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Structural Assignment of a Molybdenum-Containing Silsesquioxane which Catalyzes the Metathesis of Olefins: DPFGSE-NOE and X-Ray Diffraction Studies

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The reaction of [(c-C_6H_{11})$_7$$Si_7O_9$($OSiMe_3$)(OTl)$_2$] with [Mo($CHCMe_2Ph$)(NAr)($OSO_2CF_3$)$_2$(dme)] (Ar = 2,6-diisopropylphenyl) affords 4a as the predominant (>99%) molybdenum-containing product. Assignment of 4a as the *syn*-isomer with juxtaposed arylimido and Me_3Si groups was made on the basis of double pulsed field gradient spin echo (DPFGSE) NOE experiments and confirmed by a single-crystal x-ray diffraction study. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

In a recent paper,[1] we reported the synthesis of a molybdenum-containing silsesquioxane which rapidly catalyzed the metathesis of olefins. This metallasilsesquioxane was formed in virtually quantitative yield from the reaction of [(c-C_6H_{11})$_7$$Si_7O_9$($OSiMe_3$)(OTl)$_2$] (**1**)[2] with [Mo($CHCMe_2Ph$)(NAr)($OSO_2CF_3$)$_2$($MeOCH_2CH_2OMe$)] (Ar = 2,6-diisopropylphenyl) (**2**),[3] but its structure could not be assigned on the basis of data available at the time. In this paper we report the use of a powerful pulsed NMR technique for detecting NOE effects to assign the structure of this compound. This assignment was corroborated by a single-crystal x-ray diffraction study.

RESULTS AND DISCUSSION

In principle, the reaction of **1** with **2** can afford four possible structures, **4a–d**. On the basis of the ^{1}H chemical shift and coupling constant for the alkylidene CH resonance (δ 11.83, $^1J_{CH} = 118$ Hz), and the observation that many Schrock-type metathesis catalysts [i.e. $(RO)_2M(CHR^1)(NAr)$, M = Mo (**3a**)[3] or W (**3b**)[4,5]] adopt '*syn*' structures in the solid-state,[4] *syn* isomers **4a** and **4c** seem most likely.[6–9] These isomers adopt the same coordination geometry within the immediate vicinity of Mo, but differ in the orientation of their silsesquioxane framework. In **4a** and **4b** the Me_3Si group on the silsesquioxane faces the imido ligand, whereas in **4c** and **4d** it faces the alkylidene ligand. A small singlet resonance at δ 12.04 is consistently observed in all spectra of **4**, suggesting that another alkylidene complex is present to the extent of *ca.* 0.7%.[7] The intensity of this resonance doubles upon brief UV irradiation (at −80 °C) and then rapidly returns to its original intensity upon warming to room temperature. All of these observations are consistent with an equilibrium mixture of two alkylidene complexes which differ by a 180° rotation about the Mo=C bond,[7] but they provide no objective basis for determining which pair of alkylidene complexes are present (i.e. **4a**/**4b** *vs.* **4c**/**4d**).

Numerous attempts over 2 years to obtain x-ray quality crystals of **4** were unsuccessful. The complex is highly air-sensitive, extremely soluble in most solvents with which it does not react and tends to form poorly diffracting microcrystals which are too small for a single-crystal x-ray diffraction study. Efforts were therefore undertaken to determine the structure on the basis of NMR data.

