coupling reaction we have developed for this synthesis represents a highly useful chemoselective method for preparing hitherto inaccessible α-C-homologated piperazinediones and, potentially, other α-amino acid derivatives.[9] The methodology described herein is *uniquely* adaptable to the preparation of many structurally diverse bicyclomycin analogues that cannot be prepared by modification of the abundantly available natural product nor from any of the other published[5,6] synthetic efforts. Finally, we have found that the p-methoxybenzyl groups can be cleanly and *reliably* removed from any of these bicyclic structures[17] (i.e., **2** (R = CH_2Ph-p-OCH_3), **8b**, **9b**, and **10b**) to afford the hydrophilic "free" amides. Biological and mechanistic studies utilizing this chemistry shall be reported in due course from these laboratories.

Acknowledgment. We gratefully acknowledge the National Institutes of Health Grant RO1AIGM 18957 for financial support of this work. We thank Fujisawa Pharmaceutical Co., Ltd., Japan, for the generous gift of natural bicyclomycin used for comparison. NMR measurements at 360 MHz were obtained at the Colorado State University Regional NMR Center, funded by the National Science Foundation Grant CHE 78-18581.

Supplementary Material Available: Complete spectroscopic and analytical data for all new compounds (12 pages). Ordering information is given on any current masthead page.

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(17) Preliminary antimicrobial assays of totally synthetic (±)-bicyclomycin against *E. coli 94* and *Klebsiella pneumoniae 369* show that the racemic material exhibits half the activity of the natural compound; numerous N-deprotected bicyclic analogues have been evaluated for antimicrobial activity: Williams, R. M.; Armstrong, R. W.; Dung, J.-S., unpublished results. We thank Drs. Hans Maag and David Pruess of Hoffman La-Roche, Inc., for performing the assay.

Fast Atom Bombardment Mass Spectroscopy (FABMS) of Polyoxoanions

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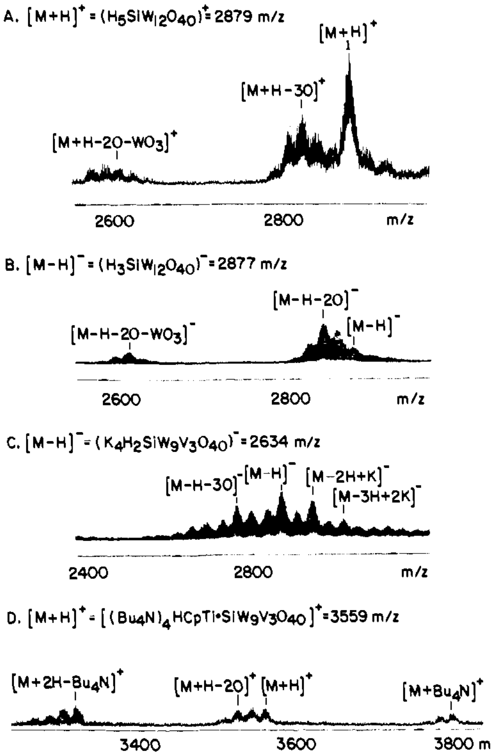

Figure 1. (A) Positive-ion spectrum of $H_4SiW_{12}O_{40}$. (B) Negative-ion spectrum of $H_4SiW_{12}O_{40}$. Note that molecular ion and the loss of O and WO_3 are observed in both spectra A and B. Not shown are the sequential losses of WO_3 in both spectra and much smaller peaks above 3000 *m/z* due to the attachment of WO_3 fragments or of thioglycerol in the negative-ion spectrum. (C) Negative-ion spectrum of $K_4H_3SiW_9V_3O_{40}$. Extensive exchange of cations (cationization) is observed. Sequential loss of O and WO_3 (not shown) is also observed. (D) Positive-ion spectrum of $(Bu_4N)_4CpTi\cdot SiW_9V_3O_{40}$. Only peaks corresponding to cation exchange and loss of O are observed. The sequential loss of WO_3 is not observed.

