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Alignment Of A Nonaqueous Lyotropic Liquid Crystalline Phase With Lecithin

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are outlined in Scheme I.¹³ Mass spectroscopic analysis clearly shows that the product of thermolysis of $\text{Ta}(\text{OAr}')_2(\text{CD}_3)_3$ is $\text{Ta}(\text{OC}_6\text{H}_3\text{-}t\text{-BuCM}_2\text{CH}_2)(\text{OAr}')(\text{CD}_3)_2$ whereas photolysis followed by room-temperature metalation leads to $\text{Ta}(\text{OC}_6\text{H}_3\text{-}t\text{-BuCM}_2\text{CH}_2)(\text{OAr}')(\text{CD}_3)(\text{CD}_2\text{H})$, the proton being incorporated from the *tert*-butyl group.

These results prove that the methylidene compound is not generated during the thermal reaction, and the thermal metalation step probably proceeds in a four-center pathway.¹⁴ The structure of the methylidene compound is at present unknown although it should be very similar to that of the related compound $\text{Ta}(\text{OAr}')_2(=\text{CHSiMe}_3)(\text{CH}_2\text{SiMe}_3)$.¹⁵ This latter compound also undergoes cyclometalation on thermolysis (80 °C), but a number of pathways are possible.¹⁵ The fact that II converts directly to III at room temperature indicates that methylidene functions have a higher activity for aliphatic CH bond activation (at least intramolecularly) than simple alkyl groups. This metalation step can be thought of as an intramolecular reverse of the α -hydride abstraction process, the aliphatic CH bond adding to the tantalum-carbon double bond.

The question arises as to the pathway of the photochemical α -hydride abstraction itself. Figure 1 shows that the electronic spectrum of I contains a strong absorption in the ultraviolet with $\lambda_{\text{max}} = 307 \text{ nm}$ and a molar extinction coefficient $\epsilon_{\text{max}} = 7300 \text{ L mol}^{-1} \text{ cm}^{-1}$. This band we assign as a ligand to metal charge-transfer process from the aryl oxide oxygen atoms to tantalum,¹⁶ being neither in the right position or of the correct shape or intensity to be due to the lowest lying $\pi-\pi^*$ transition ($A_{1g}-B_{2u}$) of the aromatic ring of the OAr' ligands. Irradiation into this band at 313 nm results in the generation of II with a high quantum efficiency of 0.95 ± 0.1 .¹¹ Further evidence for the assignment of this band comes from the spectrum of the yellow compound $\text{TaCl}_2(\text{CH}_2\text{SiMe}_3)_3$. Here the band is of comparable intensity but is red shifted to $\lambda_{\text{max}} = 344 \text{ nm}$, as would be expected for this less electronegative donor atom.

Evidence for the possible generality of this process comes from a study of the compound $\text{Ta}(\text{OAr}'')_2(\text{CH}_2\text{SiMe}_3)_3$ (OAr'' = 2,6-di-isopropylphenoxide). Thermolysis of this compound at 120 °C (toluene-*d*₈/sealed ¹H NMR tube) for 7 days causes little change in the spectrum, approximately 5% Me₄Si being generated with no other identifiable products. In contrast photolysis leads to the rapid formation of 1 equiv of Me₄Si and the alkylidene $\text{Ta}(\text{OAr}'')_2(=\text{CHSiMe}_3)(\text{CH}_2\text{SiMe}_3)$.¹⁷ Further work is in progress to more fully study the possible generality of this process in compounds of this type and to try and ascertain the mechanism of this photoreaction.¹⁸

(13) $\text{Ta}(\text{OAr}')_2(\text{CD}_3)_3$ was prepared as described previously.¹³ Analysis of samples of III generated from $\text{Ta}(\text{OAr}')_2(\text{CH}_3)_3$ either by thermolysis⁸ or photolysis followed by room-temperature metalation showed identical mass spectral patterns. A parent molecular ion peak at 620 (100%) was accompanied by peaks at 621 (35%) and 622 ($\approx 5\%$) due to the ¹³C natural abundances in this C₃₀ molecule. In contrast, the thermolysis of $\text{Ta}(\text{OAr}')_2(\text{CD}_3)_3$ led to a sample of III with a base peak at 626 (i.e., III-*d*₆) with less than 4% 625, whereas the sample of III from photolysis of $\text{Ta}(\text{OAr}')_2(\text{CD}_3)_3$ gave a base peak of 625 (i.e., III-*d*₅) and approximately 40% 626 (as expected from ¹³C natural abundance). In the ¹H NMR of III generated via the photochemical route from $\text{Ta}(\text{OAr}')_2(\text{CD}_3)_3$, a broad, weak multiplet at $\delta 1.05$ was observed and assigned to the TaCD₂H group. No such multiplet could be resolved for the thermally generated compound.

