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Reaction of Phosphoranes with $Mo(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(CHCMe_3)[OCMe(CF_3)_2]_2$: Synthesis and Reactivity of an Anionic Imido Alkylidyne Complex

Zachary J. Tonzetich, Richard R. Schrock,* and Peter Müller

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

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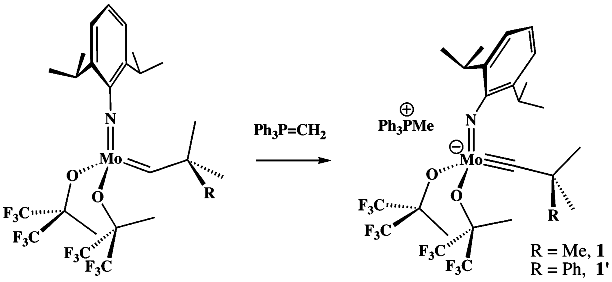
The reaction of $Ph_3P{=}CH_2$ with $Mo(NAr)(CHCMe_3)[OCMe(CF_3)_2]_2$ (Ar = 2,6-*i*-$Pr_2C_6H_3$) produces the anionic alkylidyne complex $\{Ph_3PMe\}\{Mo(NAr)(CCMe_3)[OCMe(CF_3)_2]_2\}$. An X-ray structure determination of the complex reveals a bent Mo−N−C angle for the imido group, as expected when a metal−carbon triple bond is present. The anion has been shown to react with electrophiles predominantly at the imido nitrogen.

Introduction

Olefin metathesis catalysts of the type $Mo(NR)(CHR')(OR'')_2$,[1] and variations that contain chiral diolates,[2] are known to decompose either via bimolecular decomposition of alkylidenes or via rearrangement of some intermediate metalacyclobutane complex. The metal is "reduced" in the process by two electrons to a d^2 species of some type (e.g., a bimetallic species that contains a M=M bond[3]). It would be highly desirable to discover a way of regenerating the catalyst through the use of an alkylidene source such as a phosphorus or sulfur ylide. The first demonstration of a reaction of this type was transfer of an alkylidene from an alkylidene phosphorane to a Ta(III) species to generate a Ta(V) bis-cyclopentadienyl complex.[4] Alkylidenes also have been transferred from phosphorus to W(IV) species to yield W(VI) alkylidene complexes.[5] However, in no case was the resulting alkylidene species a known metathesis catalyst. Therefore we decided to turn to an exploration of potential reactions between the prototypical metathesis catalyst $Mo(NAr)(CHCMe_3)[OCMe(CF_3)_2]_2$ (Ar = 2,6-*i*-$Pr_2C_6H_3$) and phosphorus ylides, reasoning that if a $Mo(NAr)(CHR)[OCMe(CF_3)_2]_2$ species were to be regenerated from some "$Mo(NAr)[OCMe(CF_3)_2]_2$" species in a reaction involving an alkylidene phosphorane, then the resulting alkylidene ideally would have to react relatively slowly with that phosphorane in order to avoid potentially destructive secondary reactions. We report here reactions between $Mo(NAr)(CHCMe_3)[OCMe(CF_3)_2]_2$ and several phosphoranes. Only one clean reaction was observed in the case of one phosphorane; $Mo(NAr)(CHCMe_3)[OCMe(CF_3)_2]_2$ reacts with $Ph_3P{=}CH_2$ to give an anionic imido alkylidyne complex, $\{Ph_3PMe\}\{Mo(NAr)(CCMe_3)[OCMe(CF_3)_2]_2\}$.

Results

Addition of 1 equiv of $Ph_3P{=}CH_2$ to $Mo(NAr)(CHCMe_2R)[OCMe(CF_3)_2]_2$ (R = Me or Ph) in benzene-d_6 resulted in an immediate color change from yellow to deep orange. The ^1H NMR spectrum of the product showed it to be a single compound that has no alkylidene H_α resonance. The ^1H and ^{13}C NMR features are consistent with the product being an anionic alkylidyne complex (R = Me, **1**, *or* R = Ph, **1′**; eq 1). The product can be isolated readily in high yield. Proton NMR spectra reveal broad resonances for the isopropyl methyl groups of the arylimido ligand, consistent with hindered rotation about the $N{-}C_{ipso}$ bond. For **1**, these resonances coalesce near 40 °C at 500 MHz in benzene-d_6. Spectra in tetrahydrofuran-d_8 show coalescence of the isopropyl methyl groups at 20 °C. Therefore ion pairing may be responsible for a slightly more hindered rotation in benzene. A ^{13}C NMR spectrum of purified **1** shows a resonance at 300.75 ppm in C_6D_6 that can be assigned to the alkylidyne carbon atom. No J_{CP} coupling was observed, consistent with the ionic formulation shown in eq 1, while the ^{19}F NMR spectrum displays two resonances for the diastereotopic trifluoromethyl groups, as anticipated.



