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Communications

Reactions of $Mo(NAr)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_2$ with Alcohols To Give Metathesis Catalysts of the Type $Mo(NAr)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)(OR)$

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Summary: The reaction between Mo(NAr)(CH-t-Bu)-(CH_2-t-Bu)$_2$ and 1 equiv of an alcohol yields either Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes or Mo-(NAr)(CH_2-t-Bu)$_3$(OR) complexes, which evolve neopentane to yield the former. Preliminary experiments have shown that Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$(OR) complexes are active for metathesis conversion of diallyl ether to dihydrofuran and ethylene.

We have been interested in olefin metathesis by well-defined molybdenum imido alkylidene complexes, most recently asymmetric metathesis reactions catalyzed by complexes of the type Mo(NR)($CHCMe_2R'$)(diolate) ($R' = Me$, Ph) that contain an enantiomerically pure biphenolate or binaphtholate ligand.[1] During the search for new asymmetric catalysts we became attracted to the possibility of preparing catalysts of the type Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) (Ar = 2,6-i-$Pr_2C_6H_3$). Such species would be chiral at the metal center, and possible approaches of an olefin either trans to OR or trans to a neopentyl ligand could differ significantly in energy. For asymmetric reactions OR would have to be enantiomerically pure and one diastereomer of the complex either would have to be the only one present or would have to be vastly more reactive than the other diastereomer. Of course the neopentyl group would have to survive any metathesis reactions without complications. One possible approach to Mo(NAr)(CH-t-Bu)-(CH_2-t-Bu)(OR) complexes would be to add 1 equiv of ROH to a Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ species. Only one example of a complex of this general type has been reported[2] (prepared through addition of Ph_3SiOH to Mo(N-t-Bu)(CH-t-Bu)(CH_2-t-Bu)$_2$), although it was not characterized, and its metathesis activity was not explored. In this communication we report that reactions of simple alcohols with Mo imido dialkyl/alkylidene complexes proceed through two pathways, and preliminary evidence suggests that Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes are active metathesis catalysts.

Addition of 2 equiv of neopentylmagnesium chloride in ether to Mo(NAr)(CH-t-Bu)(triflate)$_2$(dme)[3] (Ar = 2,6-i-$Pr_2C_6H_3$) in ether gives the red-orange complex Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ (**1a**) in 93% isolated yield. (Full details can be found in the Supporting Information.) Highly soluble **1a** has been prepared on a 10 g scale and can be used in "crude" form if pure Mo(NAr)-(CH-t-Bu)(triflate)$_2$(dme) and accurately titrated Me_3CCH_2MgCl are employed. Proton and ^{13}C NMR spectra of **1a** in C_6D_6 show resonances at 9.50 and 255.0 ppm ($J_{CH} = 108$ Hz) for the (syn) alkylidene ligand and at 2.75 and 0.65 ppm ($\delta(CH_2)$; $J_{HH} = 12$ Hz) for the diastereotopic methylene protons in the neopentyl

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[1] Schrock, R. R.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4592.

[2] Ehrenfeld, D.; Kress, J.; Moore, B. D.; Osborn, J. A.; Schoettel, G. *J. Chem. Soc., Chem. Commun.* **1987**, 129.

[3] Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

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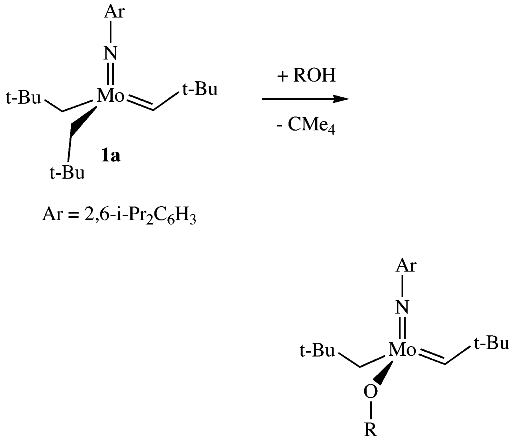
ligands. These chemical shifts are what one might expect for a high-oxidation-state syn alkylidene complex[4,5] and should be compared to $\delta(H_\alpha)$ 9.22 ppm and $\delta(C_\alpha)$ 249.3 ppm ($J_{CH} = 106$ Hz) in Mo(N-t-Bu)(CH-t-Bu)(CH_2-t-Bu)$_2$, which was reported as a brown oil,[2] and $\delta(H_\alpha)$ 6.74 ppm, $\delta(C_\alpha)$ 247.2 ppm ($J_{CH} = 102$ Hz), and $\delta(CH_2)$ 2.72 and 0.41 ppm in W(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$.[6] One similarly can prepare Mo(NAr)($CHCMe_2Ph$)(CH_2-t-Bu)$_2$ (**1b**) and Mo(NAr)(CH-t-Bu)(CH_2CMe_2Ph)$_2$ (**1c**) through alkylation of Mo(NAr)($CHCMe_2Ph$)(triflate)$_2$(dme) and Mo(NAr)(CH-t-Bu)(triflate)$_2$(dme), respectively.

