions

We have demonstrated that either an imido alkylidene complex or, in the presence of triethylamine, an amido alkylidyne complex can form upon addition of K_2[Biphen] to Mo(NAr_{Cl})(CH-*t*-Bu)$(OTf)_2$(dme). Moving a proton from carbon to nitrogen is the reverse of a step in the original syntheses of imido alkylidene dichloride complexes of Mo and W from amido alkylidyne dichloride complexes (e.g. as shown in Scheme 1). Therefore, it is clear that an imido alkylidene and an amido alkylidyne can be close in energy and that a proton can move from nitrogen to carbon or the reverse. However, even two decades after the first such reactions were observed [38], it is not clear exactly what mechanism or mechanisms are operative. In these first studies, it was found that W(NHPh)(C-*t*-Bu)$(PEt_3)_2Cl_2$ reacts with $Ph_3P{=}CH_2$ to yield [Ph_3PCH_3]Cl and W(NPh)(C-*t*-Bu)$(PEt_3)_2$Cl, which subsequently can be treated with HCl to yield W(NPh)(CH-*t*-Bu)$(PEt_3)_2Cl_2$ [38]. Interestingly, later it was also found that both W(NAr)(CH-*t*-Bu)$[OCMe(CF_3)_2]_2$ and W(NHAr)(C-*t*-Bu)$[OCMe(CF_3)_2]_2$(dme) can be prepared, and neither can be converted into the other in the presence of a catalytic amount of triethylamine [39]. Therefore we might propose that a good leaving group (e.g. chloride or triflate) must be present so that [BaseH]X (X = chloride or triflate) can be lost from either an imido alkylidene or an amido alkylidyne to yield a neutral imido alkylidyne intermediate, one that is likely to be stabilized by coordination of some donor ligand such as dme (cf. W(NPh)(C-*t*-Bu)$(PEt_3)_2$Cl [38]). Of course, [BaseH]X must also be acidic enough to *reprotonate* N or C in the imido alkylidyne intermediate if the proton transfer is to be completed. The required loss of [BaseH]X to yield a neutral imido alkylidyne intermediate would account for the failure to interconvert imido alkylidene and amido alkylidyne complexes that contain only alkoxides, at least with triethylamine as the base. Since it is known that W(NHPh)(C-*t*-Bu)$(PEt_3)_2Cl_2$ is converted into W(NPh)(CH-*t*-Bu)$(PEt_3)_2Cl_2$ simply through heating [38], donor ligands (e.g. a phosphine) might dissociate and play the role as a base in certain circumstances. Finally, we still cannot exclude the possibility that a proton can transfer directly from N to C or from C to N in the right circumstances, without any external base being required. This proton migration reaction would be related to an α hydrogen abstraction, which produces an alkylidene from a dialkyl complex [26]. Exactly how the proton is transferred (irreproducibly) when K_2[Biphen] is added to various bis(triflates) is still a puzzle.

The proton transfer reaction (N to C or vice versa) is likely to be delicately balanced, and the nature of the substituent on nitrogen (in an amido or imido group) is likely to be one of several important variables. A proton might be transferred to the Mo=NAr_{Cl} group relatively easily because of a weak interaction between an ortho chloride and the metal in the developing amido ligand, as shown in the crystal structure of Mo($NHAr_{Cl}$)($CCMe_2Ph$)[*S*-Biphen] (Fig. 1). No proton transfer to a 2,6-diisopropylphenylimido or a 2,6-dimethylphenylimido ligand has been observed, and transfer to an ortho(trifluoromethyl)phenylimido ligand has not been reproducible.

