range studied (−80 to −120 °C) ethoxy always gave relatively less **2** than did *tert*-butoxy: the data could be represented by $1.6\,([\mathbf{1}]/[\mathbf{2}])_{t\text{-BuO}\cdot} \approx ([\mathbf{1}]/[\mathbf{2}])_{\text{EtO}\cdot}$.

The relative thermodynamic stabilities of **1** and **2** and the barrier to their interconversion could not be determined.[17] However, the fairly large positive temperature coefficients for a^{H_2} and a^{H_4} in both **1** and **2** suggests that there is an appreciable degree of torsional motion about the C_2–C_3 and C_3–C_4 bonds in both conformers. That is, additional positive spin will reach these hydrogens as the vinyl group to which they are attached is twisted out of the radical plane, because hyperconjugation to the partly occupied $C_3\ 2p_z$ orbital will improve. A similar phenomenon has been observed in the allyl radical[18] and, in fact, $\partial a^{\mathrm{H}_2}/\partial T$ for allyl is of similar magnitude to $\partial a^{\mathrm{H}_2}/\partial T$ and $\partial a^{\mathrm{H}_4}/\partial T$ for pentadienyl.

Additional experimental work and the results of INDO molecular orbital calculations on pentadienyl and on a variety of substituted pentadienyl radicals will be reported in a full paper.

Acknowledgment. We are grateful to Professor A. G. Davies for many helpful and stimulating discussions and for a gift of *trans*-bromo-2,4-pentadiene.

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$$\log [1]/[\mathbf{2}] = 0.97 \pm 0.12 - (0.71 \pm 0.07)/\theta$$

where $\theta = 2.303RT$ kcal/mol.
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Derivatives of Heteropolyanions. 1. Organic Derivatives of $W_{12}SiO_{40}^{4-}$, $W_{12}PO_{40}^{3-}$, and $Mo_{12}SiO_{40}^{4-}$

Sir:

This communication reports the facile preparation of organic derivatives of the Keggin-type (Figure 1) heteropolyanions $W_{12}SiO_{40}^{4-}$, $W_{12}PO_{40}^{3-}$, and $Mo_{12}SiO_{40}^{4-}$. The few previous reports[1,2] of organic derivatives of heteropolyanions were restricted to organoheteropolymolybdates such as $(RP)_2Mo_5O_{21}^{6-}$, $(RAs)_2Mo_6O_{26}^{6-}$, and $(RAs)_4Mo_{12}O_{46}^{4-}$ in which the structure permits bonding of an organic group to a surface heteroatom (phosphorus or arsenic) of the parent anion. No organic derivatives of Keggin-type anions, in which the heteroatom is buried in the middle of the structure, have been reported, nor have any heteropolyanion derivatives been described which contain a carbon–*metal* bond. Such species promise to be attractive models for solution studies of metal carbon bonds in a metal-oxide-like environment.

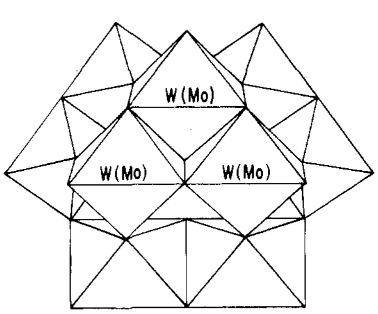

Figure 1. The Keggin structure, shared by $W_{12}SiO_{40}^{4-}$, $W_{12}PO_{40}^{3-}$, $Mo_{12}SiO_{40}^{4-}$, and many other heteropolyanions. It consists of four sets of three metal-centered octahedra symmetrically located around a central tetrahedrally coordinated heteroatom. This perspective does not show the heteroatom or all the octahedra but was chosen to permit better correlation with Figure 2 and 3. For a better depiction and description of the Keggin structure as a whole see ref 14.

Organometal and organometalloidal halides including $RSnCl_3$, $RSiCl_3$, $RGeCl_3$, $RAsCl_2$, and $C_5H_5TiCl_3$ were reacted with the "unsaturated" Keggin fragments $W_{11}SiO_{39}^{8-}$, $W_{11}PO_{39}^{7-}$, or $Mo_{11}SiO_{39}^{8-}$. The latter were prepared either in a prior separate step or in situ by standard techniques.[3] In each case heteropolyanions which contained the corresponding RM group were formed. These were precipitated as trimethylammonium or tetramethylammonium salts, recrystallized from water and characterized by elemental analysis and by infrared and NMR spectroscopy. NMR integration of the substituent protons relative to those of the alkylammonium cations served as a further check on composition.

Three structurally different classes of derivatives were encountered.

