J. Am. Chem. Soc. **1994,** *116,* 2145–2146

Synthesis of a Molybdenum-Containing Silsesquioxane Which Rapidly Catalyzes the Metathesis of Olefins

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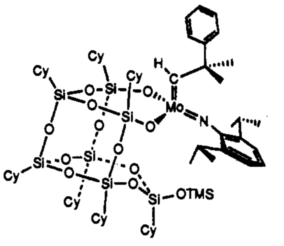
Received September 13, 1993

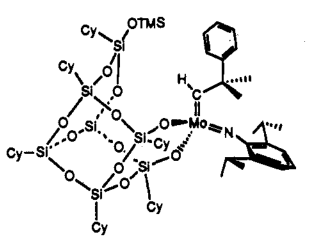
Olefin metathesis can be initiated by a very large number of molybdenum and tungsten complexes and numerous catalysts have been reported.[1-4] Many factors influence the activity of Mo and W-containing metathesis catalysts, but in the absence of differential steric effects, catalytic activity appears to correlate best with the electron-withdrawing ability of the alkoxide ligands.[2-4] In the case of Schrock's well-known family of catalysts, an appropriate balance between steric and electronic effects was achieved by using strongly σ-withdrawing hexafluoro-t-butoxide ligands (i.e., $[(CF_3)_2(CH_3)CO]_2M(CHR)(NAr)$; M = Mo (**1a**) or W (**1b**)).[4]

During recent studies of olefin polymerization by vanadium-containing silsesquioxanes,[5] we suggested that coordination of d^0 metals to a silsesquioxane framework instead of conventional alkoxide or siloxide ligands could produce more electrophilic metal centers; the Si atoms of a silsesquioxane framework are approximately as electron-withdrawing as CF_3 groups[6] and most silsesquioxanes coordinate to metals with acute M-O-Si bond angles, which limits the extent of $O(p\pi)$-$M(d\pi)$ bonding possible. Since the activity of a Schrock-type olefin metathesis catalyst is very sensitive to the nature of its alkoxide ligands, we decided to prepare a silsesquioxane analog of **1a** in order to evaluate the electronic properties of silsesquioxane ligands and to test the utility of silsesquioxanes as ancillary ligands for metathesis catalysts. In this paper we report the synthesis of such a complex, as well as the results from preliminary reactivity studies which suggest that its activity for the metathesis of internal olefins (e.g., cis-2-octene) is comparable to **1a** and **1b**.

The reaction of $[(c\text{-}C_6H_{11})_7Si_7O_9(OSiMe_3)(OH)_2]$ (**2**)[7] with TlOEt (2 equiv) affords $[(c\text{-}C_6H_{11})_7Si_7O_9(OSiMe_3)(OTl)_2]$ (**3**),[8] which upon addition of $[Mo(CHCMe_2Ph)(NAr)(OSO_2CF_3)_2(dme)]$ (Ar = 2,6-diisopropylphenyl)[4a] affords a quantitative (by NMR) yield of a single molybdenum-containing silsesquioxane.[9] There are four possible structures for this product, but isomers **4a** and **4b** seem most likely[10] on the basis of the ^1H chemical shift for the alkylidene CH, molecular models, and the fact that **1a** adopts a "syn" structures in the solid state.[4]



4a



4b

At high-temperature (70 °C), ^1H, ^{13}C, and ^{29}Si NMR spectra of the product are consistent with a time-averaged structure resulting from rapid rotation about N-Arylimido, Arylimido-$CHMe_2$, and perhaps Mo═C bonds.[11] Upon cooling to −30 °C, resonances for the isopropyl CH_3 groups decoalesce into two sets of CH_3 resonances, and the complex multi-line pattern observed between 6.9 and 7.05 ppm for the three aromatic arylimido protons appears to coalesce into a broad singlet.[12] The multiplicities of all other resonances in the ^1H, ^{13}C and ^{29}Si NMR spectra are

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(8) (a) In a typical reaction,[8bc] TlOEt (460 mg, 1.84 mmol) is added to a solution of disilanol **2a** (965 mg, 0.923 mmol) in toluene (25 mL). After the mixture has been stirred for 3.5 h at 25 °C, the volatiles are evaporated (25 °C, 0.1 Torr, 3 h), and the remaining white solid is washed with hexanes (3 × 8 mL) and dried. The product obtained in this manner is pure by ^1H and ^{13}C NMR spectroscopy, but it can be recrystallized from toluene/hexanes. (b) Budzichowski, T. A.; Ph.D. Thesis, University of California, Irvine, CA, 1991, pg 117. (c) Feher, F. J.; Budzichowski, T. A.; Rahimian, K.; Ziller, J. W. *Inorg. Chem.*, submitted.

