Organometallics 1987, *6*, 1373-1374

Well-Characterized Olefin Metathesis Catalysts That Contain Molybdenum

John S. Murdzek and Richard R. Schrock*

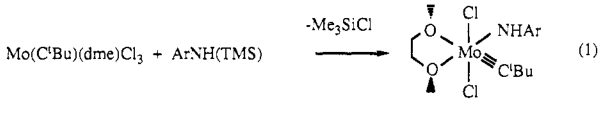
Department of Chemistry, 6-331
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received March 16, 1987

Summary: The reaction between Mo(C-*t*-Bu)(dme)Cl_3 (dme = 1,2-dimethoxyethane) and $Me_3SiNHAr$ (Ar = 2,6-diisopropylphenyl) yields Mo(C-*t*-Bu)(NHAr)(dme)Cl_2 (**1**), which upon treatment with a catalytic amount of NEt_3 is transformed into Mo(CH-*t*-Bu)(NAr)(dme)Cl_2 (**2**) virtually quantitatively. Complexes of the type Mo(CH-*t*-Bu)(NAr)$(OR)_2$ (OR = $OCMe(CF_3)_2$, $OCMe_2(CF_3)$, or $OCMe_3$) have been prepared. Mo(CH-*t*-Bu)(NAr)$[OCMe(CF_3)_2]_2$ is an active metathesis catalyst (but less active than the tungsten analogue) while Mo(CH-*t*-Bu)(NAr)$(OCMe_3)_2$ does not react with ordinary olefins. Addition of $Me_3SiCH{=}CH_2$ to Mo(CH-*t*-Bu)(NAr)$[OCMe(CF_3)_2]_2$ to yield Mo$(CHSiMe_3)$(NAr)$[OCMe(CF_3)_2]_2$ is taken as evidence that molybdacyclobutane complexes lose an olefin more readily than analogous tungstacyclobutane complexes.

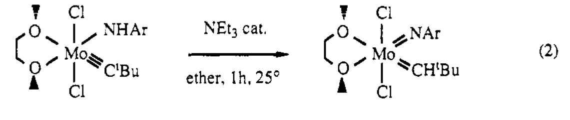
Molybdenum, tungsten, and rhenium are the three metals that are most active by far in classical catalyst systems for the metathesis of olefins.[1] Of these, tungsten-based homogeneous catalyst systems have been the most studied and used, since they appear to have some of the highest activities. But high activity has its costs, among them short catalyst lifetimes (probably), high reactivity toward functional groups, and lack of control over ring-opening polymerization of cyclic olefins. Since we have observed that molybdenum[2] acetylene metathesis catalysts of the type $Mo(CR)(OR')_3$ are much less active than analogous tungsten catalysts,[3] we felt compelled to explore the possibility of preparing molybdenum analogues of the recently described tungsten complexes of the type $W(CHR)(NAr)[OCMe(CF_3)_2]_2$ (Ar = 2,6-diisopropylphenyl).[4] Here we report the synthesis and some reactions of molybdenum complexes of this type.

The approach we took to the synthesis of the molybdenum complexes was identical with that used to prepare the tungsten complexes.[4] Fortunately the two crucial reactions (eq 1 and 2) proceed smoothly in high yield.[5] All evidence suggests that in both **1** and **2** the chloride ligands are mutually trans and the carbon atom cis to the nitrogen atom. In the ^1H NMR spectrum of **2** a signal for the neopentylidene α proton is observed at 12.91 ppm. However, another signal can be observed at 14.10 ppm in samples of **2** that have been recrystallized from pentane. A less soluble, dme-free species can be crystallized selectively from solution. Upon addition of dme to it in solution the spectrum of **2** is regenerated. We propose that the dme-free species is a dimer (**3**, *x* = 2) containing two bridging chloride ligands, although it could easily be a polymer. A species analogous to **3** was not observed in the tungsten system probably because dme is more firmly bound in the tungsten analogue of **2**.[4]



(1)

1



(2)

1 2

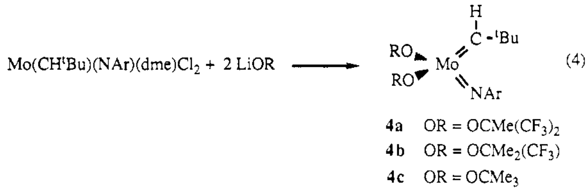
Table I. Selected ^1H and ^{13}C NMR Data for Molybdenum Alkylidene Complexes[a]

