ORGANOMETALLICS

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Syntheses of "Phosphine-Free" Molybdenum Oxo Alkylidene Complexes through Addition of Water to Alkylidyne Complexes

Feng Zhai, Richard R. Schrock,* Amir H. Hoveyda, and Peter Müller

Cite This: https://dx.doi.org/10.1021/acs.organomet.0c00275 Read Online

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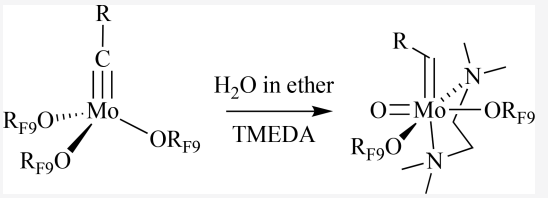
ABSTRACT: Addition of 1 equiv of water to $Mo(CAr_p)(OR_{F9})_3$ (Ar_p = *p*-methoxyphenyl; OR_{F9} = $OC(CF_3)_3$) in the presence of 5% NEt_3 (vs Mo) in THF led to the formation of $Mo(O)(CHAr_p)(OR_{F9})_2(THF)_2$ in good yield. $Mo(O)(CHAr_p)(OR_{F9})_2(THF)_2$ reacts with 2 equiv of LiOHMT (OHMT = *O*-2,6-mesityl$_2$C$_6$H$_3$) at room temperature to yield $Mo(O)(CHAr_p)(OHMT)_2$ and with 2 equiv of NaOTPP (OTPP = 2,3,5,6-tetraphenylphenoxide) to yield $Mo(O)(CHAr_p)(OTPP)_2$. In the presence of TMEDA (2.5 equiv), $Mo(CR)(OR_{F9})_3$ (R = Ar_p, mesityl, or *t*-Bu) reacts with 1 equiv of water to yield $Mo(O)(CHR)(OR_{F9})_2$(TMEDA) complexes, from which (when R = *t*-Bu) TMEDA is readily displaced by 2,2′-bipyridyl to give $Mo(O)(CH\text{-}t\text{-}Bu)(OR_{F9})_2$(bipy). $Mo(O)(CH\text{-}t\text{-}Bu)(OR_{F9})_2$(bipy) was converted into $Mo(O)(CH\text{-}t\text{-}Bu)Cl_2$(bipy) readily, from which $Mo(O)(CH\text{-}t\text{-}Bu)Cl$(OHMT)(3-Brpy) (3-Brpy = 3-bromopyridine) and $Mo(O)(CH\text{-}t\text{-}Bu)Cl$(OHIPT)(3-Brpy) (OHIPT = *O*-2,6-(2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$) were prepared. X-ray studies were carried out on $Mo(O)(CHAr_p)(OR_{F9})_2(THF)_2$, $Mo(O)(CH\text{-}t\text{-}Bu)(OR_{F9})_2$(TMEDA), $Mo(O)(CHAr_p)(OTPP)_2$, $Mo(O)(CH\text{-}t\text{-}Bu)Cl$(OHMT)(3-Brpy), and $Mo(O)(CH\text{-}t\text{-}Bu)Cl$(OHIPT)(3-Brpy).



INTRODUCTION

High oxidation state molybdenum and tungsten oxo alkylidene complexes are analogues of the much-studied molybdenum and tungsten imido alkylidene families of complexes that have been known for approximately three decades.[1] Interest in oxo alkylidene complexes derives (in part) from the fact that they are likely to be the active catalysts in "classical" olefin metathesis systems where no primary amine is present. Tungsten oxo alkylidenes were prepared through α hydrogen abstraction in tungsten oxo dineopentyl complexes in 2012.[2] However, syntheses of molybdenum oxo alkylidene complexes that are active for metathesis of olefins remained elusive[3] until we found that addition of 1 equiv of water to benzylidyne complexes $Mo(CAr)(OR)_3(L')$ (where Ar = *ortho*- or *para*-methoxyphenyl and OR = $OC(CF_3)_2Me$ or $OC(CF_3)_3$ (OR_{F9}) and L′ = DME or two THFs) in the presence of a phosphine L (e.g., PMe_2Ph, $PMePh_2$, PEt_3, or $P(i\text{-}Pr)_3$) led, with varying degrees of success, to formation of $Mo(O)(CHAr)(OR)_2(L)$ complexes.[4] If the phosphine is not present, hydroxy alkylidyne dimers, $\{Mo(CAr)(OR)_2(\mu\text{-}OH)\}_2(\mu\text{-}L')$ (L′ = ether, THF, DME), are formed. In some cases, the hydroxy alkylidyne complexes are converted into $Mo(O)(CHAr)(OR)_2(L)$ complexes upon addition of a phosphine. Addition of the phosphine first to $Mo(CAr)(OR_{F9})_3(THF)_2$ complexes, followed by 1 equiv of water, often produces the $Mo(O)(CHAr)(OR)_2(L)$ product in better yields, which suggests that L attacks on some monomeric Mo hydroxy alkylidyne intermediate may be the more desirable and more controllable reaction. A key question is whether another ligand/base besides a phosphine can promote the hydrogen migration reaction from O to C. For this reason, we turned to an exploration of syntheses of Mo oxo alkylidene complexes under "phosphine-free" conditions. We report here a variety of Mo oxo alkylidene syntheses that do not require a phosphine.