Reactions between **1a** and the four alcohols shown in eq 1 (Ad = 1-adamantyl) in benzene or toluene (22 °C, 0.1−0.2 M, up to 24 h reaction time) give isolable complexes of the type Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR).



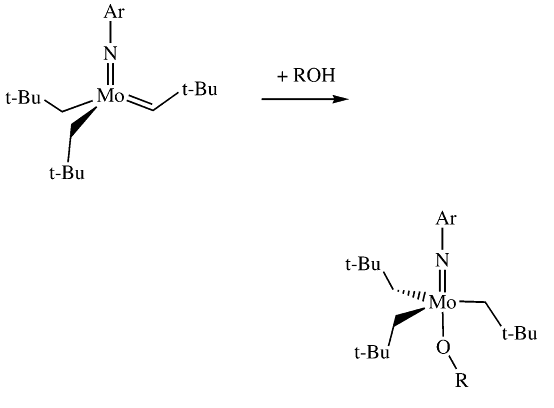
Ar = 2,6-i-Pr$_2$C$_6$H$_3$

(1)

OR = OCH(CF_3)$_2$ (**2a**), OAd (**2b**), OCMe$_3$ (**2c**), or OAr (**2d**)

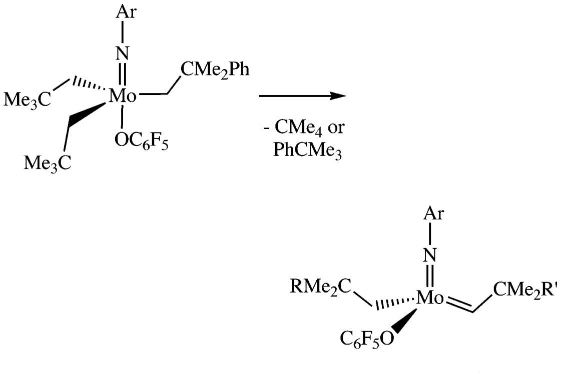
(See the Supporting Information.) Species **2a**−**d** have been isolated on scales between ∼0.15 and ∼1 g. We can confirm that AdOH or t-BuOH adds across a Mo−C bond directly, since addition of ROH to **1b** gives Mo(NAr)($CHCMe_2Ph$)(CH_2-t-Bu)(OR) exclusively.

In contrast, the reaction between **1a** and C_6F_5OH in benzene-d_6 or *neat* $(CF_3)_2CHOH$ at 22 °C gives the trineopentyl species **3a** or **3e** shown in eq 2 rapidly (minutes) and exclusively.[7] When solutions of **3a** or **3e** are heated to 60 °C over a period of hours, neopentane evolves smoothly to yield Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) species (OR = OC_6F_5 (**2e**), OCH(CF_3)$_2$ (**2a**)). The conversion of **3e** to **2e** was shown to be unimolecular with $k = 1.0 \times 10^{-4}$ s^{-1} in benzene-d_6 at 60 °C. Addition of C_6F_5OH to Mo(NAr)($CHCMe_2Ph$)(CH_2-t-Bu)$_2$ yields Mo(NAr)(CH_2CMe_2Ph)(CH_2-t-Bu)$_2$(OC_6F_5), which upon heating is transformed into a mixture of the expected three compounds (approximately 1:1:1) shown in eq 3, along with neopentane and *tert*-butylbenzene.



(2)

OR = OC_6F_5 (**3e**) or OCH(CF_3)$_2$ (**3a**)
(in *neat* $(CF_3)_2HCOH$)



(3)