Class I. This includes 12-tungstosilicate and 12-molybdosilicate derivatives such as $CH_3SnW_{11}SiO_{39}^{5-}$ $C_6H_5SnW_{11}SiO_{39}^{5-}$, $C_2H_5SnMo_{11}SiO_{39}^{5-}$, $C_3H_5SnW_{11}SiO_{39}^{5-}$, $HOC(O)CH_2CH_2SnW_{11}SiO_{39}^{5-}$, $C_2H_5GeW_{11}SiO_{39}^{5-}$, and $C_6H_5AsW_{11}SiO_{39}^{4-}$. In addition, it includes both monosubstituted and disubstituted 12-tungstophosphate derivatives such as $CH_3SnW_{11}PO_{39}^{4-}$ and $C_6H_5SnW_{11}PO_{39}^{4-}$ (formed at pH 5) and $(CH_3Sn)_2W_{10}PO_{38}^{5-}$ and $(C_6H_5Sn)_2W_{10}PO_{38}^{5-}$ (formed at pH 7). In all of these derivatives the replacement of a tungsten- or molybdenum-oxygen moiety by an RM group is one for one.[4] The infrared spectra of the products are exceedingly similar to those of the corresponding salts of the parent heteropolyanions in the 1100–700-cm^{-1} region. This strongly suggests that the Keggin structure is retained, with the organic substituents at the unshared, terminal vertices of octahedrally coordinated tin, germanium, or arsenic atoms.

The ^{31}P NMR spectrum[5] of $C_6H_5SnW_{11}PO_{39}^{4-}$ exhibits only one resonance in D_2O, at −12.2 ppm from external H_3PO_4. The ^{31}P NMR spectrum of $(C_6H_5Sn)_2W_{10}PO_{38}^{5-}$ exhibits at least four resonances, at −8 to −9.2 ppm. All of these signals exhibit $^{2}J_{^{31}\mathrm{P}-^{117}\mathrm{Sn}^{119}\mathrm{Sn}}$ of 16–20 Hz. These spectra are consistent with the single isomer possible for $C_6H_5SnW_{11}PO_{39}^{4-}$ and the maximum five geometric isomers possible for $(C_6H_5Sn)_2W_{10}PO_{38}^{5-}$ based on the Keggin structure. If isomerization of the Keggin skeleton had occurred,[6] more isomers would be possible for both the mono- and disubstituted derivatives although, of course, all possible isomers might not be formed or be separately observable.

Class II. Reaction of $RSiCl_3$ (R = C_2H_5, C_6H_5, $NC(CH_2)_3$, C_3H_5) with $W_{11}SiO_{39}^{8-}$ in unbuffered aqueous solution gives

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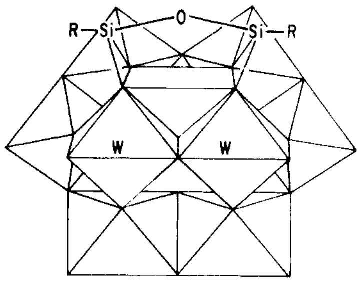

Figure 2. Proposed structure for $(RSi)_2W_{11}SiO_{40}{}^{4-}$

anions of the composition $(RSi)_2W_{11}SiO_{40}{}^{4-}$.[7] One WO^{4+} unit has been replaced by an $(RSi)_2O^{4+}$ group. The infrared spectra of these products are somewhat perturbed from that of $W_{12}SiO_{40}{}^{4-}$ in the 1100-700-cm^{-1} region. The most striking variation is the appearance of a strong band at ~1040 cm^{-1}, which can be assigned to the Si-O-Si group,[8] in the spectra of the derivatives. A structure is postulated (Figure 2) for these anions in which one tungsten-centered octahedral array of six oxygen atoms in $W_{12}SiO_{40}{}^{4-}$ is replaced by a similar array which is not metal centered. The oxygen atom located at the normally unshared vertex of this array is bridging the two tetrahedrally coordinated silicon atoms, giving rise to the 1040-cm^{-1} band. ^{1}H NMR suggests that the two R groups in these $(RSi)_2W_{11}SiO_{40}{}^{4-}$ anions are equivalent, which is consistent with the proposed structure.