(1)

Slow cooling of a saturated toluene/pentane solution of **1** afforded red spars suitable for X-ray diffraction. The solid-state structure contains two independent ion pairs in the asymmetric unit. A POV-ray rendering of one of the molecules is displayed in Figure 1, and relevant crystallographic details are listed in Table 1. The imido alkylidyne formulation is consistent with the large Mo1−C1−C2 bond angle (168.2(2)°) and the bent Mo1−N1−C21 angle (141.16(17)°; cf. 169−175° in typical four-coordinate alkylidenes of this type[1]). The anions in each molecule are virtually identical except for the $Mo{-}N_{imido}{-}C_{ipso}$ bond angle, which is 141.16(17)° in the compound shown in Figure 1 and 158.66(17)° in the other (see Table S1 in the Supporting Information). The reason for the large difference in bond angles might be ascribed to a closer approach of the phosphonium cation in the compound shown in Figure 1 versus the

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* To whom corresondence should be addressed. E-mail: rrs@mit.edu.

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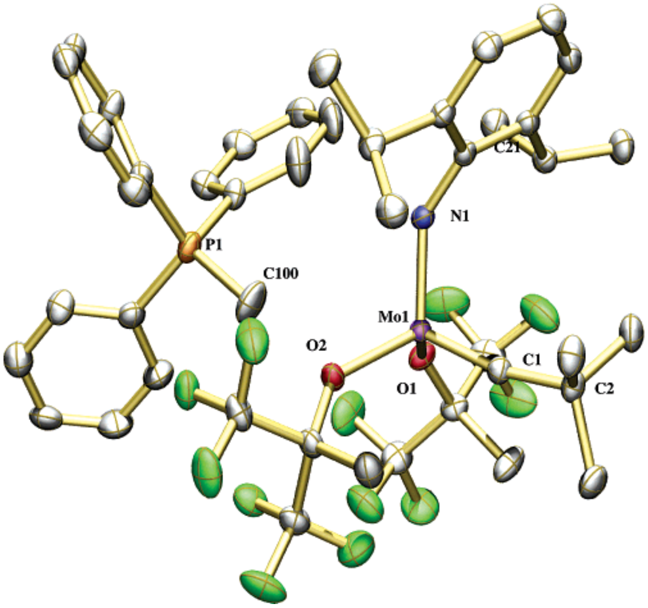

Figure 1. POV-ray rendering (thermal ellipsoids at 50%) of one of the two independent molecules of {Ph_3PMe}{Mo(NAr)($CCMe_3$)-[$OCMe(CF_3)_2]_2$} in the unit cell. Hydrogen atoms are removed for clarity. Molybdenum is shown in purple, oxygen in red, nitrogen in blue, fluorine in green, and phosphorus in orange. Relevant bond distances (Å) and angles (deg): Mo1−C1, 1.754(2); Mo1−N1, 1.813(2); Mo1−O1, 1.9838(18); Mo1−O2, 1.9763(18); C100−Mo1, 3.566(3); Mo1−C1−C2, 168.2 (2); Mo1−N1−C23, 141.16-(17); N1−Mo1−C1, 105.82(11).

Table 1. Crystallographic Data and Refinement Parameters for 1

empirical formula	$C_{44}H_{50}F_{12}MoNO_2P$
fw	979.76 g/mol
temperature	100(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	$P2_1/c$
unit cell dimens	a = 25.3522(10) Å, $\alpha = 90°$ b = 17.7046(7) Å, $\beta = 97.2830(10)°$ c = 20.2127(8) Å, $\gamma = 90°$
volume	8999.3(6) $Å^3$
Z	8
density (calcd)	1.446 g/cm^3
absorp coeff	0.413 mm^{-1}
F(000)	4016
cryst size	0.30 × 0.25 × 0.10 mm^3
θ range for data collection	1.67 to 29.57°
index ranges	$-34 \leq h \leq 35$, $-24 \leq k \leq 24$, $-28 \leq l \leq 27$
no. of reflns collected	198 822
no. of indep reflns	25 247 [*R*(int) = 0.0558]
completeness to $\theta = 29.57°$	100%
absorp corr	semiempirical from equivalents
max. and min. transmn	0.9598 and 0.8860
refinement method	full-matrix least-squares on F^2
no. of data/restraints/ params	25 247/2270/1299
goodness-of-fit on F^2	1.031
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0374, wR2 = 0.0841
R indices (all data)	R1 = 0.0549, wR2 = 0.0928
largest diff peak and hole	0.844 and −0.502 e·$Å^{-3}$

latter (compare 3.566(3) versus 4.054(3) Å for the distance from the carbon atom of the methyl group of the phosphonium cation to the molybdenum center). Only one species is observed in solution, and the low barrier to $N_{imido}-C_{ipso}$ bond rotation in arene solvents suggests that the potential energy surface for flexing of the $Mo-N_{imido}-C_{ipso}$ angle may be quite flat and sensitive to ion pairing. Therefore it is likely that crystal-packing effects are responsible for the observed differences in the solid state. Because of the presence of the triple bond to carbon and π bonding of the imido group to the metal, C_{ipso} of the aryl group must lie in the N−Mo−C plane. The aryl group points toward the alkylidyne ligand, away from the phosphonium cation, which is nestled into the NOO face of the tetrahedral central core.

{Ph_3PMe}{Mo(NAr)($CCMe_3$)[$OCMe(CF_3)_2]_2$} is isoelectronic with the known rhenium(VII) complex Re(NAr)($CCMe_3$)-[$OCMe(CF_3)_2]_2$.[6] In the Re compound, the C_α resonance is found at 304.28 ppm (vs 300.75 ppm in the Mo species above) and the isopropyl methyl groups appear as a single doublet resonance at room temperature, consistent with facile rotation of the aryl ring about the $N_{imido}-C_{ipso}$ bond on the NMR time scale. No structural study of Re(NAr)($CCMe_3$)[$OCMe(CF_3)_2]_2$ was carried out.