(9) (a) A solution of $[Mo(CHCMe_2Ph)(NAr)(OSO_2CF_3)_2(dme)]$ (0.866 g, 1.09 mmol) in benzene (10 mL) was added dropwise over a period of 10 min to a solution of **3** in benzene (20 mL). After being stirred for 2 h at 25 °C, the solution was filtered through alumina and the volatiles were evaporated (25 °C, 0.01 Torr). Recrystallization from a minimum amount of ether at −30 °C afforded orange microcrystals (1.37 g, 86%). The stoichiometry of the product was unequivocally established by multinuclear NMR spectroscopy,[9b] but the exact structure cannot be assigned at this time.[9c] Structures **4a** and **4b** are most likely.[10] For the sake of discussion, the product will be referred to only as **4**. (b) For **4**: mp 122–158 °C dec; ^1H NMR (500.1 MHz, C_6D_6, 22 °C) δ 11.83 (s, 1H, MoC*H*), 7.39 (d, *J* = 8 Hz, 2H, *o*-Ph), 7.24 (t, H = 8 Hz, 2H, *m*-Ph), 7.01 (t, *J* = 8 Hz, 1H, *p*-Ph), 7.02–6.92 (≥7 lines, 3H, arylimido), 3.86 (sept, *J* = 7 Hz, 2H, C*H*Me_2), 2.1–1.0 (br m, 77H), 1.78 (s, 6H, C*Me_2*Ph), 1.37 (d, *J* = 7 Hz, 6H, CH*Me_2*), 0.24 (s, 9H, Si*Me_3*); ^{13}C NMR (125.03 MHz, C_6D_6, 22 °C) δ 268.17 (Mo*C*H), 154.27, 149.94, 146.42, 128.45, 128.37, 126.19, 126.09, 123.33 (aromatic), 54.56 (*C*Me_2Ph), 31.47 (C*Me_2*Ph), 29.37 (*C*HMe_2), 28.00, 27.82, 27.77, 27.61, 27.50, 27.43, 27.35, 27.22, 27.16 (CH_2), 25.33, 24.93, 24.88, 24.36, 23.78 (1:2:2:1:1 for Si*C*H), 23.78 (v br s, CH*Me_2*), 2.13 (s, Si*Me_3*); ^{29}Si NMR (99.35 MHz, C_6D_6, 22 °C) δ 10.01 (*Si*Me_3), −61.78, −67.02, −67.77, −68.53, −70.23 (2:1:1:1:2). At 70 °C, the ^{13}C resonance for the isopropyl methyl groups (δ 23.78) sharpens to a singlet, and the ^1H arylamido resonances at δ 7.02–6.92 collapse to a broad singlet at δ 7.00. At −30 °C, the broad ^{13}C NMR resonance at δ 23.78 resolves into two CH_3 resonances at δ 24.54 and 23.02. Anal. Calcd for $C_{67}H_{115}MoNO_{12}Si_8$ (Found): C, 55.60 (56.17); H, 8.01 (7.81). (c) Numerous attempts to obtain crystals suitable for an X-ray crystal structure have produced microcrystals which are too small for a single-crystal X-ray diffraction study.

(10) The other two isomers differ by formal 180° rotations about the Mo═C bonds in **4a** and **4b**.

(11) Rotation about the Mo═C bond is only required to explain our NMR data if both syn and anti rotamers are present in spectroscopically significant amounts,[4] but there is no spectroscopic evidence (^1H NMR, 70 to −50 °C) for more than a single rotamer.

(12) It appears that one resonance (probably for the two meta protons) has a small temperature-dependent chemical shift, which profoundly effects the observed AB_2 pattern because $\Delta\nu \sim J$.

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uneffected, and no new resonances appear at –30 °C. From these observations, it appears that: (i) the product is a single isomer (e.g., **4a** or **4b**); (ii) as in the case of **1a**,[4] the arylimido ligand is perpendicularly-bisected by the molecular plane of symmetry in the ground state structure; and (iii) there is a significant barrier to rotation about the N-Ar bond ($\Delta G^{\ddagger} \sim 14$ kcal/mole at 298 K).[13]

In C_6D_6 solution, the ^1H and ^{13}C NMR resonances for **4** are unaffected by the addition of DME, diethyl ether, CH_3CN, or ethyl acetate. Upon the addition of olefins, however, resonances for **4** quickly disappear as olefin metathesis products are produced.[14] In the case of 1-pentene or 2-pentene (20 equiv), characteristic vinylic resonances attributable to $C_6H_5(CH_3)_2CCH{=}CH_2$ and $C_6H_5(CH_3)_2CCH{=}CH(CH_3)$ quickly appear in the ^1H NMR spectrum and an equilibrium mixture of metathesis products is obtained within a matter of minutes. New alkylidene resonances can also be observed at $\sim \delta$ 12.3 in the ^1H NMR spectrum,[15] and the solution remains catalytically active for as long as these resonance are observable (at least 1.5 days in an NMR tube at 25 °C).

