Figure 3. ^{29}Si CP/MAS NMR spectra of reaction products of methyltrichlorosilane and silica gel (A) directly after silation, (B) exposed to air for 0.5 h, (C) exposed to air for 6 h. Spectrum 3D was obtained after heating the sample corresponding to 3C for 24 h at 200 °C.

surface silanol intensity remains essentially constant in this series of spectra.[13]

The high functionality of the methyltrichlorosilane reagent allows for a much more diverse set of derived surface structures than the reaction products of trimethylchlorosilane and dimethyldichlorosilane. This diversity is reflected in the ^{29}Si spectra of Figure 3, which were taken on the silation product from silica gel and CH₃SiCl₃ after various stages of exposure of the sample to the atmosphere (Figure 3A–C) and heating the hydrolyzed surface at 200 °C (Figure 3D). In general the spectral changes associated with this series of samples parallel the behavior observed for the dimethyldichlorosilane reactions.[14] The progression of changes from Figure 3A to 3D can be interpreted therefore as reflecting an increasing degree of hydrolysis and condensation of the silane phase on the silica surface.

Work is in progress to further elucidate the nature of these and other siloxane bonding reactions.

(13) Considering the fact that peak f in Figure 2A implies some contamination by water in the "nearly anhydrous" sample of this spectrum, it is entirely possible that all or most of the intensity at about −15 ppm in all three spectra of Figure 2 can be attributed to structure e′, rather than e or a combination of e and e′. This view would be consistent with the conclusions of Gilpin and Burke.[1]

(14) An alternative chemical interpretation of the siloxane peak in Figure 3A is a species with two links to the surface, e.g., CH₃SiCl(–O–surface)₂ (e.g., see: Evans, B.; White, T. E. *J. Catal.* **1968**, *11*, 336–341. Hair, M. L.; Herth, W. *Ibid.* **1969**, *15*, 307–309). However, chemical shift correlations and patterns of spectral changes upon sample treatment lead us to prefer the interpretation stated in the text.[12]

Derivatives of Heteropolyanions. 3. O-Alkylation of Mo₁₂PO₄₀³⁻ and W₁₂PO₄₀³⁻

Walter H. Knoth* and Richard L. Harlow

Contribution No. 2906
Central Research and Development Department
E. I. du Pont de Nemours & Company
Experimental Station
Wilmington, Delaware 19898

The derivative chemistry previously reported for Keggin-structure[1] heteropolyanions has involved replacement of peripheral metal–oxygen groups by other metal–ligand groups. For example, W₁₂PO₄₀³⁻ has been converted to H₂OCoW₁₁PO₃₉⁵⁻,[2] CpTiW₁₁PO₃₉⁴⁻,[3,4] CH₃SnW₁₁PO₃₉⁴⁻,[4,5] and CpFe(CO)₂SnW₁₁PO₃₉⁴⁻.[6] No derivatives have been reported which result from attack on surface oxygen of a Keggin-structure anion without accompanying degradation of the anion nor have experimental studies been reported which bear on the relative reactivities of the various types of surface oxygen atoms in this structure. Heteropolyanions and related metal oxides are becoming increasingly important as olefin oxidation catalysts; information on the reactivity of the surface oxygen atoms is of obvious significance. We wish to report the electrophilic O-alkylation of Mo₁₂PO₄₀³⁻ and W₁₂PO₄₀³⁻ and a crystal-structure determination which shows that the preferred alkylation site is a bridging, rather than a terminal, oxygen atom.

Trimethyloxonium tetrafluoroborate (4 mol equiv) was stirred with [(n-C₆H₁₃)₄N]₃Mo₁₂PO₄₀ in 1,2-dichloroethane to give [C₆H₁₃)₄N]₂CH₃OMo₁₂PO₃₉[7] in 76% yield (16-h reaction period, ambient temperature, nitrogen atmosphere, recrystallization from acetonitrile). The infrared spectrum (mineral oil mull) of the product is very similar to that of [(n-C₆H₁₃)₄N]₃Mo₁₂PO₄₀ except that the P–O stretching band is split (1070, 1050 cm⁻¹) and a new, weak band appears at 1005 cm⁻¹. The ^{31}P NMR spectrum in dichloroethane exhibits a single resonance at −3.4 ppm compared to −3.7 ppm found for [(n-C₆H₁₃)₄N]₃MO₁₂PO₄₀ in the same solvent. The ^{1}H NMR spectrum in dideuteriotetrachloroethane includes a singlet for the CH₃OMo₂ protons at δ 4.5.

