2:1 ratio suggesting $D°(FeCo^+-Co) \sim D°(Co_2^+-Fe)$.

Dioxygen reacts rapidly with both $FeCo_2(CO)_5^+$ and $Co_3-(CO)_6^+$, resulting in carbonyl eliminations, reactions 24–26. These

$$FeCo_2(CO)_5^+ + O_2 \longrightarrow FeCo_2(CO)(O)_2^+ + 4CO \quad (24)$$

$$Co_3(CO)_6^+ + O_2 \longrightarrow \begin{cases} \xrightarrow{27\%} Co_3(CO)_3(O)_2^+ + 3CO \quad (25) \\ \\ \xrightarrow{73\%} Co_3(CO)_2(O)_2^+ + 4CO \quad (26) \end{cases}$$
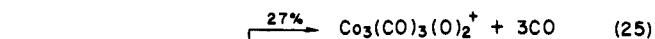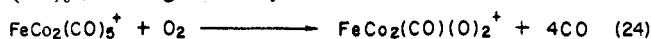
products react a second time with dioxygen to yield reactions 27–32. Both the $FeCo_3(CO)(O)_2^+$ and $Co_3(CO)_2(O)_2^+$ reactions are rapid ($k > 5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) whereas the $Co_3-(CO)_3(O)_2^+$ reaction is markedly slower ($k < 1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}). This may be attributed once again to the higher degree of coordination in the latter case.

$$FeCo_2(CO)(O)_2^+ + O_2 \longrightarrow \begin{cases} \xrightarrow{70\%} FeCo_2O_4^+ + CO \quad (27) \\ \\ \xrightarrow{30\%} FeCo_2O_3^+ + (CO_2) \quad (28) \end{cases}$$

$$Co_3(CO)_2(O)_2^+ + O_2 \longrightarrow \begin{cases} \xrightarrow{75\%} Co_3O_4^+ + 2CO \quad (29) \\ \\ \xrightarrow{25\%} Co_3O_3^+ + (CO + CO_2) \quad (30) \end{cases}$$

$$Co_3(CO)_3(O)_2^+ + O_2 \longrightarrow \begin{cases} \xrightarrow{30\%} Co_3O_4^+ + 3CO \quad (31) \\ \\ \xrightarrow{70\%} Co_3O_3^+ + (2CO + CO_2) \quad (32) \end{cases}$$
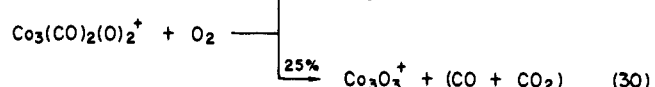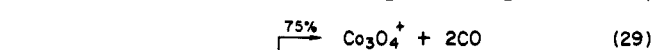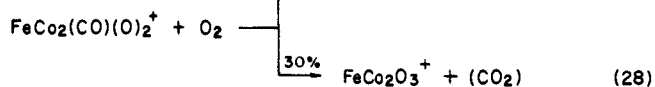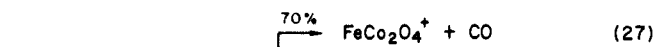
Both $FeCo_2O_3^+$ and $Co_3O_3^+$ are unreactive with dioxygen; however, the $M'M_2O_4^+$ species react according to eq 33. This

$$M'M_2O_4^+ + O_2 \rightarrow M'M_2O_3^+ + O_3 \quad (33)$$
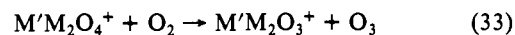
implies that $D°(M'M_2O_3^+-O) < D°(O_2-O) = 25.5$ kcal/mol.[34] This compares with $D°(M'M_2O_2^+-O) > 85$ kcal/mol from reaction 14.[34] The weakness of the $M'M_2O_3^+-O$ bond is surprising since Fe_3O_4 and Co_3O_4 are much more stable oxides than Fe_3O_3 and Co_3O_3.[48]

Collisional activation of $Co_3O_4^+$ yields predominantly elimination of an oxygen atom forming $Co_3O_3^+$ with a small amount of CoO_2 elimination also observed. Collisional activation of $FeCo_2O_4^+$ is similar with O elimination forming $FeCo_2O_3^+$ dominating with a small amount of CoO_2 and FeO_2 elimination also observed. In contrast the $M'M_2O_3^+$ ions do *not* undergo fragmentation upon collisional activation at 75 eV kinetic energy suggesting that they are very stable. These $M'M_2O_3^+$ ions may consist of a triangular array of metals bridged by three oxides similar to structure **2**.