compd	$\delta(H_\alpha)$	$\delta(C_\alpha)$	J_{CH}, Hz
Mo(CH-*t*-Bu)(NAr)(dme)-Cl_2[b] (**2**)	12.91 (9.97)	312.2 (283.8)	115
[Mo(CH-*t*-Bu)(NAr)$Cl_2]_x$[b] (**3**)	14.10	326.2	124
Mo(CH-*t*-Bu)(NAr)[OCMe-$(CF_3)_2]_2$ (**4a**)	12.06 (8.87)	288.2 (253.9)	117
Mo(CH-*t*-Bu)(NAr)[$OCMe_2$-$(CF_3)]_2$ (**4b**)	11.61 (8.41)	276.8 (244.9)	118
Mo(CH-*t*-Bu)(NAr)-$(OCMe_3)_2$ (**4c**)	11.23 (8.05)	265.8 (236.5)	117
Mo$(CHSiMe_3)$(NAr)[OCMe-$(CF_3)_2]_2$ (**4d**)	13.86 (9.97)	289.8 (242.8)	113
Mo(CHEt)(NAr)[OCMe-$(CF_3)_2]_2$[c] (**5**)	12.44 (9.22)		

[a] Values for the corresponding tungsten complexes[4,7] are shown in parentheses. All spectra were obtained in C_6D_6 unless otherwise noted. [b] Solvent = CD_2Cl_2. [c] Observed in situ.

$$\mathrm{Mo(CH^tBu)(NAr)(dme)Cl_2} \underset{+\,\mathrm{dme}}{\overset{-\,\mathrm{dme}}{\rightleftharpoons}} \underset{\mathbf{3}}{[\mathrm{Mo(CH^tBu)(NAr)Cl_2}]_x} \qquad (3)$$

Replacing the two chloride ligands in **2** with alkoxide ligands yields the extremely soluble, presumably pseudotetrahedral orange neopentylidene complexes shown in eq 4.[6] ^1H and ^{13}C NMR data (Table I) are similar to those



(4)

4a OR = $OCMe(CF_3)_2$
4b OR = $OCMe_2(CF_3)$
4c OR = $OCMe_3$

---

[1] (a) Ivin, K. J. *Olefin Metathesis*; Academic: New York 1983. (b) Dragutan, V.; Balaban, A. T.; Dimonie, M. *Olefin Metathesis and Ring Opening Polymerization of Cyclo-Olefins*, 2nd ed.; Wiley Interscience: New York, 1985.

[2] McCullough, L. G.; Schrock, R. R.; Dewan, J. C.; Murdzek, J. S. *J. Am. Chem. Soc.* **1985**, *107*, 5987.

[3] (a) Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1554. (b) Freudenberger, J. H.; Schrock, R. R.; Churchill, M. R.; Rheingold, A. L.; Ziller, J. W. *Organometallics* **1984**, *3*, 1563.

[4] Schaverien, C. J.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2771.

[5] (a) $Me_3SiNHAr$ (0.69 g, 2.77 mmol), dissolved in ether (6.0 mL), was added dropwise over 5 min to a blue solution of Mo(C-*t*-Bu)(dme)Cl_3 (dme = dimethoxyethane) (1.00 g, 2.77 mmol) in ether (45 mL) while the solution was stirred at −30 °C. The resulting orange-red solution was allowed to warm to room temperature over 90 min. The volatile components were removed in vacuo. The orange residue of crude **1** thus obtained was pure enough for subsequent reactions. It can be recrystallized from a minimum amount of ether at −40 °C to yield analytically pure Mo(C-*t*-Bu)(NHAr)(dme)Cl_2 (**1**) as yellow-orange needles (1.06 g, 76%) in three crops: partial ^1H NMR (CD_2Cl_2) δ 12.49 (br s, 1, N*H*Ar); partial ^{13}C NMR (CD_2Cl_2) δ 321.2 ($CCMe_3$); IR (Nujol) 3204 cm^{-1} (s, ν_{NH}). Anal. Calcd for $MoC_{21}H_{37}O_2Cl_2N$: C, 50.21; H, 7.42. Found: C. 49.88; H, 7.35. (b) A sample of crude Mo(C-*t*-Bu)(NHAr)(dme)Cl_2 prepared from 0.24 g (0.66 mmol) of Mo(C-t-Bu)(dme)Cl_3 as described above was dissolved in ether (20 mL). While the solution was stirred at −30 °C, dimethoxyethane (70 mL, 0.67 mmol) and then NEt_3 (25 mL, 0.18 mmol) were added. The solution was allowed to warm to ambient temperature over the next twenty minutes. The volatile components were then removed in vacuo, leaving an orange-red residue that was pure enough for subsequent reactions. ^1H and ^{13}C NMR spectra of this residue showed it to be a mixture of **2** and the dme-free complex, [Mo(CH-*t*-Bu)(NAr)$Cl_2]_x$ (**3**). **3** selectively crystallized out as an orange solid (0.15 g, 45%) from a minimum amount of pentane at −40 °C. It was too unstable for elemental analysis. We have not yet obtained crystalline **2** completely free of **3**.

