ORGANOMETALLICS

Synthesis of Molybdenum(VI) Neopentylidene Neopentylidyne **Complexes**

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Supporting Information

ABSTRACT: Mo(C-t-Bu)(CH-t-Bu)(Cl)(PMe₂Ph)₂ (1) was prepared as off-white crystals in 26% yield through addition of 2.5 equiv of $Mg(CH_2-t-Bu)_2$ to $Mo(O)[OC(CF_3)_3]_4$ in diethyl ether followed by 3 equiv of PMe₂Ph and a workup that includes dichloromethane (the source of Cl). Compound 1 is largely a syn isomer initially that equilibrates to give approximately a 1:1 mixture of syn and anti isomers within 1-2 h. Compound 1 reacts with Li(3,5-dimethylpyrrolide) to give $Mo(C-t-Bu)(CH-t-Bu)(\eta^1-Me_2Pyr)(PMe_2Ph)_2$ (2a) as a pale



yellow solid in 76% yield, and 2a reacts with Ph₃SiOH to give a mixture of syn and anti Mo(C-t-Bu)(CH-t- $Bu)(OSiPh_3)(PMe_2Ph)_2$ (3a) in 84% yield. All three compounds tend to lose PMe_2Ph to give 14e monophosphine complexes with the formulas $Mo(C-t-Bu)(CH-t-Bu)(X)(PMe_2Ph)$ (X = Cl, Me_2Pyr, or OSiPh_3), none of which could be isolated. X-ray studies show the structures of 1, 2a, and 3a to be analogous with τ values of 0.45, 0.53, and 0.69, respectively.

mido alkyl complexes such as $M(NR')_2(CH_2R)_2$ (M = Mo I or W; $\dot{R'}$ = aryl, *tert*-butyl, or adamantyl and CH_2R = neopentyl or neophyl), which can be prepared readily from $M(NR')_2(dme)Cl_2$ complexes and magnesium or lithium alkyls, yield $M(NR')(CHR)X_2$ complexes when one of the imido ligands is protonated with 2 equiv of HX (e.g., X =triflate).¹ However, analogous approaches to oxo alkylidene complexes usually are thwarted by the fact that oxo ligands are attacked by the alkylating agent and removed from the metal. Attempted alkylations of Mo oxo complexes more often give rise to low yields of oxo products, or none at all. For example, Osborn reported the synthesis of Mo(O)(CH₂-t-Bu)₃Cl and "Mo(O)(CH₂-t-Bu)₄" through addition of Mg(CH₂-t-Bu)₂ to $Mo(O)Cl_{4}^{2}$ but experimental details (including yields) were not provided in either of the succinct reports, and Mo(O)- $(CH_2-t-Bu)_4$ had to be reformulated (as noted in footnote 1 in ref 2b, without further details) as $Mo(O)(CH_2-t-Bu)_3(O$ *t*-Bu). The neopentoxide in $Mo(O)(CH_2-t-Bu)_3(OCH_2-t-Bu)$ could arise through attack by the alkylating agent on the oxo ligand.³ It also has been reported that addition of 6 equiv of (t-BuCH₂)MgCl to MoO₂Cl₂ in diethyl ether gives the best reported yield (~35%) of Mo(C-t-Bu)(CH₂-t-Bu)₃.⁴ The analogous trimethylsilylmethylidyne complex, Mo(CSiMe₃)-(CH₂SiMe₃)₃ (8% yield; liquid at 22 °C), has been prepared similarly with (Me₃SiCH₂)₃Mo=Mo(CH₂SiMe₃)₃ (25% yield; crystalline) and unstable (Me₃SiCH₂)₃Mo=CHSiMe₃ (proposed) being two other metal-containing products.⁵