Conclusions

The oxide chemistry of these dimeric and trimeric cluster ions is much richer than that for the corresponding monomeric transition-metal ions. This is due in large part to the very strong oxide bonds in these clusters relative to the monomeric species. Armentrout and co-workers observed similar behavior for reaction of Mn_2^+ with dioxygen.[21] Although these limited results increase our understanding of small transition-metal clusters, clearly additional experimental and detailed theoretical studies are needed before these clusters are well understood.

Silicon-29 NMR Structural Characterization of Two Novel Germanosilicate Cages in a Tetramethylammonium Germanosilicate Solution[†]

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Abstract: We have identified two novel germanium-substituted silicate cages in an aqueous tetramethylammonium germanosilicate solution by means of high-field (11.7 T) silicon-29 NMR spectroscopy, with ^{29}Si isotopic enrichment. Our results indicate that these anions exist in the form of a double four-membered ring (cubic octameric cage) and a double three-membered ring (prismatic hexameric cage), in which a single silicon site is replaced by germanium. Introduction of chemical shift nonequivalence by means of heteroatom incorporation leads to complex spin–spin splitting patterns, which may, however, be readily interpreted by means of two-dimensional homonuclear correlated spectroscopy (2D-COSY) or by spectral simulation. The ^2J couplings are 7.5 Hz in the double four-membered ring and 4.3 Hz in the double three-membered ring. A ^4J coupling of ~ 1.0 Hz is also deduced for the double three-membered ring. These results represent the first solution NMR observation of heteroatom incorporation into silicate cages and provide a novel means for investigating the structures and stabilities of such species.

The structures of the various species formed during the hydrolysis of silica or various silicates are of interest for a number of reasons, including the mechanism(s) of the sol–gel process (used in glass manufacture), the nature of the species present in zeolite precursor solutions, and the nature of the species formed during the weathering of minerals.[1–3] We are interested in all three topics, and in this article we describe a novel nuclear magnetic resonance (NMR) spectroscopic approach to the determination

(1) R. K. Iler, "The Chemistry of Silica", Wiley-Interscience, New York, 1969.
(2) J. G. Vail, "Soluble Silicates: Their Properties and Usage", Vol. 2, Reinhold, New York, 1952.
(3) W. M. Meier In "Molecular Sieves", Society for Chemical Industry, London, 1968, p 100.

^{29}Si NMR of Silicate Solutions

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of the structures of the various silicate anions that may exist in such solutions, in addition to providing a novel approach to the topic of isomorphous replacement[4] in zeolites and their precursors. In particular, we focus on methods for detecting the symmetric double four- and double three-membered ring silicate ions, and their germanium-atom substituted derivatives, in aqueous solutions.

Crystalline tetramethylammonium silicate has long been known to adopt the cubic, double four-membered ring structure in the solid-state, X-ray diffraction studies[5] revealing a complex of the formula $[(CH_3)_4N]_8[Si_8O_{20}]\cdot\sim69H_2O$. More recently, several investigations have indicated[6-8] that the double four-membered ring structure may be retained in aqueous solution, and indeed it is held to be the primary constituent of aqueous tetramethylammonium silicate solutions. Results from ^{29}Si NMR studies of isotopically enriched silicate solutions imply[8,9] that under many conditions the double three-membered ring, or prismatic hexameric cage, is also stable in solution. However, unambigous evidence for the existence of silicate cages in alkaline solution is still lacking. For example, established methods of chemical analysis, particularly trimethylsilylation followed by chromatographic separation, involve the chemical modification of the solution by acidification. Although it was at first thought that the modified solutions accurately reflected the distribution and structure of the anions originally present, it is now becoming clear[10] that silicate anions may undergo rapid and substantial rearrangement during acidification, especially in concentrated solutions, so that the silicate species observed in acidified solutions are not necessarily those that existed in the parent solution. Results from NMR spectroscopy, which does not chemically interfere with the polysilicate equilibrium, are, unfortunately, often no less ambiguous. Because silicon-29 is a "rare spin", each chemically distinguishable silicon site yields a single resonance, making assignment of individual signals to specific structures largely a matter of speculation. Isotopically enriched samples have been used[8,9] to overcome this problem for molecules containing more than one chemical environment, but in regular silicate cages all the silicon sites are chemically equivalent, with the consequence that even isotopically enriched silicate cages exhibit a single resonance, precluding any unambiguous structural assignment.