0276-7333/87/2306-1373$01.50/0

for the analogous tungsten species[4,7] (values in parentheses). The trend seems to be toward a smaller chemical shift for H$_\alpha$ and C$_\alpha$ in the more electron-donating alkoxide complexes and a larger chemical shift for H$_\alpha$ and C$_\alpha$ in the molybdenum complexes relative to the tungsten complexes. So far we have not found any clear cut correlation between such relatively small changes in chemical shifts and how such complexes react with olefins.

Addition of Me$_3$SiCH=CH$_2$ to **4a** yields Me$_3$CCH=CH$_2$ and Mo(CHSiMe$_3$)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (**4d**) by ^{1}H NMR. **4d** can be isolated readily as orange crystals.[8] This result differs significantly from that reported for the analogous tungsten system where W[CH(SiMe$_3$)CH(SiMe$_3$)CH$_2$](NAr)[OCMe(CF$_3$)$_2$]$_2$ can be isolated and structurally characterized.[4] Therefore we can conclude that in this particular case the α,β-bis(trimethylsilyl)molybdacyclobutane complex loses olefin more readily than the tungstacyclobutane analog.[10] (The conclusion ultimately should prove to be more general.) This finding parallels that found for metallacyclobutadiene complexes of the type M(C$_3$Et$_3$)(O-2,6-C$_6$H$_3$-*i*-Pr$_2$)$_3$; when M = W, the MC$_3$ ring is stable toward loss of 3-hexyne[3a] while when M = Mo, the MC$_3$ ring loses 3-hexyne completely at 25 °C in C$_6$D$_6$ to give Mo(CEt)(O-2,6-C$_6$H$_3$-*i*-Pr$_2$)$_3$.[2]

Addition of 20 equiv of *cis*-3-hexene to **4a** in C$_6$D$_6$ generates Mo(CHEt)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (**5**) in equilibrium with **4a** (1:1). Addition of 500 equiv of *cis*-2-pentene to this mixture results in metathesis to give the expected mixture of 2-pentenes, 2-butenes, and 3-hexenes, at a rate that is of the order of 250 turnovers/min. This reaction should be compared with that between *cis*-2-pentene and W(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ to yield metathesis products at a rate of 10^3 turnovers/min (lower limit).[4] Therefore in spite of the uncertainties that result from a lack of knowledge of how much faster ethylidene and propylidene complexes react with olefins than neopentylidene complexes react with olefins, we can say that the molybdenum metathesis catalysts are approximately an order of magnitude less reactive than the tungsten metathesis catalysts. Like W(CHEt)(NAr)[OCMe(CF$_3$)$_2$]$_2$[4] Mo(CHEt)(NAr)[OCMe(CF$_3$)$_2$]$_2$ slowly decomposes over a period of 1–2 days to as yet unknown products.

In contrast to the high activity of **4a**, **4c** *does not react* with ordinary olefins. With time (1 day) a small amount of isomerization and metathesis of *cis*-2-pentene is observed, but **4c** also decomposes slightly during this time. Therefore we cannot say for certain that **4c** (or an analogue) is responsible for metathesis-like activity over an extended period of time. Like W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$,[7] **4c** will react with norbornene and other olefins to produce living polymers. These results will be reported separately. We expect the activity of **4b** to be intermediate between that of **4a** and **4c**, as has been found in the tungsten system.[7,9]

An important question is whether molybdenum complexes will react in a Wittig-like fashion with carbonyl groups, a type of reaction that seems to be fairly general for the well-characterized tungsten complexes that have been prepared so far.[4,11] We find that both **4a** and **4c** react very rapidly with benzaldehyde (1 equiv) to yield *trans*-PhCH=CH-*t*-Bu and a single product in each case whose ^{1}H and IR spectra are consistent with their being the expected products of the type Mo(O)(NAr)(OR)$_2$. We are in the process of devising a set of reactions that would provide a comparison of the rate of reaction of a given Mo complex vs. that of the analogous W complex with a carbonyl group.

To our knowledge the compounds reported here, along with related species reported recently by Osborn,[12] are the first examples of high oxidation state molybdenum alkylidene complexes and their reaction with olefins is the first example of olefin metathesis by a well-characterized molybdenum alkylidene complex. Their preparation clearly establishes the analogy between the high oxidation state chemistry of molybdenum and that of tungsten. We are in the process of exploring in detail the differences and similarities between molybdenum and tungsten complexes in metathetical and Wittig-like reactions.

