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Syntheses of Molybdenum Adamantylimido and *t*-Butylimido Alkylidene Chloride Complexes Using HCl and Diphenylmethylphosphine

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Abstract

Reactions between Mo(N-*t*-Bu)$_2$(CH$_2$-*t*-Bu)$_2$ or Mo(NAdamantyl)$_2$(CH$_2$CMe$_2$Ph)$_2$ and 3 equiv of HCl in the presence of 1 equiv of PPh$_2$Me yield Mo(NR)(CHR')(PPh$_2$Me)Cl$_2$ complexes, from which Mo(NR)(CHR')(PPh$_2$Me)(OAr)Cl complexes (OAr = a 2,6-terphenoxide) can be prepared. The Mo(NR)(CHR')(PPh$_2$Me)(OAr)Cl complexes were evaluated as cross-metathesis catalysts between cyclooctene and *Z*-1,2-dichloroethylene. The efficiencies of the test reaction for complexes in which OAr = OTPP, OHMT, OHIPT, or OHTBT (where OTPP is 2,3,5,6-tetraphenylphenoxide, OHMT is hexamethylterphenoxide, OHIPT is hexaisopropylterphenoxide, and OHTBT is hexa-*t*-butylterphenoxide) maximize when OAr is OHMT or OHIPT. Mo(N-*t*-Bu)(CH-*t*-Bu)(PPh$_2$Me)Cl$_2$ is essentially inactive for the reaction between cyclooctene and *Z*-1,2-dichloroethylene. X-ray structural studies were carried out on Mo(NAd)(CHCMe$_2$Ph)(PPh$_2$Me)Cl$_2$, Mo(N-*t*-Bu)(CH-*t*-Bu)(PPh$_2$Me)(OHMT)Cl, Mo(NAd)(CHCMe$_2$Ph)(Cl)(OHTBT)(PMe$_3$), and [Mo(NAd)(CHCMe$_2$Ph)(PMe$_3$)(Cl)]$_2$(μ-O), the product of the reaction between Mo(NAd)(CHCMe$_2$Ph)(Cl)(OHTBT)(PMe$_3$) and 0.5 equiv of water.

Graphical Abstract

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ASSOCIATED CONTENT

Supporting Information

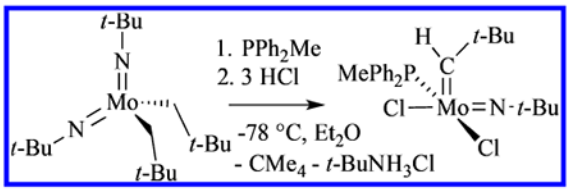
The Supporting Information is available free of charge on the ACSPublicationswebsite at DOI: 10.1021/acs.organomet.7b00647.

NMR data and spectra for all compounds, details of the cross-metathesis experiments, and X-ray data for the four structures (PDF)

Accession Codes

CCDC 1572637–1572640 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.

The authors declare no competing financial interest.



INTRODUCTION

A key step in the synthesis of molybdenum and tungsten imido alkylidene complexes traditionally has been the addition of 3 equiv of triflic acid to a $M(NR)_2(CH_2R')_2$ complex (R = aryl, *t*-butyl, or 1-adamantyl; R' = *t*-Bu or CMe_2Ph) in the presence of dimethoxyethane to give RNH_3OTf, CH_3R', and a $M(NR)(CHR')(OTf)_2(DME)$ complex.[1] The triflate ligands can be replaced with a variety of sterically demanding alkoxide (or aryloxide; X) or pyrrolide (Y) ligands to give 14e $M(NR)(CHR')(X)_2$, $M(NR)(CHR')(Y)_2$, or M(NR)(CHR')(X)(Y) complexes. Monoaryloxide pyrrolide M(NR)(CHR')(X)(Y) complexes have proven useful for *E*-selective or *Z*-selective reactions,[2] including stereoselective ROMP reactions,[3] when the aryloxide is a sterically demanding 2,6-terphenoxide such as 2,6-dimesitylphenoxide (OHMT = hexamethylterphenoxide). In the process of exploring cross-metathesis reactions in which one of the olefins is *Z*-ClCH=CHCl,[4] we discovered that M(NR)(CHR')(OAr)(L)Cl complexes are especially reactive if the donor ligand (L = a 2e donor such as a pyridine or a nitrile) is labile enough to expose the 14e M(NR)(CHR')(OAr)Cl core. Although we devised methods of preparing some M(NR)(CHR')(OAr)(L)Cl complexes,[5] the monochloride complexes would be more directly accessible from $M(NR)(CHR')(L)Cl_2$ or $M(NR)(CHR')(L)_2Cl_2$ complexes simply through substitution of one chloride with a sterically demanding aryloxide. They should be useful catalysts if L readily dissociates from M(NR)(CHR')(OAr)(L)Cl to a significant degree.

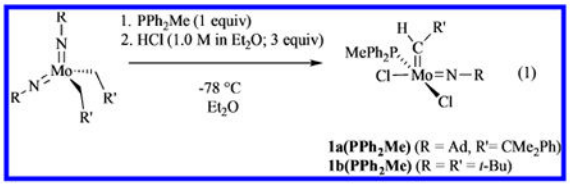
$M(NR)(CHR')(L)Cl_2$ or $M(NR)(CHR')(L)_2Cl_2$ complexes (M = Mo or W) are relatively rare. The first $M(NR)(CHR')(L)_2Cl_2$ complexes were prepared through addition of 3 equiv of HCl (as pyridinium chloride) to $M(NR)_2(CH_2R')_2$, where NR is N-2,6-$(mesityl)_2C_6H_3$ (NAr*).[6] Molybdenum and tungsten complexes that contain a N-2,6-(2,4,6-*i*-$Pr_3C_6H_2)_2C_6H_3$ (NAr**) ligand were prepared in a similar manner.[7] The steric demand of the NAr** ligand even allowed a $W(NAr^{**})(CHCMe_2Ph)Cl_2$ complex to be prepared, the only isolable monomeric 14e dichloride complex of this general type. W(NR)$(CHR')Cl_2(pyridine)_2$ complexes (R = adamantylimido or *t*-butylimido) were reported soon thereafter,[8] as were similar dichlorides in reactions between $W(N\text{-}t\text{-}Bu)_2(CH_2\text{-}2\text{-}OMeC_6H_4)_2$ and pyridine hydrochloride.[9] Unfortunately, in most cases pyridine is bound too strongly to the metal in the resulting M(NR)(CHR')(OAr)(L)Cl complexes for them to be highly active in olefin metathesis reactions. In some cases the pyridine is labile enough to be removed from solution through addition of $B(C_6F_5)_3$ to yield $(py)B(C_6F_5)_3$, in which case the 14e complexes can be generated *in situ*.

Phosphine adducts of imido alkylidene complexes are relatively well-known.[1] Therefore, we explored the possibility of using phosphonium chlorides as the means of delivering HCl and

chloride to generate imido alkylidene dichloride complexes as phosphine adducts. We discovered that addition of 2 equiv of $PhMe_2PHCl$ to $Mo(NC_6F_5)_2(CH_2CMe_2Ph)_2$ led to formation of $Mo(NC_6F_5)(CHCMe_2Ph)(PhMe_2P)_2Cl_2$ complexes in good yield.[5] In that paper, we reported that "treatment of Mo(N-*t*-Bu)$_2$(CH$_2$-*t*-Bu)$_2$ with phosphonium halides generated a complex mixture of alkylidene-containing compounds along with other unidentified products." Upon optimization of conditions and choice of phosphine, we have now found that reactions between Mo(N-*t*-Bu)$_2$(CH$_2$-*t*-Bu)$_2$ or Mo(NAdamantyl)$_2$(CH$_2$CMe$_2$Ph)$_2$ and 3 equiv of HCl in the presence of 1 equiv of PPh_2Me produce Mo(NR)(CHR')(PPh_2Me)Cl$_2$ complexes, from which Mo(NR)(CHR')(PPh_2Me)(OAr)Cl complexes can be prepared. In this paper we report the syntheses of Mo(NR)(CHR')(PPh_2Me)Cl$_2$ and Mo(NR)(CHR')(PPh_2Me)(OAr)Cl complexes, along with a side-by-side comparison of all catalysts for a ring-opening cross-metathesis between cyclooctene and *Z*-ClCH=CHCl.