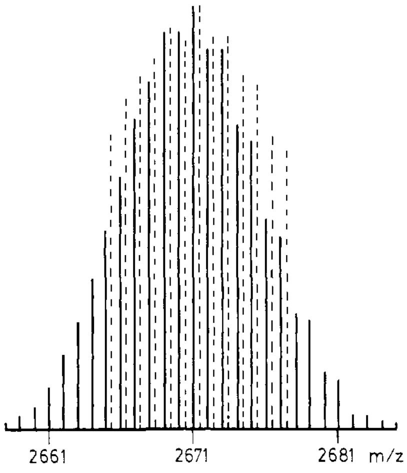

Figure 2. Calculated (solid line) vs. observed (dotted line) isotopic distribution patterns for the $[M-2H+K]^-$ (= $K_5HSiW_9V_3O_{40}^-$) ion at *m/z* 2671. Only the centermost lines of the two patterns are directly comparable due to the presence of overlapping patterns in the observed FABMS for the $K_5HSiW_9V_3O_{40}^-$ ion.

Polyoxoanion chemistry[3] is a field poised for a rapid development with a wide range of potential applications.[3a,c,4-7] Hampering this development, however, are well-known difficulties in obtaining accurate analytical[8] and molecular weight data,[3a] problems that

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(1) University of Oregon.

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(4) A large number of examples of polyoxoanions in catalysis, largely heterogeneous catalysis, exist. A few references in acid catalysis,[4a-d] oxidation catalysis,[4e-h] homogeneous Wacker-type[4i,j] chemistry, and recent reviews[4k] are provided below. (a) Onoue, Y.; Mizutani, Y.; Akiyama, S.; Izumi, Y. CHEMTECH **1978**, 432 (b) Ono, Y.; Baba, T.; Sakai, J.; Keii, T. *J. Chem. Soc., Chem. Commun.* **1981**, 400. Baba, T.; Sakai, J.; Ono, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2657. (c) Okuhara, T.; Kasai, A.; Hayakawa, N.; Yoneda, Y.; Misono, M. *J. Catal.* **1983**, *83*, 121. (d) Hayashi, H.; Moffat, J. B. *J. Catal.* **1983**, *83*, 192; *Ibid.* **1983**, *81*, 61. (e) Konishi, Y.; Sakata, K.; Misono, M.; Yoneda, Y. *J. Catal.* **1982**, *77*, 169. (f) Ai, M. *J. Catal.* **1981**, *71*, 88. (g) Akimoto, M.; Tsuchida, Y.; Echigoya, E. *Chem. Lett.* **1980**, 1205. (h) Akimoto, M.; Tsuchida, Y.; Sato, K.; Echigoya, E. *J. Catal.* **1981**, *72*, 83. (i) Ogawa, H.; Fujinami, H.; Taya, K. *J. Chem. Soc., Chem. Commun.* **1981**, 1274. (j) Taraban'ko, V. E.; Kozhevenikov, I. V.; Matreev, K. I. *Kinet. Katal.* **1978**, *19*, 1160. (k) Kozhevnikov, I. V.; Matveev, K. I. *Appl. Catal.* **1983**, *5*, 135; *Russ. Chem. Rev. (Engl. Transl.)* **1982**, *51*, 1075.

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have led to a number of misformulated polyoxoanions.[8a] Our own work, aimed at developing heteropolyanions for use as soluble metal oxide analogues in catalysis,[6] has made us keenly aware of the need for a rapid and accurate method for determining the elemental compositions and molecular weights of polyoxoanions.

Herein we report the use of fast atom bombardment mass spectroscopy (FABMS)[9,10] to obtain the first mass spectra of nonvolatile, high molecular weight salts of polyoxoanion complexes such as $SiW_{12}O_{40}{}^{4-}$, $SiW_9V_3O_{40}{}^{7-}$, and the previously unreported organometallic-polyoxoanion complex $CpTiSiW_9V_3O_{40}{}^{4-}$.[6b] The success we have experienced suggests that FABMS constitutes a significant new development in the ability to characterize polyoxoanions and similar inorganic polyanions or -cations.