One exception to low yield alkylations of Mo oxo complexes is the class of molybdenum or tungsten compounds with the formula $MO_2(CH_2R)_2(bipy)$ (CH₂R can be a variety of alkyls, including neopentyl), which can be prepared through alkylation of MO₂Cl₂(bipy) compounds with Grignard reagents.⁶ The final M(VI) complexes are formed only after exposure of the crude product to water and air, so it appears likely that at least some, if not most, of the metal is reduced and then reoxidized in the presence of water and air. $WO_2(CH_2-t-Bu)_2(bipy)$ is a precursor to W(O)(CH-t-Bu)- Cl_2L_2 upon reaction of WO₂(CH₂-t-Bu)₂(bipy) with Me₃SiCl, $ZnCl_2$, and 2 equiv of L (e.g., L = PPhMe₂); W(O)(CH₂-t- $Bu_{2}Cl_{2}(bipy)$ is a plausible intermediate.⁷ This approach to the synthesis of $Mo(O)(CH-t-Bu)Cl_2L_2$ complexes failed in our hands so far. A second exception is the reaction between $Mo(O)(Cl)_2(t-Bu_3P=N)_2$ and 2 equiv of LiCH₂SiMe₃ to give $Mo(O)(CHSiMe_3)(t-Bu_3P=N)_2$ in 87% yield;⁸ Mo(O)- $(CH_2SiMe_3)_2(t-Bu_3P=N)_2$ is the plausible intermediate in this reaction. Unfortunately, Mo(O)(CHSiMe₃)(t-Bu₃P=N)₂ and analogous molybdenum imido alkylidene complexes that contain two t-Bu₃SiO⁻ ligands (which are sterically approximately equivalent to t-Bu₃P=N⁻ligands)⁹ are relatively unreactive in olefin metathesis reactions.

We recently prepared molybdenum oxo alkylidene complexes through a controlled addition of 1 equiv of water to molybdenum(VI) $OC(CF_3)_3$ or $OC(CF_3)_2Me$ benzylidyne complexes.¹⁰ In the hope that more direct routes to these Mo oxo alkylidene complexes could be successful, we turned to alkylation of $Mo(O)[OC(CF_3)_3]_4$.¹¹ Yellow Mo(O)[OC- $(CF_3)_3]_4$ can be prepared readily from $Mo(O)Cl_4$ and 4 equiv of $NaOC(CF_3)_3$. It can be sublimed under a good vacuum ($<10^{-2}$ mm) at 60–80 °C. It is poorly soluble in organic solvents (pentane, benzene, toluene) but partially soluble in diethyl ether or dichloromethane.

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We decided to explore alkylation of $Mo(O)[OC(CF_3)_3]_4$ with $Mg(CH_2-t-Bu)_2$ in the presence of PMe₂Ph in order to trap any monometallic products. Alkylation reactions using 0.5, 1.0, 2.0, and 2.5 equiv of $Mg(CH_2CMe_3)_2$ in the presence of PMe₂Ph in diethyl ether were explored initially. Each crude sample was dissolved in C_6D_6 or CD_2Cl_2 and examined by proton and/or ³¹P NMR. A small multiplet in the region characteristic of a molybdenum alkylidene having two phosphines bound to the metal in proton NMR spectra in CD_2Cl_2 grew slightly over a day, but no other product could be identified. When 2.5 equiv of $Mg(CH_2CMe_3)_2$ were used and CH₂Cl₂ was part of the workup, the alkylidene could be extracted into pentane and crystallized reproducibly from a concentrated pentane solution at -20 °C as off-white needles in a yield of 26%. When the crude brown residue was dissolved in C_6D_6 and not exposed to dichloromethane, no alkylidene resonance was observed, even after addition of 2 equiv of PMe₂Ph. However, when a drop of CD₂Cl₂ was added to this sample, the alkylidene resonance grew in with time. The syn alkylidene resonance can be observed in the ¹H NMR spectrum 5 h after addition of CD₂Cl₂ and stops increasing after ~ 60 h. There was no further change in the ¹H NMR spectrum.