The benzylidene phosphorane, $Ph_3P{=}CHPh$, did not react with Mo(NAr)($CHCMe_3$)[$OCMe(CF_3)_2]_2$ at concentrations of ~0.01 M in benzene-d_6, even upon heating to 40 °C. Presumably for steric reasons this phosphorane can neither deprotonate the alkylidene readily nor create adducts through addition to the metal, as described below.

The reaction of Mo(NAr)($CHCMe_3$)[$OCMe(CF_3)_2]_2$ and $Me_3P{=}CHPh$ in benzene-d_6 was followed by NMR and shown to give a mixture of two compounds initially (Scheme 1). The main component of the mixture is an alkylidene-containing species with a neopentylidene H_α resonance at 11.65 ppm that is coupled weakly to phosphorus (J_{PH} = 1.5 Hz). Only one methyl resonance for the hexafluoro-*tert*-butyl group is observed, which suggests that the molecule possesses mirror symmetry. The imido aryl ring also shows free rotation, as judged by the single doublet resonance for the methyl protons of the isopropyl groups. These spectral features are all consistent with an adduct in which the ylide is bound to the NOO face of the original tetrahedral core. Base adducts of this type have been observed in several instances,[7] and some have been structurally characterized.[8] Interestingly, the ylide coordinating to the Mo center is no longer a benzylidene but rather a methylidene, as judged by the doublet resonance at 2.48 ppm that integrates to two protons (PCH_2Ph). The minor component of the initial mixture shows no alkylidene resonance. The minor species also possesses mirror symmetry, and the methyl protons of the isopropyl groups are broadened significantly. These features are consistent with an alkylidyne anion−phosphonium cation ion pair (**1″**) formed by deprotonation of the alkylidene by the ylide (Scheme 1, Figure S1). The mechanism of formation of the methylene species is not known, although formation of {Me_3PCH_2Ph}-{Mo(NAr)($CCMe_3$)[$OCMe(CF_3)_2]_2$} followed by abstraction of a methyl proton in the phosphonium salt by the alkylidyne α carbon atom is one attractive possibility.

Upon standing at room temperature for several hours, the reaction evolves into a new mixture of products. The major component is now the alkylidyne anion (>70%), and the initial adduct is gone. The minor component is again an alkylidene-containing species with the neopentylidene H_α resonance at 12.71 ppm (J_{PH} coupling could not be resolved). The spectrum is consistent with the lack of any symmetry element, suggesting

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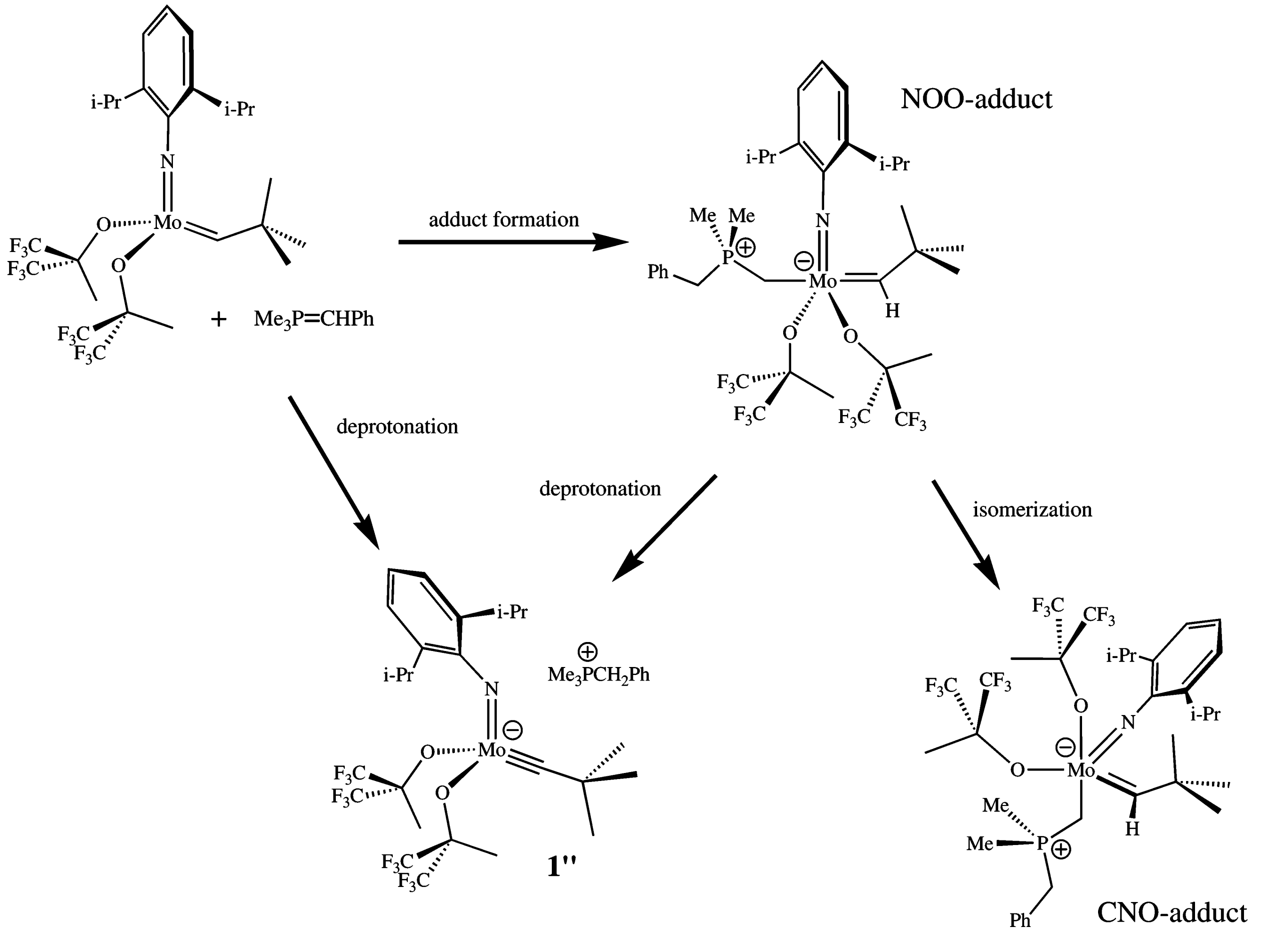
Scheme 1. Summary of Observed Reaction Products between $Mo(NAr)(CHCMe_3)[OCMe(CF_3)_2]_2$ and $Me_3P{=}CHPh$