The only isolable molybdenum alkylidyne complex in the early investigations that contains a phenoxide ligand is Mo(C-*t*-Bu)$(DIPP)_3$ (DIPP = O-2,6-*i*-$Pr_2C_6H_3$) [36]. This species will metathesize twenty equivalents of 3-heptyne in <5 min, and new alkylidyne complexes, Mo(CR)$(DIPP)_3$ (R = Me, Et, *n*-Pr, Ph) can be observed upon treating Mo(C-*t*-Bu)$(DIPP)_3$ with various alkynes. However, metallacyclobutadiene complexes of molybdenum are rare, with only Mo(C_3Et_3)$(DIPP)_3$ being observed at low temperatures; at room temperature in solution this molybdacycle dissociates into EtC≡CEt and Mo(CEt)$(DIPP)_3$. On the other hand, the tungstenacyclobutadiene species, W(C_3R_3)(O-2,6-*i*-$Pr_2C_6H_3)_3$ (R = Et, Pr) [4], can be isolated and will catalyze the metathesis of 3-heptyne readily at room temperature. Therefore we were surprised by the finding that complexes **10a** and **10b** not only would not lose alkyne reversibly and metathesize alkynes, but would decompose slowly to yield a species (in low yield) that contains a radically altered $[Biphen]^{2-}$ ligand. On the other hand, it has been known for some time that certain tungstacyclobutadiene complexes will not metathesize alkynes, but will react with alkynes to give complexes in which the metal has been reduced [3]. For example, W(C-*t*-Bu)Cl_3(dme) reacts with 2-butyne to give an observable trigonal bipyramidal tungstacyclobutadiene complex, W[C(*t*-Bu)CMeCMe]Cl_3, which reacts further with 2-butyne to give a W[η^5-C_5(*t*-Bu)Me_4]Cl_3 species, which subsequently disproportionates into W[η^5-C_5(*t*-Bu)Me_4]Cl_4 and W[η^5-C_5(*t*-Bu)Me_4]Cl_3(2-butyne) in the presence of 2-butyne [40,41]. We might expect Mo(6+) metallacyclobutadienes to be reduced more readily than W(6+) metallacyclobutadienes. However, we were not prepared for the degree of alteration of the $[Biphen]^{2-}$ ligand in **11a**, especially fusion of the C_3Me_3 fragment to the $[Biphen]^{2-}$ ligand and creation of two quaternary carbon centers in the process. Clearly Mo biphenolate alkylidyne complexes are not as stable as Mo 2,6-diisopropoxide alkylidyne complexes. Therefore the prospect of any alkyne metathesis reactions with Mo(CR)[Biphen](OR′) complexes does not seem bright. It is not yet known whether binaphtholate ligands are also unsuitable in potential alkyne metathesis reactions.

It should be noted that triphenoxide Mo alkylidyne complexes are most likely the active species in the first homogeneous alkyne metathesis system to be reported, which involved heating $Mo(CO)_6$ to high temperatures (>130 °C) in the presence of alkynes and various phenols [42,43]. Triphenoxide Mo alkylidyne complexes, many of them formed in situ, continue to be useful as alkyne metathesis catalysts [6–17]. Most recently Moore has shown that Mo[N(*t*-Bu)(Ar″)]$_3$ (Ar″ = 3,5-$Me_2C_6H_3$) will react with 1,1-dichloroalkanes, R′$CHCl_2$ (R′ = H, Me, Et), in the presence of magnesium to give high yields of Mo(CR′)[N(*t*-Bu)(Ar″)]$_3$ species [23]. Upon addition of *o*-trifluoromethylphenol or perfluoro-*t*-butanol to Mo(CR′)[N(*t*-Bu)(Ar″)]$_3$ efficient alkyne metathesis catalysts are generated in situ; presumably these are Mo(CR′)(OR)$_3$ species. Moore's method of preparing triphenoxide alkyne metathesis catalysts in situ may well turn out to be the most convenient and efficient method of generating alkyne metathesis catalysts to be reported so far.

4. Experimental

4.1. General details

All experiments were conducted under nitrogen in a Vacuum Atmospheres drybox or using standard Schlenk techniques. THF, toluene, ether, and pentane were sparged with nitrogen and passed through alumina columns. Benzene was distilled from sodium benzophenone ketyl. Benzyl potassium [44], H_2[*rac*-Biphen] [45], H_2[*S*-Biphen] [31], Mo(NAr_{Cl})(CH-*t*-Bu)$(OTf)_2$(dme) [32] and Mo$(NAr_{Cl})_2$$(CHCMe_2Ph)_2$ [32] (NAr_{Cl} = *N*-2,6-$Cl_2C_6H_3$) were prepared by reported methods. Mo(η^2-CH_2CSiMe_3)[N(*i*-Pr)Ar″]$_3$ (Ar″ = 3,5-$Me_2C_6H_3$) was a gift from Tsai et al. [13]. 1-Adamantanol was used as received from Aldrich. 2-Butyne and 3-hexyne were filtered through alumina before use. C_6D_6 and toluene-d_8 were sparged with nitrogen and stored over 4 Å molecular sieves. ^1H- and ^{13}C-NMR data are listed in parts per million downfield from tetramethylsilane and were referenced using the residual protio solvent resonance. Routine NMR coupling constants are not reported. Spectra were obtained at room temperature. Elemental analyses were performed by H. Kolbe Laboratories, Mülheim an der Ruhr, Germany.