RESULTS

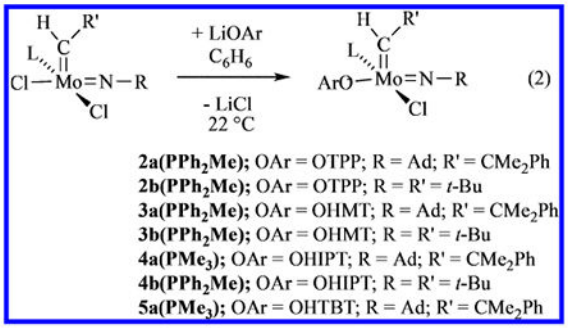
The molybdenum imido alkylidene dichloride complexes, Mo(NAd)(CHCMe$_2$Ph)(PPh_2Me)Cl$_2$ (**1a(PPh_2Me)**) and Mo(N-*t*-Bu)(CH-*t*-Bu)(PPh_2Me)Cl$_2$ (**1b(PPh_2Me)**) are obtained in approximately 50% yield from the corresponding Mo(NR)$_2$(CH$_2$R')$_2$ complexes upon addition of 1 equiv of PPh_2Me, followed by 3 equiv of HCl in diethyl ether, or alternatively, 1 equiv of PPh_2Me•HCl, followed by 2 equiv of HCl in ether (eq 1). Three equivalents of HCl are required to complete the reaction because the *t*-butylamine or adamantylamine that is formed is readily protonated to give the ammonium salt, which is not a strong enough acid to allow the reaction to be completed. The reactions typically are carried out at −78 °C initially, followed by warming the reaction mixtures slowly to 22 °C, although reactions that start at ~−30 °C have been equally successful. Exploratory reactions in the presence of 1 equiv of PPh_3 or $PPhMe_2$ so far have not led to acceptable yields of complexes analogous to **1a(PPh_2Me)** and **1b(PPh_2Me)**.



All NMR data are consistent with **1a(PPh_2Me)** and **1b(PPh_2Me)** being monophosphine complexes that do not contain a plane of symmetry. Two alkylidene doublet resonances are found in the proton NMR spectra of each. The major alkylidene α proton resonances found near 13 ppm (in CD_2Cl_2) have $^1J_{CH}$ values (123 Hz for **1a(PPh_2Me)** and 118 Hz for **1b(PPh_2Me)**) that are consistent with the alkylidene being in the *syn* orientation. In the minor isomer (5–10 % of the mixture) the value for $^1J_{CH}$ (148 Hz for **1a(PPh_2Me)**) is characteristic of an *anti* isomer. The doublet resonance for the *syn* alkylidene α carbon in **1a(PPh_2Me)** is found at 309.8 ppm ($^2J_{CP}$ = 18.9 Hz; CD_2Cl_2) and in **1b(PPh_2Me)** is found at 314.5 ppm ($^2J_{CP}$ = 18.7 Hz; CD_2Cl_2). Recrystallization of mixtures of *syn* and *anti* isomers leads to samples that are essentially pure *syn* isomers, which suggests that *syn* and

anti isomers do not interconvert readily in solution, most likely because alkylidenes can interconvert only as 14e phosphine-free species[10,11] and PPh_2Me is bound too strongly in **1a(PPh_2Me)** and **1b(PPh_2Me)**.

An X-ray structural study of **1a(PPh_2Me)** (Figure 1) shows the overall structure to be approximately halfway between a trigonal bipyramid and a square pyramid (τ[11] = 0.54) with the alkylidene in the *syn* orientation. Relevant bond angles at the metal are N1–Mo–Cl1 = 132.38(7)°, Cl1–Mo–C1 = 120.92(8)°, C1–Mo–N1 = 106.24(10)°, Cl2–Mo–P1 = 164.85(2)°, C1–Mo–P1 = 89.15(8)°, and C1–Mo–Cl2 = 96.40(7)°. The Mo=C1 (1.887 (2) Å) and Mo=N1 (1.717 (2) Å) distances and Mo=C–C (147.39(19)°) and Mo=N–C (163.15(17)°) angles are normal for five-coordinate complexes of this general type.



Monoaryloxide monochloride complexes were prepared in reactions between **1a(PPh_2Me)** or **1b(PPh_2Me)** and 1 equiv of LiOAr (OAr = OTPP, OHMT, OHIPT, OHTBT) in benzene, where OTPP is 2,3,5,6-tetraphenylphenoxide, OHMT is hexamethylterphenoxide (2,6-dimesitylphenoxide), OHIPT is hexaisopropylterphenoxide, and OHTBT is hexa-*t*-butylterphenoxide.[12] We chose OTPP, OHMT, OHIPT, and OHTBT because of the dramatic degree to which their steric properties vary in the order OTPP<OHMT<OHIPT<OHTBT. Compound **5a(PMe_3)** is the first alkylidene complex to be prepared that contains the OHTBT ligand.[12]

Proton NMR spectra of complexes **2a(PPh_2Me)** and **2b(PPh_2Me)** reveal largely a doublet resonance for a *syn* alkylidene isomer, and under some conditions a small doublet for an *anti* alkylidene isomer, as found for **1a(PPh_2Me)** and **1b(PPh_2Me)**. However, a few percent of each sample (~5%, depending upon the concentration) are the phosphine-free 14e complexes, **2a** and **2b**, respectively, as *syn* isomers, according to ^{1}H NMR spectra. Free phosphine also can be observed in the ^{31}P NMR spectra (see the SI). The amount of free phosphine increases for **3a(PPh_2Me)** and **3b(PPh_2Me)**, and again for **4b(PPh_2Me)**. As expected, addition of PPh_2Me shifts the equilibrium toward the PPh_2Me adduct (as a *syn* isomer), while addition of 1 equiv of $B(C_6F_5)_3$ results in scavenging of the PPh_2Me to produce spectra consistent with formation of the phosphine-free species. It is clear that the phosphine-free complexes are extremely soluble, even in pentane, and none has been isolated in crystalline form. Mo(NR)(CHR')(OAr)Cl complexes also appear to be exceedingly sensitive to water (*vide infra*).

An X-ray crystallographic study of **3b(PPh$_2$Me)** reveals that the crystals contain two molecules that are enantiomers,[13] with equal occupancy over the entire unit cell (see the SI for details). The disorder could be resolved and both structures of **3b(PPh$_2$Me)** solved. They are best described as approximately square pyramids (τ = 0.24 and 0.36) with the apical alkylidene in a *syn* conformation and the PPh$_2$Me bound *trans* to the chloride. Solvents are commonly found in the crystal lattices of the compounds reported here (sometimes partial occupation; see the SI), a complication that has compromised the precision of elemental analyses in some cases.

The structure of the isomer of **3b(PPh$_2$Me)** with τ = 0.24 is shown in Figure 2. Relevant bond angles around the metal are Cl1–Mo1–P1 = 167.39(4)°, N1–Mo1–O1 = 153.12(9)°, C1–Mo1–N1 = 101.32(11)°, C1–Mo1–O1 = 105.51(9)°, C1–Mo1–Cl1 = 100.33(8)° and C1–Mo1–P1 = 89.01(8)°. The Mo=C1 (1.921(2) Å), Mo=N1 (1.722(2) Å), Mo–Cl1 (2.4457(7) Å), Mo–P1 (2.5587(13) Å), and Mo–O1 (1.9895(14) Å) distances and Mo=C1–C2 (142.4(2)°), Mo=N1–C6 (160.15 (19)°), and Mo–O1–C10 (146.90(12)°) angles are typical of other five-coordinate complexes of this general type.[5]

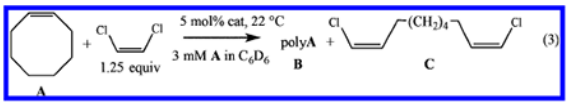
The reaction of **1a(PPh$_2$Me)** with KOHTBT (OHTBT = hexa-*t*-butylterphenoxide) gives essentially phosphine-free 4-coordinate **5a**, according to NMR studies; it is too soluble, even in pentane, to be crystallized (so far). However, a PMe$_3$ complex, **5a(PMe$_3$)**, could be isolated in crystalline form in 47% yield upon addition of 5 equiv of PMe$_3$ to **5a** in dichloromethane. Compound **5a(PMe$_3$)** is an off-white powder in the solid state, but its solutions are yellow because PMe$_3$ dissociates to a significant degree to give yellow **5a**, as can be shown upon scavenging PMe$_3$ in solutions of **5a(PMe$_3$)** with B(C$_6$F$_5$)$_3$. The proton NMR spectrum of **5a(PMe$_3$)** in Figure 3 (top) shows that the ratio of **5a(PMe$_3$)** to **5a** is 73:27 (20 mg of **5a(PMe$_3$)** in 0.6 mL of C$_6$D$_6$, 31 mM initial concentration); therefore K_{eq} is 3.1 mM in C$_6$D$_6$ at 20 °C. The rate of PMe$_3$ exchange in **5a(PMe$_3$)** is such that the alkylidene proton is essentially decoupled from phosphorus. Addition of 2 equiv of PMe$_3$ to the solution of **5a(PMe$_3$)** results in a mixture that is ~97% **5a(PMe$_3$)** (Figure 3 bottom). The small doublet alkylidene resonance at 13.55 ppm in the spectra in Figure 3 is the result of a reaction between **5a(PMe$_3$)** and traces of water (*vide infra*).