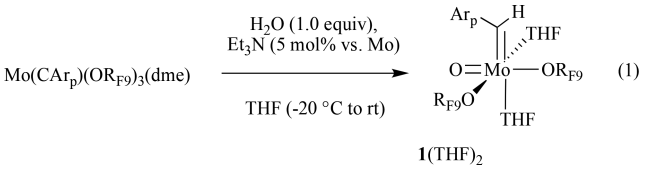
RESULTS AND DISCUSSION

Addition of Water to Alkylidynes. We decided to focus on $OC(CF_3)_3$ (OR_{F9}) alkylidyne complexes because of the significant steric protection and electron-withdrawing ability that perfluoro-*t*-butoxide affords and because OR_{F9} complexes may allow access to a variety of alkylidyne complexes through alkyne metathesis.[5]

Key findings in 1982 provided some clues as to what syntheses of Mo oxo alkylidenes might be successful. The first imido alkylidene complex (of W) was prepared through conversion of an amido neopentylidyne complex into an imido neopentylidene complex, thermally or (more rapidly) upon addition of triethylamine.[6] Second, addition of 1 equiv of water to $W(C\text{-}t\text{-}Bu)(PMe_3)_3Cl_3$[7] gave $W(O)(CH\text{-}t\text{-}Bu)(PMe_3)_2Cl_2$ and Me_3PHCl.[8] Finally, as noted above, addition of 1 equiv of water (in THF) to $Mo(CAr_p)(OR_{F9})_3(THF)_2$ in CH_2Cl_2 led to formation of $\{Mo(CAr_p)(OR_{F9})_2(\mu\text{-}OH)\}_2(\mu\text{-}THF)$.[4b]

Received: April 22, 2020

The above observations led to an experiment in which we added water (1 equiv in THF) to $Mo(CAr_p)(OR_{F9})_3(DME)$ in THF in the presence of Et_3N (5 mol % vs Mo). The experiment yielded $Mo(O)(CHAr_p)(OR_{F9})_2(THF)_2$ (**1**$(THF)_2$; 47% isolated; eq 1) as red crystals. The yield



(1)

greatly depends upon the Mo concentration and other variables that have yet to be fully explored. Using $Mo(CAr_p)(OR_{F9})_3(THF)_2$ instead of $Mo(CAr_p)(OR_{F9})_3(DME)$ did not change the outcome or improve the yield dramatically. Increasing the loading of Et_3N to 1 equiv led to formation of a messy mixture containing several unidentified alkylidenes.

The structure of **1**$(THF)_2$ was established through X-ray diffraction (Figure 1). One of the THF ligands is *trans* to the

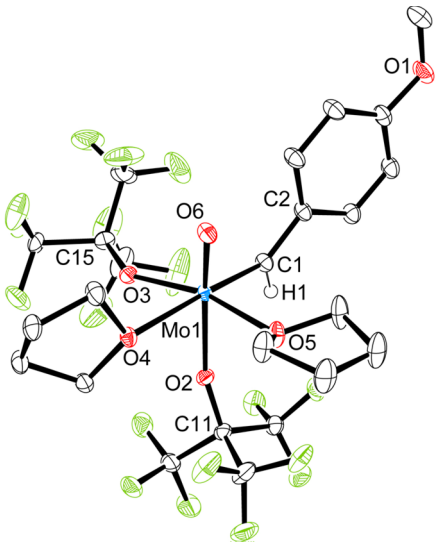
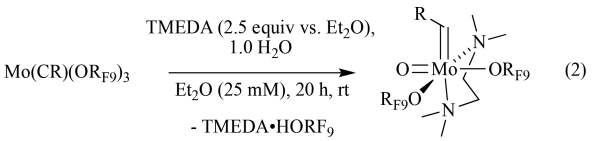


Figure 1. Thermal ellipsoid plot (50% probability) of **1**$(THF)_2$. Hydrogen atoms except for the alkylidene hydrogen (H1) are omitted for clarity. Mo1−O6 = 1.6785(5) Å, Mo1−C1 = 1.9398(7) Å, Mo1−O4 = 2.3938(5) Å, Mo1−O5 = 2.2226(5) Å; Mo1−O2 = 2.0249(5); Mo1−O3 = 2.0049(5).

benzylidene ligand and the other *trans* to one OR_{F9} ligand. The former THF ligand exhibits a Mo−O(THF) bond (2.3938(5) Å) significantly longer than that of the latter (2.2226(5) Å). The alkylidene proton resonance of **1**$(THF)_2$ in C_6D_6 (δ 13.85) is slightly broadened, which suggests that THF is relatively labile. ^1H, ^{19}F, and ^{13}C NMR spectra at 24 °C also show fast exchange between the two THF ligands (and exchange with added THF) and only one type of OR_{F9} ligand. Reversible dissociation of one THF and rearrangement of five-coordinate $Mo(O)(CHAr_p)(OR_{F9})_2(THF)$ is a plausible explanation of the NMR observations.

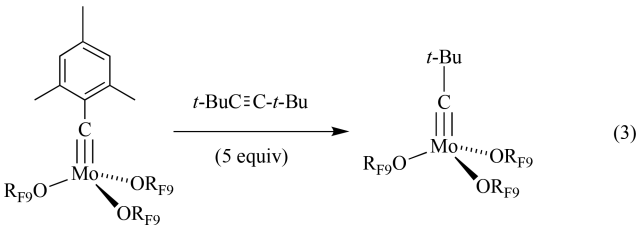
Addition of water (1 equiv; in THF or DME) to a mixture of $Mo(CAr_p)(OR_{F9})_3(L)$ (L = DME or 2THF) and TMEDA (2.5 equiv) in diethyl ether ([Mo] = 25 mM) at room temperature furnishes $Mo(O)(CHAr_p)(OR_{F9})_2(TMEDA)$ (**2a**) in 78% yield (eq 2). The reaction is equally efficient in CH_2Cl_2, THF, or DME. Mo(C-*t*-Bu)$(OR_{F9})_3$ was prepared



(2)

2a; R = Ar_p, 74%
2b; R = *t*-Bu, 78%
2c; R = Mes, 64%

through the reaction shown in eq 3. Reactions analogous to that yielding **2a** involving Mo(C-*t*-Bu)$(OR_{F9})_3$ or Mo-



(3)

(CMesityl)$(OR_{F9})_3$[5] gave Mo(O)(CH-*t*-Bu)-$(OR_{F9})_2$(TMEDA) (**2b**) and Mo(O)(CHMesityl)-$(OR_{F9})_2$(TMEDA) (**2c**), respectively (eq 2). These results suggest that water addition has some generality with respect to the alkylidyne. The alkylidene resonances in **2a** and **2c** appear at δ 13.88 (J_{CH} = 129 Hz) and 13.89 (J_{CH} = 116 Hz), respectively. The NMR data revealed hindered rotation of the mesityl group in **2c**. Decreasing the amount of TMEDA to 1 equiv led to much lower yields of **2b** (one experiment). It should be noted that the $R_{F9}OH$ (pK_a = 5.4 in water) that is formed in any of these reactions could protonate TMEDA.