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(17) The compound $\text{Ta}(\text{OAr}'')_2(\text{CH}_2\text{SiMe}_3)_3$ was prepared either by treatment of $\text{Ta}(\text{OAr}'')_2\text{Cl}_3$ with LiCH₂SiMe₃ or by reacting TaCl₂(CH₂SiMe₃)₃ with excess LiOAr'', both in hydrocarbon solvents. The product is a white solid extremely soluble in hexane. ¹H NMR (30 °C, C₆D₆) δ 1.11 (s, CH₂SiMe₃), 0.11 (s, SiMe₃), 3.84 (septet, CHMe₂), 1.36 (d, CHMe₂), 6.8-7.3 (m, OC₆H₃). The electronic spectrum shows a band with $\lambda_{\text{max}} = 302 \text{ nm}$ and $\epsilon = 9900 \text{ L mol}^{-1} \text{ cm}^{-1}$. On photolysis Me₄Si was rapidly generated along with a solution of $\text{Ta}(\text{OAr}'')_2(=\text{CHSiMe}_3)(\text{CH}_2\text{SiMe}_3)$. ¹H NMR (30 °C, C₆D₅CD₃) δ 8.68 (s, Ta=CHSiMe₃), 0.24 and (s) 0.29 (s, CHSiMe₃ and CH₂SiMe₃), 3.47 (septet, CHMe₂), 1.17 (d) and 1.20 (d, CHMe₂), 6.7-7.2 (m, OC₆H₃). The CH₂SiMe₃ signals could not be resolved.

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Registry No. I, 82182-23-8; II, 88915-83-7; III, 88915-84-8; Ta(OAr'')₂(CH₂SiMe₃)₃, 88915-85-9.

(18) Since the submission of this manuscript, experimental details of the photochemical generation of $\text{Re}(\text{N-}t\text{-Bu})_2(=\text{CHSiMe}_3)(\text{CH}_2\text{SiMe}_3)$ from $\text{Re}(\text{N-}t\text{-Bu})_2(\text{CH}_2\text{SiMe}_3)_3$ have appeared, see: Edwards, D. S.; Blondi, L. V.; Ziller, J. W.; Churchill, M. R.; Schrock, R. R. *Organometallics* **1983**, *2*, 1505.

Alignment of a Nonaqueous Lyotropic Liquid Crystalline Phase with Lecithin

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The aqueous lyotropic liquid crystalline phases based on phosphatidyl cholines (lecithins) have been widely studied by NMR in recent years. The important NMR parameters can be obtained most easily from oriented samples. For example, following the discovery that the aqueous phase can be aligned on glass plates, it was relatively straightforward to show that the proton broadening is orientation dependent.¹ Surface orientation of samples is now the normal technique used in preparing samples prior to study by NMR.² To our knowledge, spontaneous magnetic alignment for lyotropic phases based on lecithin has not been observed.

We are currently conducting studies on the nonaqueous lamellar liquid crystalline phase composed of lecithin and various organic diols.^{3-6,10} In the course of these studies, we have observed ³¹P NMR line shapes that exhibit effects consistent with the sample being aligned under certain conditions. Figure 1 shows several ³¹P NMR spectra for a lamellar sample 70/30 (w/w) soy lecithin/ethylene glycol (I). Proton decoupled and nondecoupled spectra are presented for two Zeeman field strengths. In the case of $B_0 = 2.35 \text{ T}$ (Figure 1A), the sample yields a spectrum that is roughly a randomly oriented (three-dimensional) powder pattern⁷ for a spin ¹/₂ nucleus. There is no evidence for alignment under these conditions. A distinctly different spectrum is observed for $B_0 = 4.70 \text{ T}$ (Figure 1C). This spectrum has the qualitative appearance of a 2-dimensional spin ¹/₂ powder pattern.⁷ This type spectrum is derived from a random distribution of directors in a plane passing through B_0 ; however, the only definite conclusion

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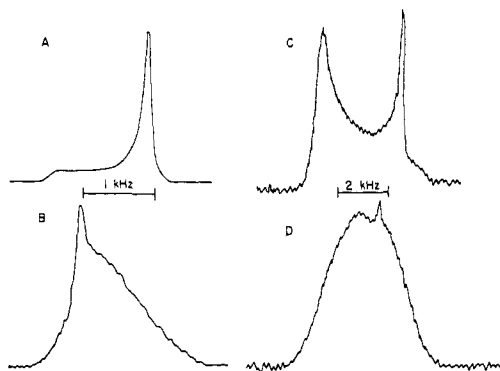


Figure 1. ^{31}P NMR Spectra of I taken at 22 °C, (A) $B_0 = 2.35$ T, proton decoupler on; (B) $B_0 = 2.35$ T, proton decoupler off; (C) $B_0 = 4.70$ T, proton decoupler on; (D) $B_0 = 4.70$ T, proton decoupler off. Removal of the orientation-dependent proton broadening⁹ reveals an approximately axially symmetric line shape for (A) and line shape suggesting alignment for (C). The line shape arises from chemical shift anisotropy, and thus the two spectra (A and C) differ by a factor of 2 in frequency scale, consistent with the different spectrometer frequencies. Frequency increases from left to right.

