Table I. Thermodynamic Parameters Used in the Calculation of $\Delta H_{f,300}(R'\cdot)^a$

| R' | $K_{300}{}^b$ | $S°_{300}(R'\cdot)$ | $S°_{300}(R'I)$ | $\Delta H_{f,300}(R'I)^c$ | $\Delta H_{f,300}(R'\cdot)$ | $BDE_{300}(R'-H)$ |
|---|---|---|---|---|---|---|
| Me | 1 | $46.4^d$ | $60.5^e$ | 3.4 ± 0.3 | $34.4^f$ | $104.4^f$ |
| Et | 20.1 | $59.2^d$ | $70.7^g$ | −2.0 ± 0.4 | $28.0 \pm 1.0^h$ | 100.3 ± 1.0 |
| *t*-Bu | $1.67 \times 10^4$ | $73.0^i$ | $82.5^j$ | −17.2 ± 0.3 | $9.4 \pm 1.0^h$ | 93.9 ± 1.0 |

[a] $\Delta H_f$, kcal mol$^{-1}$; $S°$, cal deg$^{-1}$ mol$^{-1}$. [b] For reaction 5, R = Me. [c] From ref 8; see also ref 16. [d] Reference 18. [e] Gelles, E.; Pitzer, K. S. *J. Am. Chem. Soc.* 1953, *75*, 5259–5267. [f] Reference standard.[10] [g] Benson, S. W.; Amano, A. *J. Chem. Phys.* 1962, *36*, 3464–3471. [h] Error limits derive mainly from uncertainties in $\Delta H_{f,300}(R'I)$ but allow a contribution of ±1 cal deg$^{-1}$ mol$^{-1}$ for $\Delta S°_{300}$; errors in $K_{300}$ are less significant. [i] Reference 19. [j] Benson, S. W.; Amano, A. *J. Chem. Phys.* 1962, *37*, 197–198.

ation. Photolysis of an isooctane solution of hexa-*n*-butylditin, RI, and R′I (eq 9 and 10) led to values for *K* which were the same

$$n\text{-}Bu_3SnSnBu_3\text{-}n \xrightarrow{h\nu} 2n\text{-}Bu_3Sn\cdot \qquad (9)$$

$$n\text{-}Bu_3Sn\cdot + RI/R'I \rightarrow n\text{-}Bu_3SnI + R\cdot/R'\cdot \qquad (10)$$

as those obtained by the thermal route. The photolysis procedure was used at 0 °C for experiments involving methyl, since, in thermolysis experiments at 60 °C, there was some evidence that this radical was abstracting hydrogen from the solvent.

The values obtained for *K* are shown in Scheme I and generally represent an average obtained from five experiments. The equilibrium involving ethyl and *tert*-butyl radicals could not be established directly because of the magnitude of *K*, and hence cyclopentyl and *sec*-butyl radicals were used as intermediates linking these two.

The values of *K* measured in these experiments are solution values. However, if we assume that the free energies of mixing and vaporization of the radicals are similar to those of their parent alkanes, we can treat these values as being equivalent to gas-phase data. This is because heats of mixing of alkyl iodides and alkanes with hydrocarbons are small (<100 cal mol$^{-1}$),[15] and since only differences in these values alter *K*, their effect is negligible. Moreover, corrections to the free energies of the radicals and iodides for vaporization are subject to "compensation effect"[16] and are also negligible. Values of $K_{333}$ were corrected to $K_{300}$ by using the entropies and heat capacities of the components in equilibria[9c,16] and are shown in Table I along with the other thermodynamic parameters used in the calculation of $\Delta H_{f,300}(R'\cdot)$ and $BDE_{300}(R-H)$.

The value of $\Delta H_{f300}(Et\cdot)$ obtained in this work is higher than the normally accepted value of 25.9 ± 1.3 kcal mol$^{-1}$ [20] and leads to a value for the C–H bond dissociation energy in ethane of 100.7 ± 1.0 kcal mol$^{-1}$. We note that the higher value for $\Delta H_{f,300}(Et\cdot)$ leads to a reconciliation of currently conflicting data on the self-reaction of the ethyl radical,[6,9a] which enhances our confidence in the accuracy of this method.