An X-ray study of **2b** (Figure 2) was plagued with whole-molecule disorder, but the connectivity is assured (see

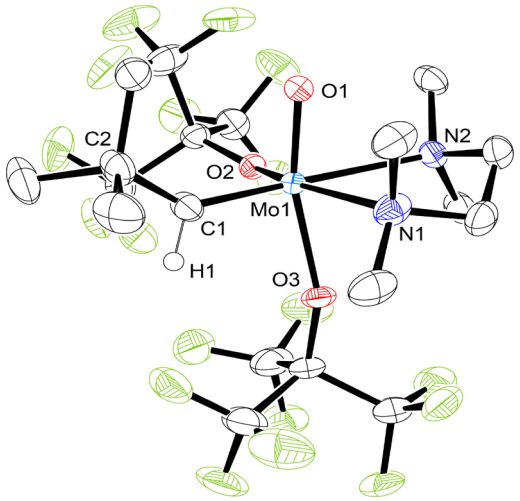


Figure 2. Thermal ellipsoid plot (50% probability) of **2b**. Hydrogen atoms except for the alkylidene hydrogen (H1) are omitted for clarity.

Supporting Information (SI) for details and discussion). The TMEDA ligand coordinates in a bidentate fashion *cis* to the oxo ligand. The NMR spectra (^1H, ^{13}C, ^{19}F) in CD_2Cl_2 show an unsymmetrically bound TMEDA ligand and inequivalent OR_{F9} ligands, as found in the solid state. The alkylidene proton resonance appears at δ 13.98 with a J_{CH} (125 Hz), consistent with the observed *syn* configuration of the alkylidene ligand.

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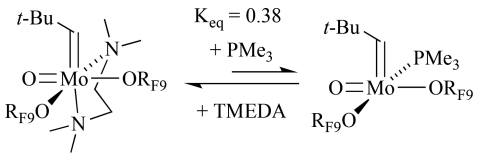
TMEDA is not strongly bound in **2a**–**2c**. For example, the addition of PMe_3 to a solution of **2b** in C_6D_6 resulted in formation of $Mo(O)(CH\text{-}t\text{-}Bu)(OR_{F9})_2(PMe_3)$ (eq 4). A



(4)

small amount of what we propose is $Mo(O)(CH\text{-}t\text{-}Bu)(OR_{F9})_2(PMe_3)_2$, on the basis of a triplet alkylidene ^1H NMR resonance, is also observed. We found K_{eq} to be 0.38 for $[Mo(O)(CH\text{-}t\text{-}Bu)(OR_{F9})_2(PMe_3)][TMEDA]/[\mathbf{2b}][PMe_3]$ (see Figure S34 in SI). The addition of 2,2′-bipyridyl (bipy; 1.0 equiv) to **2b** resulted in complete replacement of TMEDA by bipy and formation of $Mo(O)(CH\text{-}t\text{-}Bu)(OR_{F9})_2(bipy)$ (**2d**); a 10:1 mixture of two *syn*-alkylidene isomers is found in the proton NMR spectrum of **2d** in CD_2Cl_2 at 24 °C.

Synthesis of Other Oxo Alkylidenes. We showed that $\mathbf{1}(THF)_2$ is a starting point to make two bisaryloxides. The reaction between $\mathbf{1}(THF)_2$ and 2 equiv of LiOHMT at room temperature gave known[4b] $Mo(O)(CHAr_p)(OHMT)_2$ (**3a**) in 66% yield and with 2 equiv of NaOTPP (OTPP = 2,3,5,6-tetraphenylphenoxide) gave dark red $Mo(O)(CHAr_p)(OTPP)_2$ (**3b**) in 39% yield. The structure of **3b** was confirmed through X-ray diffraction analysis (Figure 3). Compound **3b** is essentially insoluble in C_6H_6 and ether and only moderately soluble in CD_2Cl_2.

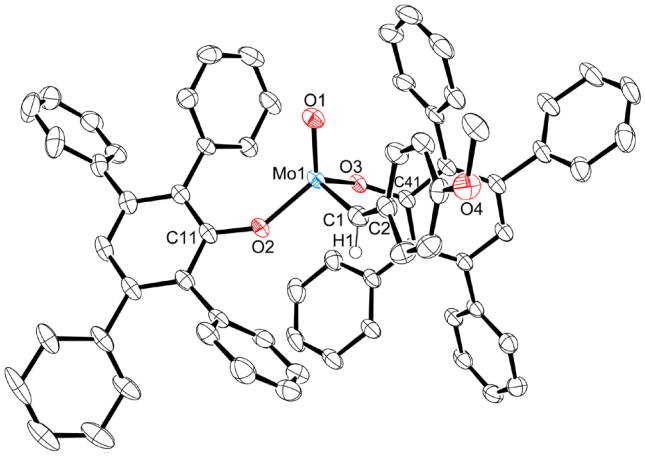
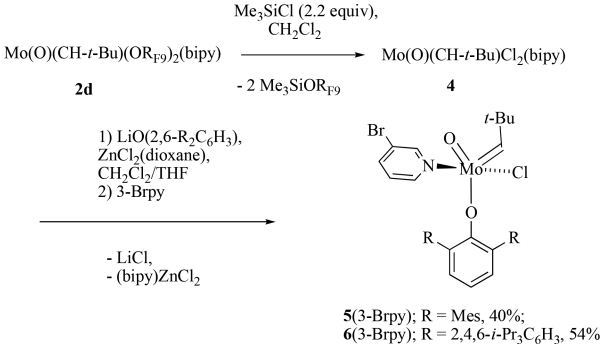


Figure 3. Thermal ellipsoid plot (50% probability) for **3b**. Hydrogen atoms except for the alkylidene hydrogen (H1) are omitted for clarity. Mo1–O1 = 1.6723(15) Å, Mo1–C1 = 1.913(2) Å, Mo1–O2 = 1.9086(14) Å, Mo1–O3 = 1.9332(14) Å, C11–O2–Mo1 = 145.58(14)°, C41–O3–Mo1 = 131.21(13)°.