Since heteroatom-substituted silicate structures are common in many minerals and zeolites, experiments aimed at lifting the chemical degeneracy of the silicon sites in silicate cages by replacing silicon with another element have been undertaken in this work. Our initial studies have focussed on germanium substitutions because germanium closely resembles silicon in many of its chemical properties, and it is well established that germanium can partially or completely replace silicon in zeolites.[11] Furthermore, germanium-68 is commonly used as a radio-tracer for investigating silicon metabolic pathways in plants and animals.[12]

Experimental Aspects

Silicate Chemistry. Samples containing SiO_2 at natural abundance of ^{29}Si were prepared by dissolving silica (prepared from the hydrolysis of doubly-distilled $SiCl_4$) in a tetramethylammonium hydroxide solution (tetramethylammonium hydroxide pentahydrate, 97%, Aldrich Chemicals) and heating to boiling until dissolution was complete. Care was taken to exclude atmospheric carbon dioxide, samples and reagents being stored under nitrogen whenever possible.

(4) R. M. Barrer, "Hydrothermal Chemistry of Zeolites", Academic Press, London, 1982.

(5) D. Hoebbel and W. Wieker, Z. Anorg. Allg. Chem., **384**, 43 (1971).

(6) R. K. Harris and C. T. G. Knight, J. Mol. Struct., **78**, 273 (1982).

(7) D. Hoebbel, G. Garzo, G. Engelhardt, and A. Vargha, Z. Anorg. Allg. Chem., **494**, 31 (1982).

(8) R. K. Harris, C. T. G. Knight, and W. E. Hull, J. Am. Chem. Soc., **103**, 1577 (1981).

(9) R. K. Harris and C. T. G. Knight, J. Chem. Soc., Faraday Trans. 2, **79**, 1525, 1539 (1983).

(10) L. S. Dent-Glasser and E. E. Lachowski, J. Chem. Soc., Dalton Trans., 393, (1980).

(11) R. M. Barrer, J. W. Baynham, F. W. Bultitude, and W. M. Meier, J. Chem. Soc., 195 (1959); L. Lerot, G. Poncelet, and J. J. Fripiat, Mat. Res. Bull., **9**, 979 (1974).

(12) F. Azam and B. E. Volcani In "Silicon and Siliceous Structures in Biological Systems", T. L. Simpson and B. E. Volcani, Eds., Springer-Verlag, New York, 1981.
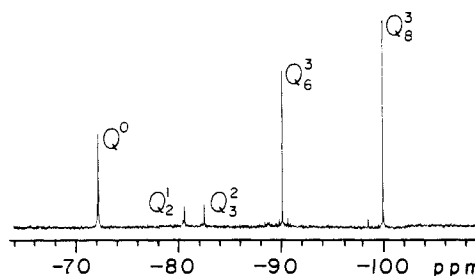

Figure 1. 99.32-MHz (11.7 T) ^{29}Si NMR spectrum of a freshly prepared 1.1 M tetramethylammonium silicate solution (N:Si = 2:1), at 25 °C. The spectrum was recorded with a 5000-Hz sweep width, 1179 30-μs (90°) pulses, and a recycle time of 20 s. Chemical shifts are referenced to the ^{29}Si signal of external Me$_4$Si, high-frequency signals being denoted as positive. Methanol-d_4 (20% v/v) was added to the silicate solution to provide a ^{2}H lock signal.

Because paramagnetic contamination of silicate solutions results from prolonged contact with glass surfaces and has a deleterious effect upon the ^{29}Si NMR spectra, samples and reagents were mixed, heated, and stored in polyethylene containers. Glassware used in sample preparation was soaked in an alkaline silicate solution, and then in an EDTA solution, for several days prior to use. Germanium dioxide (Aldrich Gold Label, 99.999%) was added directly to the samples during heating.