An X-ray structural study confirms that 1 is the "Ene/Yne" complex, $Mo(C-t-Bu)(CH-t-Bu)(PPhMe_2)_2Cl$ (1; eq 1 and

$$MoO[OC(CF_{3})_{4}]_{4} + 2.5 Mg(CH_{2}-t-Bu)_{2} + 3 L \xrightarrow{1. Et_{2}O}_{2. CH_{2}Cl_{2}} Cl \longrightarrow M_{0} \overset{t-Bu}{\underset{L = PPhMe_{2}}{}} Cl \longrightarrow M_{0} \overset{t-Bu}{\underset{L = PPhMe_{2}}{}} (1)$$



Figure 1. Structure of 1 ($\tau = 0.45$).

Figure 1), not an oxo alkylidene complex. The overall geometry is approximately halfway between a TBP and an SP ($\tau^{12} = 0.45$), although 1 (and related derivatives described below) will be drawn as a TBP with L in the apical positions for convenience. The bond lengths and angles (Table 1) are not unusual for neopentylidyne ligands (1.691(3) Å, 166.80°) or *syn* neopentylidene ligands (1.985(3) Å, 152.57°). The chloride must come from dichloromethane, a phenomenon that has been reported in the literature for certain Mo^{13a,b} and Re^{13c} compounds. No mechanistic details have been reported for formation of chloride complexes in the presence of

Table 1. Selected Bond Lengths and Angles in 1, 2a, and 3a

	1	2a	3a
Mo1-C1	1.691(3)	1.661(11)	1.764(6)
Mo1-C6	1.985(3)	2.000(9)	1.9214(14)
Mo1-P1	2.5089(3)	2.5092(10)	2.5202(3)
Mo1-P2	2.5196(3)	2.5092(10)	2.5366(4)
Mo1-C1-t-Bu	166.80	172.59	170.61
Mo1–C6–t-Bu	152.57	151.52	152.16
P1-Mo1-P2	160.28	164.97	171.25
C1-Mo1-C6	104.33	102.49	103.51
Mo1-X ^a	2.5197(3)	2.227(3)	2.0748(9)
${}^{4}X = Cl (in 1), N (in 2a), or O (in 3a).$			

dichloromethane, and we also do not want to propose any for forming 1 at this stage.

Compound 1 is related to tantalum bisneopentylidene complexes (e.g., $Ta(CH-t-Bu)_2(PMe_3)_2Cl$) which contain two different neopentylidene ligands, one of which has a significantly greater agostic interaction of its alkylidene CH_{α} bond with the metal than does the other.¹⁴ It also is related to $W(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)(PMe_3)_2$,¹⁵ square pyramidal $W(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)(dmpe)$,¹⁶ and trimethylsilyl relatives.¹⁶ The alkylidene is in the *syn* orientation in the crystal chosen for the X-ray study. Compound 1 is stable in benzene solution for several days at temperatures as high as 80 °C. Attempts to remove one of the phosphines from a C_6D_6 solution of 1 through addition of 1 equiv of $B(C_6F_5)_3$ to 1 in 0.5 mL of C_6D_6 (0.04 M) led only to decomposition to unidentified products. We propose that loss of phosphine in the solid state at 1 atm is the reason for a failure to obtain satisfactory elemental analyses for 1 and related derivatives 2a and 3a described below.

Proton NMR spectra of 1 usually show two triplet alkylidene resonances at 13.87 ppm (*anti*, ${}^{1}J_{CH} = 137.0$ Hz) and 12.26 ppm (*syn*, ${}^{1}J_{CH} = 100.6$ Hz). Freshly isolated 1 is usually *syn*rich, occasionally as high as 95% *syn* (see SI). Upon recrystallizations of 1, the *syn/anti* ratio approaches 1:1 and remains so.

Compound 1 reacts with Li(2,5-dimethylpyrrolide) to yield the monopyrrolide complex, 2a (eq 2). Compound 2a can be



crystallized from pentane as off-white needles in 76% yield. An X-ray study showed the structure of **2a** (Figure 2) to be analogous to that of **1**, with the pyrrolide bound to the metal in an η^1 fashion. The overall geometry and bond lengths and angles in **2a** are similar to those found in **1** (Table 1).