Bisaryloxides have not proven to be as "tunable" to give highly reactive and *Z*-selective catalysts, unlike monoaryloxide pyrrolide (MAP)[9] or monoaryloxide chloride (MAC)[10] complexes. In order to prepare MAC complexes, we turned to **2d** and approaches analogous to those used to make the first MAC complexes that contain an imido ligand.[10a] As shown in Scheme 1, **2d** reacts with Me_3SiCl (2.2 equiv) in CH_2Cl_2 ([Mo] = 48 mM) at room temperature to yield $Mo(O)(CH\text{-}t\text{-}Bu)Cl_2(bipy)$ (**4**), which precipitated upon addition of Et_2O and was isolated in 70% yield. Compound **4** is a mixture of isomers that is dominated by one *syn*-alkylidene species (96%)

Scheme 1. Synthetic Route to Mo Oxo MAC Neopentylidene Complexes



on the basis of ^1H NMR data; **4** is moderately soluble in chlorinated solvents and insoluble in ether or pentane. Monitoring the reaction progress by ^1H NMR (Figure S35 in SI) revealed the generation and consumption of an intermediate which we propose is a single isomer of $Mo(O)(CH\text{-}t\text{-}Bu)Cl(OR_{F9})(bipy)$. The formation of Me_3SiOR_{F9} was confirmed through independent synthesis.[11] A minor side product was identified as $(Me_3Si)_2O$, which we presume is formed through a slow oxo abstraction reaction.

The reaction between **2d**, LiOHMT (OHMT = *O*-2,6-mesityl$_2$C$_6$H$_3$), and $ZnCl_2$(dioxane) in CH_2Cl_2/THF yields an ether-soluble, pentane-insoluble alkylidene intermediate (^1H δ 12.47 in C_6D_6), which we propose is $Mo(O)(CH\text{-}t\text{-}Bu)Cl(OHMT)$ (**5**) or its THF adduct, **5**(THF). This MAC species was separated by extraction into Et_2O and was treated with 3-bromopyridine (3-Brpy) to form $Mo(O)(CH\text{-}t\text{-}Bu)Cl(OHMT)$(3-Brpy) (**5**(3-Brpy)) in 40% isolated yield. Similarly, the reaction between **2d**, LiOHIPT (OHIPT = *O*-2,6-(2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$), and $ZnCl_2$(dioxane) in CH_2Cl_2/THF yields a pentane-soluble intermediate (^1H δ 12.66 in $CDCl_3$), which was extracted with pentane and treated with 3-Brpy to yield $Mo(O)(CH\text{-}t\text{-}Bu)Cl(OHIPT)$(3-Brpy) (**6**(3-Brpy)) in 54% isolated yield. 3-Bromopyridine was found to be a labile ligand in previous studies of Mo and W imido MAC alkylidene catalysts for alkene metathesis.[10b]

The structure of **5**(3-Brpy) (Figure 4) was found to be halfway between a square pyramidal and a trigonal bipyramidal (τ = 0.41)[12] with the 3-Brpy ligand approximately *trans* to the chloride ligand (N1–Mo1–Cl1 = 168.49(3)°). **5**(3-Brpy) forms dimers through intermolecular short contacts including C–Br···O=Mo halogen bonds between a 3-Brpy ligand and an adjacent oxo ligand in the solid state (see SI). The structure of **6**(3-Brpy) is closer to a square pyramid (τ = 0.33; Figure 5) and does not feature significant intermolecular halogen bonding in the solid state, which we propose as a consequence of the greater steric demand of the OHIPT ligand versus the OHMT ligand.

Compound **5**(3-Brpy) has a sharp, concentration-independent alkylidene resonance (δ 12.71) in its ^1H NMR spectrum, consistent with no significant degree of dissociation of 3-Brpy in solution. In contrast, the ^1H alkylidene singlet in the proton NMR spectrum of compound **6**(3-Brpy) broadens without shifting significantly upon dilution in CD_2Cl_2 at room temperature (see SI) and becomes sharp upon addition of free 3-Brpy, behavior that is consistent with the greater lability of 3-Brpy in **6**(3-Brpy) as a consequence of the greater steric demand of the OHIPT ligand versus the OHMT ligand. The

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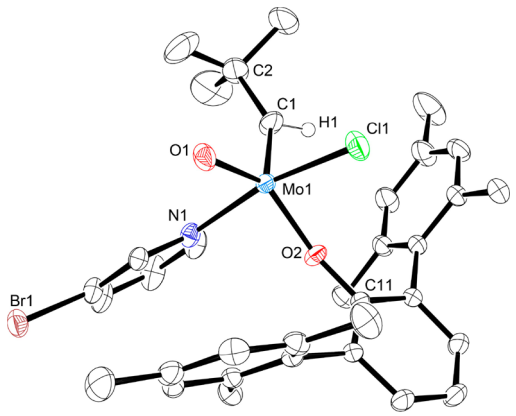

Figure 4. Thermal ellipsoid plot (50% probability) for **5**(3-Brpy). Solvent molecules and hydrogen atoms except for the alkylidene hydrogen (H1) are omitted for clarity. Mo1−O1 = 1.6920(9) Å, Mo1−C1 = 1.8881(13) Å, Mo1−O2 = 1.9102(9) Å, Mo1−N1 = 2.2503(11) Å, Mo1−O2−C11 = 152.76(8)°; τ = 0.41.

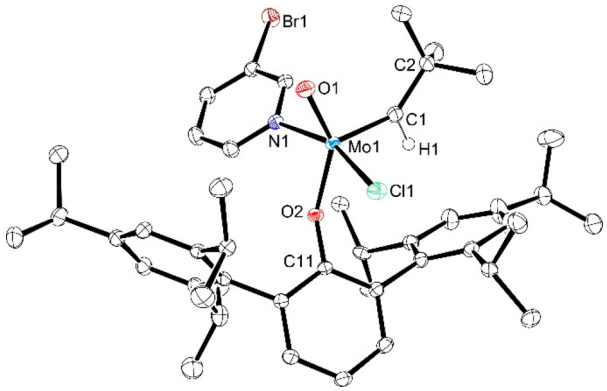

Figure 5. Thermal ellipsoid plot (50% probability) for **6**(3-Brpy). Hydrogen atoms except for the alkylidene hydrogen (H1) are omitted for clarity. Mo1−O1 = 1.6880(9) Å, Mo1−C1 = 1.8946(12) Å, Mo1−O2 = 1.9617(8) Å, Mo1−N1 = 2.2619(10) Å, Mo1−O2−C11 = 137.30(7)°; τ = 0.33.