FABMS were obtained on samples of $H_4SiW_{12}O_{40}{\cdot}26H_2O$,[11a] $K_4H_3SiW_9V_3O_{40}{\cdot}3H_2O$,[6b,11b] and $(Bu_4N)_4CpTiSiW_9V_3O_{40}$[6b] in thioglycerol in both the negative and positive ion modes,[12] as shown in Figure 1. The parent or molecular ion peaks show an isotopic distribution which agrees with the calculated envelope, as shown in Figure 2.

Cation exchange processes are clearly observed in several of our FABMS spectra. For example, K^+ replacement of H^+ in negative-ion FABMS spectra of $K_4H_3SiW_9V_3O_{40}$ produces the progression shown in Figure 1C corresponding to $K_4H_2SiW_9V_3O_{40}{}^-$, $K_5HSiW_9V_3O_{40}{}^-$, and $K_6SiW_9V_3O_{40}{}^-$. Similarly, Bu_4N^+ exchange with H^+ in positive ion FABMS of $(Bu_4N)_4CpTiSiW_9V_3O_{40}$ produces the series shown in Figure 1D corresponding to $(Bu_4N)_3H_2CpTiSiW_9V_3O_{40}{}^+$, $(Bu_4N)_4HCpTiSiW_9V_3O_{40}{}^+$, and $(Bu_4N)_5CpTiSiW_9V_3O_{40}{}^+$. The latter FABMS spectrum is particularly significant, since it illustrates the ability of this technique to characterize the previously unknown $CpTiSiW_9V_3O_{40}{}^{4-}$, which we have synthesized as a discrete, soluble analogue of $CpTi^{3+}$ supported on metal oxide surfaces.[6b]

The fragmentation patterns are dominated by multiple loss of O (*m*/*z* 16), consistent with other mass spectral data[10c,13] and by multiple loss of WO_3 (*m*/*z* 232). The former is seen in all FABMS spectra, both positive and negative ion, which we have examined, whereas the latter has not been observed with Bu_4N^+ salts (i.e., Figure 1D). The observation of positive-ion FABMS is remarkable due to the high acidity of some of these ions, and the recent report that FABMS ion currents can reflect solution concentrations.[9h] It appears from the data in Figure 1 and from FABMS spectral data on other related complexes that optimal spectra are obtained for positive ions from Bu_4N^+ salts.

In summary, fast atom bombardment mass spectroscopy has provided the first mass spectra of high molecular weight, nonvolatile salts of polyoxoanion complexes. The results obtained suggest that FABMS constitutes a significant development in the ability to characterize polyoxoanions and similar inorganic materials.

Acknowledgment. Support at Oregon by NSF Grant CHE-8313459 and a Dreyfus Teacher–Scholar (1982–1987) and Alfred P. Sloan Foundation Fellowship (1982–1984) to R.G.F. and at Illinois by NSF CHE-8020006 to K.S.S. are gratefully acknowledged. FAB mass spectra were obtained in the mass spectroscopy facility of the School of Chemical Sciences, University of Illinois, supported in part by NIH GM-27029; the ZAB mass spectrometer was purchased in part by grants from the Division of Research Resources, NIH (RR01575), and from the NSF (PCM-8121494).

Registry No. $H_4SiW_{12}O_{40}$, 12027-38-2; $K_4H_3SiW_9V_3O_{40}$, 91523-04-5.

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Polar Transition State for the [1,5]-Sigmatropic Shift in Cyclopentadienes

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The model that we have developed[1] for analyzing substituent effects on thermal pericyclic reactions suggests that the transition state for the [1,5]-sigmatropic shift in cyclopentadienes should be π-isoconjugate[2] with bicyclo[3.1.0]hexatriene, which, being a lower homologue of azulene, should have a dipole moment with the negative end directed toward the five-membered ring (see structure at the top of Figure 2). In this communication we present data that support this idea. In addition we show that the same model provides a convenient way to rationalize and predict the regiochemistry of [1,5] migrations in substituted cyclopentadienes.

The parent[3] **1** and five-substituted[4] spiro[4.4]nona-1,3-dienes **2–6** were synthesized and subjected to thermal rearrangement. The products underwent facile [1,5]-hydrogen shifts, as antici-

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