In an attempt to obtain quantitative rate data, catalytic amounts of **4** were separately added to 4800 equiv of neat 1-octene and 9300 equiv of cis-2-octene at 25 °C.[16] In the case of 1-octene, more than 150 turnovers occurred within 20 seconds of mixing. As expected, the rate of productive metathesis slowed as ethylene accumulated,[17] but the system clearly remains active for much longer. Although an apparent equilibrium was established within 2 h with 1-octene and 7-tetradecenes in an approximate 1:1 ratio, total conversion of 1-octene to 7-tetradecenes could still be accomplished more than 4 h after the start of the reaction of actively purging ethylene from the system with nitrogen.[17] In the case of cis-2-octene, the initiation of metathesis was somewhat slower and only 100 turnovers were observed within the first 60 seconds of the reaction (presumably because **4** reacts more slowly with internal olefins). However, the rate of metathesis quickly accelerated, and complete equilibration of 9300 equivalents of 2-octene with 2-butenes and 6-dodecenes occurred within 10 minutes. As in the case of 1-octene, total conversion could be quickly accomplished by purging butenes from the system with nitrogen. It is not possible to extract meaningful rate constants from this data, but it appears that the activity of **4** is comparable to the activity of **1a** and **1b**,[4] as well as other high activity metathesis catalysts which have been reported recently.[2a]

The ability of **4** to tolerate a variety of functional groups suggested that it might be able to metathesize functionalized olefins. This is indeed the case, but the susceptibility of **4** toward hydrolysis requires that all functionalized olefins be rigorously anhydrous. In the case of methyl oleate (400 equiv), complete equilibration occurs within 2 h, and the system remains catalytically active for at least 24 hours.[16]

The surprisingly high activity of **4** presents a number of exciting opportunities for the development of new metathesis catalysts. One of the more intriguing possibilities is the use of chiral chelating silsesquioxanes (e.g., **2** with Me_3Si replaced by a chiral silane) to effect stereospecific metathesis reactions, including ring-opening metathesis polymerization. The results from our work in this area, our attempts to prepare W-containing catalysts, and our efforts to establish an unambiguous structure for **4**, will be reported in due course.

Acknowledgment. These studies were supported by the National Science Foundation. Acknowledgement is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. We gratefully acknowledge Professor R. R. Schrock (MIT) for his helpful suggestions and for providing a sample of $[Mo(CHCMe_2Ph)(NAr)(OSO_2CF_3)_2(dme)]$. We also thank Dr. J. Feldman (Dupont) for his helpful comments.

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[13] (a) $\Delta G^{\ddagger}$ was estimated from the temperature (T_c = 295 K) at which coalescence of the isopropyl ^{13}C resonances ($\delta\nu$ = 190 Hz) was first observed.[13b] (b) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; pp 79 and 96.

[14] In a typical NMR tube reaction, freshly distilled olefin (20 equiv) was syringed into a 5-mm NMR tube containing a solution of **4** (10 mg, 6.9 μmol) in C_6D_6 (0.4 mL). After the solution was mixed, a series of ^1H NMR spectra were periodically recorded over 24 h. The progress of each metathesis reaction was determined by monitoring characteristic ^1H NMR resonances for both the starting olefins and the expected metathesis products.

[15] A poorly defined singlet (δ 12.33) and an apparent triplet (δ 12.254, J = 6 Hz) are observed during active metathesis reactions of 1-pentene and 2-pentene, respectively.

[16] The course of each reaction was monitored by gas chromatography using benzene from the stock solution as an integration standard. Control experiments unequivocally established that the observed catalysis occurs in the reaction mixture (and not in a hot syringe needle or the injector port of the GC). In the case of octene, 0.500 mL of a stock solution of **4** in benzene (7–14 mM) was added to 5–10 mL of olefin under an atmosphere of nitrogen at 25 °C. In the case of methyl oleate, a solution of **4** (4.8 μmol) in benzene (1.00 mL) was added to a solution prepared by adding methyl oleate (1.93 mmol) to 0.350 mL of benzene.

[17] (a) Ethylene is quite soluble in benzene at 25 °C, and ΔG°_{298} for the metathesis of two terminal olefins to ethylene and an internal olefin is unfavorable by approximately 1.2 kcal/mol.[17b] Without active purging, the accumulation of ethylene prevents the reaction from going to completion. (b) Calculated at 298 K for the gas-phase metathesis of 1-butene using thermodynamic data from: Karapet'yants, M. Kh. *Thermodynamic Constants of Inorganic and Organic Compounds*; Humphrey Science Publishers: Ann Arbor, London, 1970.