Isotopically enriched silicates were prepared in an identical manner, using SiO_2 enriched to the 95.28% level in ^{29}Si, obtained from Oak Ridge National Laboratories. Dissolution of the enriched material required prolonged sample heating and was never fully accomplished. Consequently, quoted sample concentrations and ratios must be taken as nominal values, although the discrepancy is estimated at 10% or less, in all cases. Samples were generally prepared and centrifuged immediately before use, 20% v/v methanol-d_4 being added to provide an internal ^{2}H-lock signal.

Nuclear Magnetic Resonance Spectroscopy. All ^{29}Si NMR spectra were recorded on a "homebuilt" 11.7-T NMR spectrometer, which consists of an 11.7-T 52-mm bore superconducting solenoid (Oxford Instruments, Osney Mead, U.K.), a Nicolet (Madison, WI) Model 1280 data aquisition system, an Amplifier Research (Souderton, PA) Model 200L amplifier for final radio frequency pulse generation, and a 10-mm multinuclear probe (Cryomagnet Systems, Indianapolis, IN). A homebuilt interface between the Nicolet computer and radio frequency gating sections was used in order to make most efficient use of the Nicolet software commands (for 2D NMR experiments). Spectra were simulated by using the Nicolet program NMRSIM. Chemical shifts are reported with respect to an external standard of Me$_4$Si, using the sign convention of high-frequency (low field, paramagnetic, deshielded) shifts being positive.

Results and Discussion

We show in Figure 1 the 99.32-MHz (11.7 T) ^{29}Si NMR spectrum of a freshly prepared 1.1 M tetramethylammonium silicate solution with N:Si of 2. In agreement with previous work,[6] the strong peak at $\delta = -100.0$ ppm is assigned to the double four-membered ring, and the signal at $\delta = -90.2$ ppm is attributed to the double three-membered ring. The signals at $\delta = -72.2$, -80.6, and -82.6 ppm are assigned to the monomer, dimer, and cyclic trimer, respectively. (The terms n-mer and n-membered ring refer to the condensed species containing n-SiO groups, plus the appropriate number of additional oxygen atoms. The extent of protonation of the species is ignored.) Addition of GeO$_2$ to this solution causes several new ^{29}Si NMR peaks to appear. For the double four-membered ring, replacement of a single silicon site by germanium will yield a molecule containing three distinct silicon environments:

O = Si,   ● = Ge

I
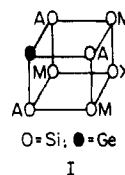
The resulting ^{29}Si NMR spectrum is expected to show three signals, having intensity ratios of 3:3:1. Figure 2A shows an expansion of the spectrum shown in Figure 1 in the region ascribed to the cubic octamer. Figure 2B shows the same region of a similar
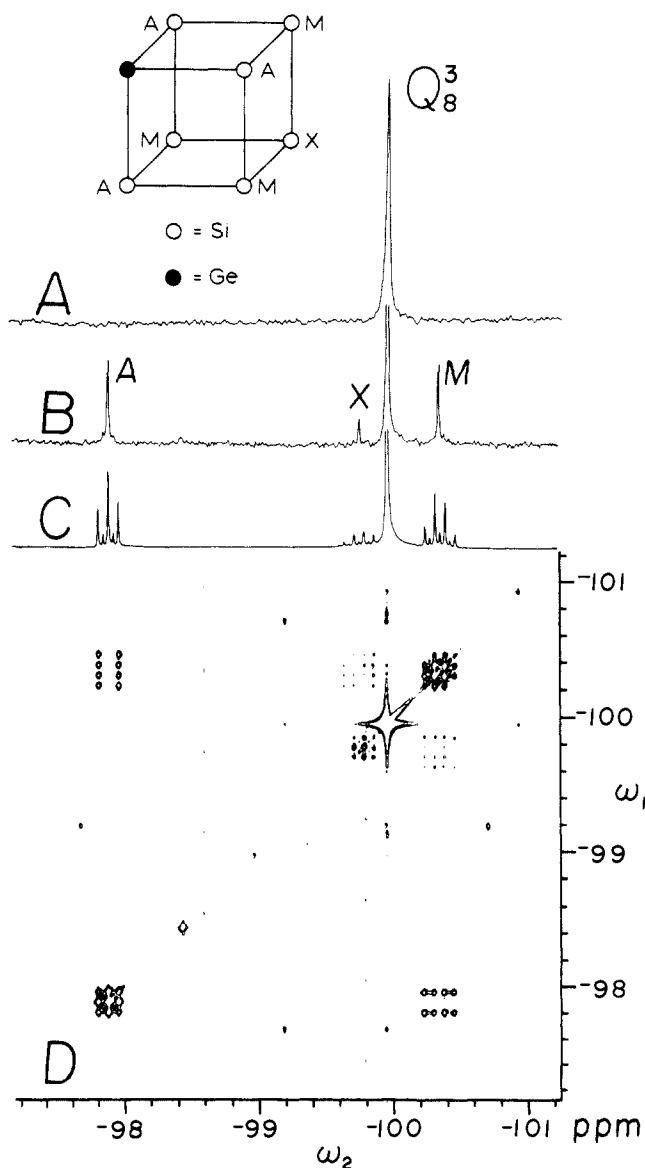
Figure 2. 99.32-MHz (11.7 T) ^{29}Si NMR spectra of tetramethyl-ammonium silicate and germanosilicate solutions, at 25 °C. (A) Expansion of the spectrum shown in Figure 1, the single peak is ascribed to the cubic octamer. (B) 1 M SiO$_2$, 2:1 (N:Si) tetramethylammonium germanosilicate solution, 0.25 M in GeO$_2$. The spectrum was recorded by using a 20 000-Hz sweep width, 8000 10-μs (23°) pulses, and a recycle time of 5 s. (C) Solution basically as in B but prepared with SiO$_2$ enriched to the 95.3% level in ^{29}Si. The spectrum was recorded by using a sweep width of 5000 Hz, 592 37-μs (90°) pulses, and a recycle time of 10 s. (D) ^{29}Si 2D homonuclear correlation (COSY) spectrum obtained with a four-step phase-cycling and *n*-type peak-selection routine. The spectral width in each dimension was 400 Hz, obtained from 512 t_1-points, using 16 transients for each point, and a recycle time of 5 s.

solution, to which GeO$_2$ (0.25 M) has been added. Three new peaks are apparent, and their relative intensities are consistent with structure I. This is confirmed in Figure 2C, which is the ^{29}Si NMR spectrum of the same germanosilicate solution prepared, however, using SiO$_2$ isotopically enriched in ^{29}Si to 95.3%. Under these conditions, $^2J_{Si-O-Si}$ spin–spin couplings split signals from chemically distinguishable sites into characteristic spin-multiplets. Signals from molecules in which all sites are chemically equivalent remain unsplit.

For an enrichment of 100% in ^{29}Si, and assuming 4-bond J coupling to be negligible, structure I will yield an [AM]$_3$X splitting pattern. In principle, the spectrum will be second order although computer simulation suggests a deceptively simple appearance, with site "A" giving a triplet due to equal coupling to both "M" sites. Similarly, site "X" will show a quartet pattern, as a result
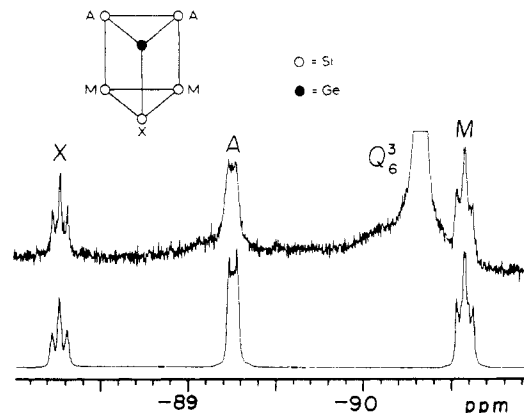

Figure 3. 99.32-MHz (11.7 T) ^{29}Si NMR spectrum of the solution described in Figure 2C, in the region of the double three-membered ring resonances, together with its spectral simulation. The spectrum was recorded by using a 5000-Hz sweep width, 2000 15-μs (34°) pulses, and a recycle time of 3 s.

of equal coupling to three "M" sites. Site "M" will yield a quartet only if the magnitude of the coupling constant between site "A" and site "M" is equal to that between sites "M" and "X", otherwise a doublet of triplets is expected. Figure 2C exhibits the splitting patterns predicted for structure I and strongly suggests that the coupling constant is unaffected by germanium substitution, presumably because the cage geometry is essentially unchanged. The small peaks occurring between the binomial multiplets arise from the ~4.7% of sites occupied by magnetically inactive ^{28}Si(I = 0) and ^{30}Si(I = 0).