that the minor species is an adduct in which the ylide is bound to the CNO face of the original tetrahedral MoCNOO core. The spectrum shows a doublet resonance at 1.92 ppm with a relative integration of two, demonstrating that the ylide is coordinating through a methylidene carbon as above. It remains a possibility that the NOO adduct is the initial product of reaction between the benzylidene ylide and that both the alkylidyne anion and the CNO adduct form from this initial complex (Scheme 1, Figure S1). A variable-temperature NMR study between 20 and 80 °C revealed no exchange between the alkylidyne anion and the ylide (CNO) adduct. Preparative-scale reactions in toluene yielded the same mixture of compounds even after recrystallization from toluene.

The reaction between $Me_3P{=}CH_2$ and $Mo(NAr)(CHCMe_3)[OCMe(CF_3)_2]_2$ produced a crystalline product for which proton and phosphorus NMR spectra suggest it to be a mixture of the NOO (10%) adduct, the CNO (26%) adduct, and the alkylidyne anion (64%).

The reactivity of **1** has been explored briefly. Treatment of **1** with $[Me_3O]BF_4$ in methylene chloride generates the new alkylidyne species $Mo(CCMe_3)[N(Me)Ar][OCMe(CF_3)_2]_2$ (**2**, Scheme 2). This new species is a pentane-soluble, colorless solid, consistent with an alkylidyne amido bis-alkoxide complex formed by methylation at nitrogen.[9] The alkylidyne carbon resonance appears at 319.47 ppm in benzene-d_6 and the isopropyl methyl groups appear as well-resolved doublets in the ^1H NMR spectrum, consistent with locked rotation about the $N_{imido}-C_{ipso}$ bond. Treatment of the alkylidyne anion with $Me_3SiOSO_2CF_3$ yields the related species $Mo(CCMe_3)[N(SiMe_3)Ar][OCMe(CF_3)_2]_2$ (**3**). This compound is also colorless and displays a resonance for C_α at 322.79 ppm (benzene-d_6). Both reactions appear to be quantitative by NMR; however isolated yields were only moderate due to the high solubility of the alkylidyne complexes in pentane.

The net result of protonation of $\{Ph_3PMe\}\{Mo(NAr)(CCMe_3)[OCMe(CF_3)_2]_2\}$ with $[HNMe_2Ph]Cl$ or $[Et_3NH]Cl$ is formation of $Mo(NAr)(CHCMe_3)[OCMe(CF_3)_2]_2$, as judged by ^1H NMR. In the case of $[HNMe_2Ph]Cl$, the dimethylaniline byproduct does not coordinate to the metal and $Mo(NAr)(CHCMe_3)[OCMe(CF_3)_2]_2$ is formed cleanly (Scheme 2). With $[Et_3NH]Cl$, the triethylamine appears to coordinate weakly to the metal, giving rise to two observed alkylidene species. The reaction between $\{Ph_3PMe\}\{Mo(NAr)(CCMe_3)[OCMe(CF_3)_2]_2\}$ and $[H(OEt_2)_2]B[3,5\text{-}(CF_3)_2C_6H_3]_4$ appeared to be instantaneous in benzene-d_6, as judged by immediate precipitation of $[Ph_3PMe]B[3,5\text{-}(CF_3)_2C_6H_3]_4$ as a brown oil. Spectra indicated that the major species formed was again $Mo(NAr)(CHCMe_3)[OCMe(CF_3)_2]_2$, though several resonances in the region of 8−9 ppm suggest that Mo(NHAr) species are present.