The heat of formation for *tert*-butyl (Table I) is within experimental error of recent measurements[4,6,7] which cover the range $\Delta H_{f,300}(t\text{-}Bu\cdot) = 8.4–10.5$ kcal mol$^{-1}$ and is in excellent agreement with the results of two unpublished determinations.[19,22] Since our value falls (albeit fortuitously) at the mean of the best available data, we recommend its use until a more accurate method of measurement becomes available. This work is being extended to measure the heats of formation of a variety of radicals.

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(17) $\Delta H_{f,300}(R'I)^8$ were checked by measuring the heats of reaction for the reductions of the iodides by tri-*n*-butyltin hydride in isooctane solvent. Taking $\Delta H_{f,300}(CH_3I) = 3.4$ kcal mol$^{-1}$ as a standard, $\Delta H_{f,300}(EtI)$ and $\Delta H_{f,300}(t\text{-}BuI)$ were found to be −3.3 ± 1.0 and −16.7 ± 1.0 kcal mol$^{-1}$, in good agreement with the gas-phase data. Castelhano, A. L.; Marriott, P. R.; Griller, D., unpublished results.

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## $^{29}$Si CP/MAS NMR Studies of Methylchlorosilane Reactions on Silica Gel

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Covalently attached bonded-phase materials prepared by the reaction of silating agents with the surface of silica gel have found important applications in many areas.[1–4] As part of a continuing study of such systems by $^{29}$Si and $^{13}$C cross-polarization and magic-angle spinning (CP/MAS) NMR[5,6] spectroscopy, we wish to report some preliminary observations on the reactions of a homologous series of methylchlorosilanes with a commercial silica gel (Fisher S-157). Recent CP and MAS studies of related materials have shown great promise for structure elucidation.[5–8]

Surface–silane reactions were carried out by exposing samples of silica gel, prepared under vacuum at 240 °C, to vapors from refluxing methylchlorosilane reagent for a period of about 12 h. The reaction temperature was maintained at 200 °C by independent heating of the sample cell and subsequently for an additional 4 h while the cell was evacuated to remove any unreacted, physically adsorbed reagent. Solid-state $^{29}$Si spectra were obtained at 11.88 MHz on a JEOL FX-60QS spectrometer.[9]

We recently reported $^{29}$Si chemical shift assignments for the three observable resonances of the silica gel surface.[6] These are labeled a, b, and c in Figure 1A which also shows a hypothetical surface segment suggested by the $^{29}$Si data. Resonance a cor-

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(9) All $^{29}$Si CP/MAS spectra employed contact times of 10 ms and repetition times of 0.50 s. The spectra shown represent 10 000 to 60 000 repetitions. Peak intensities in the −109-ppm region are especially sensitive to the quality of the Hartmann–Hahn match[10] and should therefore be viewed with caution. $^{13}$C CP/MAS spectra of the particular systems discussed here were found to show just one line due to ($CH_3Si<$) carbons and were therefore not very informative. However, $^{13}$C spectra of systems with more complex carbon frameworks are sometimes very useful.[6,12]

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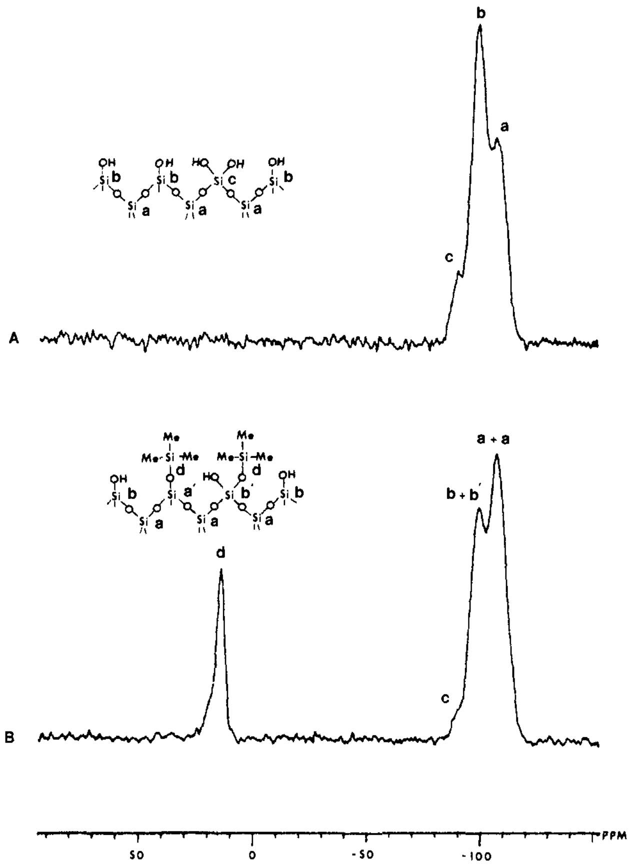