NMR resonances for the aryloxide ligands in both **5**(3-Brpy) and **6**(3-Brpy) are broad at room temperature due to hindered rotation of the aryloxide. At −20 °C, the ^{1}H NMR spectrum of **6**(3-Brpy) was sharp and allowed the resonances for the HIPTO ligand to be assigned.

CONCLUSIONS

We conclude that triethylamine and TMEDA both promote the conversion of Mo alkylidyne complexes into oxo alkylidene complexes, although we still have no information concerning mechanistic details of those transformations. Yields can depend to a significant degree upon the alkylidyne and conditions, but a thorough study has not yet been carried out. These "phosphine-free" methods, and in particular, the synthesis of TMEDA complexes, allow access to monoaryloxide chloride complexes. Complex **6**(3-Brpy) is the first Mo oxo MAC complex that is an active olefin metathesis catalyst as a consequence of the likely lability of 3-Brpy to give four-coordinate **6**. (Mo(CHAr$_o$)(OHIPT)Cl(PMe$_3$) (Ar$_o$ = *o*-methoxyphenyl) reacts slowly only with norbornenes or norbornadienes.[4a] Although preliminary studies confirm that **6**(3-Brpy) will polymerize cyclooctene (86% in 1 h with 5 mol % of initiator), we chose to postpone thorough studies until side-by-side comparisons become possible, that is, a comparison of **6**(3-Brpy) with Mo imido MAC complexes and other five-coordinate Mo oxo MAC complexes to be prepared that contain a labile ligand in a variety of metathesis reactions.

EXPERIMENTAL SECTION

All air- and moisture-sensitive materials were manipulated under a nitrogen atmosphere in a glovebox or on a dual-manifold Schlenk line. Glassware was either oven-dried or flame-dried prior to use. Toluene, C_6H_6, MeCN, CH_2Cl_2, Et_2O, tetrahydrofuran (THF), and 1,2-dimethoxyethane (DME) were degassed, passed through activated alumina columns, and stored over 4 Å Linde-type molecular sieves (4 Å MS). Pentane was washed with H_2SO_4, followed by water and a saturated solution of aqueous $NaHCO_3$, and dried over $CaCl_2$ pellets for at least 2 weeks prior to use in the solvent purification system. Deuterated solvents were dried over 4 Å MS prior to use. *tert*-Butyl chloride was dried over CaH_2 and distilled under nitrogen (1 atm). *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (TMEDA) was dried over 4 Å MS, degassed by two freeze−pump−thaw cycles, and transferred under vacuum.

^{1}H, ^{19}F, ^{13}C, and 2D NMR spectra were acquired on Bruker Avance 400 MHz and Bruker Neo 500 MHz NMR spectrometers at ambient temperature (24 °C) under arbitrary concentration unless otherwise noted. Chemical shifts for ^{1}H and ^{13}C NMR spectra are reported as parts per million (ppm) relative to tetramethylsilane and referenced to the residual ^{1}H or ^{13}C resonances of the deuterated solvent (^{1}H δ: C_6D_6 7.16, CD_2Cl_2 5.32, $CDCl_3$ 7.26; ^{13}C δ: C_6D_6 128.06, CD_2Cl_2 53.84, $CDCl_3$ 77.16).[13] Chemical shifts for ^{31}P and ^{19}F NMR spectra are reported as ppm relative to 85% H_3PO_4 (^{31}P δ 0) and $CFCl_3$ (^{19}F δ 0), respectively. Coupling constants are reported in hertz (Hz). Elemental analyses were performed at Atlantic Microlab, Inc., Norcross, GA.

Mo(CAr$_p$)Br$_3$(DME) (Ar$_p$ = *p*-methoxyphenyl),[14] Mo(Cmesityl)-(OR$_{F9}$)$_3$,[5] ZnCl$_2$(dioxane),[15] 2,3,5,6-tetraphenylphenol (HOTPP),[16] 2,6-bis(2,4,6-trimethylphenyl)phenol (HOHMT),[17] and 2,6-bis-(2,4,6-triisopropylphenyl)phenol (HOHIPT)[10b] were synthesized according to literature procedures. Mo(CAr$_p$)(OR$_{F9}$)$_3$(DME) was prepared according to literature procedure[4b] and sublimed twice (60−85 °C, 30 mTorr) until the purple pure material was devoid of brown impurities. KOR$_{F9}$ (or NaOR$_{F9}$) was prepared by reacting HOR$_{F9}$ with 1 equiv of KH (or NaH) in Et_2O, removing all volatiles, and drying the white solid residue at 60 °C under high vacuum. LiOHMT was prepared through addition of 1 equiv of *n*-BuLi to a cold Et_2O solution of HOHMT, and the solid was collected on a glass frit, washed with pentane, and dried under vacuum. LiOHIPT was prepared through addition of 1 equiv of *n*-BuLi to a cold pentane solution of HOHIPT, and the solid was collected on a glass frit, washed with pentane, and dried under vacuum. NaOTPP was prepared by reacting HOTPP with 1 equiv of NaH in THF at room temperature and removing all volatiles, and the solid was collected on a glass frit, washed with pentane, and dried under vacuum; the amount of residual THF was quantified using ^{1}H NMR integration in C_6D_6.