Reaction of **1** with carbon dioxide was rapid upon warming the reaction mixture from 77 K to room temperature; the solution decolorized and a white precipitate formed. NMR examination of the precipitate in methylene chloride-d_2 showed it to be the κ^2-carbamate complex (**4**, Scheme 2). The IR spectrum in methylene chloride shows a strong peak at 1658 cm^{-1}, consistent with the CO stretch of the carbamate ligand.[10] Heating the

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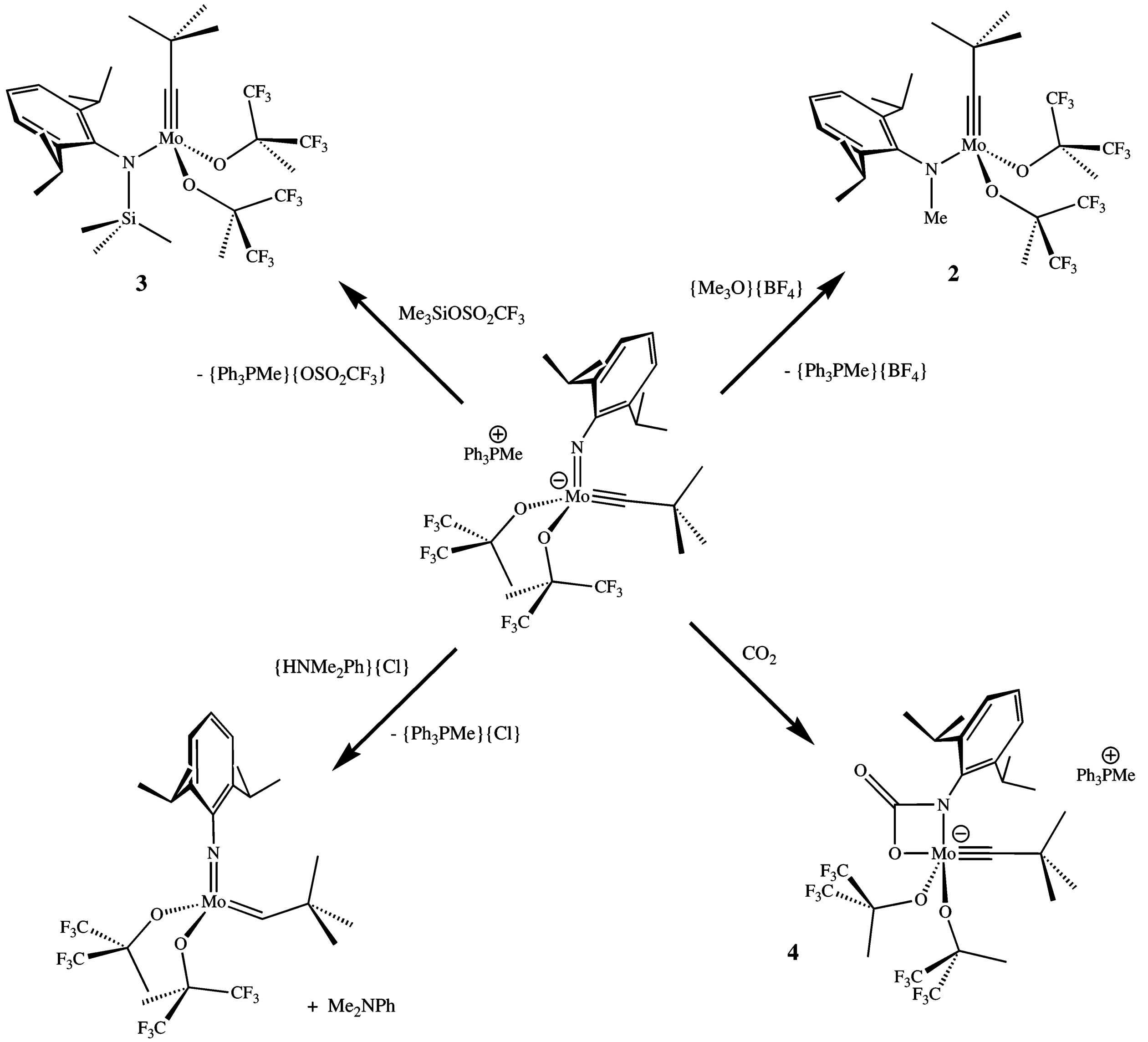
Scheme 2. Reaction of $\{Ph_3PMe\{Mo(NAr)(CCMe_3)[OCMe(CF_3)_2]_2\}$ with Electrophiles



carbamate did not result in extrusion of aryl isocyante, but rather decomposition to unidentifiable products.

Addition of several equivalents of 3-hexyne to $\{Ph_3PMe\}\{Mo(NAr)(CCMe_3)[OCMe(CF_3)_2]_2\}$ led to no reaction at room temperature after several days. In contrast, $Re(NAr)(CCMe_3)[OCMe(CF_3)_2]_2$ has been reported to react with 3-hexyne to give metallacyclobutadiene species.[6] The more electron-rich nature of the alkylidyne anion may disfavor alkyne binding.