Acknowledgment. We thank the National Science Foundation for supporting this research (Grant CHE 84-02892).

---

(6) **Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$.** A sample of crude Mo(CH-*t*-Bu)(NAr)(dme)Cl$_2$ prepared from 1.00 g (2.76 mmol) of Mo(C-*t*-Bu)(dme)Cl$_3$ as described above was dissolved in ether (60 mL). LiOCMe(CF$_3$)$_2$ (1.04 g, 5.53 mmol) was added as a solid over 5 min while the solution was stirred at −30 °C. The solution lightened slightly from red-orange to yellow-orange, and LiCl precipitated as the reaction mixture was allowed to warm to room temperature the next 3 h. The volatile components were removed in vacuo, and the residue was extracted with pentane. The extracts were filtered through Celite and evaporated to dryness in vacuo. The residue thus obtained was virtually pure by ^{1}H NMR. Analytically pure material suitable for catalytic studies recrystallized from a minimum amount of pentane at −40 °C as a yellow-orange solid (1.49 g, 77% from Mo(C-*t*-Bu)(dme)Cl$_3$, three crops). Anal. Calcd for MoC$_{25}$H$_{33}$O$_2$NF$_{12}$: C, 42.69; H, 4.73. Found: C, 42.87; H, 4.55. **Mo(CH-*t*-Bu)(NAr)[OCMe$_2$(CF$_3$)]$_2$.** A sample of crude Mo(CH-*t*-Bu)(NAr)(dme)Cl$_2$ prepared from 0.55 g (1.52 mmol) of Mo(C-*t*-Bu)(dme)Cl$_3$ as described above was dissolved in ether (35 mL). LiOCMe$_2$(CF$_3$) (0.41 g, 3.04 mmol) was added as a solid over several minutes to the solution at −30 °C while it was being stirred. The solution lightened slightly from red-orange to yellow-orange, and LiCl precipitated as the reaction mixture was allowed to warm to room temperature over the next 3 h. All volatile components were then removed in vacuo, and the residue was extracted with pentane. The extracts were filtered through Celite, and the filtrate was evaporated to dryness in vacuo. This orange residue (0.88 g, 97%) was virtually pure by NMR spectroscopy. **Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$.** A sample of crude Mo(CH-*t*-Bu)(NAr)(dme)Cl$_2$ prepared from 1.00 g (2.76 mmol) of Mo(C-*t*-Bu)(dme)Cl$_3$ as described above was dissolved in ether (60 mL). LiOCMe$_3$ (0.67 g, 8.37 mmol) was added as a solid over several minutes to the solution at −30 °C while it was being stirred. The solution lightened slightly from red-orange to yellow-orange, and LiCl precipitated as the reaction mixture was allowed to warm to room temperature over the next 3 h. All volatile components were then removed in vacuo, and the residue was extracted with pentane. The extracts were filtered through Celite, and the filtrate was evaporated to dryness in vacuo. The residue was recrystallized from a minimum amount of pentane at −40 °C to yield an orange solid (0.94 g, 70%) in three crops. An analysis sample was prepared by subliming the recrystallized solid at 60 °C and 0.1 μm. Anal. Calcd for MoC$_{25}$H$_{45}$O$_2$N: C, 61.59; H, 9.30. Found: C, 61.84; H, 9.16.

(7) Schrock, R. R.; Feldman, J.; Grubbs, R. H.; Cannizzo, L. *Macromolecules* **1987**, *20*, 1169.

(8) Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (0.10 g, 0.14 mmol) was dissolved in pentane (20 mL). Vinyltrimethylsilane (62 μL, 0.43 mmol) was added all at once to this yellow-orange solution at −30 °C. The solution turned dark green upon warming to room temperature over a period of 2.5 h. Removing all volatile components in vacuo yielded a dark residue that was recrystallized from a minimum amount of pentane at −40 °C to give Mo(CHSiMe$_3$)(NAr)[OCMe(CF$_3$)$_2$]$_2$ as a greenish yellow solid (0.080 g, 74%).

(9) Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. submitted for publication.

(10) Recently we have found that W[CH(SiMe$_3$)CH(SiMe$_3$)CH$_2$](NAr)[OCMe(CF$_3$)$_2$]$_2$ is in equilibrium with W(CHSiMe$_3$)(NAr)[OCMe(CF$_3$)$_2$]$_2$ in C$_6$D$_6$ ($K_{eq} \approx 5 \times 10^{-3}$ M at 40 °C).[9]

(11) Aguero, A.; Kress, J.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1986**, 531.

(12) Ehrenfeld, D.; Kress, J.; Moore, B. D.; Osborn, J. A.; Schoettel, G. *J. Chem. Soc., Chem. Commun.* **1987**, 129.