An X-ray study of **5a(PMe$_3$)** (Figure 4) shows its structure to be closer to a square pyramid (τ = 0.27) with the alkylidene in the *syn* orientation, analogous to that of **3b(PPh$_2$Me)** (Figure 2). Relevant bond angles at the metal are Cl1–Mo–P1 = 168.122 (13)°, N1–Mo–O1 = 151.86(5)°, C1–Mo–O1 = 106.44(5)°, C1–Mo–N1 = 101.36(6)°, C1–Mo1–Cl1 = 97.67(4)°, and C1–Mo1–P1 = 94.21(4)°. The Mo=C1 (1.8973(14) Å), Mo=N1 (1.7345(12) Å), Mo–Cl1 (2.4480(5) Å), and Mo–P (2.5168(5) Å) distances are similar to what they are in **3b(PPh$_2$Me)**. The Mo-O1 (2.0243(10) Å) distance is slightly longer than what it is in **3b(PPh$_2$Me)**, presumably as a consequence of the extreme steric bulk of the OHTBT ligand. The steric bulk of the OHTBT ligand must also be the origin of the relatively large Mo–O1–C21 (159.86(9)°) angle. For comparison, in Mo(N-*t*-Bu)(CH-*t*-Bu)Cl(OHIPT)(3-Bromopyridine) the Mo–O–C$_{aryl}$ angle is 151.4(3)°.[4] The Mo=C-C (142.48(11)°) and Mo=N–C (166.59(11)°) angles within **5a(PMe$_3$)** are consistent with complexes of this type.

In an attempt to remove PMe_3 from **5a(PMe$_3$)** in the solid state to give **5a**, a sample of 50 mg of **5a(PMe$_3$)** in a Pyrex tube was exposed to a vacuum (25 mTorr) for 24 h. We were surprised to find that **5a(PMe$_3$)** decomposed under these conditions to give HTBTOH and a single alkylidene complex that is relatively insoluble in pentane and that contains PMe_3, but not OHTBT. HTBTOH can be separated from the decomposition product (**6a(PMe$_3$)**) through addition of a small quantity of pentane to the mixture of **6a(PMe$_3$)** and HTBTOH. A ^{1}H NMR spectrum of **6a(PMe$_3$)** shows that the *syn*-alkylidene proton resonance is a doublet at 13.55 ppm ($^3J_{PH}$ = 6.4 Hz; $^1J_{CH}$ = 127 Hz). Because **6a(PMe$_3$)** also could be obtained in 67% yield in a reaction between **5a(PMe$_3$)** and 0.5 equiv of water in ether, we suspect that **6a(PMe$_3$)** is formed from a selective hydrolysis of the OHTBT ligand in **5a(PMe$_3$)**, even *in vacuo* in the particular experiment described above.

An X-ray study of **6a(PMe$_3$)** (Figure 5) showed it to be [Mo(NAd)(CHCMe$_2$Ph)(PMe$_3$)(Cl)]$_2$(μ-O). The overall structure of each Mo center is close to a square pyramid (τ = 0.21 at Mo1 and τ = 0.16 at Mo2) with each alkylidene in the *syn* orientation. Relevant bond angles at the metal are Mo1–O–Mo2 = 120.37(7)°, N1–Mo1–O1 = 149.41(7)°, Cl1–Mo1–P1 = 161.730(19)°, N2–Mo2–O1 = 152.02 (7)°, Cl2–Mo2–P2 = 161.34(2)°. The Mo1–O1 (1.9423(13) Å), Mo2–O1 (1.9774(13) Å), Mo1=C101 (1.907(2) Å), Mo2=C201 (1.907(2) Å), Mo1=N1 (1.7507(17) Å), Mo2=N2 (1.7492(17) Å), Mo1–Cl1 (2.4871(6) Å), Mo2–Cl2 (2.4870(6) Å), Mo1–P1 (2.4980(6) Å), Mo2–P2 (2.4894(7) Å) distances and Mo1=C–C (141.95(6)°), Mo2=C–C (143.61(16)°), Mo1=N–C (158.81(14)°), and Mo2=N–C (160.82(15)°). In view of the steric crowding within **6a(PMe$_3$)**, we were surprised to find that the Mo1–O1–Mo2 angle is only 120°.

We evaluated the efficacy of **1b**, **2b**, **3b**, **4b**, **5a**, and **6a**, and their phosphine adducts), for the ring-opening cross-metathesis of cyclooctene and *Z*-dichloroethylene (equation 3), as has been described in an earlier paper for closely related monomeric complexes.[5] The results are shown in Table 1.



We found that product **C** is formed readily when **3b** and **4b**, in which the PPh_2Me is dissociated to the greatest extent, are the initiators. Compound **C** is essentially 100% *Z,Z* when **4b(PPh$_2$Me)** is the initiator and 86.4% *Z,Z* when **3b(PPh$_2$Me)** is the initiator, as a consequence of the greater steric demand of the OHIPT versus the OHMT terphenoxide ligand.[5] Some poly(cyclooctene) is formed when **2b(PPh$_2$Me)** is the initiator, but the cross-metathesis reaction is comparatively sluggish unless $B(C_6F_5)_3$ is added, in which case the activity is high, but the stereoselectivity is only ~90%. Compound **1b(PPh$_2$Me)** is inactive for the cross-metathesis reaction, most likely because PPh_2Me is too tightly bound to the metal. **1b(PPh$_2$Me),** cyclooctene, and ClCH=CHCl are still present after 10 h and no initial metathesis product (*t*-BuCH=CHCl) is formed. We were surprised to find that **5a(PMe$_3$)** is inactive, even though PMe_3 is dissociated to a significant degree from Mo in 5a(PMe_3)

(Figure 3, top) and even when $B(C_6F_5)_3$ has been added to **5a(PMe$_3$)** to give **5a**. No **C** is formed using **6a(PMe$_3$)** or **6a**.

DISCUSSION

It has long been known through experiments,[1,14] and has now been confirmed through extensive calculations,[15] that the 14e core of a high oxidation state Mo or W complex must be accessible in order to be an efficient olefin metathesis catalyst, and the metallacyclobutane intermediate must be a trigonal bipyramid with the MC_3 ring in two equatorial positions.[15] As we have shown here and elsewhere,[4,5] monoaryloxide monochloride complexes are unusually reactive and capable of cross-metathesizing electron-poor Z-ClCH=CHCl with an "ordinary" olefin such as cyclooctene. Fortunately, the adamantylimido and *t*-butylimido alkylidene complexes now can be prepared relatively directly as diphenylmethylphosphine adducts using HCl to trigger formation of the alkylidene through protonation and removal of one imido ligand and to provide the chloride anion, all in one event. Phosphine is required in order to isolate the dichloride or monochloride complexes, but in the right circumstances the phosphine is labile enough for the compound to initiate and sustain a metathesis reaction that involves Z-ClCH=CHCl. The degree of dissociation of PPh_2Me depends dramatically upon the size of the aryloxide (OAr) ligand in the order OTPP < OHMT < OHIPT < OHTBT, but the reactivity of the resulting 14e complex is likely to follow the opposite trend (OTPP > OHMT > OHIPT > OHTBT). These opposing trends result in **3b(PPh$_2$Me)** and **4b(PPh$_2$Me)** being the "best compromise" for the reaction shown in equation 3. Sterically less demanding and more strongly bound phosphines (PMe_3) or other ligands (e.g., pyridine) are more likely to hinder or block reaction with an olefin through formation of a 16e or 18e complex. More reactive, smaller olefins (e.g., ethylene) *may* be able to compete successfully for a 14e complex, whereas Z-ClCH=CHCl, or even cyclooctene, cannot.