In principle, the proximity of the Me_3Si group to either the imido ligand or the alkylidene ligand could have allowed an unambiguous structural assignment to be made on the basis of simple NOE experiments. In practice, however, these effects are very small and extremely difficult to detect by traditional NOE experiments. We therefore performed a series of NOE experiments using the double pulsed field gradient spin echo (DPFGSE) technique developed by Hwang and

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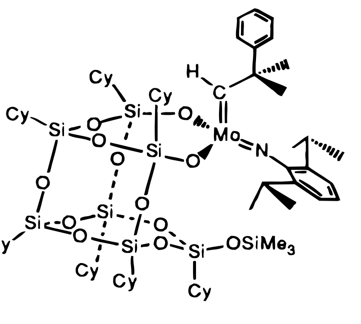
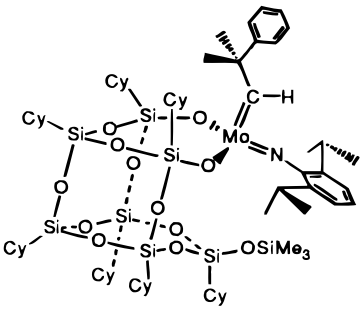
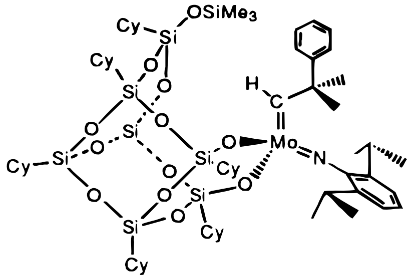


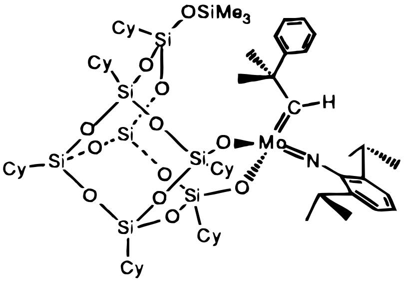
4a Cy = c-C$_6$H$_{11}$



4b



4c



4d

Shaka[10] and recently applied to the NOE difference experiment.[11] This technique, which reliably detects very small NOE effects, represents a powerful tool for resolving structural ambiguities such as the one presented here.

The pulse sequence timing diagram for the DPFGSE-NOE technique is shown in Fig. 1. A strong 90° pulse excites all the proton resonances over the spectral width of interest, and is then immediately followed by a DPFGSE sequence, where the selective 180° pulses are applied to the desired target spin multiplet. Particularly good results are obtained using a frequency modulated (FM) pulse[11] based on the well understood hyperbolic secant family of waveforms.[12,13] The strong PFGs destroy all magnetization except that receiving a proper 180° pulse, so that only the target remains at the end of the DPFGSE. A further 90° pulse then inverts the target, a purging gradient removing any transverse magnetization that remains. Cross-relaxation occurring during the subsequent mixing time τ_m is then observed by a 90° read pulse. Advancing the phase of the first 180° pulse by 90° each scan while subtracting alternate scans removes unwanted contributions from longitudinal relaxation during τ_m.

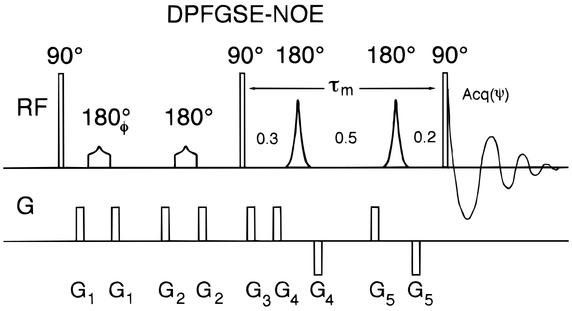


Figure 1. A typical pulse sequence timing diagram for the DPFGSE-NOE method. The PFGs are z-axis gradients, all 1 ms in duration, with levels G_1 = 10.7 G cm^{-1}, G_2 = 3.1 G cm^{-1} and G_3 = 0.5 G cm^{-1}; G_4 and G_5 are less than 0.2 G cm^{-1}. The first two 180° pulses are identical FM waveforms described in Ref. 11. Their duration depends on the target region to be selected, but ranges from 10 to 40 ms. The two 180° pulses in the mixing time were broadband hyperbolic secant pulses with a typical duration of 1.5 ms. These pulses are spaced through the mixing period as shown (0.3 τ_m–180°–0.5 τ_m–180°–0.2 τ_m) and serve to keep unwanted residual magnetization from recovering. The phases ϕ and ψ are cycled through four steps as follows: ϕ = (0°, 90°, 180°, 270°), ψ = (0°, 180°, 0°, 180°). This phase cycling accomplishes the desired difference step, as all magnetization not experiencing the selective pulse is removed.