2,2,5,5-Tetramethylhex-3-yne (*t*-BuC≡C-*t*-Bu). Adapted from literature procedures.[18,19] A Schlenk flask was charged with $AlCl_3$ (3.91 g, 29.3 mmol, 0.10 equiv) and CH_2Cl_2 (400 mL). The mixture was cooled to −78 °C and stirred for 10 min. In a second Schlenk flask, bis(trimethylsilyl)acetylene (50.0 g, 293 mmol) and *tert*-butyl chloride (64.7 mL, 587 mmol, 2.00 equiv) were mixed, and the mixture was transferred into the cold mixture of $AlCl_3$ and CH_2Cl_2 via cannula. After the addition was complete, the mixture was warmed to −20 °C and stirred at −20 °C for 1.5 h to afford a red homogeneous mixture. The mixture was warmed to 0 °C, and most of the CH_2Cl_2 and the byproduct Me_3SiCl were removed on a rotovap at 0 °C (ice bath) to yield a biphasic mixture of a colorless liquid and a dense red liquid. The mixture was extracted with pentane (150 mL) under air, and the pentane extract was transferred into a clean flask and then distilled under air (ambient pressure, oil bath up to 120 °C, circulating water at 10 °C for cooling) to completely remove pentane

https://dx.doi.org/10.1021/acs.organomet.0c00275
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and the remaining Me_3SiCl. The residue was further distilled under air (ambient pressure, oil bath at 140−170 °C, static water for cooling; bp 110 °C) to yield 17.85 g (129 mmol, 44%) of 2,2,5,5-tetramethylhex-3-yne as a colorless liquid. The product was degassed and dried over 4 Å MS prior to synthetic use. The observed boiling point is consistent with literature value (111.9 °C at 746 Torr, ref 19): ^{1}H NMR (400 MHz, C_6D_6) δ 1.23 (s).[20]

Me_3SiOR_{F9}. A Schlenk storage flask was charged with $NaOR_{F9}$ (4.75 g, 18.4 mmol) and Et_2O (20 mL). A Et_2O solution (5 mL) of Me_3SiCl (2.00 g, 18.4 mmol) was added. The mixture was stirred at room temperature for 2 days and then filtered. The filtrate was fractionally distilled under nitrogen (1 atm), and the fraction at ∼85 °C was condensed and collected as a colorless liquid. Yield: 1.74 g (30%). The NMR data are in line with literature report:[11] ^{1}H NMR (500 MHz, CD_2Cl_2) δ 0.28 (s); ^{19}F NMR (470 MHz, CD_2Cl_2) δ −74.0.

Mo(C-*t*-Bu)$(OR_{F9})_3$. A Schlenk storage flask was charged with Mo(CMesityl)$(OR_{F9})_3$ (20.2 g, 21.7 mmol), C_6H_6 (450 mL), and *t*-BuC≡C-*t*-Bu (15.0 g, 108 mmol, 5.0 equiv). The flask was sealed, and the mixture was stirred at 100 °C for 3 days to afford a pale red clear mixture. The mixture was cooled to room temperature, and formation of a yellow flaky precipitate was complete within a few hours. The flask was transferred into a glovebox, and the solid was collected by filtration. The filtrate was concentrated under vacuum to 200 mL, and the resulting yellow precipitate was collected by filtration. The combined solid was extracted with pentane (200 mL). The extract was filtered through a pad of Celite and concentrated to dryness to yield a crude product, which was recrystallized in pentane at −20 °C to afford 16.20 g (86%, 3 crops) of Mo(C-*t*-Bu)$(OR_{F9})_3$ as yellow flakes. Alternatively, the crude product can be purified by sublimation under high vacuum (35 °C, 20 mTorr). Anal. Calcd for $C_{17}H_9F_{27}MoO_3$ (870.16 g/mol): C, 23.47%; H, 1.04%. Found: C, 23.59%; H, 1.07%.

Mo(O)$(CHAr_p)(OR_{F9})_2(THF)_2$ (1$(THF)_2$). A vial was charged with Mo$(CAr_p)(OR_{F9})_3$(DME) (500 mg, 495 μmol) and THF (8 mL, [Mo] = 62 mM) to form a green solution. Et_3N (3.5 μL, 25 μmol, 5 mol %) was added, and the mixture was chilled at −20 °C for 10 min. Water (10 wt % in THF, 99 μL, 495 μmol, 1.00 equiv) was quickly injected into the vigorously stirred mixture, and the mixture was stirred and allowed to warm to room temperature over 30 min. The volatiles were removed under vacuum to yield an orange solid residue. The residue was extracted in THF (1 mL)/pentane (20 mL), and the clear liquid was stored at −20 °C to yield a mixture of red **1**$(THF)_2$ and green Mo$(CAr_p)(OR_{F9})_3(THF)_2$ crystals. The solid mixture was separated from the mother liquor and dissolved in DME (10 mL). The mixture was concentrated to dryness, and the residue was dissolved in CH_2Cl_2 (10 mL). The mixture was stored at −20 °C to give purple needles of unreacted Mo$(CAr_p)(OR_{F9})_3$(DME) (113 mg, 23%), which was collected by filtration, washed with cold CH_2Cl_2, and dried under vacuum. The mother liquor was concentrated to dryness, and the residue was dissolved with THF (10 mL). The volatiles were concentrated to dryness. The residue was extracted with THF (1 mL)/pentane (20 mL), and the clear liquid was separated from trace insoluble impurities by filtration and stored at −20 °C to yield pure product as red crystals (198 mg, 2 crops, 47%). Anal. Calcd for $C_{24}H_{24}F_{18}MoO_6$ (846.37 g/mol): C, 34.06%; H, 2.86%. Found: C, 34.22%; H, 2.73%. Single crystal sample of **1**$(THF)_2$ for X-ray analysis was obtained from diffusion of pentane into a THF solution at −20 °C.

Mo(O)$(CHAr_p)(OR_{F9})_2$(TMEDA) (2a). A vial was charged with Mo$(CAr_p)(OR_{F9})_3$(DME) (50.0 mg, 49.5 μmol), TMEDA (18.6 μL, 124 μmol, 2.5 equiv), and Et_2O (2 mL) to form a pale yellow mixture. Water (10 wt % in THF, 9.9 μL, 49 μmol, 1.0 equiv) was added in one portion under vigorous stirring to form a red mixture, which turned dark red within a few minutes. The mixture was stirred for 20 h at room temperature and then filtered through a pad of Celite. The red filtrate was concentrated to 1 mL under vacuum and treated with pentane (5 mL). The mixture was stored at −20 °C overnight to give pure product as a red microcrystalline solid, which was collected by filtration, washed with cold pentane, and dried under vacuum. Yield: 29.8 mg (74%). Anal. Calcd. for $C_{22}H_{24}F_{18}MoN_2O_4$ (818.37 g/mol): C, 32.29%; H, 2.96%; N, 3.42%. Found: C, 32.58%; H, 3.11%; N, 3.37%.