We have to ascribe the low activity of phosphine-free **5a** entirely to the fact that OHTBT is simply too sterically demanding for the reaction shown in equation 3, or even polymerization of cyclooctene, under the conditions employed. Low reactivity has been observed, largely for steric reasons, for other 14e imido alkylidene complexes. One example is $Mo(NAd)(CHCMe_2Ph)[OSi(t\text{-}Bu)_3]_2$, which does not react readily with ethylene at 5 atm and 120 °C.[16] The low reactivity of phosphine-free **6a** also can be ascribed to the steric demand of one of the Mo entities with respect to reaction of substrate at the other Mo center.

Detailed studies that document the consequence of reaction of water with high oxidation state Mo or W alkylidene complexes[17] (or alkylidyne complexes[18]) are rare. What we have found here in the case of **6a(PMe$_3$)** is that the alkylidene ligand is not necessarily the first ligand to be protonated upon addition of water. The protonation process is likely to consist of water first binding to the metal followed by a proton being transferred (intramolecularly or intermolecularly) to the aryloxide oxygen. It also cannot be assumed that, if an alkylidene ligand survives partial hydrolysis, the resulting complex will be a *more* active catalyst than the original alkylidene complex, especially if a μ-oxo dimer or larger cluster is formed, as is found for **6a(PMe$_3$)**. In fact, a lower reactivity may be more likely in view of the propensity of an oxo ligand to bridge between metals in many circumstances.

CONCLUSIONS

We have shown that adamantylimido and *t*-butylimido alkylidene dichloride complexes can be prepared in the presence of diphenylmethylphosphine and 3 equiv of HCl. These serve as starting materials for the synthesis of monoaryloxide chloride complexes in which the aryloxide is a terphenoxide (OTPP, OHMT, OHIPT, or OHTBT). A 16e monoaryloxide monochloride complex is active in metathesis reactions when the terphenoxide is large enough to labilize the phosphine, but small enough to allow reactions at the 14e metal center to proceed. The metathesis reaction is most stereoselective when the terphenoxide is OHIPT.

Experimental Section

General Procedures.

All air- and moisture-sensitive materials were manipulated under a nitrogen atmosphere in a Vacuum Atmospheres glovebox or on a dual-manifold Schlenk line. Glassware was either oven-dried or flame-dried prior to use. Acetonitrile, benzene, methylene chloride, diethyl ether, 1,2-dimethoxyethane, and toluene were degassed, passed through activated alumina columns, and stored over 4 Å Linde-type molecular sieves. 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 Linde-type molecular sieves prior to use. ^1H and $^{31}P\{^1H\}$ NMR spectra were acquired on a Varian Mercury 300 MHz or a Varian Inova-500 MHz NMR spectrometer. $^{13}C\{^1H\}$ NMR spectra were acquired on a Varian Inova-500 MHz NMR spectrometer. 2D NMR spectra were acquired on a Varian Inova-500 MHz NMR spectrometer. Chemical shifts for ^1H, ^{31}P, and ^{13}C NMR spectra are reported as parts per million relative to tetramethylsilane and referenced to the residual ^1H or ^{13}C resonances of the deuterated solvent (^1H δ: benzene 7.16 ppm, methylene chloride 5.32 ppm; ^{13}C δ: benzene 128.06 ppm, methylene chloride 53.84 ppm). Gas Chromatography was performed on an Agilent system equipped with an HP-5 column (ID 320 μm, 0.25 μm, and length 30 m). TMSCl was purchased from Alfa Aesar and degassed by a free-pump-thaw method prior to use. $B(C_6F_5)_3$ was purchased from Strem and used as received. LiOAr was prepared by the addition of 1 equiv of *n*-butyllithium to a cold pentane or Et_2O solution of ArOH, and the solid was collected on a glass frit, washed with pentane, and dried *in vacuo*. PMe_3, $PPhMe_2$, and PPh_2Me were purchased from Strem chemicals and used as received. The hydrochloride salts of the phosphines were prepared through addition of ethereal HCl (1.0 M; Sigma Aldrich) to the phosphine in diethyl ether while stirring the mixture; the phosphine hydrochloride salt was collected on a glass frit, washed with minimal ether, and dried *in vacuo*. $Mo(NAd)_2Cl_2(DME)$,[19] $Mo(NAd)_2(CH_2CMe_2Ph)_2$,[9] and $Mo(N\text{-}t\text{-}Bu)_2Cl_2(DME)$[20] were prepared as described in the literature. Syntheses of $Mo(N\text{-}t\text{-}Bu)_2(CH_2\text{-}t\text{-}Bu)_2$ from $Mo(N\text{-}t\text{-}Bu)_2Cl_2$ and neopentyllithium[21] and from $Mo(N\text{-}t\text{-}Bu)_2Cl_2(DME)$ and neopentyl Grignard[22] have been reported in the literature, but no detailed procedures were provided; we provide a procedure here. Elemental analyses were performed at the CENTC Elemental Analysis Facility at the University of Rochester, New York.

Mo(N-*t*-Bu)$_2$(CH$_2$-*t*-Bu)$_2$.

Mo(N-*t*-Bu)$_2$Cl$_2$(DME) (4.01 g, 10.03 mmol) was dissolved in ~30 mL of diethyl ether in a glovebox under nitrogen. The reaction vessel was connected to a Schlenk manifold and cooled to −78 °C with a dry ice/acetone bath. Neopentylmagnesium chloride (20.1 mL, 20.09 mmol, 2 equiv., 1.0 M in THF) was syringed into the reaction vessel over a few minutes. The reaction mixture was stirred overnight to give a turbid brown-orange solution. All volatiles were removed *in vacuo*. In a glovebox ~30 mL of pentane was added and the mixture was filtered through Celite. All volatiles were removed from the filtrate *in vacuo* to yield Mo(N-*t*-Bu)$_2$(CH$_2$-*t*-Bu)$_2$ as a brown oil that was used without purification; crude yield 3.77 g (99%): ^{1}H NMR (500 MHz, C_6D_6, 22 °C) 1.76 (s, 4H), 1.41 (s, 18 H), 1.19 (s, 18 H) ppm.

Mo(NAd)(CHCMe$_2$Ph)(PPh$_2$Me)Cl$_2$ (1a(PPh$_2$Me)).

Mo(NAd)$_2$(CH$_2$CMe$_2$Ph)$_2$ (1.05 g, 1.59 mmol, 1.00 equiv) was dissolved in 30 mL of diethyl ether. The solution was stirred rapidly and solid PPh$_2$Me·HCl (0.375 g, 1.59 mmol, 1.00 equiv) was added. The reaction mixture was stirred for 30 min at room temperature and then chilled to – 78 °C. HCl (1.0 M in diethyl ether; 3.17 mL, 2.00 equiv) was added to the mixture with a syringe. The cooling bath was removed and the mixture was stirred overnight. The volatiles were removed from the reaction *in vacuo*, the crude residue was triturated with 1–2 mL of diethyl ether, and the off-white solid was collected on a glass frit. The crude product was dissolved in ~20 mL of a mixture of benzene and toluene (1:1 v/v) and the solution was filtered through Celite to remove the *t*-butylammonium chloride. The solvents were removed from the extract *in vacuo* to afford the product; yield 0.540 g (53 %). *Only alkylidene NMR resonances are listed here*: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 13.10 (d, $^3J_{HP}$ = 4.9 Hz, $^1J_{CH}$ = 123 Hz, 1H, Mo=CH_{syn}); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 309.8 (d, $^2J_{CP}$ = 22.4 Hz, Mo=*C*). Anal. Calcd for $C_{33}H_{40}Cl_2MoNP$ (648.52 g/mol): C, 61.12%; H, 6.22%; N, 2.16%. Found: C, 61.21%; H, 6.19%; N, 2.51%.

Slow evaporation of benzene from a saturated solution of **1a(PPh$_2$Me)** at room temperature gave crystals suitable for X-ray data collection.

