Table I. Average Molybdenum-Oxygen Distances for the α-$Mo_8O_{26}^{4-}$ ion in α-$[(n\text{-}C_3H_7)(C_6H_5)_3P]_4Mo_8O_{26}\cdot CH_3CN\cdot H_2O$

Type[a]	Distance,[b] Å
Mo_I-O_A	1.696 (3, 2, 3)
Mo_I-O_D	1.904 (3, 4, 9)
Mo_I-O_C	2.425 (3, 19, 56)
Mo_{II}-O_C	1.783 (3, 3, 5)
Mo_{II}-O_B	1.708 (3)

[a] See Figure 1a for labeling scheme. [b] The first number in parentheses following an average value is the root mean squared value of the estimated standard deviation for an individual datum. The second and third numbers, when given, are the mean and maximum deviations from the averaged value, respectively.

formula $(MoO_4^{2-})_2(Mo_6O_{18})$ which characterizes the weak interactions between the two MoO_4^{2-} ions and a ring of six distorted MoO_4 tetrahedra sharing corners.[9] This representation is also in accord with the existence of stable rings $(MoO_3)_n$, $n = 3$, 4, and 5, studied in the vapor phase by Berkowitz et al.

The simple relationship between kinetic lability and low bond order established here is consistent with previous exchange studies[12] and may be extended in an attempt to predict the kinetic behavior of other polyoxomolybdates. Several heteropolyanions may be viewed as structurally related to the α-$Mo_8O_{26}^{4-}$ ion and represented as $(AsO_4^{3-})_2(Mo_6O_{18})$,[13] $(C_6H_5AsO_3^{2-})_2(Mo_6O_{18})$,[13] $(PO_4^{3-})_2(Mo_5O_{15})$,[14] $(CH_3PO_3^{2-})_2(Mo_5O_{15})$,[15] and $((CH_3)_2AsO_2^-)(OH^-)$-(Mo_4O_{12}),[16] which in turn implies potential lability with respect to dissociation of AsO_4^{3-}, $C_6H_5AsO_3^{2-}$, PO_4^{3-}, $CH_3PO_3^{2-}$, and $(CH_3)_2AsO_2^-$, respectively. One may speculate further into the more general case where a large polyoxomolybdate cluster may be dissected into smaller clusters by breaking only weak bonds. For example, β-$Mo_8O_{26}^{4-}$ may be accurately represented by $((O^{2-})(Mo_4O_{12})_2$ since the β-$Mo_8O_{26}^{4-}$ cluster can be dissected into two $(O^{2-})(Mo_4O_{12})$ subunits by breaking only bonds whose lengths exceed 2.22 Å[17] and hence have bond orders less than 0.2.[6] This fact points toward a mechanistic pathway for the reaction of $((O^{2-})$-$(Mo_4O_{12})_2$ with $(CH_3)_2AsO_2H$ to form the $((CH_3)_2AsO_2^-)$-$(OH^-)(Mo_4O_{12})$ ion mentioned above. We are currently attempting to verify some of these speculations using dynamic ^{17}O NMR techniques.

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(5) Compound **3** crystallizes in the centrosymmetric monoclinic space group, $C2/c$-C_{2h}^6 (No. 15) with $a = 28.096$ (6) Å, $b = 14.313$ (2) Å, $c = 27.116$ (5) Å, $\beta = 121.32$ (1)°, and $Z = 4$ (formula units as given above). Diffracted intensities were measured on a spherical crystal having $\mu r = 0.28$ for 12 892 independent reflections having $2\theta_{MoK\bar{\alpha}} < 59°$ (the equivalent of 1.2 limiting Cu $K\bar{\alpha}$ spheres) on a computer-controlled four-circle Syntex $P\bar{1}$ autodiffractometer using Nb-filtered Mo $K\bar{\alpha}$ radiation and θ–2θ scans. The four molybdenum atoms of the asymmetric unit were located using direct methods (MULTAN) and the remaining atoms by standard difference Fourier techniques. The resulting structural parameters have been refined to convergence ($R = 0.031$ for 4611 independent reflections having $2\theta_{MoK\bar{\alpha}} < 43°$ (the equivalent of 0.50 limiting Cu $K\bar{\alpha}$ sphere) and $I > 3\theta(I)$) using unit-weighted full-matrix least-squares techniques with anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. Refinement is continuing with those reflections having $2\theta_{MoK\bar{\alpha}} < 59°$.
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Intercalate of Xenon Tetrafluoride with Graphite