4.2. Mo(NH-2,6-$Cl_2C_6H_3$)($CCMe_3$)[Biphen] (**4a**)

4.2.1. Method A

Benzyl potassium (96 mg, 0.58 mmol) was added to H_2[rac-Biphen] (104 mg, 0.29 mmol) in THF (2 ml). Mo(NAr_{Cl})(CH-*t*-Bu)$(OTf)_2$(dme) (200 mg, 0.29 mmol) was then added and the mixture turned dark red. After 24 h, the solvent was removed in vacuo. The residue was dissolved in benzene and the solution was filtered through Celite. The benzene was evaporated, the residue was dissolved in ether. A yellow powder was filtered off after storing the mixture at −30 °C for 1 month; yield 32 mg (17%): ^1H-NMR (500 MHz, C_6D_6) δ 11.73 (s, 1, N*H*), 7.40 (s, 1, Ar*H*), 7.25 (s, 1, Ar*H*), 6.69 (d, 2, Ar*H*), 6.05 (t, 1, Ar*H*), 2.20 (s, 3, ArCH_3), 2.17 (s, 3, ArCH_3), 1.75 (s, 3+9, ArCH_3+ArC$(CH_3)_3$), 1.67 (s, 3, ArCH_3), 1.39 (s, 9, ArC$(CH_3)_3$), 1.01 (s, 9, Mo≡CC$(CH_3)_3$); ^{13}C-NMR (125 MHz, C_6D_6) δ 327.74, 160.63, 155.81, 147.20, 137.15, 135.74, 135.06, 131.16, 130.34, 129.91, 129.75, 129.69, 128.67, 128.32, 127.70, 121.42, 54.96, 36.12, 35.63, 30.97, 30.22, 28.84, 20.89, 20.85, 17.18, 17.03. Anal. Calcd for $MoC_{35}H_{45}Cl_2NO_2$: C, 61.95; H, 6.68; N, 2.06; Cl, 10.45. Found: C, 62.08; H, 6.75; N, 1.98; Cl, 10.31%.

4.2.2. Method B

Benzylpotassium (0.740 g, 5.70 mmol) was added in portions to a stirred solution of H_2[*rac*-Biphen] (1.010 g, 2.80 mmol) in 40 ml of THF until a slightly yellow color persisted. The solution was chilled to −30 °C and added drop-wise to a stirred, prechilled solution of Mo(*N*-2,6-$Cl_2C_6H_3$)(CH-*t*-Bu)$(OTf)_2$(dme) (2.030 g, 2.84 mmol) and ten equivalents of triethylamine (5 ml, 28.4 mmol) in 75 ml THF. The resulting deep red solution was stirred for 2 h at room temperature and the volatile solvents were removed in vacuo to give an orange–brown solid. This solid was dissolved in toluene and the solution was filtered through a pad of Celite. The toluene was removed and the product was dissolved in a minimum amount of pentane. Bright orange crystals were obtained in 40% yield from a concentrated pentane solution at −30 °C. NMR spectra of this material were identical to those of the product produced by Method A.