Mo(N-*t*-Bu)(CH-*t*-Bu)Cl$_2$(PPh$_2$Me) (1b(PPh$_2$Me)).

The procedure was virtually the same as that for **1a(PPh$_2$Me)** starting with Mo(N-*t*-Bu)$_2$(CH$_2$-*t*-Bu)$_2$ (2.00 g, 5.26 mmol, 1.00 equiv) in 30 mL of diethyl ether, PPh$_2$Me·HCl (1.24 g, 5.26 mmol, 1.00 equiv), and HCl (1.0 M in diethyl ether; 10.5 mL, 2.00 equiv); yield 1.31 g (49 %). *Only alkylidene NMR resonances are listed here*: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 13.01 (d, $^3J_{HP}$ = 4.9 Hz, $^1J_{CH}$ = 118 Hz, 1H, Mo=CH_{syn}); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 314.5 (d, $^2J_{CP}$ = 22.7 Hz, Mo=*C*). Anal. Calcd for $C_{22}H_{32}Cl_2MoNP$ (508.34 g/mol): C, 51.98%; H, 6.35%; N, 2.76%. Found: C, 52.04%; H, 6.29%; N, 2.61%.

Mo(NAd)(CHCMe$_2$Ph)(Cl)(OTPP)(PPh$_2$Me) (2a(PPh$_2$Me)).

A solution of LiOTPP (0.218 g, 0.216 mmol, 1 equiv) in benzene solution was added dropwise to **1a(PPh$_2$Me)** (0.140 g, 0.216 mmol, 1 equiv) in benzene. The reaction was stirred overnight and filtered through Celite. The solvents were removed *in vacuo* and the

tacky yellow solid was triturated in 5 mL of pentane to afford the product as an off-white solid; yield 0.187 g (86%). *Only alkylidene NMR resonances are listed here*: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 11.55 (d, $^{3}J_{HP}$ = 4.4 Hz, 1H, Mo=C*H*); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 311.9 (d, $^{2}J_{CP}$ = 16.7 Hz, Mo=*C*). Anal. Calcd for $C_{63}H_{61}ClMoNOP$ (1010.57 g/mol): C, 74.88%; H, 6.08%; N, 1.39%. So far elemental analyses that agree with the calculated figures has not been successful.

Mo(N-*t*-Bu)(CHCMe$_2$Ph)(Cl)(OTPP)(PPh$_2$Me) (2b(PPh$_2$Me)).

A solution of LiOTPP (0.114 g, 0.238 mmol, 1 equiv) in benzene was added dropwise to **1b(PPh$_2$Me)** (0.121 g, 0.238 mmol, 1 equiv) in benzene. The isolation procedure was the same as that for **2a(PPh$_2$Me)**; yield 0.151 g (72.9%). *Only alkylidene NMR resonances are listed here*: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 11.58 (d, $^{3}J_{HP}$ = 4.5 Hz, 1H, Mo=C*H*); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 316.5 (d, $^{2}J_{CP}$ = 16.9 Hz, Mo=*C*). Anal. Calcd for $C_{52}H_{53}ClMoNOP$ (870.39 g/mol): C, 71.76%; H, 6.14%; N, 1.61%. Found: C, 72.05%; H, 6.25%; N, 1.19%.

Mo(NAd)(CHCMe$_2$Ph)(Cl)(OHMT)(PPh$_2$Me) (3a(PPh$_2$Me)).

A solution of LiOHMT (0.063 g, 0.154 mmol, 1 equiv) was added dropwise to **1a(PPh$_2$Me)** (0.100 g, 0.154 mmol, 1 equiv) in benzene. The isolation procedure was the same as that for **2a(PPh$_2$Me)**; yield 0.111 g (76.4%). *Only alkylidene NMR resonances are listed here*: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 12.45 (d, $^{3}J_{HP}$ = 4.6 Hz, 1H, Mo=C*H*); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 313.6 (d, $^{2}J_{CP}$ = 17.9 Hz, Mo=*C*). Anal. Calcd for $C_{57}H_{65}ClMoNOP$ (942.54 g/mol): C, 72.64%; H, 6.95%; N, 1.49%. Found: C, 72.13%; H, 6.88%; N, 1.31%.

Mo(N-*t*-Bu)(CH-*t*-Bu)(Cl)(OHMT)(PPh$_2$Me) (3b(PPh$_2$Me)).

A solution of LiOHMT (0.067 g, 0.163 mmol, 1 equiv) in benzene solution was added dropwise to **1b(PPh$_2$Me)** (0.083 g, 0.163 mmol, 1 equiv) in benzene. The isolation procedure was the same as that for **2a(PPh$_2$Me)**; yield 0.072 g (55%). *Only alkylidene NMR resonances are listed here*: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 12.27 (d, $^{3}J_{HP}$ = 4.7 Hz, 1H, Mo=C*H*); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 318.5 (d, $^{2}J_{CP}$ = 17.7 Hz, Mo=*C*). Anal. Calcd for $C_{49.5}H_{61}ClMoNOP$ (848.42 g/mol): C, 70.07%; H, 7.25%; N, 1.65%. Found: C, 70.05%; H, 7.27%; N, 1.51%.

X-ray quality crystals were grown from a saturated toluene solution at –25 °C. The lattice contains 0.5 molecules of toluene per **3b(PPh$_2$Me)**.

Mo(NAd)(CHCMe$_2$Ph)(Cl)(OHIPT)(PPh$_2$Me) (4a(PMe$_3$)).

A solution of LiOHIPT (0.089 g, 0.177 mmol, 1 equiv) was added dropwise to **1a(PPh$_2$Me)** (0.115 g, 0.177 mmol, 1 equiv) in benzene. The solution was stirred for 30 h and filtered through Celite. The solvents were removed from the filtrate *in vacuo* and the tacky residue was extracted with pentane to give an orange solution. PMe_3 (0.100 g, 1.31 mmol, 7.4 equiv) was added to the orange pentane solution. The crystals that grew when the solution was cooled to – 25 °C were collected by filtration; yield 0.040 g (23%). *Only alkylidene NMR resonances are listed here*: ^{1}H NMR (500 MHz, C_6D_6) δ 12.74 (d, $^{3}J_{HP}$ = 4.8 Hz, 1H, Mo=C*H*); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 300.9 (d, $^{2}J_{CP}$ = 18.4 Hz, Mo=*C*). Anal.

Calcd for $C_{59}H_{85}ClMoNOP$ (986.72 g/mol): C, 71.82%; H, 8.68%; N, 1.42%. Found: C, 71.49%; 8.55%; N, 1.20%.

Mo(N-*t*-Bu)(CH-*t*-Bu)(Cl)(OHIPT)(PPh_2Me) (4b(PPh_2Me)).

A solution of LiOHIPT (0.139 g, 0.275 mmol, 1 equiv) in benzene solution was added drop wise to a solution of Mo(N-*t*-Bu)(CH-*t*-Bu)(PPh_2Me)Cl_2, **1b(PPh_2Me)** (0.140 g, 0.275 mmol, 1 equiv) in benzene. The solution was stirred rapidly overnight. The mixture was filtered through Celite, and the volatiles were removed from the filtrate *in vacuo*. The tacky yellow solid was stirred in 5 mL pentane to afford **4b(PPh_2Me)** as an off-white solid; yield 0.168 g (62.8%). *Only alkylidene NMR resonances are listed here*: ^{1}H NMR (500 MHz, C_6D_6) δ 12.99 (br d, 1H, 5-coordinate Mo=C*H*), 11.62 (s, 1H, 4-coordinate Mo=C*H*); ^{13}C NMR (obtained from ^{1}H-^{13}C deHSQC spectrum 500 MHz, C_6D_6) δ 292.9 (4-coordinate Mo=*C*). Anal. Calcd for $C_{58}H_{81}ClMoNOP$ (970.68 g/mol): C, 71.77%; H, 8.41%; N, 1.44%. Found: C, 71.39%; H, 8.27%; N, 1.22%.

Mo(NAd)($CHCMe_2Ph$)(Cl)(OHTBT)(PMe_3) (5a(PMe_3)).