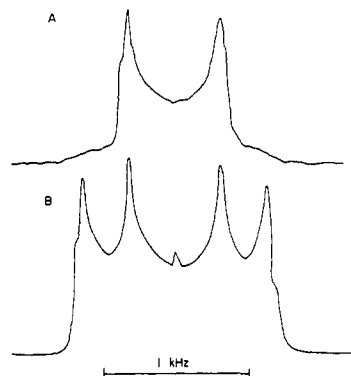


Figure 2. ^2H NMR Spectra of II taken at 22 °C. (A) $B_0 = 2.35$ T; (B) $B_0 = 4.70$ T. No proton decoupling.

to be drawn from Figure 1C is that the directors are not randomly distributed and that there is partial alignment within the sample. This apparent field-dependent alignment is consistent with the anticipated result⁸ that the free energy change on alignment is proportional to B_0^2 . The type line shape shown in Figure 1C has not been observed previously for ^{31}P NMR to our knowledge.

We have also observed strong evidence for spontaneous alignment in ^2H NMR spectra. Figure 2 shows spectra for a sample of composition identical with I but with specific solvent labeling as $(\text{HOCD}_2)_2$, which we designate II. These two spectra taken at different B_0 clearly show random orientation and alignment effects for the sample at $B_0 = 2.35$ and 4.70 T, respectively. The observed ^2H spectrum for $B_0 = 4.70$ T appears to be a two-dimensional spin 1 powder pattern,⁷ which has been observed previously only for type I phases⁷ that have been specially prepared. The preparation involves equilibration of the stationary sample in the magnetic field followed by prolonged spinning of the sample for 2 h and, finally, observation of the spectrum immediately after stopping the spinning.⁷ The sample is not at equilibrium at the time of spectrum observation. In contrast, we have observed all our spectra using stationary samples that had been allowed to equilibrate in the magnetic field. Furthermore, only a few minutes were required for the equilibration.

Spontaneous alignment has been observed by us using both egg yolk and soy lecithin amphiphiles, as well as with various short-chain diol solvents. A variety of samples, ranging in age

from a few months to 3 years, were used for the studies. These samples were carefully prepared under inert atmosphere. After equilibration, the lamellar structure was confirmed by polarizing microscopy, which showed typical myelin figures. Within a 2-min time frame, samples within the lecithin/ethylene glycol composition range 60:40–90:10 (w/w) have been observed to align for $B_0 = 4.70$ T. No alignment has been observed for $B_0 = 2.25$ T. The degree of alignment appears to be slightly temperature dependent.

The present apparent two-dimensional powder pattern behavior is very unusual. One additional feature is that sample probe orientations were different for the two fields (iron core magnet vs. superconducting solenoid). There may be a complex interaction involving the sample, the magnetic field, and the glass container walls. A suggestion that this is the case has been made by Forrest and Reeves,⁷ but the present results put the problem in a new context. We are currently conducting further studies on this system.

Registry No. Ethylene glycol, 107-21-1.

Synthesis, Structure, and Reactivity of $[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Mo}_3(\mu^3\text{-S})(\mu^2\text{-S})_3(\text{SCH}_2\text{CH}_2\text{S})_3]$: A Cluster with Sulfur "Vacancies" and Resonance Raman Spectral Similarity to Fe_3S_4 Proteins

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Multinuclear transition-metal-sulfur complexes (clusters) are of well-established significance in biochemistry,^{2a} while extended-lattice transition-metal-sulfur solids (e.g., MoS_2) are ubiquitous in industrial hydrotreating catalysis.^{2b} In both these contexts, it is important to develop rational, high-yield, general synthetic techniques for the construction and elaboration of transition-metal-sulfur clusters. Recently,^{3a} a synthetic approach to complexes containing the $\text{Mo}_2\text{S}_4^{2+}$ core has been reported, via reduction of the persulfide ligands in $\text{Mo}_2(\text{S}_2)_6^{2-}$.^{3b} We have now been able to extend this approach⁴ to prepare complexes containing the $\text{Mo}_3\text{S}_4^{4+}$ core by starting with the cluster anion $\text{Mo}_3\text{S}(\text{S}_2)_6^{2-}$. Here, we report the synthesis and structure of $\text{Mo}_3\text{S}(\text{SCH}_2\text{CH}_2\text{S})_3^{2-}$ (1). This anion bears an unexpected relation to the layered structure of molybdenum disulfide, while its resonance Raman spectrum resembles that of putative Fe_3S_4 clusters in proteins.

Solid $(\text{NH}_4)_2[\text{Mo}_3\text{S}(\text{S}_2)_6]$ and dry $[\text{N}(\text{C}_2\text{H}_5)_4]\text{Br}$ were added to excess (>9 equiv) $\text{Na}_2(\text{SCH}_2\text{CH}_2\text{S})$ in acetonitrile, and the mixture was stirred at room temperature for 5 h. The deep violet, air-sensitive solution was filtered to remove insoluble oxidized mercaptide polymer, treated with 3:1 diethyl ether/isopropyl alcohol to incipient crystallization and cooled to -10 °C overnight.

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