**Figure 1.** $^{29}$Si NMR spectra of Fisher S-157 silica gel (A) before and (B) after reaction with trimethylchlorosilane.[12] Chemical shift scale is in ppm with respect to liquid Me$_4$Si, with larger numbers corresponding to lower shielding.

responds to surface silicon atoms with four siloxane (−OSi<) attachments (interconnecting lattice sites), resonance b to species with three siloxane bonds and one hydroxyl group (silanol sites), and resonance c to silicon atoms with two siloxane bonds and two hydroxyls (silanediol sites). Spectral contributions from silicon atoms deeper in the lattice are strongly discriminated against in the cross-polarization experiment because of their prohibitively long Si–H distances.[5,10,11]

The $^{29}$Si spectrum of a sample prepared with trimethylchlorosilane is shown in Figure 1B. This reaction is thought to proceed by direct substitution of surface hydroxyl hydrogens with trimethylsilyl groups. In the silicon spectrum these changes are manifested by the appearance of a strong resonance at 13 ppm (peak d in Figure 1B), corresponding to the attached Si(Me)$_3$ moiety, and a redistribution of intensity in peaks, a, b, and c in the "silica region" at higher shielding than −80 ppm. Differences in spectral intensities between Figures 1A and 1B can, in principle, be used to extract information relating to the degree of coverage of the silating agent on the surface, as well as the relative reactivity of the different surface hydroxyl types. Reaction on silanol sites, for example, results in a transfer of intensity from resonance b to resonance a, since following the reaction these b-type surface silicon atoms become species containing four siloxane bonds (a′).

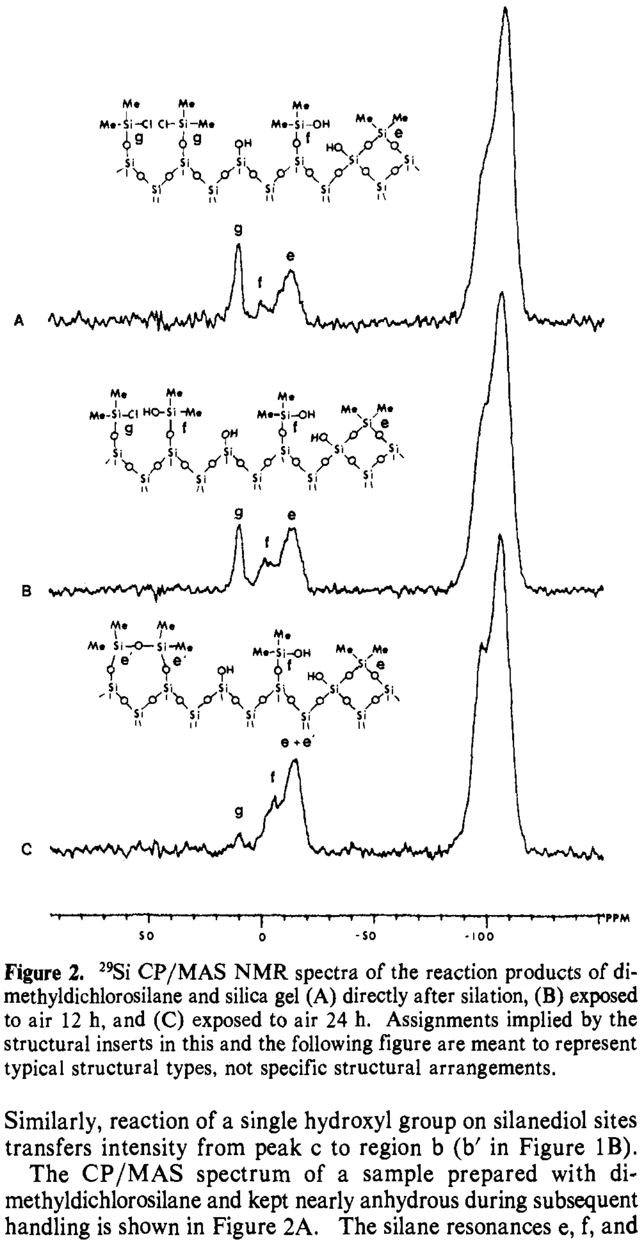

**Figure 2.** $^{29}$Si CP/MAS NMR spectra of the reaction products of dimethyldichlorosilane and silica gel (A) directly after silation, (B) exposed to air 12 h, and (C) exposed to air 24 h. Assignments implied by the structural inserts in this and the following figure are meant to represent typical structural types, not specific structural arrangements.