KOHTBT (300 mg, 0.482 mmol, 1 equiv) was added to 20 mL of benzene containing Mo(NAd)($CHCMe_2Ph$)$(Cl)_2$(PPh_2Me) **1a(PPh_2Me)** (313 mg, 0.482 mmol, 1 equiv), and the mixture was heated at 60 °C for 18 h. The benzene was evaporated *in vacuo*, 5 mL of dichloromethane was added, and the mixture filtered through Celite to give a red solution. PMe_3 (0.245 mL, 184 mg, 2.41 mmol, 5 equiv) was added, and the resulting solution was kept at −20 °C overnight. During this time, pale off-white crystals formed, which were filtered off and washed with 1 mL of cold dichloromethane. The product was dried *in vacuo* to give Mo(NAd)($CHCMe_2Ph$)(OHTBT)(Cl)(PMe_3).2CH_2Cl_2 as off-white crystals; yield 280 mg (47%). The product was stored in the glovebox refrigerator at – 20 °C in order to avoid slow decomposition. *Only alkylidene NMR resonances are listed here*: ^{1}H NMR (400 MHz, C_6D_6) δ 13.47 (br s, 1H, Mo=C*H*); ^{13}C{^{1}H} NMR (151 MHz, C_6D_6) δ 311.1 (d, $^2J_{CP}$ = 15.1 Hz, Mo=*C*). Anal. Calcd for $C_{65}H_{97}ClMoNOP$ (1070.88 g/mol): C, 72.90%; H, 9.13%; N, 1.31%. Found: C, 73.49%; H, 9.40%; N, 1.05%.

Crystals suitable for X-ray data collection were obtained by crystallizing **5a(PMe_3)** from dichloromethane in the presence of 2 equiv of PMe_3 at room temperature.

[Mo(NAd)($CHCMe_2Ph$)(Cl)(PMe_3)]$_2$(μ-O) (6a(PMe_3)).

Mo(NAd)($CHCMe_2Ph$)(OHTBT)(Cl)(PMe_3).2CH_2Cl_2 (**5a(PMe_3)**) (100 mg, 0.08 mmol, 1 equiv) was suspended in 2 mL of ether and the mixture was cooled to – 78 °C. A stock solution of wet ether was prepared through addition of 0.005 mL of water to 1 mL ether. A 0.145 mL (0.726 mg, 0.04 mmol, 0.5 equiv of water) of this solution was added, and the resulting suspension was stirred at room temperature overnight. The solid was filtered and washed by 1 mL of ether. All solvent was removed *in vacuo* to give [Mo(NAd)($CHCMe_2Ph$)(Cl)(PMe_3)]$_2$(μ-O) **(6a(PMe_3)** as an off-white powder; yield 27 mg (67%). *Only alkylidene NMR resonances are listed here*: ^{1}H NMR (400 MHz, C_6D_6) δ 13.57 (d, $^3J_{HP}$ = 6.3 Hz, 2H, Mo=C*H*); ^{13}C{^{1}H} NMR (151 MHz, C_6D_6) δ 307.7 (d, $^2J_{CP}$ = 19.8 Hz, Mo=*C*). Anal. Calcd for $C_{46}H_{72}Cl_2Mo_2N_2OP_2$ (993.86 g/mol): C, 55.59%; H, 7.30%; N, 2.82%. Found: C, 55.60%; H, 7.11%; N, 2.24%.

Crystals of **6a(PMe$_3$)** suitable for X-ray data collection were obtained through crystallization from a mixture of pentane and toluene – 20 °C.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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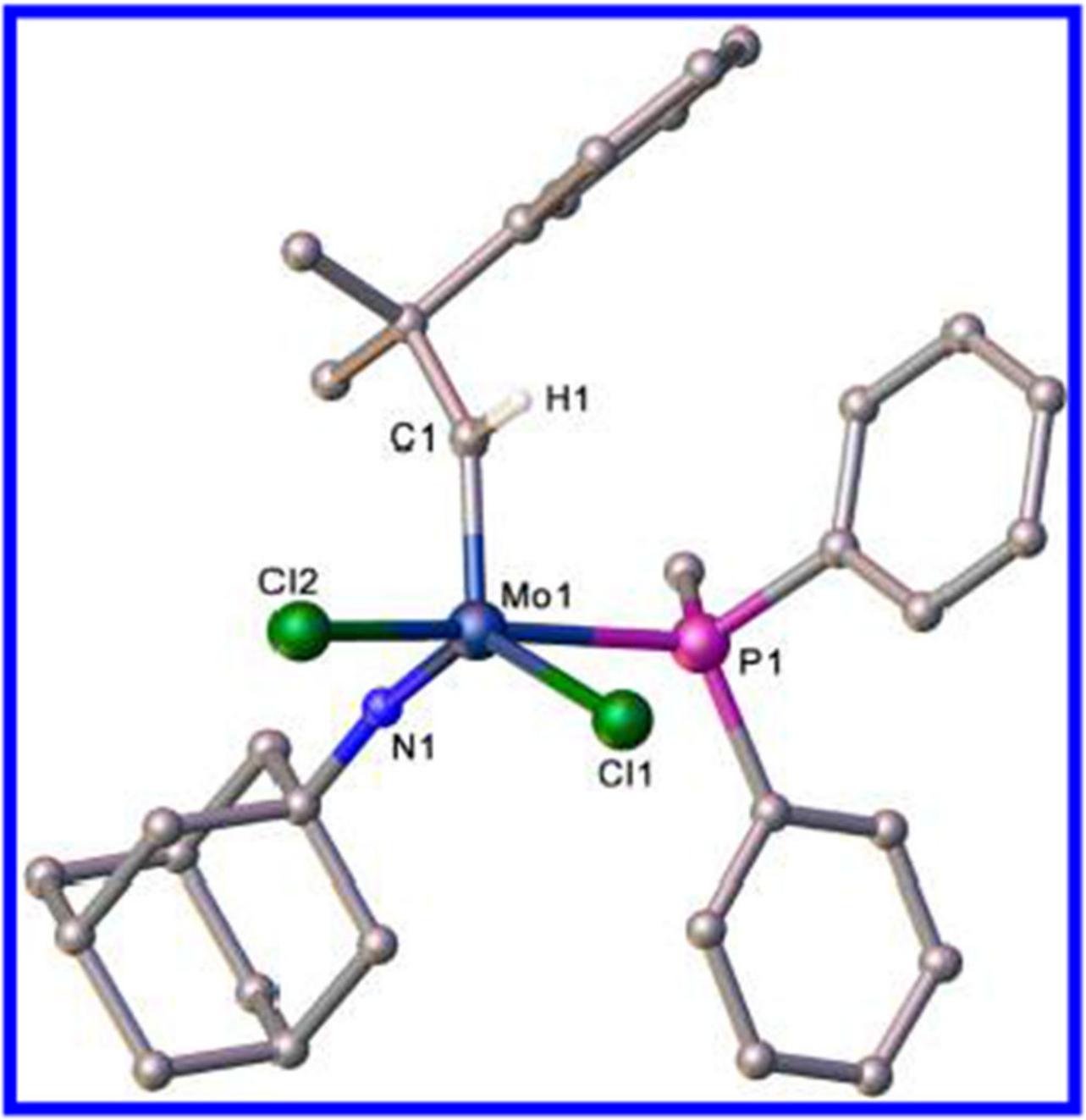

Figure 1.

Structure of Mo(NAd)(CHCMe$_2$Ph)(PPh$_2$Me)Cl$_2$ (**1a(PPh$_2$Me)**). Hydrogen atoms, except on C1, have been omitted for clarity.