An [AM]$_3$X spin system of this sort provides an ideal candidate for a ^{29}Si NMR two-dimensional homonuclear correlation (COSY) experiment,[13] the results of which are illustrated in Figure 2D. It is clear that site "M" is coupled to both sites "A" and "X", which are not mutually coupled. This experiment is taken as providing unequivocal evidence in support of structure I and also supports the idea that the single peak of δ = –100.0 ppm does indeed arise from the cubic octamer, confirming the widely held view that this anion is particularly stable across a wide range of solution conditions.

The double three-membered ring has also been suggested as a component of tetralkylammonium silicate solutions, and indeed it has been evoked as the major constituent of tetraethyl-[6] and tetrapropylammonium[6,14] silicate solutions. However, the existence of three-membered rings in silicate solutions has traditionally been viewed with some scepticism,[15] in view of the ring strain expected.[16] In this anion, replacement of a silicon site yields an [AM]$_2$X spin system for the isotopically enriched situation (structure II). A

II
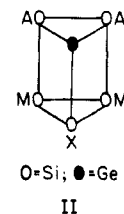
second-order splitting pattern is expected, due to the chemical equivalence of the two "A" sites and the chemical equivalence of the two "M" sites. Figure 3 shows a portion of the ^{29}Si NMR spectrum of a 1 M 95.3% ^{29}Si-enriched tetramethylammonium silicate solution, 0.25 M in GeO$_2$. The singlet at δ = –90.3 ppm is that ascribed in Figure 1 to the double three-membered ring. On the basis of a computer simulation (lower spectrum), the three multiplets observed are assigned to the three sites of structure II.
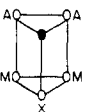
(13) A. Bax, "Two-Dimensional Nuclear Magnetic Resonance in Liquids", Reidel, Dordrecht, 1982.

(14) K. J. Cavell, A. F. Masters, and K. G. Wilshier, *Zeolites* **2**, 244 (1982).

(15) See, for example, ref 1, p 216.

(16) M. O'Keefe and B. G. Hyde, *Acta Crystallogr.*, **B34**, 27 (1978).

Table I. Silicon-29 Isotropic Chemical Shifts and Spin–Spin Coupling Constants for Singly Substituted Double Three- and Double Four-Membered Germanosilicate Rings[a]

species		δ_i (ppm)[b]	^2J (Hz)	^4J (Hz)
	A	−97.86$_7$	7.5	0.0
	M	−100.32$_5$	7.5	0.0
	X	−99.73$_6$	7.5	0.0
	A	−89.26$_3$	4.3	1.0
	M	−90.57$_8$	4.3	1.0
	X	−88.27$_1$	4.3	1.0

[a] Data from an isotopically enriched, 2:1 (N:Si) tetramethylammonium germanosilicate solution, 1 M in Si and 0.25 M in Ge (Figures 2 and 3), at 25 °C. [b] In parts per million from an external standard of tetramethylsilane.

In this case, computer simulation reveals that four bond couplings cannot be neglected, and a value of ^4J of ~1.0 Hz gives the best fit. (We must emphasize that the accuracy of this measurement is low, due to the relatively poor resolution and signal to noise of the experimental spectrum.) The good agreement between the simulated and observed spectra nevertheless provides particularly convincing evidence in support of the existence of the double three-membered ring in solution and confirms the earlier assignment[6] of the peak at δ = −90.3 ppm to this structure. Table I compiles the chemical shifts and coupling constants observed in the spectra of the enriched tetramethylammonium germanosilicate solutions. Additional support for both structures is provided by comparing the coupling constants deduced in this work with those of similar structures reported elsewhere.[9]

Concluding Remarks

The results we have presented above are of interest for two reasons. First, they demonstrate that soluble heteroatom-substituted silicate cages may be prepared, and their ^{29}Si NMR solution spectra may be resolved and assigned. Further substitutions are also possible (e.g., double Ge substitution) and will be discussed elsewhere. Second, these results enable us to more definitely assign the peaks at −100.0 and −90.2 ppm, in solution, to the unsubstituted double four- and double three-membered cage structures. We thus believe that the combined used of ^{29}Si enrichment and heteroatom substitution may be a useful technique with which to assign novel silicate species in solution, which should be of relevance to structural studies of the sol–gel process, zeolite synthesis, and the speciation of silicate anions during various weathering processes.