Similarly, reaction of a single hydroxyl group on silanediol sites transfers intensity from peak c to region b (b′ in Figure 1B).

The CP/MAS spectrum of a sample prepared with dimethyldichlorosilane and kept nearly anhydrous during subsequent handling is shown in Figure 2A. The silane resonances e, f, and g have been assigned to the surface structures pictured in the figure insert on the basis of comparisons with relevant solution data[12] and consistent patterns of chemistry implied by these spectra. The relative intensities of the three peaks in this region suggest that at this level of surface loading about half of the attached silane is involved in two surface bonds (e). The presence of the low-intensity peak (f) at −6 ppm in Figure 2A may reflect partial contamination of the sample by surface water, resulting in a partial conversion of the singly attached dimethylchlorosiloxane species (g) to its hydrolysis product (f).

Spectra shown in Figure 2B,C were taken following exposure of the sample to atmospheric water vapor for periods of 12 h and 24 h, respectively. The ratio of integrated intensity of the region associated with peaks g and f to the total silane intensity (g + f + e) changes from a value of 0.49 in Figure 2A to 0.46 in Figure 2B and 0.29 in Figure 2C. We believe that these observations are indicative of an additional surface reaction involving the condensation of adjacent dimethylchlorosiloxane groups (g) to form cross-linked structures containing two siloxane bonds per silicon atom (e.g., e′ in Figure 2C). The possibility of further participation of surface hydroxyls in this secondary reaction to yield additional doubly attached e-type structures is unlikely, because the measured ratio of total silane intensity to unreacted

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(10) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569–589.

(11) Another possible interpretation of the three peaks in Figure 1A is that they represent surface silicons with four (O—Si<) attachments and surface silicons with three (O—Si<) attachments and one OH group, with the silanol hydroxyls either hydrogen bonded or not (e.g., see: Iler, R. K. "The Chemistry of Silica"; Wiley: New York, 1979). However, empirical chemical shift correlations, patterns of $^{29}$Si spectral changes of silica gels treated by humidifying and drying procedures,[12] and known effects of hydrogen bonding on $^{29}$Si shifts of silanols (Williams, E. A.; Cargioli, J. D.; Larochelle, R. W. *J. Organomet. Chem.* **1976**, *108*, 153–159) lead us at the present time to consider this alternative interpretation incorrect.

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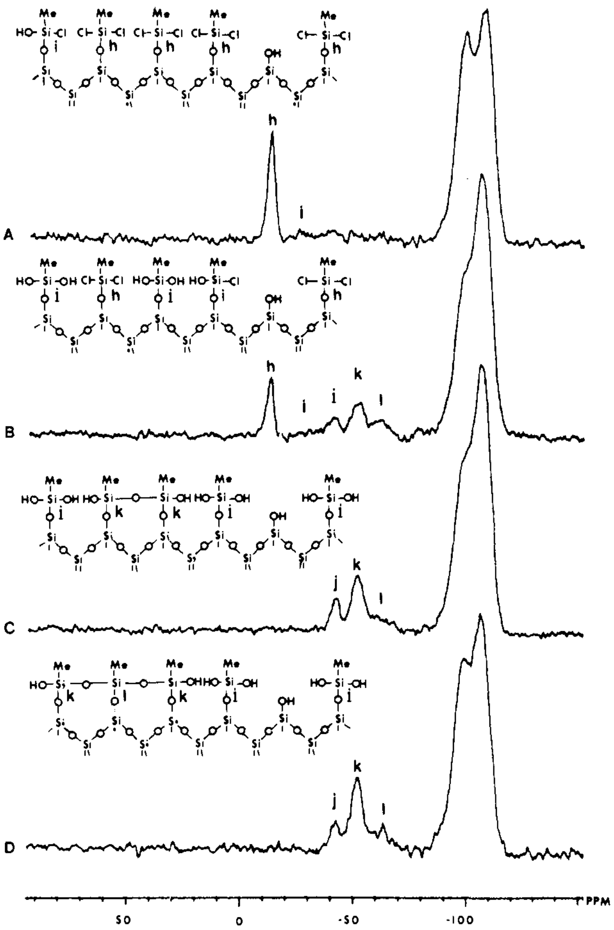