A similar reaction with triethyloxonium tetrafluoroborate gave [(n-C₆H₁₃)₄N]₂C₂H₅OMo₁₂PO₃₉,[7] which has an infrared spectrum almost identical with that of the methylated analogue. The reaction of [(n-C₆H₁₃)₄N]₃W₁₂PO₄₀ with trimethyloxonium tetrafluoroborate in 1,2-dichloroethane gave mainly a trimethyloxonium salt, [(CH₃)₃O]₃W₁₂PO₄₀, but an 11% yield of [(C₆H₁₃)₄N]₂CH₃OW₁₂PO₃₉ was also obtained.[7] The differences between the infrared spectra of [(n-C₆H₁₃)₄N]₃W₁₂PO₄₀ and [(n-C₆H₁₃)₄N]₂CH₃OW₁₂PO₃₉ are very similar to the differences between the spectra of the analogous molybdenum compounds. The P–O stretching band is split (1090, 1062 cm⁻¹), and a new band appears at 1002 cm⁻¹. The ^{1}H NMR spectrum in dideuteriotetrachloroethane includes a singlet at δ 4.49, assigned to the CH₃OW₂ protons (cation: CH₃OW₂ proton ratio, calcd 2:1; found 2:0.9). The ^{31}P NMR spectrum of [(n-C₆H₁₃)₄N]₂CH₃OW₁₂PO₃₉ in dichloroethane consists of one resonance, which is at −13.9 ppm, compared to −15.1 ppm observed for [(n-C₆H₁₃)₄N]₃W₁₂PO₄₀ in the same solvent.

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(7) Anal. Calcd for [(C₆H₁₃)₄N]₂CH₃OMo₁₂PO₃₉: C, 23.11; H, 4.23; N, 1.10. Found: C, 23.25; H, 4.13; N, 1.10. Calcd for [(C₆H₁₃)₄N]₂C₂H₅OMo₁₂PO₃₉: C, 23.45; H, 4.29; N, 1.09; Mo, 44.96. Found: C, 23.94; H, 4.32; N, 1.00, Mo, 45.0. Calcd for [(CH₃)₃O]₃W₁₂PO₄₀: C, 3.53; H, 0.89; N, 0.0. Found: C, 3.82; H, 0.97; N, 0.3. Calcd for [(C₆H₁₃)₄N]₂CH₃OW₁₂PO₃₉: C, 16.34; H, 2.99; N, 0.78. Found: C, 16.57; H, 2.99; N, 0.72.
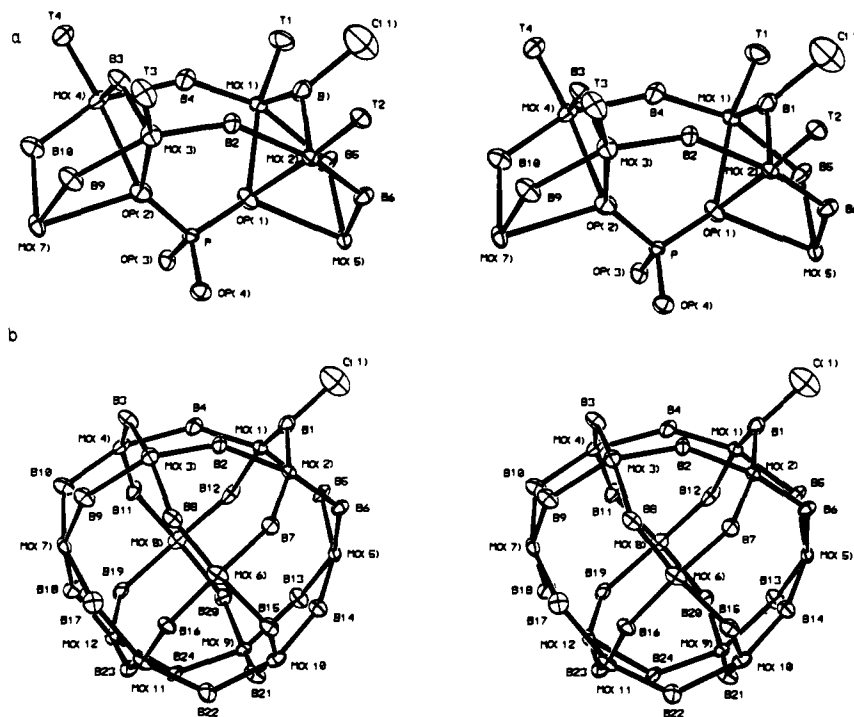
Figure 1. Stereodrawings of (a) the immediate neighborhood of the –OCH$_3$ group and (b) the Mo–O$_B$–MO framework. Ignoring the atoms bonded to Mo(1) and Mo(2), the average bond distances for the Keggin structure are P–O$_p$, 1.533; Mo–O$_p$, 2.447; Mo–O$_B$ (short), 1.846; Mo–O$_B$ (long), 1.966; Mo–O$_T$, 1.653 Å. The bridging oxygens labeled as "B" can be divided into corner sharing and edge sharing; bond distances for the two groups cannot be distinguished, but the average Mo–O$_B$–Mo angles are quite different: corner sharing, 150.4; edge sharing, 128.0°. Selected individual bond distances and angles are Mo(1)–O$_p$(1), 2.429 (8); Mo(1)–O$_B$(1), 1.980 (9); Mo–O$_B$(4), 1.845 (8), Mo(1)–O$_B$(5), 1.971 (8); Mo(1)–O$_B$(12), 1.890 (9); Mo–O$_T$(1), 1.655 (9); Mo(2)–O$_p$(1), 2.455 (8); Mo(2)–O$_B$(1), 2.059 (9); Mo–O$_B$(2), 1.934 (9); Mo(2)–O$_B$(6), 1.843 (8); Mo(2)–O$_B$(7), 1.811 (9); Mo–O$_T$(2), 1.648 (8); O$_B$(1)–C(1), 1.64 (2) Å; Mo(1)–O$_B$(1)–Mo (2), 124.0 (5); Mo(1)–O$_B$(1)–C(1), 113 (1); Mo(2)–O$_B$(1)–C(1), 115 (1)°.