Discussion

Deprotonation of a high oxidation state alkylidene was first demonstrated in a reaction between $Ta(CHCMe_3)(CH_2CMe_3)_3$ and LiBu.[11] Dehydrohalogenation of $W(NPh)(CHCMe_3)(PEt_3)_2Cl_2$ with $Ph_3P{=}CH_2$ has been shown to lead to $W(NPh)(CCMe_3)(PEt_3)_2Cl$.[12] Addition of HCl to this species regenerated $W(NPh)(CHCMe_3)(PEt_3)_2Cl_2$. Moving a proton from an amido nitrogen to a neopentylidyne α carbon atom was the first general method of preparing imido alkylidene complexes of tungsten,[13] while the reverse, deprotonation of a neopentylidene or neophylidene, has been a troublesome side reaction whenever alkoxides or diolates are added to $Mo(NAr)(CHR)(OTf)_2(dme)$ ($R = CMe_3$ or CMe_2Ph) species.[14] (This approach has been the standard method of preparing bis-alkoxide catalysts such as $Mo(NAr)(CHCMe_3)[OCMe(CF_3)_2]_2$.) Phosphorus ylides have been employed as bases in early experiments; for example, $Me_3P{=}CH_2$ was employed as a base in order to cleanly deprotonate $[Cp_2TaMe_2]BF_4$ to yield $Cp_2TaMe(CH_2)$.[15] For all of these reasons, therefore, we did not find deprotonation of the neopentylidene ligand in $Mo(NAr)(CHCMe_3)[OCMe(CF_3)_2]_2$ to be especially surprising. Nevertheless unambiguous examples are relatively rare, and the example described here is first to our knowledge of a structurally characterized four-coordinate high oxidation state imido alkylidyne species. These species represent isolable versions of intermediates thought to be present along the proton transfer pathway from $Mo(NR)(CHR')(OR'')_2$ to $Mo(NHR)(CR')(OR'')_2$.[14]

On the basis of the results described here, it would seem that regeneration of a metathetically active alkylidene complex

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through transfer of an alkylidene from an alkylidene phosphorane could be problematic. From this point of view, the fact that $Ph_3P{=}CHPh$ did *not* deprotonate $Mo(NAr)(CHCMe_3)[OCMe(CF_3)_2]_2$ is one of the more interesting results. However, whether $Ph_3P{=}CHPh$ could serve as a source of a benzylidene ligand in a reaction with some "$Mo(NAr)[OCMe(CF_3)_2]_2$" species to yield $Mo(NAr)(CHPh)[OCMe(CF_3)_2]_2$ remains unknown. We hope to explore such possibilities in future studies.

Experimental Section

General Comments. All manipulations were performed in oven-dried (200 °C) glassware under an atmosphere of nitrogen in a Vacuum Atmospheres glovebox. HPLC-grade toluene, pentane, and methylene chloride were purified by passage through an alumina column and stored over 4 Å Linde-type molecular sieves prior to use. Benzene-d_6 was dried over sodium benzophenone ketyl and distilled prior to use. Methylene chloride-d_2 was dried over CaH_2, vacuum distilled, and stored over molecular sieves prior to use. NMR spectra were recorded on a Varian Mercury or Varian Inova spectrometer operating at 300 or 500 MHz (^1H), respectively. Spectra are referenced to the residual $^1H/^{13}C$ peaks of the solvent (^1H: C_6D_6, 7.16; CD_2Cl_2, 5.32; ^{13}C: C_6D_6, 128.39; CD_2Cl_2, 54.00) and are listed in ppm relative to tetramethylsilane. ^{19}F and ^{31}P NMR were referenced externally to fluorobenzene (δ −113.15 ppm upfield of $CFCl_3$) and 80% H_3PO_4 (δ 0.00 ppm), respectively. Combustion analyses were performed by H. Kolbe Mikroanalitisches Laboratorium, Mülheim an der Ruhr, Germany.

$Mo(NAr)(CHCMe_2R)[OCMe(CF_3)_2]_2$ (R = Me and Ph) were prepared according to published procedures. $Me_3P{=}CHPh$, $Ph_3P{=}CHPh$, and $Me_3P{=}CH_2$ were prepared by addition of *n*-BuLi to a toluene suspension of the corresponding phosphonium halide salt, followed by filtration and crystallization from pentane or toluene ($Me_3P{=}CHPh$ and $Ph_3P{=}CHPh$) or distillation ($Me_3P{=}CH_2$). $Ph_3P{=}CH_2$ was prepared with $LiN(SiMe_3)_2$ in a similar fashion and crystallized from toluene. $[Me_3O]BF_4$, $Me_3SiOSO_2CF_3$, and CO_2 were purchased from commercial vendors and used as received.

Crystallography. Low-temperature diffraction data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), performing θ- and ω-scans. The structure was solved by direct methods using SHELXS[16] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[17] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. Two disordered $CMe(CF_3)_2$ groups in one of the two crystallographically independent molecules were refined with the help of similarity restraints on 1−2 and 1−3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. Similar ADP restraints were also applied to all atoms of the two $[Ph_3PMe]^+$ ions.