**Figure 3.** $^{29}Si$ CP/MAS NMR spectra of reaction products of methyltrichlorosilane and silica gel (A) directly after silation, (B) exposed to air for 0.5 h, (C) exposed to air for 6 h. Spectrum 3D was obtained after heating the sample corresponding to 3C for 24 h at 200 °C.

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 $CH_3SiCl_3$ 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.

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[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., $CH_3SiCl(-O-surface)_2$ (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]

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# Derivatives of Heteropolyanions. 3. O-Alkylation of $Mo_{12}PO_{40}^{3-}$ and $W_{12}PO_{40}^{3-}$

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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, $W_{12}PO_{40}^{3-}$ has been converted to $H_2OCoW_{11}PO_{39}^{5-}$,[2] $CpTiW_{11}PO_{39}^{4-}$,[3,4] $CH_3SnW_{11}PO_{39}^{4-}$,[4,5] and $CpFe(CO)_2SnW_{11}PO_{39}^{4-}$.[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 $Mo_{12}PO_{40}^{3-}$ and $W_{12}PO_{40}^{3-}$ 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 $[(n\text{-}C_6H_{13})_4N]_3Mo_{12}PO_{40}$ in 1,2-dichloroethane to give $[C_6H_{13})_4N]_2CH_3OMo_{12}PO_{39}$[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 $[(n\text{-}C_6H_{13})_4N]_3Mo_{12}PO_{40}$ 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 $[(n\text{-}C_6H_{13})_4N]_3MO_{12}PO_{40}$ in the same solvent. The $^1H$ NMR spectrum in dideuteriotetrachloroethane includes a singlet for the $CH_3OMo_2$ protons at δ 4.5.

A similar reaction with triethyloxonium tetrafluoroborate gave $[(n\text{-}C_6H_{13})_4N]_2C_2H_5OMo_{12}PO_{39}$,[7] which has an infrared spectrum almost identical with that of the methylated analogue. The reaction of $[(n\text{-}C_6H_{13})_4N]_3W_{12}PO_{40}$ with trimethyloxonium tetrafluoroborate in 1,2-dichloroethane gave mainly a trimethyloxonium salt, $[(CH_3)_3O]_3W_{12}PO_{40}$, but an 11% yield of $[(C_6H_{13})_4N]_2CH_3OW_{12}PO_{39}$ was also obtained.[7] The differences between the infrared spectra of $[(n\text{-}C_6H_{13})_4N]_3W_{12}PO_{40}$ and $[(n\text{-}C_6H_{13})_4N]_2CH_3OW_{12}PO_{39}$ 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 $^1H$ NMR spectrum in dideuteriotetrachloroethane includes a singlet at δ 4.49, assigned to the $CH_3OW_2$ protons (cation: $CH_3OW_2$ proton ratio, calcd 2:1; found 2:0.9). The $^{31}P$ NMR spectrum of $[(n\text{-}C_6H_{13})_4N]_2CH_3OW_{12}PO_{39}$ in dichloroethane consists of one resonance, which is at −13.9 ppm, compared to −15.1 ppm observed for $[(n\text{-}C_6H_{13})_4N]_3W_{12}PO_{40}$ in the same solvent.

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[6] Knoth, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 2211–2213.

[7] Anal. Calcd for $[(C_6H_{13})_4N]_2CH_3OMo_{12}PO_{39}$: C, 23.11; H, 4.23; N, 1.10. Found: C, 23.25; H, 4.13; N, 1.10. Calcd for $[(C_6H_{13})_4N]_2C_2H_5OMo_{12}PO_{39}$: 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 $[(CH_3)_3O]_3W_{12}PO_{40}$: C, 3.53; H, 0.89; N, 0.0. Found: C, 3.82; H, 0.97; N, 0.3. Calcd for $[(C_6H_{13})_4N]_2CH_3OW_{12}PO_{39}$: C, 16.34; H, 2.99; N, 0.78. Found: C, 16.57; H, 2.99; N, 0.72.

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