Class III. The reaction of $CpTiCl_3$ with preformed $W_{11}SiO_{39}{}^{8-}$ or with $W_{12}PO_{40}{}^{3-}$ at pH 7 or with $Mo_{12}SiO_{40}{}^{4-}$ at pH 5 gives $CpTiW_{11}SiO_{39}{}^{5-}$, $CpTiW_{11}PO_{39}{}^{4-}$, or $CpTiMo_{11}SiO_{39}{}^{5-}$, respectively.[9,10] The ^{1}H NMR spectrum of the tungstates includes one sharp resonance for the cyclopentadienyl ring; two sharp unequal resonances were observed for $CpTiMo_{11}SiO_{39}{}^{5-}$. These varied in intensity from one recrystallization fraction to another and fractions were obtained which had only one such resonance. The analyses were correct for salts of $CpTiMo_{11}SiO_{39}{}^{5-}$ regardless of the ratio of these peaks, implying they were due to isomers and not to compositionally different species. The ^{31}P spectrum of $CpTiW_{11}PO_{39}{}^{4-}$ revealed two singlets in a 40:60 ratio, again suggesting the presence of two isomers despite the singlet observed in the proton nmr spectrum. The infrared spectra of $CpTiW_{11}SiO_{39}{}^{5-}$, $CpTiW_{11}PO_{39}{}^{4-}$, and $CpTiMo_{11}SiO_{39}{}^{5-}$ are exceedingly similar to those of the parent Keggin anions in the 700-1100-cm^{-1} region. The one exception is that the phosphate stretching band at 1080 cm^{-1}, which is a singlet in $W_{12}PO_{40}{}^{3-}$ is split into two bands in $CpTiW_{11}PO_{40}{}^{4-}$. This splitting is not observed in the spectra of the $RSnW_{11}PO_{39}{}^{4-}$ or $(RSn)_2W_{10}PO_{38}{}^{5-}$ derivatives.

It is proposed that the titanium in these anions is formally eight coordinate, as in Cp_2TiCl_2; three coordination sites are formally occupied by the π-bonded cyclopentadienyl ring while the remaining five coordination sites are bonded to the W_{11} or Mo_{11} Keggin fragment. Several possible explanations for the apparent "isomers" are being investigated. It is not believed that isomerization of the M_{11} portion of the Keggin fragment has occurred.

In related work, reaction of $C_6H_5SnCl_3$ with $W_{17}P_2O_{61}{}^{10-}$ [11] and with $W_{16}P_2O_{59}{}^{12-}$ [12] has given $C_6H_5SnW_{17}P_2O_{61}{}^{7-}$ and $(C_6H_5Sn)_2W_{16}P_2O_{60}{}^{8-}$, respectively. Studies on the chemistry described here and on related heteropolyanion derivatives are continuing and will be reported shortly.[13]

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(5) Acknowledgement is given to F. Davidson for determining the ^{31}P spectra.

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(9) Since this manscript was first submitted, Professor W. G. Klemperer has published a nonaqueous preparation of $CpTiW_{11}PO_{39}{}^{4-}$ [R. K. C. Ho and W. G. Klemperer, *J. Am. Chem. Soc.*, **100**, 6772 (1978)].

(10) Typical analyses: Calcd (found) for $[(CH_3)NH]_5CpTiW_{11}SiO_{39}\cdot H_2O$: C, 7.73 (7.78); H, 1.85 (1.81); N, 2.25 (2.26); Ti, 1.54 (1.39); Si, 0.90 (0.88); W, 65.11 (65.15); H_2O, 0.58 (0.53); CH_3:Cp proton ratio 9:1 (9.7:1). Calcd (found) for $[(CH_3)_3NH]_4KCpTiMo_{11}SiO_{39}\cdot H_2O$: C, 9.64 (10.03); H, 2.24 (2.25); N, 2.64 (2.62); K, 1.85 (1.83); Ti, 2.26 (1.83); H_2O, 0.85 (1.31); CH_3:Cp proton ratio, 7.2:1 (8:1).

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Enhancement of Nuclear Magnetic Resonance Signals by Polarization Transfer

Sir:

We report here a new method for enhancing the intensity of NMR signals from nuclei of low magnetogyric ratio. The method is independent of relaxation mechanisms, unlike the nuclear Overhauser effect,[1] and hence is likely to be particularly useful for nuclei such as ^{15}N and ^{29}Si which have negative magnetogyric ratios. The enhancement arises from the transfer of nuclear spin polarization from the *S* spins (usually protons) with large Boltzmann population differences, to the nuclear species under investigation, the *I* spins. It provides an alternative to rotating frame cross-polarization experiments,[2,3] which have recently been used on liquid-phase systems.[4]

The pulse sequence for the proposed experiment can be written

$$90°_S(X) - \tau - 180°_S(X),$$
$$180°_I - \tau - 90°_S(Y),\ 90°_I - \text{acquisition}$$

where the transmitter pulses applied to the *S* spins can be phase shifted so that the B_1 field is directed along either the *X* or *Y* axes of the appropriate rotating reference frame. This pulse sequence is closely related to one used in heteronuclear two-dimensional Fourier transform spectroscopy[5-8] but relies on the excitation of spin echoes and employs a fixed delay τ, equal to $1/(4J_{IS})$ s. For a simple system of two spins *I* and *S*, the components of *S* magnetization M(α) and M(β) corresponding to the two *I* spin states can be represented by the vectors α and β (Figure 1). The first two pulses excite a spin echo for the *S*

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