R = R' = Me; 36%
R = Ph; R' = Me; 31%
R = Me; R' = Ph; 33%

When $(CF_3)_3COH$ is added to **1a** in benzene-d_6, both Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)[OC(CF_3)$_3$] (**2f**) and Mo(NAr)(CH_2-t-Bu)$_3$[OC(CF_3)$_3$] (**3f**) are formed in a ratio of 1:1.2, while the reaction between Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ and *neat* $(CF_3)_3COH$ affords a mixture which contains >95% **3f** and <5% **2f**. Compound **3f** is converted into **2f** at 60 °C in benzene-d_6 with a rate constant of 7.2×10^{-4} s^{-1} (cf. $k = 1.0 \times 10^{-4}$ s^{-1} for conversion of **3e** to **2e**). Therefore, the rate of α abstraction is accelerated by a factor of ∼7 upon changing OC_6F_5 to OC(CF_3)$_3$. Since the pK_a's of OC(CF_3)$_3$ and OC_6F_5 in water are similar (5.4 and 5.5, respectively), these results again demonstrate that α-hydrogen abstraction is accelerated under the electronically similar but sterically more crowded circumstances.[4,5,8] If $(CF_3)_3COH$ is added to Mo(NAr)($CHCMe_2Ph$)(CH_2-t-Bu)$_2$ (**1b**) in benzene-d_6, the alkylidene that is formed initially (∼50% of the mixture) is only Mo(NAr)($CHCMe_2Ph$)(CH_2-t-Bu)[OC(CF_3)$_3$], thus confirming that a Mo−C bond is cleaved directly, in competition with addition of $(CF_3)_3COH$ to the Mo═C bond to give Mo(NAr)(CH_2CMe_2Ph)(CH_2-t-Bu)$_2$[OC(CF_3)$_3$]. When Mo(NAr)(CH_2CMe_2Ph)(CH_2-t-Bu)$_2$[OC(CF_3)$_3$] decomposes, it yields all possible alkylidenes analogous to those shown in eq 3 in approximately a 1:1:1 ratio.

We have shown in preliminary experiments that selected Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes will convert diallyl ether to dihydrofuran and ethylene (Table 1). Complexes **2b**,**c** are slower reacting catalysts, as expected, since the metal center is likely to be less electrophilic. Reactions that involve **2e** are not as long-lived as reactions that involve **2d**, most likely as a consequence of the greater protection against bimolecular decomposition of intermediate alkylidenes that the

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(7) The structure of Mo(NAr)(CH_2-t-Bu)$_3$(OC_6F_5) has been confirmed in an X-ray study, details of which will be provided in a future paper.

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Table 1. Ring-Closing Metathesis of Diallyl Ether with Mo(NAr)(CH-*t*-Bu)(CH_2-*t*-Bu)(OR) Catalysts at Room Temperature

OR[a]	loading (%)	time (h)	conversn (%)
OAd (**2b**)	5, 2.5	6.5, 17.5	88, 52
O−t-Bu (**2c**)	5, 2.5	6.5, 17.5	79, 48
OAr (**2d**)	5, 2.5, 1.7	0.1, 0.2, 0.2	92,[b] 92, 88
OC_6F_5 (**2e**)	5, 2.5	0.1, 0.2	93,[c] 85

[a] All reactions were carried out in C_6D_6 at room temperature and followed by proton NMR. The ethylene formed in the reaction was released only if a second aliquot was added. [b] An additional 20 equiv of diallyl ether was converted to product in 91% yield in 1.1 h. [c] An additional 20 equiv of diallyl ether was not metathesized over a period of 2.3 h.

bulkier OAr ligand offers. It should be noted that Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ shows poor catalytic activity (27% in 20 h) with no improvement in another 24 h.

There are no reports of reactions between the known[6] W(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ and alcohols. However, there are some parallels between the reactions reported here and those that involve Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)$_2$.[9] The reaction between Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)$_2$ and a silica surface produces a Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)(OSi_{surf}) species that has been deduced to form via addition of Si_{surf}OH to both the Re−C and Re═C bonds (followed by rapid α abstraction at the high temperatures employed);[10,11] no addition of Si_{surf}OH to the neopentylidyne ligand took place. The Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)(OSi_{surf}) species is an active olefin metathesis catalyst at room temperature. In solution Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)$_2$ was shown to react with Ph_3SiOH over a period of 12 h at room temperature to yield Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)($OSiPh_3$) as a 10:1 mixture of syn and anti isomers.[10] It is also known that HX ($X^- = C_6F_5O^-$, $CF_3SO_3^-$, BF_4^-) reacts with Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)$_2$ rapidly in solution to give Re(C-t-Bu)(CH_2-t-Bu)$_3$X species, which upon subsequent treatment with L (L = py, CH_3CN, CD_3OD, THF) yield neopentane and Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)$(L)_n$X ($n = 1-3$) species.[12]

The results reported here suggest that the mode of addition of alcohols to Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ (and related) species varies dramatically with the size and pK_a of the alcohol and the conditions under which the reaction is run. They also suggest that Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) and related species do not react rapidly with another 1 equiv of ROH to give known Mo(NAr)(CH-t-Bu)$(OR)_2$ species, a result that we initially found surprising. Unfortunately, the first experiments designed to prepare one diastereomer of an asymmetric metathesis catalyst of the type Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR*) (where R* is enantiomerically pure) by the methods outlined here have led to mixtures of diastereomers.[13] Therefore, alternative methods may be required in order to prepare enantiomerically and diastereomerically pure asymmetric metathesis catalysts of this type.

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Supporting Information Available: Text giving experimental procedures for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) An example of R*OH is monomethyl-protected (*R*)-binaphthol. Similar results have been obtained by M. Duval-Lungulescu with a variety of chiral alcohols.