The DPFGSE-NOE method has a sensitivity identical with that of the conventional transient NOE difference experiment,[14] but offers much better performance because all signals except the target are nulled at the start of the mixing time. The unwanted magnetization can be kept close to the null position by spacing one or more 180° pulses throughout τ_m, and in practice a factor of at least 100 suppression of this background can be obtained for a broad range of mixing times and a reasonable range of longitudinal relaxation times by the timing diagram shown in Fig. 1. It is thus possible to detect, with complete confidence, NOEs in the 0.01% range. The build-up of the NOE enhancements remains unaffected by these inversion pulses.[15] The repetition rate for the experiment is set only by the relaxation time of the target, a decided advantage when searching for small NOEs to slowly relaxing methyl groups.

Figure 2 shows a series of DPFGSE-NOE spectra obtained on a dilute solution of **4** in benzene-d_6 using a 500 ms mixing time. Spectra B and D show that there is

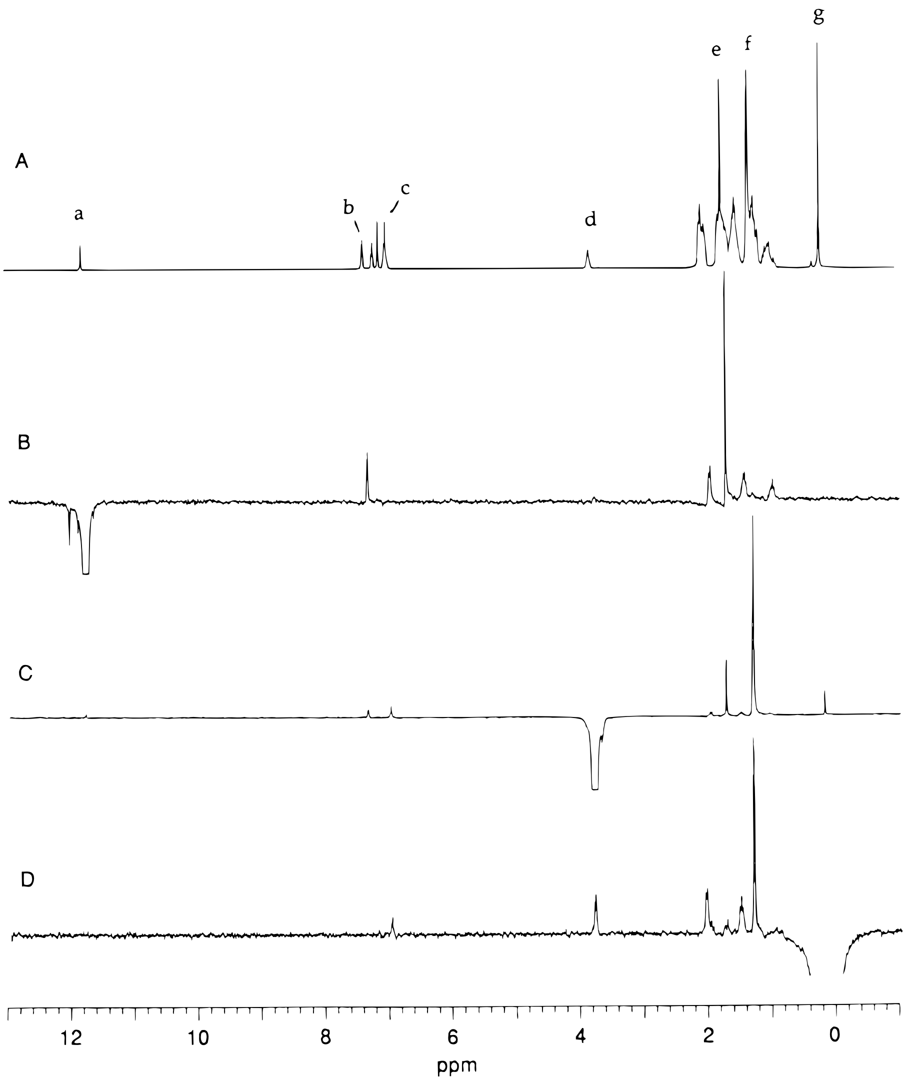


Figure 2. (A) Normal 500 MHz ^{1}H NMR spectrum of **4a**. Resonances a–g in spectrum (A) are assigned as follows: (a) MoC*H*; (b) *o*-C_6H_5; (c) *N*-aryl; (d) C*H*Me$_2$; (e) PhC*Me*$_2$; (f) CH*Me*$_2$; (g) Si*Me*$_3$. (B)–(D) Spectra from DPFGSE-NOE experiments. The target resonances for selective 180° pulses are (B) MoC*H*, (C) C*H*Me$_2$ and (D) Si(C*H*$_3$)$_3$.

no evidence for proximity between the alkylidene proton an the TMS group, while spectrum C shows that an NOE to the TMS group can be reliably detected when the isopropyl group on the aniline ring is the target.