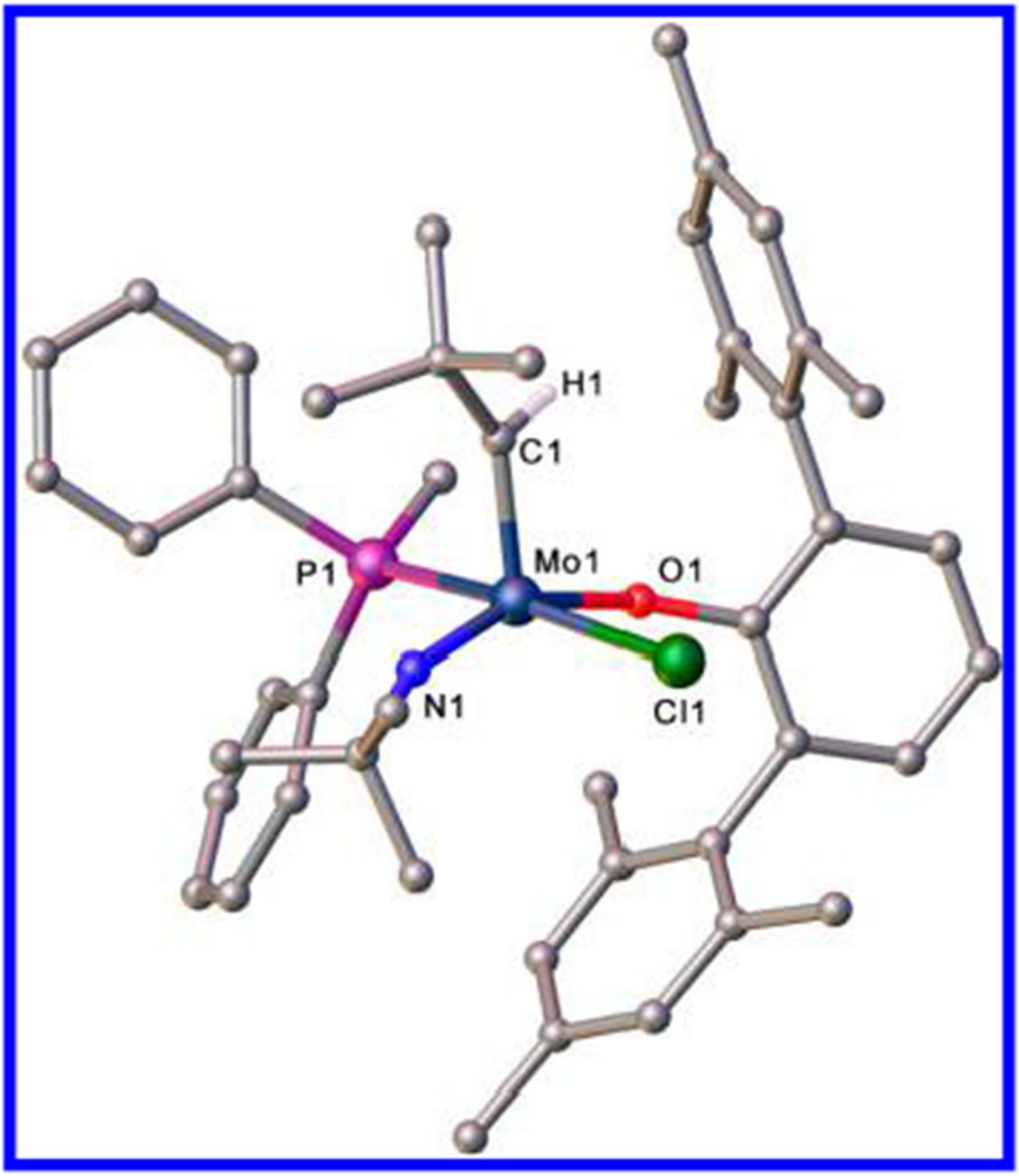

Figure 2.

Structure of one of the molecules of Mo(N-*t*-Bu)(CH-*t*-Bu)(PPh_2Me)(OHMT)Cl (**3b(PPh$_2$Me)**); τ = 0.24. Hydrogen atoms (except on C1), disordered atoms, and lattice solvent toluene have been omitted for clarity.

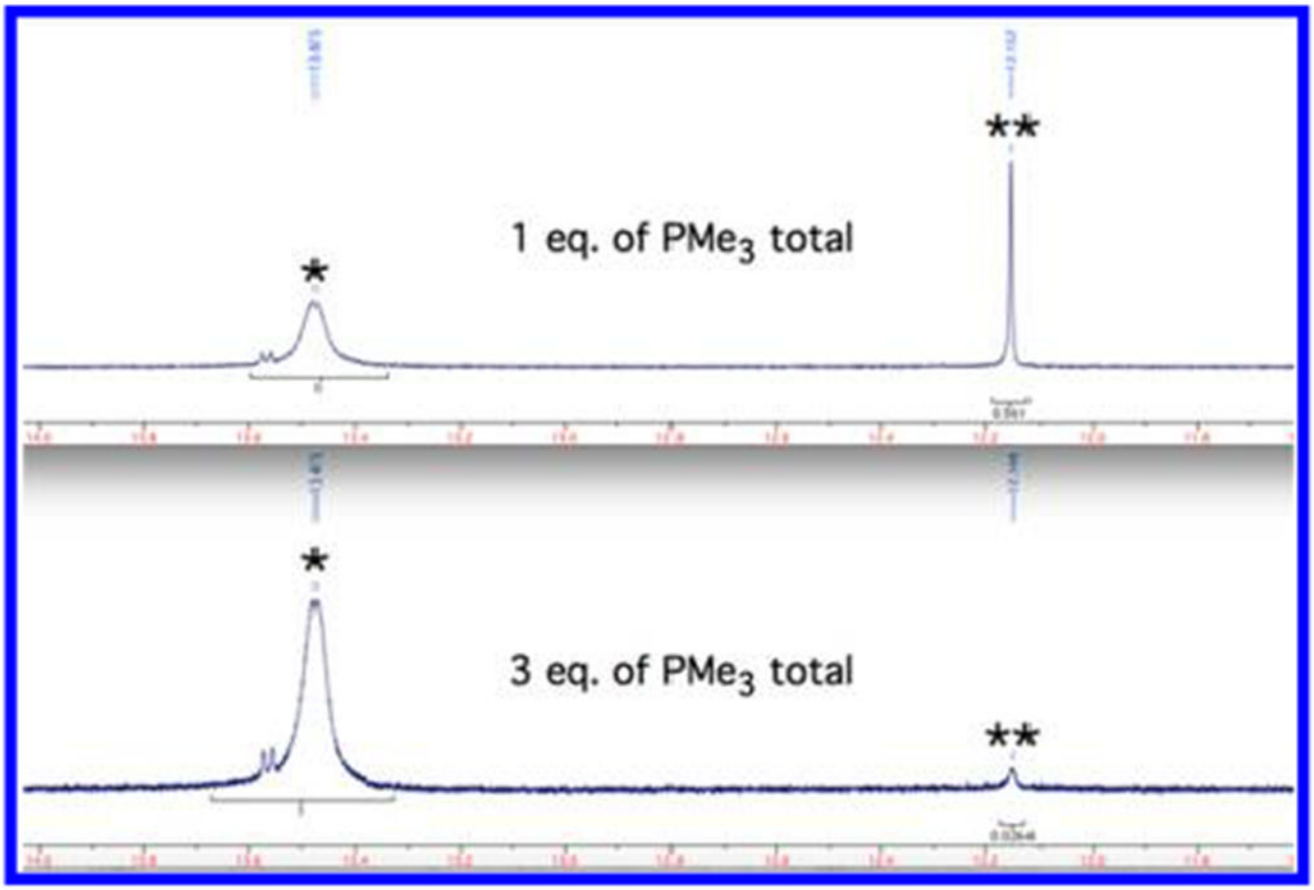

Figure 3.

Alkylidene resonances in proton NMR spectra of Mo(NAd)($CHCMe_2Ph$)(Cl)(OHTBT)(PMe_3) **5a(PMe$_3$)** in C_6D_6 at 20 °C; ***5a(PMe$_3$)**; ****5a**.