{Ph_3PMe}{$Mo(NAr)(CCMe_3)[OCMe(CF_3)_2]_2$}, 1. A round-bottom flask was charged with 1.035 g (1.47 mmol) of $Mo(NAr)(CHCMe_3)[OCMe(CF_3)_2]_2$ and 25 mL of toluene. To the stirring yellow solution was added 0.410 g (1.48 mmol) of $Ph_3P{=}CH_2$ as a solid in one portion, at which point the reaction solution became orange-red. The mixture was stirred for 90 min at room temperature, and the volatiles were removed in vacuo. The residue was dissolved in toluene, and pentane was added until the solution became turbid. The solution was set aside at −25 °C for 18 h, during which time 1.093 g (76%) of orange microcrystals formed. Crystals suitable for X-ray diffraction were grown by slow cooling of a saturated toluene/pentane solution: NMR (C_6D_6) ^1H (500 MHz) δ 7.33 (d, 2 Ar*H*), 7.02 (m, 10 Ar*H*), 6.89 (m, 6 Ar*H*), 3.79 (sep, 2 C*H*Me_2), 3.10 (d, $J_{PH} = 12.6$ Hz, 3 P*Me*), 2.07 (s, 6 *Me*−R_{F6}), 1.8−1.0 (v br, 12 CHMe_2), 1.29 (s, 9 CMe_3); $^{13}C\{^1H\}$ (125 MHz) δ 300.75 ($Mo{\equiv}C_\alpha$), 163.70, 137.99, 135.14 (d, $J_{CP} = 3.0$ Hz), 133.20 (d, $J_{CP} = 10.8$ Hz), 130.69 (d, $J_{CP} = 12.3$ Hz), 126.28 (q, $J_{CF} = 288$ Hz), 125.94 (q, $J_{CF} = 289$ Hz), 122.41, 120.30, 119.45 (d, $J_{CP} = 89.2$ Hz), 80.08 (sep, $C_{quat}{-}R_{F6}$), 52.63, 32.29, 28.34, 24.2 (br, CHMe_2), 21.81, 9.91 (d, $J_{CP} = 56.9$ Hz); $^{31}P\{^1H\}$ (121 MHz) δ 22.29; ^{19}F (282 MHz) δ −77.52 (q), −78.15 (q). Anal. Calcd for $C_{44}H_{50}F_{12}MoNO_2P$: C, 53.94; H, 5.14; N, 1.43. Found: C, 54.08; H, 5.17; N, 1.36.

{Ph_3PMe}{$Mo(NAr)(CCMe_2Ph)[OCMe(CF_3)_2]_2$}, 1′. A J-Young type NMR tube was charged with 38.5 mg (50.3 μmol) of $Mo(NAr)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ and 14.2 mg (51.4 μmol) of $Ph_3P{=}CH_2$. Approximately 0.7 mL of C_6D_6 was added to the solids, producing an orange solution. ^1H NMR observation of the mixture indicated that the desired complex was present in ~90% along with a minor species that was not identified completely but appeared to be a phosphorane adduct of the alkylidene. The C_6D_6 was removed in vacuo and the residue dissolved in a minimal amount of 3:1 pentane/toluene. The solution was set aside at −25 °C for several days, during which time the complex precipitated as 33.2 mg (63%) of orange needles: NMR (C_6D_6) ^1H (300 MHz) δ 7.74 (d, 2 Ar*H*), 7.37 (d, 2 Ar*H*), 7.23 (t, 2 Ar*H*), 7.13 (t, 1 Ar*H*), 6.99 (m, 10 Ar*H*), 6.87 (m, 6 Ar*H*), 3.80 (sep, 2 C*H*Me_2), 3.08 (d, $J_{HP} = 12.6$ Hz, 3 P*Me*), 1.80 (s, 6 *Me*−R_{F6}), 1.72 (s, 6 CMe_2Ph), 1.56 (v br, 6 CHMe_2), 1.09 (v br, 6 CHMe_2); $^{31}P\{^1H\}$ (121 MHz) δ 21.70; ^{19}F (282 MHz) δ −77.58 (q), −78.12 (q). Anal. Calcd for $C_{49}H_{52}F_{12}MoNO_2P$: C, 56.59; H, 5.03; N, 1.34. Found: C, 56.36; H, 5.12; N, 1.29.

$Mo(CCMe_3)[N(Me)Ar][OCMe(CF_3)_2]_2$, 2. A flask was charged with 0.147 g (0.15 mmol) of {Ph_3PMe}{$Mo(NAr)(CCMe_3)[OCMe(CF_3)_2]_2$} and 8 mL of methylene chloride. The solution was cooled to −25 °C, at which point 0.029 g (0.20 mmol) of $[Me_3O]BF_4$ was added as a solid. The mixture was stirred at room temperature for 45 min, during which time the solution became pale yellow. All volatiles were removed in vacuo, and the residue was extracted with pentane. The pentane extract was filtered through Celite and the solution volume reduced to ~1 mL in vacuo. Slow cooling of the pentane solution at −25 °C afforded 0.067 g (65%) of pale yellow to colorless crystals: NMR (C_6D_6) ^1H (500 MHz) δ 7.03 (m, 3 Ar*H*), 3.28 (s, 3 N*Me*), 3.02 (sep, 2 C*H*Me_2), 1.69 (s, 6 *Me*−R_{F6}), 1.26 (d, 6 CHMe_2), 1.03 (d, 6 CHMe_2), 0.66 (s, 9 CMe_3); $^{13}C\{^1H\}$ (125 MHz) δ 319.47 ($Mo{\equiv}C_\alpha$), 157.62, 142.07, 127.94, 124.61 (q, $J_{CF} = 286$ Hz, CF_3), 124.41, 124.21 (q, $J_{CF} = 287$ Hz, CF_3), 81.59 (sep, $J_{CF} = 29.4$ Hz, $C_{quat}{-}R_{F6}$), 54.99, 45.25 (N*Me*), 29.97, 28.05, 26.73, 23.79, 20.79; ^{19}F (470 MHz) δ −78.26 (q), −78.97 (q). Anal. Calcd for $C_{26}H_{35}F_{12}MoNO_2$: C, 43.52; H, 4.92; N, 1.95. Found: C, 43.64; H, 5.05; N, 1.87.