The DPFGSE-NOE experiments convincingly established **4a** as the product obtained from the reaction of **1** with **2**. Shortly after the conclusion of these NOE experiments, we succeeded in obtaining crystals of **4a** suitable for a single crystal x-ray diffraction study. The ORTEP plot, which is illustrated in Fig. 3, confirms the structural assignment of **4a**.

Complex **4a** crystallizes from diethyl ether as well formed, but poorly diffracting, crystals in the space group $P\bar{1}$. Although the quality of the structure (current $R_F \approx 13\%$) does not warrant a detailed discussion of metrical data, it provides reasonably accurate values for distances and angles involving bonds to Mo, and also the Si and O atoms within the silsesquioxane framework. The coordination geometry around Mo, which is approximately tetrahedral, is very similar to that observed for **3b**. The arylimido ligand is nearly linear (Mo—N—C > 170°), and the alkylidene ligand possesses a characteristically obtuse Mo═C—C angle (*ca.* 144°). Bond distances and angles within the silsesquioxane framework are normal and are very similar to those observed for the chromate ester of **1**.[16] The Si—O—Mo angles in **4a** are more acute than the C—O—W angles observed in **3b** and also the C—O—Mo are angles in the Me_3P adduct of **3a**,[9] but these differences are small and probably not chemically significant.

In conclusion, we have established that the product obtained from the reaction of **1** and **2** is **4a**, the *syn*-isomer with juxtaposed arylimido and Me_3Si groups. Although final confirmation of the structure of **4a** was made by a single-crystal x-ray diffraction study, unambiguous assignment of **4a** could be made on the basis of a new pulsed NMR technique for reliably detecting very small NOE effects. This technique, which represents a major improvement over conventional NOE experiments, can quickly resolve many stereochemical ambiguities that would have previously required resolution