4.3. $Mo(N\text{-}2,6\text{-}Cl_2C_6H_3)(CHCMe_2Ph)(OTf)_2(THF)$

Triflic acid (3.77 g, 25.15 mmol) was added to a −30 °C solution of $Mo(NAr_{Cl})_2(CH_2CMe_2Ph)_2$ (5.72 g, 8.38 mmol) in dme (80 ml). After stirring the solution for 16 h, the dme was evaporated in vacuo. The resulting brown oil was dissolved in toluene and the solution was filtered through Celite. Evaporation of the toluene yielded a brown oily solid that was dissolved in ether. A brown–yellow solid formed and was triturated with THF and ether several times to give a yellow powder; yield 1.75 g, 28%. According to elemental analyses the complex exists as a mono(THF) adduct in the solid state. In THF-d_8, $Mo(N\text{-}2,6\text{-}Cl_2C_6H_3)(CHCMe_2Ph)(OTf)_2(THF)_2$ is observed as a 1:1 mixture of two isomers: ^{1}H-NMR (500 MHz, THF-d_8) δ 14.21 (s, 1, Mo=C*H*, $J_{CH} = 126$ Hz), 14.17 (s, 1, Mo=C*H*, $J_{CH} = 124$ Hz), 6.96 (d, 4, Ar*H*), 6.92 (d, 2, Ar*H*), 6.87 (d, 2, Ar*H*), 6.78 (t, 1, Ar*H*), 6.71 (m, 3, Ar*H*), 6.55 (m, 3, Ar*H*), 6.30 (t, 1, Ar*H*), 3.69 (m, 4, THF), 3.54 (m, 4, THF), 3.44 (m, 4, THF), 2.82 (m, 4, THF), 1.21 (s, 3, C*H*$_3$), 1.20 (s, 6, C*H*$_3$), 0.94 (s, 3, C*H*$_3$); ^{19}F-NMR (282 MHz, THF-d_8) δ −80.14 (s), −80.52 (s), −81.10 (s), −81.33 (s). Anal. Calcd for $MoC_{22}H_{23}Cl_2NO_7F_6S_2$: C 34.84; H 3.06; N 1.85; Cl 9.35. Found: C 34.68; H 2.93; N 1.81; Cl 9.39%.

4.4. $Mo(NH\text{-}2,6\text{-}Cl_2C_6H_3)(CCMe_2Ph)[S\text{-}Biphen]$ (**4b**)

Benzyl potassium (151 mg, 1.16 mmol) in THF (2 ml) was added to H_2[*S*-Biphen] (187 mg, 0.53 mmol) in THF (2 ml) until a slight orange color persisted. The mixture was stirred for 10 min and added dropwise to a suspension of $Mo(NAr_{Cl})(CHCMe_2Ph)(OTf)_2(THF)_x$ (400 mg, 0.53 mmol) in THF (5 ml). The mixture turned dark red and homogeneous. After stirring the mixture for 20 h, the solvent was evaporated in vacuo. The residue was suspended in toluene, the mixture was filtered through Celite, and the solvent was evaporated to give a red oil. The red oil was dissolved in ether (2 ml) and stored at −30 °C to give $Mo(NHAr_{Cl})(CCMe_2Ph)$[*S*-Biphen] as a yellow powder that was isolated by filtration; yield 147 mg (38%): ^{1}H-NMR (500 MHz, C_6D_6) δ 11.59 (s, 1, N*H*), 7.45 (d, 2, Ar*H*), 7.33 (s, 1, Ar*H*), 7.26 (s, 1, Ar*H*), 7.21 (t, 2, Ar*H*), 7.09 (t, 1, Ar*H*), 6.66 (br s, 2, Ar*H*), 6.03 (t, 1, Ar*H*), 2.20 (s, 3, ArC*H*$_3$), 2.17 (s, 3, ArC*H*$_3$), 1.78 (s, 3, ArC*H*$_3$), 1.67 (s, 3, ArC*H*$_3$), 1.65 (s, 9, C(C*H*$_3$)$_3$), 1.45 (s, 3, C(C*H*$_3$)$_2$Ph), 1.38 (s, 9+3, C(C*H*$_3$)$_3$+C(C*H*$_3$)$_2$Ph); ^{13}C-NMR (125 MHz, C_6D_6) δ 322.13 (*C*CMe$_2$Ph), 160.68, 155.92, 147.21, 146.31, 137.36, 137.17, 135.67, 135.13, 131.37, 130.38, 129.99, 129.88, 129.74, 129.17, 127.62, 126.88, 126.82, 121.48, 61.77, 36.06, 35.62, 30.86, 30.21, 29.59, 28.79, 20.91, 17.20, 17.05. Anal. Calc. for $MoC_{40}H_{47}NCl_2O_2$: C, 64.87; H, 6.40; N, 1.89; Cl, 9.57. Found: C, 64.75; H, 6.48; N, 1.77; Cl, 9.71%.