$Mo(CCMe_3)[N(SiMe_3)Ar][OCMe(CF_3)_2]_2$, 3. A flask was charged with 0.174 g (0.178 mmol) of {Ph_3PMe}{$Mo(NAr)(CCMe_3)[OCMe(CF_3)_2]_2$} and 8 mL of toluene and chilled to −25 °C. To the cold solution was added 40 uL (0.20 mmol) of $Me_3SiOSO_2CF_3$, at which point the solution became pale yellow and cloudy. The reaction was stirred at room temperature for 15 min, and all volatiles were removed in vacuo. The residue was extracted into pentane and filtered through Celite. The solvent volume was reduced to ~1 mL in vacuo and set aside at −25 °C. The product crystallized as 0.0503 g (39%) of pale yellow to colorless cubes in two crops: NMR (C_6D_6) ^1H (500 MHz) δ 7.06 (m, 3 Ar*H*), 3.09 (sep, 2 C*H*Me_2), 1.71 (s, 6 *Me*−R_{F6}), 1.32 (d, 6 CHMe_2), 1.13 (d, 6 CHMe_2), 0.65 (s, 9 CMe_3), 0.23 (s, 9 Me_3Si); $^{13}C\{^1H\}$ (125 MHz) δ 322.79 ($Mo{\equiv}C_\alpha$), 156.76, 140.93, 126.47, 124.52, 124.50 (q, $J_{CF} = 287$ Hz, CF_3), 124.15 (q, $J_{CF} = 287$ Hz, CF_3), 82.19 (sep, $J_{CF} = 29.7$ Hz, $C_{quat}{-}R_{F6}$), 56.05, 30.41, 28.27, 25.81, 25.68, 20.44, 0.98 (SiMe_3); ^{19}F (470 MHz) δ −77.14 (q), −78.55 (q). Anal. Calcd

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for $C_{28}H_{41}F_{12}MoNO_2Si$: C, 43.36; H, 5.33; N, 1.81. Found: C, 43.28; H, 5.30; N, 1.77.

$\{Ph_3PMe\}\{Mo(CCMe_3)[\kappa^2\text{-}OC(O)NAr][OCMe(CF_3)_2]_2\}$, 4. A round-bottom flask was charged with 0.185 g (0.189 mmol) of $\{Ph_3PMe\}\{Mo(NAr)(CCMe_3)[OCMe(CF_3)_2]_2\}$ and 10 mL of toluene. To the flask was connected a needle valve. The solution was degassed by two consecutive freeze−pump−thaw cycles. The degassed solution was then exposed to 1 atm of CO_2 for 10 min while stirring and warming from the melting point of the solvent to room temperature. The flask was sealed and allowed to stir for an additional 20 min at room temperature, during which time the solution turned from orange to pale yellow with formation of a white precipitate. All volatiles were removed in vacuo, and the residue was triturated in a 10:1 mixture of pentane to toluene, causing formation of a white solid. The solid was collected by filtration, yielding 0.177 g (91%) of a white powder: NMR (CD_2Cl_2) ^1H (300 MHz) δ 7.72 (m, 15 Ar*H*), 7.14 (m, 3 Ar*H*), 3.08 (sep, 2 C*H*Me$_2$), 3.00 (d, J_{PH} = 13.2 Hz, P*Me*), 1.88 (s, 6 *Me*−R_{F6}), 1.21 (d, 6 CH*Me*$_2$), 1.03 (d, 6 CH*Me*$_2$), 0.70 (s, 9 C*Me*$_3$); $^{13}C\{^1H\}$ (125 MHz) δ 309.25 ($Mo{\equiv}C_\alpha$), 165.54 ($C{=}O$), 151.673, 143.81, 135.32 (d, J_{CP} = 2.3 Hz), 133.87 (d, J_{CP} = 10.7 Hz), 130.70 (d, J_{CP} = 13.0 Hz), 126.17, 124.62 (q, J_{CF} = 288 Hz), 124.37 (q, J_{CF} = 287 Hz), 123.01, 120.12 (d, J_{CP} = 88.3 Hz), 81.21 (sep, J_{CF} = 28.4 Hz), 51.07, 29.83, 28.84, 25.22, 22.70, 20.19, 9.29 (J_{CP} = 57.5 Hz); $^{31}P\{^1H\}$ (121 MHz) δ 22.58; ^{19}F (470 MHz) δ −78.32 (q), −78.60 (q); IR (CH_2Cl_2) 1658 cm^{-1} (νCO). Anal. Calcd for $C_{45}H_{50}F_{12}MoNO_4P$: C, 52.79; H, 4.92; N, 1.37. Found: C, 52.64; H, 5.08; N, 1.34.

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Supporting Information Available: Crystallographic details, fully labeled thermal ellipsoid diagrams for both molecules of $\{Ph_3PMe\}\{Mo(NAr)(CCMe)[OCMe(CF_3)_2]_2$, and crystallographic information files. This material is available free of charge via the Internet at http://pubs.acs.org. Data for the X-ray structure is also available to the public at http://www.reciprocalnet.org/(number 06013).

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