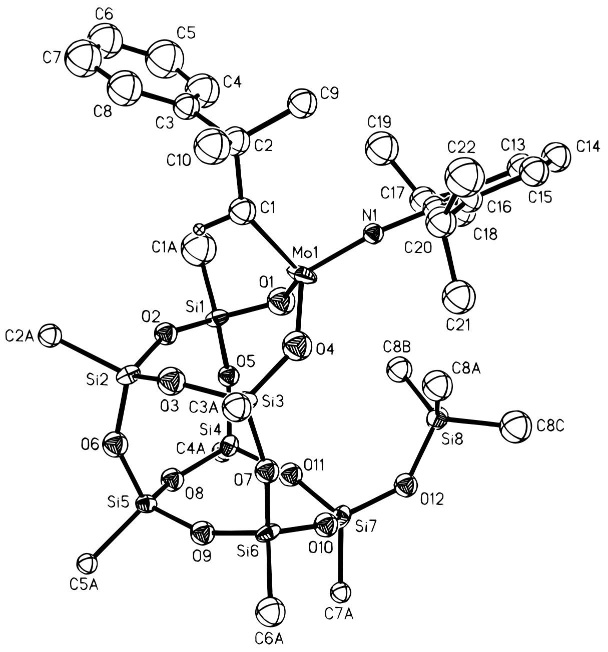


Figure 3. ORTEP plot of **4a**. For clarity, thermal ellipsoids have been plotted at the 50% probability level, and only C attached to Si are shown for cyclohexyl groups. Selected distances (Å) and angles (degrees) are as follows: Mo—O1, 1.904 (13); Mo—O4, 1.900 (10); Mo—N1, 1.712 (11); Mo—C1, 1.891 (16); Si1—O1, 1.627 (13); Si3—O4, 1.608 (10); C11—N1, 1.395 (19); C1—C2, 1.511 (22); Mo—O1—Si1, 132.3 (7); Mo—O4—Si3, 140.4 (8); Mo—C1—C2, 144.0 (13); Mo—N1—C11, 172.6 (10); C1—Mo—N1, 101.9 (6); C1—Mo—O4, 106.4 (5); C1—Mo—O1, 110.9 (7); O1—Mo—O4, 110.0 (5); O1—Mo—N1, 113.7 (5); O4—Mo—N1, 113.5 (5).

by a single-crystal x-ray diffraction study. Our use of the DPFGSE-NOE technique to assign structures for other metallasilsesquioxanes derived from **1** will appear in due course.

EXPERIMENTAL

General experimental protocol and procedures for the synthesis of **4a** are reported elsewhere.[1,17] Crystals suitable for single-crystal x-ray diffraction were obtained by slowly evaporating a saturated solution of **4a** in Et_2O.

Crystallographic data for 4a

$C_{67}H_{115}NO_{12}Si_8Mo$, $M = 1447.3$, triclinic space groups $P\bar{1}$, $a = 12.463$ (2), $b = 14.461$ (2), $c = 23.566$ (5) Å, $\alpha = 94.673$ (14), $\beta = 98.346$ (13), $\gamma = 106.986°$ (11), $U = 3984.2$ (12) Å^3, $Z = 2$.

X-ray diffraction data was collected on Siemens P4 rotating-anode diffractometer. Intensities were measured at 158 K with Mo Kα radiation ($\lambda = 0.71073$ Å) and corrected for Lorentz and polarization effects. The mean intensity of three standard reflections decreased by $<1\%$ during the experiment. The structure was solved by direct methods; final refinements were carried out with anisotropic thermal parameters for Mo and Si and isotropic thermal parameters for all non-H atoms: 9000 unique reflections collected; 403 parameters refined; $R_1 = 0.132$, $wR_2 = 0.168$ for 7107 reflections with $I > 3\sigma I$. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for this material should quote the full literature citation.

Details of the NMR experiment

Spectra were acquired on a Varian UnityPlus NMR spectrometer operating at 500 MHz for protons using the supplied waveform generator to create shaped pulses. A Varian triple-resonance *z*-axis pulsed field gradient probe was used. Experimental parameters are given in the caption to Fig. 1 and are all well within the capability of the hardware. For comparison, a number of conventional NOE experiments (data not shown) were attempted. In no case could the NOE to the trimethylsilyl group be detected above the floor set by subtraction artifacts. In part the long T_1 of this group makes the conventional NOE experiment difficult, and the nine equivalent protons lead to sharp resonance that challenges the field stability of even the most modern instruments. In contrast, a complete build-up curve of the trimethylsilyl group, from $\tau_m = 5$ to 2000 ms, could be measured with the DPFGSE-NOE sequence.

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