A crystal-structure determination on [(n-C$_6$H$_{13}$)$_4$N]$_2$CH$_3$OMo$_{12}$PO$_{39}$ (Figure 1) shows that the methyl group is bonded to an oxygen which bridges two edge-shared molybdenum octahedra.[8] This strongly suggests that these bridging oxygen atoms are more nucleophilic than the terminal oxygen atoms. The latter are more sterically accessible, and if they were also more electron rich, electrophilic substitution should occur on them regardless of whether the reaction is kinetically or thermodynamically controlled. The other set of bridging surface oxygen atoms, those bridging two corner-shared molybdenum octahedra, are the least sterically accessible of all the surface oxygen atoms. We therefore cannot use the available evidence to form conclusions about their relative basicity.

An earlier structure determination on H$_3$MO$_{12}$PO$_{40}$·(13–14)H$_2$O found that this heteropolyanion has approximate 23 symmetry.[9] The Mo–O$_B$ bonds were not equal but alternately long and short (on average, 1.96 and 1.86 Å, respectively). This type of bonding, where each O$_B$ bridging oxygen forms one long and one short Mo–O$_B$ bond and where each long Mo–O$_B$ bond is trans to a short Mo–O$_B$ bonds, is also found in the present structure. We are attempting a structure determination on CH$_3$OW$_{12}$PO$_{39}$$^{2-}$ to determine if the bond alternation persists in this tungsten analogue.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and structure amplitudes (54 pages). Ordering information is given on any current masthead page.

(8) Crystal-structure information: Monoclinic, space group $P2_1/c$; at –100 °C, a = 13.987 (2), b = 20.975 (3), c = 28.576 (3) Å; β = 101.04 (1)°; V = 8228 Å^3; Z = 4. Syntex P3 diffractometer, graphite monochromator, MoKα radiation, λ = 0.71069 Å, omega scans of 1.0°, 4 < 2θ < 45°, 10758 reflections. An empirical absorption correction based on psi-scan data was applied; the "transmission factors" ranged from 0.79 to 1.00. The structure was refined by full-matrix, least-squares techniques: 5519 reflections with I > 2σ(I), 701 variables (Mo, P, O, N, and C(1) with anisotropic thermal parameters; the remaining C's with isotropic parameters; hydrogen atoms were not included), R = 0.057, R_w = 0.054. Four of the eight n-hexyl chains suffered from disorder problems. The last carbon in the second chain [atoms C(21)–C(26)] occupied two sites which were denoted by C(26) and C(26)P; these sites were assigned occupation factors of 0.55 and 0.45, respectively, on the basis of their Fourier magnitudes. The disorder in chains 4, 6, and 8 was ill-defined and could not be modeled; the poor refinement of these chains is reflected in the thermal parameters, the bond distances, and residual peaks in the final difference Fourier. The mathematical and computational details may be found in the following reference: Nugent, W. A.; Harlow, R. L. *Inorg. Chem.* **1979**, *18*, 2030.

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Synthesis and Ammonium Cryptates of Triply Bridged Cylindrical Macrotetracycles

Florence Kotzyba-Hibert, Jean-Marie Lehn,* and Kazuhiko Saigo†

*Institut Le Bel, Université Louis Pasteua
4, rue Blaise Pascal
67000 Strasbourg, France*‡

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Multisite receptor molecules contain several binding subunits which may cooperate for the complexation of either several singly bound substrates or a multiply bound polyfunctional species. They are *cosystems* which may potentially function as coreceptors, cocarriers, or cocatalysts.[1]

The cylindrical macrotricycles, formed by two macrocyclic binding subunits linked by two bridges, yield dinuclear cryptates by inclusion of two metal cations.[2] Several new polyaza–polyoxa macrotricycles, incorporating different macrocyclic and bridging units, have been reported recently.[1,3,4] Complexation studies by

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