Mo(O)(CH-*t*-Bu)$(OR_{F9})_2$(TMEDA) (2b). A round-bottom flask was charged with Mo(C-*t*-Bu)$(OR_{F9})_3$ (1.08 g, 1.24 mmol), TMEDA (465 μL, 3.10 mmol, 2.5 equiv), and Et_2O (50 mL) to form a yellow clear mixture. Water (10 wt % in THF, 248 μL, 1.24 mmol, 1.0 equiv) was added dropwise at room temperature under vigorous stirring to form a dark orange mixture. The mixture was stirred for 20 h at room temperature and turned dark yellow. The volatiles were removed under vacuum. The solid residue was triturated with pentane (20 mL) and collected by filtration to yield 650 mg of pure product as a yellow powder. The filtrate was concentrated to 5 mL and chilled at −20 °C for a few hours to yield a second crop of yellow solid (92 mg). Total yield: 742 mg (78%). Anal. Calcd for $C_{19}H_{26}F_{18}MoN_2O_3$ (768.35 g/mol): C, 29.70%; H, 3.41%; N, 3.65%. Found: C, 29.53%; H, 3.40%; N, 3.56%. %. Single crystal sample of **2b** for X-ray analysis was obtained from diffusion of pentane into a solution of diethyl ether at −20 °C.

Mo(O)(CHMesityl)$(OR_{F9})_2$(TMEDA) (2c). A vial was charged with Mo(CMesityl)$(OR_{F9})_3$ (50.0 mg, 53.6 μmol), TMEDA (20.1 μL, 134 μmol, 2.5 equiv), and Et_2O (2 mL) to form a red mixture. Water (10 wt % in THF, 10.7 μL, 53.6 μmol, 1.0 equiv) was added in one portion under vigorous stirring to form a dark yellow mixture. The mixture was stirred for 20 h at room temperature and turned dark red. The mixture was filtered through a pad of Celite. The red filtrate was concentrated to 1 mL under vacuum and treated with pentane (5 mL). The mixture was stored at −20 °C overnight to give pure product as an orange microcrystalline solid, which was collected by filtration, washed with cold pentane, and dried under vacuum. Yield: 28.3 mg (64%). Anal. Calcd for $C_{24}H_{28}F_{18}MoN_2O_3$ (830.42 g/mol): C, 34.71%; H, 3.40%; N, 3.37%. Found: C, 34.95%; H, 3.55%; N, 3.37%.

Mo(O)(CH-*t*-Bu)$(OR_{F9})_2$(bipy) (2d). A vial was charged with **2b** (300 mg, 390 μmol) and CH_2Cl_2 (3 mL) to form a dark yellow solution. A CH_2Cl_2 solution (1 mL) of 2,2′-bipyridyl (62.0 mg, 396 μmol, 1.02 equiv) was added, and the mixture was stirred at room temperature for 15 min. The mixture was concentrated under vacuum to 1 mL and treated with pentane (8 mL). The mixture was chilled at −20 °C for 1 h, and the yellow precipitate was collected by filtration, washed with cold pentane, and dried under vacuum. Yield: 230 mg (73%). The compound exists as a 10:1 equilibrium mixture of two *syn*-alkylidene isomers at room temperature in CD_2Cl_2 solvent. Anal. Calcd for $C_{23}H_{18}F_{18}MoN_2O_3$ (808.33 g/mol): C, 34.18%; H, 2.24%; N, 3.47%. Found: C, 34.09%; H, 2.08%; N, 3.54%.

Mo(O)$(CHAr_p)(OHMT)_2$ (3a). A vial was charged with **1**$(THF)_2$ (200 mg, 236 μmol) and C_6H_6 (15 mL, [Mo] = 16 mM). LiOHMT (196 mg, 583 μmol, 2.5 equiv) was added in one portion, and the mixture was stirred at room temperature for 24 h to yield a purple suspension. The mixture was filtered through a pad of Celite to remove the white precipitate. The filtrate was loaded into a Schlenk bomb, and the volatiles were removed under Schlenk vacuum at 60 °C. The purple residue was extracted with pentane (20 mL), and the extract was stored at −20 °C to yield purple crystals and a small amount of colorless crystals ($LiOR_{F9}$). The solid was agitated in pentane, and the purple crystals were isolated by swiftly decanting off the pentane suspension of colorless crystals. The remaining purple solid was recrystallized in C_6H_6 (0.3 mL)/pentane (5 mL) at −20 °C to give pure product as purple needles (138 mg, 66%). The NMR data are identical to those reported in the literature.[4b]

Mo(O)$(CHAr_p)(OTPP)_2$ (3b). A flask was charged with **1**$(THF)_2$ (400 mg, 473 μmol) and Et_2O (30 mL). NaOTPP (containing 1.3 THF per Na, 515 mg, 992 μmol, 2.1 equiv) was added in one portion, and the mixture was stirred at room temperature for 1 h to yield a dark red suspension. The mixture was filtered through a pad of Celite on a frit, and CH_2Cl_2 (100 mL) was added to the frit in portions to elute the dark red component. The filtrate was concentrated to dryness to yield a red solid residue. The residue was stirred in MeCN (15 mL) for 2 h to yield a pinkish powdery precipitate, which was collected by filtration. The solid was stirred in toluene (4 mL) for 30

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min to yield a dark red powdery precipitate. The solid was stirred in MeCN (15 mL) for 2 h again, and the resulting orange precipitate was collected by filtration and stirred in toluene (4 mL) for 30 min to give the product as a dark red powder, which was collected by filtration, washed with toluene, and dried under vacuum. Yield: 194 mg (39%). This material contained 0.27 equiv of toluene per Mo; toluene-free material can be obtained by recrystallization from CH_2Cl_2/pentane. Anal. Calcd for $C_{68}H_{50}MoO_4 \cdot 0.27(C_7H_8)$ (1051.97 g/mol): C, 79.80%; H, 5.00%. Found: C, 80.20%; H, 5.49%. A single crystal of **3b** for X-ray analysis was obtained through diffusion of pentane into a CH_2Cl_2 solution at −20 °C.