4.5. $Mo(CCH_2SiMe_3)[Biphen](OAd)$ (**9**)

$Mo(\eta^2\text{-}CH_2CSiMe_3)[N(i\text{-}Pr)Ar'']_3$ (2.00 g, 2.93 mmol) was dissolved in toluene (60 ml) and the solution was heated to 80 °C in a Teflon-sealed Schlenk flask until complete conversion to the alkylidyne was observed by ^{1}H-NMR (~18 h). The reaction mixture was then cooled to room temperature and H_2[rac-Biphen] (1.04 g, 2.93 mmol) was added. The solution was heated to 80 °C until complete conversion to $Mo(CCH_2SiMe_3)[N(i\text{-}Pr)Ar'']$[Biphen] was observed by ^{1}H-NMR (18–48 h). The ^{1}H-NMR spectrum (500 MHz, toluene-d_8) of the mixture of $Mo(CCH_2SiMe_3)[N(i\text{-}Pr)Ar'']$[Biphen] and two equivalents of $HN(i\text{-}Pr)Ar''$ is assigned as follows: $Mo(CCH_2SiMe_3)[N(i\text{-}Pr)Ar'']$[Biphen] δ 7.29 (s, 1, Ar*H*), 6.73 (s, 1, Ar*H*), 6.34 (s, 1, *para* Ar*H* amido), 6.30 (s, 2, *ortho* Ar*H* amido), 4.28 (sept, 1, C*H*Me$_2$), 2.85 (s, 2, MoCC*H*$_2$), 2.17 (s, 3, ArC*H*$_3$ Biphen), 2.03 (s, 3, ArC*H*$_3$ Biphen), 1.94 (s, 6, ArC*H*$_3$ amido), 1.73 (s, 9, C(C*H*$_3$)$_3$), 1.69 (s, 3, ArC*H*$_3$ Biphen), 1.63 (d, 6, CH(C*H*$_3$)$_2$), 1.56 (s, 3, ArC*H*$_3$ Biphen), 1.20 (s, 9, C(C*H*$_3$)$_3$), −0.02 (s, 9, Si(C*H*$_3$)$_3$); free $HN(i\text{-}Pr)Ar''$ δ 6.59 (s, 2, *para* Ar*H*), 6.05 (s, 4, *ortho* Ar*H*), 3.37–3.31 (m, 2, C*H*Me$_2$), 2.85 (br s, 2, N*H*), 2.16 (s, 12, ArC*H*$_3$), 0.92 (d, 12, CH(C*H*$_3$)$_2$). The solution was cooled to room temperature and 1-adamantanol (0.44 g, 2.93 mmol) in THF (15 ml) was added. The reaction was stirred at room temperature (~24 h) until complete conversion to $Mo(CCH_2SiMe_3)[N(i\text{-}Pr)Ar'']$[Biphen] was found, according to ^{1}H-NMR. The solvent was evaporated and the resulting residue was dissolved in minimal pentane. After storing this solution at −30 °C for 12 h, the product was isolated by filtration as a beige crystalline solid; yield 0.95 g (46.2%): ^{1}H-NMR (500 MHz, C_6D_6)δ 7.39 (s, 1, Ar*H*), 7.15 (s, 1, Ar*H*), 2.98 (m, 3, Ad), 2.20 (s, 3, ArC*H*$_3$), 2.08 (s, 6+2, Ad+MoCC*H*$_2$), 1.94 (s, 3, ArC*H*$_3$), 1.82 (s, 9, C(C*H*$_3$)$_3$), 1.74 (s, 3, ArC*H*$_3$), 1.63 (s, 3, ArC*H*$_3$), 1.61 (s, 9, C(C*H*$_3$)$_3$), 1.54–1.51 (m, 6, Ad), 0.04 (s, 9, Si(C*H*$_3$)$_3$); ^{13}C-NMR (125 MHz, C_6D_6) δ 307.76 (*C*CH$_2$SiMe$_3$), 155.58, 149.56, 140.52, 139.25, 135.88, 135.29, 131.32, 131.04, 130.69, 129.85, 129.66, 127.19, 82.58, 47.75, 47.57, 36.87, 36.25, 35.48, 32.11, 30.81, 30.77, 20.92, 20.63, 16.98, 16.68, −0.85. Anal. Calc. for $MoC_{39}H_{58}SiO_3$: C, 67.02; H, 8.36. Found: C, 67.15; H, 8.31%.