Mechanism of the Reaction of a Solvated Rhenium Acyl Complex with Neutral Transition-Metal Hydrides. Relative Nucleophilicity of Such Hydrides

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Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523. Received May 20, 1985

Abstract: The forward rate constant k_1 for EtRe(CO)$_5$ ⇌ EtC(O)(CH$_3$CN)Re(CO)$_4$, as determined by the rate of establishment of the equilibrium in CH$_3$CN, agrees with the observed first-order rate constant for the reaction of EtRe(CO)$_5$ with an excess of any of several transition-metal hydrides. The rate-determining step in the reaction of EtRe(CO)$_5$ with these hydrides is therefore the formation of a rhenium propionyl complex. The formation of EtCHO from EtC(O)(CH$_3$CN)Re(CO)$_4$ and HRe(CO)$_5$ (which occurs at much lower temperatures than the formation of EtCHO from EtRe(CO)$_5$ and HRe(CO)$_5$) is first order in EtC(O)(CH$_3$CN)Re(CO)$_4$ and first order in HRe(CO)$_5$. The second-order rate constants for the reaction of a series of transition-metal hydrides with EtC(O)(CH$_3$CN)Re(CO)$_4$ have been measured; the order of these rate constants is substantially the reverse of the order of kinetic acidities of these hydrides, implying that the hydrides react as nucleophiles with EtC(O)(CH$_3$CN)Re(CO)$_4$. The rate of dissociation of coordinated acetonitrile from EtC(O)(CH$_3$CN)Re(CO)$_4$ has been measured; the results suggest a dissociative mechanism for the reaction of EtC(O)(CH$_3$CN)Re(CO)$_4$ with transition-metal hydrides. EtC(O)Re(CO)$_5$ only reacts with HRe(CO)$_5$ after carbonyl ligand dissociation, implying that the metal and not the acyl carbonyl is the site of nucleophilic attack by transition-metal hydrides on acyl complexes.

Previous investigations of the reactions of alkyl carbonyl complexes with transition-metal hydrides have suffered from the fact that, while intermediate formation of acyl complexes has been implied by solid kinetic evidence,[1–3] these acyl intermediates have not been directly observable.[4] The *formation* of these acyls has

Table I. Equilibrium Constants for Reaction 1 at Various Temperatures

K_1[a]	T, °C	K_1[a]	T, °C	K_1[a]	T, °C
4.1	40.6	3.5	46.0	2.7	55.8
4.0	41.4	3.2	51.4	2.4	60.4
3.6	45.8	2.7	55.4	2.0	65.2

[a] Standard deviation is ±0.2.

always been the rate-determining step, and it has thus been kinetically impossible to investigate their subsequent reaction with transition-metal hydrides. We have recently discovered[5] the re-

(1) In alkane elimination from 2 equiv of Os(CO)$_4$(H)R: (a) Okrasinski, S. J.; Norton, J. R. *J. Am. Chem. Soc.* **1977**, *9*, 295. (b) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139. (c) Carter, W. J.; Okrasinski, S. J.; Norton, J. R. *Organometallics* **1985**, *4*, 1376.

(2) In aldehyde elimination from CpMo(CO)$_3$R/CpMo(CO)$_3$H: (a) Jones, W. D.; Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4415. (b) Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 5447.

(3) An aldehyde elimination from *p*-CH$_3$OC$_6$H$_4$CH$_2$Mn(CO)$_5$: (a) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332. (b) Nappa, M. J.; Santi, R.; Diefenbach, S. P.; Halpern, J. *J. Am. Chem. Soc.* **1982**, *104*, 619. (c) Nappa, M. J.; Santi, R.; Halpern, J. *Organometallics* **1985**, *4*, 34.

(4) We have shown by competition studies[1b,c] that H(CH$_3$)Os(CO)$_4$ is three times as reactive as Et$_3$P toward the acyl we believe to be formed from H(CH$_3$)Os(CO)$_4$—a result that implies that M–H attack on the acyl is nucleophilic.