Sir:

The compounds xenon hexafluoride[1] and xenon oxide tetrafluoride[2] have previously been shown to intercalate in graphite. While these compounds react directly with graphite, xenon difluoride reacts only in the presence of hydrogen fluoride to yield an intercalate of variable composition.[3] We have now found that xenon tetrafluoride also forms intercalates with graphite.

Weighed quantities of graphite and excess XeF_4 were allowed to react in preweighed Kel-F reaction vessels for periods of up to 3 weeks at room temperature. Reactions were generally complete after about 10 days, their slowness probably due to the low vapor pressure of XeF_4. The excess XeF_4 was then pumped off until the reactor attained constant weight or did not lose weight at rates exceeding 2 mg/h. Stoichiometries were calculated on the assumption that total weight gains were due to XeF_4. The latter were extrapolated back to zero pumping time.

The graphite used was either BDH powder or GTA grade Grafoil from Union Carbide Co. Considerable variations in stoichiometry were observed. The results with powder based on nine different reactions were $C_{28.3\pm2.4}XeF_4$, while those with Grafoil were $C_{41\pm1}XeF_4$ based on four experiments. In one case, however, a stoichiometry of $C_{17.8}XeF_4$ was obtained even after pumping for 27 h. Neither xenon nor carbon fluorides were liberated during the course of the reaction, and samples showed no visible changes. Fluorine analyses (Table I) correspond roughly to stoichiometries obtained from weight

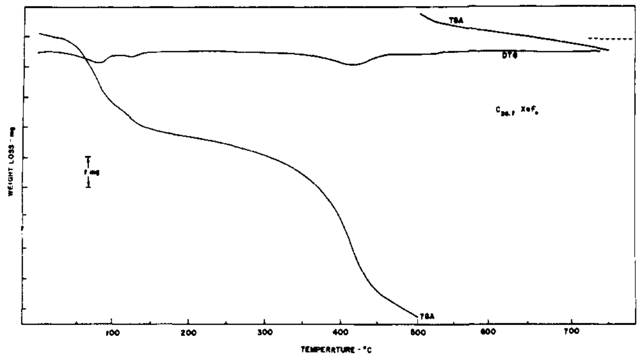

Figure 1. Thermogravimetric analysis of $C_{26.7}XeF_4$: sample weight, 25.7 mg; heating rate, 4°/min; atmosphere argon. Dashed line corresponds to calculated final weight after complete decomposition.

Table I. Analysis of C_nXeF_4

Material	mmol taken	mequiv of I titrated	mequiv of I per mmol of intercalate	% F found	% F calcd
$C_{40}XeF_4$	0.182	0.355	1.95		
$C_{24.3}XeF_4$	0.264	0.525	1.98	16.6	15.2
$C_{26.7}XeF_4$	0.241	0.534	2.21	16.6	14.5
$C_{32.5}XeF_4$	0.249	0.500	2.00	11.9	12.7

increases. Analyses of oxidizing power of the intercalates showed only 2 equiv of iodine liberated per mole of intercalate (Table I). This indicates that the XeF_4 is intercalated in the form of several species, some bound more tenaciously to the graphite than others. Indeed, preliminary wide line ^{19}F nuclear magnetic resonance spectra reveal the presence of both XeF_4 species (a doublet-singlet centered at +29 ppm with respect to $CFCl_3$ with doublet separation (3600 ± 320 Hz) and XeF_2 species (a singlet centered at +148 ppm) possessing derivative extremum line widths of 0.1 to 0.15 G).[4] Consideration of integrated absorption mode peak heights leads to a ratio of $F(XeF_2)/F(XeF_4)$ of 2.3 to 3.0. No proton resonance could be observed.