In ¹H NMR spectra of pure samples of **2a**, two *syn* alkylidene resonances are found, one triplet (at 11.65 ppm in C_6D_6) for **2a** and one doublet (~10% of the total at 13.48 ppm in C_6D_6). We ascribe the latter to a monophosphine complex, Mo(C-*t*-Bu)(CH-*t*-Bu)(PPhMe₂)(Me₂Py) (**2b**). Compounds **2a** and **2b** (plus phosphine) are in equilibrium at room temperature; in a sample of 0.033 M **2a** in C_6D_6 , the K_{eq} was found by ¹H NMR spectroscopy to be 3.7×10^{-4} M at room temperature. The ³¹P NMR of a sample of **2a** in C_6D_6 at room temperature shows three resonances at 30.4, 7.3, and -46.5



Figure 2. Structure of 2a ($\tau = 0.53$).

ppm for **2b**, **2a**, and free phosphine, respectively. The magnetization exchange rates between these two species were measured through a series of 1D EXSY experiments at different temperatures (>40 °C). For dissociation of phosphine from **2b**, the ΔH^{\ddagger} was found to be 121 (± 8) kJ/mol and ΔS^{\ddagger} was found to be 0.095 (± 0.026) kJ/mol K. For the reverse reaction, ΔH^{\ddagger} and ΔS^{\ddagger} were found to be 76(± 5) kJ/mol and -0.028 (± 0.017) kJ/mol K, respectively. **2b** was also the major product in an NMR-scale reaction in C_6D_6 of **2a** with 1 equiv of B(C_6F_5)₃ (see SI).

Compound 2a reacts cleanly with 1 equiv of triphenylsilanol to generate 3a (eq 3). An X-ray study shows the structure of 3a



to be analogous to the structures of 1 and 2a (Table 1 and Figure 3). An alkylidene multiplet can be observed in the proton NMR spectra of 3a at 13.29 ppm (in C_6D_6) with a ${}^1J_{CH}$ of 100.6 Hz that is characteristic of a *syn* alkylidene. No



doublet alkylidene resonance characteristic of a monophosphine adduct can be detected by ¹H NMR in this case, even at temperatures up to 70 °C. Nevertheless, one of the phosphines is labile enough to be scavenged as a borane adduct upon addition of 1 equiv of $B(C_6F_5)_3$ to **3a** in C_6D_6 . The resulting monophosphine adduct shows a characteristic *syn* alkylidene resonance in the ¹H NMR spectrum at 13.32 ppm (d, $J_{HP} = 3.8$ Hz, $J_{CH} = 106.1$ Hz). To date, we have not been able to isolate **3b**.

An exploratory NMR-scale ROMP reaction showed that cyclooctene was polymerized by **3a** (1%) in C_6D_6 upon addition of $B(C_6F_5)$ (1.1 equiv). The amount of cycloctene consumed was 69% in 1 h, 76% in 4 h, and 87% in 24 h.

We will seek higher yield routes to 1 and related "Ene/Yne" complexes, preferably those that do not require removal of oxo ligands from the metal and/or scavenging of chloride from dichloromethane. We are especially interested in 14e "stereogenic at metal" Mo(CR)(CH-t-Bu)(L)X complexes that contain a single donor (L) and anionic X, e.g., 2b and 3b and analogs. These are 14e relatives of (largely) imido alkylidene^{1,17} and $\cos^{7,10}$ alkylidene complexes that have been explored to date as metathesis initiators. An important question is whether an alkylidyne ligand (CR) can survive unchanged in a sustained metathesis reaction, a possibility that has not been addressed to our knowledge.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.9b00412.

Detailed NMR data and spectra for all compounds and details of X-ray studies (PDF)

Accession Codes

CCDC 1922920–1922922 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.

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Author Contributions

H.T. performed all synthetic work while P.M. performed all Xray structural studies.

Notes

The authors declare no competing financial interest.

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