Mo(O)(CH-*t*-Bu)Cl$_2$(bipy) (4). A flask was charged with **2b** (776 mg, 960 μmol) and CH_2Cl_2 (20 mL) to form a dark yellow solution. Me_3SiCl (268 μL, 2.11 mmol, 2.2 equiv) was added, and the mixture was stirred at room temperature. The reaction progress was monitored by periodically taking aliquots, removing the volatiles, dissolving the residue in CD_2Cl_2, and analyzing the NMR solution by ^{1}H NMR. The Mo starting material and the intermediate Mo(O)(CH-*t*-Bu)Cl(OR_{F9})(bipy) were fully consumed in 4 h. The volatiles were removed under vacuum. The red solid residue was extracted with CH_2Cl_2 (20 mL), and the mixture was filtered through a pad of Celite. The red filtrate was concentrated under vacuum to 10 mL and then treated with Et_2O (40 mL). A dark yellow powdery precipitate was collected by filtration, washed extensively with Et_2O, and dried under vacuum. Yield: 279 mg (71%). The compound exists as a mixture of a predominant (96%) *syn*-alkylidene and a few minor alkylidene isomers in CD_2Cl_2 solvent. Anal. Calcd for $C_{15}H_{18}Cl_2MoN_2O$ (409.17 g/mol): C, 44.03%; H, 4.43%; N, 6.85%. Found: C, 43.79%; H, 4.45%; N, 6.81%.

Mo(O)(CH-*t*-Bu)Cl(OHMT)(3-Brpy) (5(3-Brpy)). A vial was charged with LiOHMT (129 mg, 385 μmol, 1.05 equiv to Mo), $ZnCl_2$(dioxane) (90 mg, 403 μmol, 1.10 equiv to Mo), and THF (4 mL). The mixture was stirred for a few minutes at room temperature to yield a colorless solution. The mixture was slowly added to a mixture of **4** (150 mg, 367 μmol) and CH_2Cl_2 (8 mL) at room temperature under vigorous stirring. The mixture was stirred at room temperature for 1.5 h. The volatiles were completely removed under vacuum to yield a brown oily residue. The residue was extracted with Et_2O (40 mL), and then the extract was filtered through a pad of Celite to yield a red filtrate. 3-Bromopyridine (50 μL, 519 μmol, 1.4 equiv to Mo) was added to the filtrate, yielding a white solid impurity, which was removed by filtration through a pad of Celite. The filtrate was stripped to yield a yellow foamy residue. The residue was dissolved in Et_2O (2 mL) and then treated with pentane (10 mL) to yield a brown cloudy mixture; a small amount of brown precipitate quickly formed and was removed by filtration. Pentane (10 mL) was added, and the mixture was concentrated to 10 mL under vacuum. The orange clear mother liquor was transferred into a vial and stored at −20 °C to yield 105 mg (40%) of the product as yellow crystals. ^{1}H NMR analysis in CD_2Cl_2 solvent showed that the material contained 0.75 equiv of pentane to Mo and that the compound existed as a 97:3 mixture of *syn*- and *anti*-alkylidene isomers. Anal. Calcd for $C_{34}H_{39}BrClMoNO_2 \cdot 0.75(C_5H_{12})$ (759.11 g/mol): C, 59.73%; H, 6.37%; N, 1.85%. Found: C, 59.96%; H, 6.50%; N, 2.00%. A single-crystal sample of **5**(3-Brpy)·1.5(toluene) for X-ray analysis was obtained from diffusion of pentane into a toluene solution at −20 °C.

Mo(O)(CH-*t*-Bu)Cl(OHIPT)(3-Brpy) (6(3-Brpy)). A vial was charged with LiOHIPT (62 mg, 123 μmol, 1.0 equiv to Mo), $ZnCl_2$(dioxane) (28 mg, 125 μmol, 1.1 equiv to Mo), and THF (2 mL). The mixture was stirred for a few minutes at room temperature to yield a colorless solution. The mixture was slowly added to a mixture of **4** (50 mg, 122 μmol) and CH_2Cl_2 (2 mL) at room temperature under vigorous stirring. The mixture was stirred at room temperature for 18.5 h. The volatiles were completely removed under vacuum to yield a brown sticky residue. The residue was extracted with Et_2O (4 mL)/pentane (4 mL). Then, the extract was filtered through a pad of Celite to yield an orange filtrate, which was stripped to yield an orange foamy residue. The residue was redissolved in pentane (8 mL), and trace white precipitate was removed by filtration. 3-Bromopyridine (30 μL, 311 μmol, 2.6 equiv to Mo) was added to the filtrate, and the mixture was concentrated to 4 mL under vacuum and stored at −20 °C to yield a yellow fluffy solid, which was collected by filtration (using a glass frit prechilled at −20 °C), washed with a minimal volume of cold pentane, and dried under vacuum. One additional crop was isolated by crystallization from pentane at −20 °C. Yield: 58 mg (54%). Anal. Calcd for $C_{46}H_{63}BrClMoNO_2$ (873.32 g/mol): C, 63.27%; H, 7.27%; N, 1.60%. Found: C, 62.97%; H, 7.15%; N, 1.55%. A single crystal of **6**(3-Brpy) for X-ray analysis was obtained from a solution of it in a mixture of Et_2O and pentane at −20 °C.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00275.

NMR spectra, NMR chemical shift data for all compounds, details of X-ray studies, and other miscellaneous data (PDF)

Accession Codes

CCDC 1997758−1997762 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

Richard R. Schrock − *Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States;* orcid.org/0000-0001-5827-3552; Email: rrs@mit.edu

Authors

Feng Zhai − *Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States;* orcid.org/0000-0001-7892-3188

Amir H. Hoveyda − *Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467, United States;* orcid.org/0000-0002-1470-6456

Peter Müller − *Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States;* orcid.org/0000-0001-6530-3852

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.0c00275

Author Contributions

F.Z. performed all synthetic work, while P.M. performed all X-ray structural studies.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful for financial support from the National Institutes of Health (GM-59426). We also thank the NSF for support of X-ray diffraction instrumentation (CHE-0946721).

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