4.6. $Mo(C_3Me_3)[Biphen](OAd)$ (**10a**)

Addition of 2-butyne (193 mg, 3.58 mmol) to $Mo(CCH_2SiMe_3)$[Biphen](OAd) (250 mg, 0.36 mmol) in ether (2 ml) caused the colorless solution to turn dark red immediately. After 12 h, $Mo(C_3Me_3)$[Biphen](OAd) was isolated by filtration as a rosy-red powder; yield 192 mg (78%): ^{1}H-NMR (500 MHz, C_6D_6) δ 7.21 (s, 1, ArH), 6.09 (s, 1, ArH), 2.89 (br s, 3, α-C_3CH_3), 2.74 (br s, 3, α-C_3CH_3), 2.26 (s, 3, ArCH_3), 2.01 (s, 3, ArCH_3), 1.90 (s, 3, β-C_3CH_3), 1.88 (s, 3, ArCH_3), 1.86 (s, 3, ArCH_3), 1.72 (s, 9, $C(CH_3)_3$), 1.43 (s, 9, $C(CH_3)_3$), 1.41 (m, 9, OAd), 0.80 (s, 3, OAd), 0.67 (s, 3, OAd); ^{13}C-NMR (125 MHz, C_6D_6) δ 254.24 (metallacycle C), 218.03 (metallacycle C), 192.79 (metallacycle C), 169.26, 163.98, 144.85, 139.94, 137.87, 135.65, 134.16, 126.67, 125.92, 120.10, 90.48, 82.08, 64.45, 63.94, 47.04, 36.56, 35.17, 35.10, 31.73, 30.45, 30.41, 23.17, 22.22, 21.80, 21.15, 19.75, 18.09, 17.24, 15.39, 14.46. Anal. Calc. for $MoC_{40}H_{56}O_3$: C, 70.57; H, 8.29. Found: C, 70.46; H, 8.25%.

4.7. *$Mo(C_3Et_3)$[Biphen](OAd)* (**10b**)

Addition of 3-hexyne (235 mg, 2.86 mmol) to $Mo(CCH_2SiMe_3)$[Biphen](OAd) (200 mg, 0.29 mmol) in ether (2 ml) caused the colorless solution to turn dark red immediately. After 12 h, $Mo(C_3Et_3)$[Biphen](OAd) (**10b**) was isolated by filtration as a rosy-red powder; yield 122 mg (59%): ^{1}H-NMR (500 MHz, C_6D_6) δ 7.22 (s, 1, ArH), 6.45 (s, 1, ArH), 3.57–3.52 (m, 1, α-C_3CH_2), 3.07–3.00 (m, 1, α-C_3CH_2), 2.98–2.90 (m, 2, β-C_3CH_2), 2.68–2.62 (m, 1, α-C_3CH_2), 2.26 (s, 3, ArCH_3), 2.11 (s, 3, ArCH_3), 2.02–1.96 (m, 1, α-C_3CH_3), 1.78 (s, 3+9, ArCH_3+$C(CH_3)_3$), 1.73 (s, 3, ArCH_3), 1.73–1.69 (m, 3, OAd), 1.66 (s, 9, $C(CH_3)_3$), 1.31 (t, 3, β-$C_3CH_2CH_3$), 1.32–1.23 (m, 6, OAd), 0.93 (d, 6, OAd), 0.77 (t, 3, α-$C_3CH_2CH_3$), 0.64 (t, 3, α-$C_3CH_2CH_3$). Anal. Calcd for $MoC_{43}H_{62}O_3$: C, 71.44; H, 8.64. Found: C, 71.60; H, 8.56%.

4.8. *Supporting information available*

Fully labeled thermal ellipsoid drawings, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **4b**, **9** and **11a**.

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