X-ray patterns of the intercalates obtained with copper radiation showed the complete absence of the original strong graphite line at $d = 3.35$ Å and the appearance of a new pattern containing very broad, diffuse lines at approximately 3.80 and 3.24 Å for $C_{28}XeF_4$ and at 3.65 and 3.28 Å for $C_{40}XeF_4$. If one were to assume the 3.8 Å diffraction line to be [003] reflection of a second stage compound of $I_c = 11.4$ Å and the 3.65 Å line to be the [004] reflection of a third stage compound of $I_c = 14.6$ Å, as is the case in a number of graphite acid salts,[5] one would predict the ratio of carbon atoms to xenon atoms in a single layer to be 13-14/1, a result consistent with the passage of second stage $C_{28}XeF_4$ to third stage $C_{40}XeF_4$.

Thermogravimetric analyses were run on a Mettler thermoanalyzer (Figure 1). The sample begins to lose weight immediately, because $C_{26}XeF_4$ is unstable at room temperature. The first weight loss step is complete at around 150 °C and corresponds to conversion to a higher stage compound of stoichiometry $C_{40}XeF_4$, thus confirming the preparative results with Grafoil. The third stage compound decomposes rapidly above 300 °C, and decomposition is complete above 600 °C. No xenon fluorides were liberated upon heating, xenon gas and carbon tetrafluoride being the only gases detected. After decomposition, the residue again shows the characteristic graphite line at 3.35 Å.

The graphite-xenon tetrafluoride intercalate is easily handled outside the vacuum line, although part of the intercalated fluoride is slowly hydrolyzed, releasing HF. The residue is neither shock-sensitive nor exhibits appreciable oxidizing power.

Preliminary investigations show that the intercalate may also be useful as a moderate fluorinating agent in organic chemistry. Experiments with aromatic systems gave the following results: With benzene, the products were monofluorobenzene (26%), *p*-difluorobenzene (11%), and starting material (63%). Phenanthrene[6] yielded mainly 9-fluorophenanthrene (22%) and 9,9,10-trifluoro-9,10-dihydrophenanthrene (19%). As in the case of XeF_2[7] fluorination of benzene proceeds only in the presence of HF catalyst.

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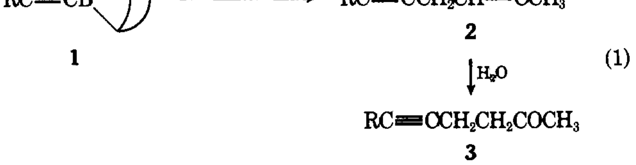
Conjugate Addition of *B*-1-Alkynyl-9-borabicyclo[3.3.1]nonanes to α,β-Unsaturated Ketones. A Convenient Synthesis of γ,δ-Acetylenic Ketones

Sir:

B-1-Alkynyl-9-borabicyclo[3.3.1]nonanes (*B*-1-alkynyl-9-BBN) (**1**), readily prepared by the reaction of boron trifluoride diethyl etherate with the corresponding lithium methyl alkynyldialkylborinate,[1] undergo a smooth 1,4-addition in pentane at room temperature to methyl vinyl ketone (MVK) and related ketones capable of adopting a cisoid conformation. Hydrolysis of the initially formed enol borinate intermediates (**2**) provide the corresponding 4-alkynyl-2-butanones (**3**) in high yields (eq 1).



The use of alkynyl copper reagents to effect the 1,4-addition of an alkynyl group to an α,β-unsaturated ketone is precluded by the tenacity with which copper binds alkynyl ligands.[2] One possible solution to this difficulty is the temporary transformation of the acetylene to a vinylstannane derivative. Thus, Corey has reported that the cuprate derived from *trans*-1,2-bis(tri-*n*-butylstannyl)ethylene reacts as a nucleophilic ethynyl group equivalent in the conjugate addition to α,β-unsaturated ketones.[3] Unfortunately, the generality of this reaction has not