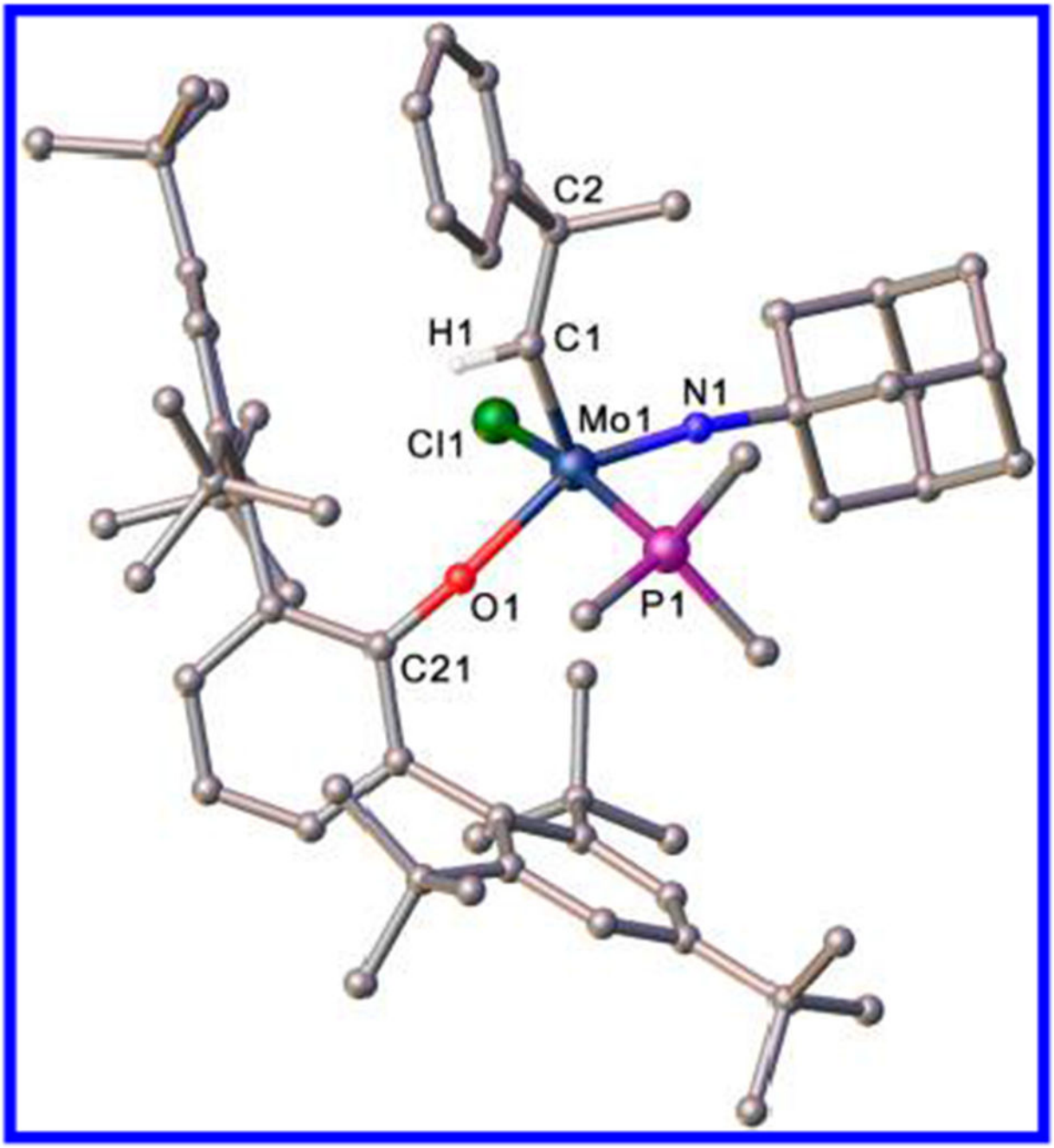

Figure 4.

Structure of Mo(NAd)(CHCMe$_2$Ph)(Cl)(OHTBT)(PMe$_3$) **5a(PMe$_3$)**; τ = 0.27. Hydrogen atoms (except on C1) and lattice solvent dichloromethane have been omitted for clarity.

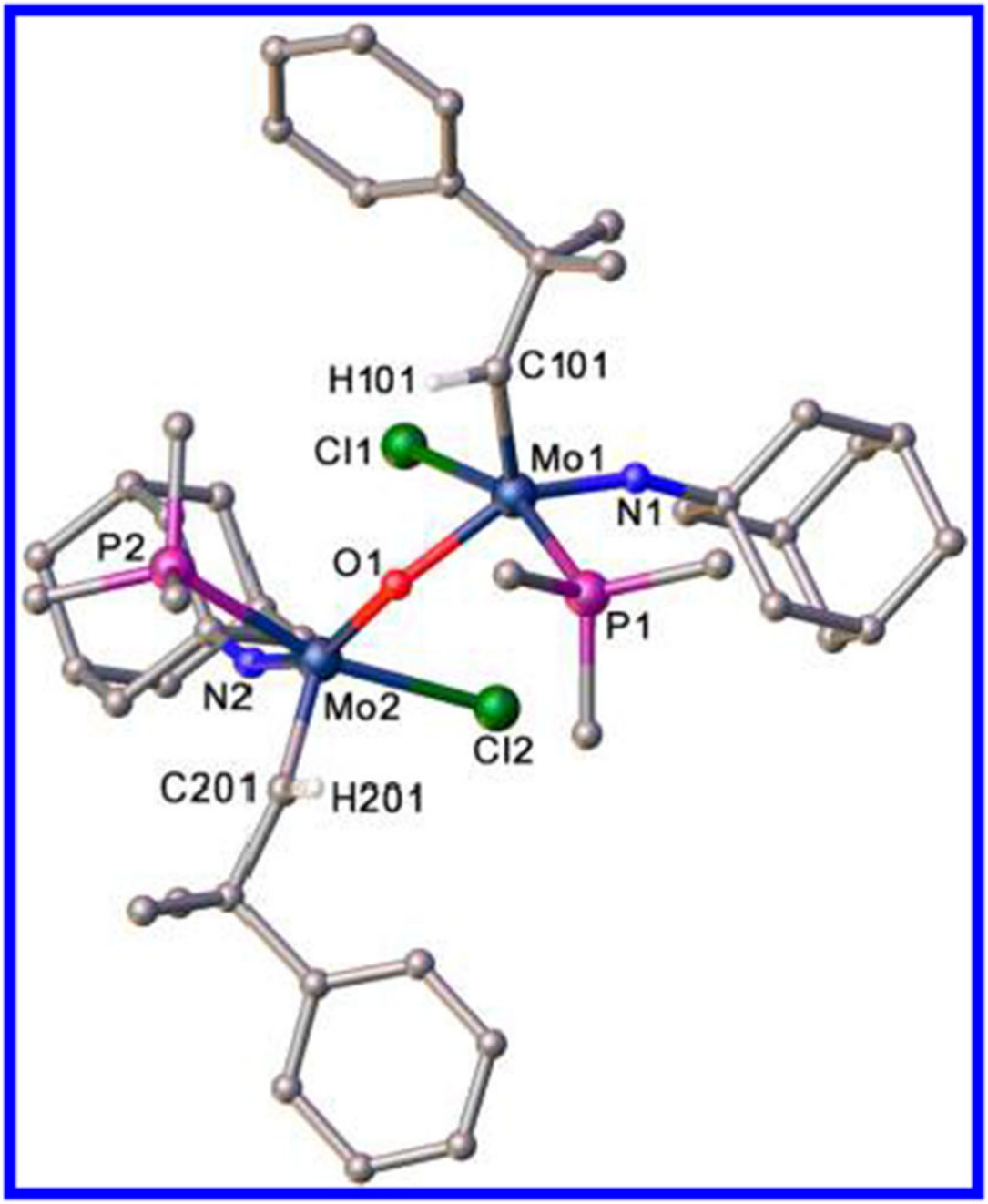

Figure 5.
Structure of [Mo(NAd)($CHCMe_2Ph$)(PMe_3)(Cl)]$_2$(μ-O) (**6a(PMe_3)**).

Table 1.

Results (A/B/C Percentages) of Reactions between Cyclooctene (A) and Z-1,2-Dichloroethylene (1.25 equiv) in C_6D_6 to Give Polycyclooctene (B) and/or the Cross-metathesis Product (C)

initiator	20 min	1 h	6 h	% Z,Z of C
1b(PPh_2Me)	100/0/0	100/0/0	100/0/0	n/a
2b(PPh_2Me)	100/0/0	92/8/0	45/55/0	
3b(PPh_2Me)	3/51/46	0/9/91	0/1/99	86.4
4b(PPh_2Me)	4/32/64	0/24/76	0/4/96	100
5a(PMe_3)	100/0/0	100/0/0	100/0/0	n/a
6a(PMe_3)	100/0/0	100/0/0	100/0/0	n/a
1b[a]	100/0/0	100/0/0	100/0/0	n/a
2b[a]	0/2/98	0/1/99		89.6
3b[a]	0/3/97	0/3/97		99.3
4b[a]	0/0/100			99.7
5a[a]	100/0/0	100/0/0	100/0/0	n/a
6a[a]	78/22/0	61/39/0	5/95/0	n/a

[a]Generated *in situ* through addition of 1 equiv of $B(C_6F_5)_3$ to the phosphine adduct.