The combination of resonance Raman and isotopic work thus demonstrates conclusively that, for $Rh_2(O_2CCH_3)_4(PPh_3)_2$, ν(RhRh) is at 289.3 cm^{-1}. Since the RhRh bond length in this complex is 2.4505 (2) Å,[11] longer than in the analogous $AsPh_3$ (2.427 (1) Å),[12] $SbPh_3$ (2.421 (4) Å),[12] and H_2O (2.3855 (5) Å)[16] complexes, the implication is that ν(RhRh) in these complexes must all lie above 289.3 cm^{-1}, as indeed is found to be the case for the $AsPh_3$ and $SbPh_3$ derivatives (vide supra). The high value for ν(RhRh) is thought to arise from the significant contribution to the RhRh restoring force brought about by the four chelating acetate groups (primarily via the four OCO bending coordinates, which are coupled only in second order to the RhRh stretching coordinate). Full details of these and related studies will be published elsewhere.

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(16) Cotton, F. A.; DeBoer, B. G.; LaPrade, M. D.; Pipal, J. R.; Ucko, D. A. *Acta Crystallogr., Sect. B* **1971**, *B27*, 1664.

Reactions of Cobalt Carbene Complexes with Alkynes—η^4-Vinylketene Complex Intermediates and a Novel Synthesis of Bovolide[†]

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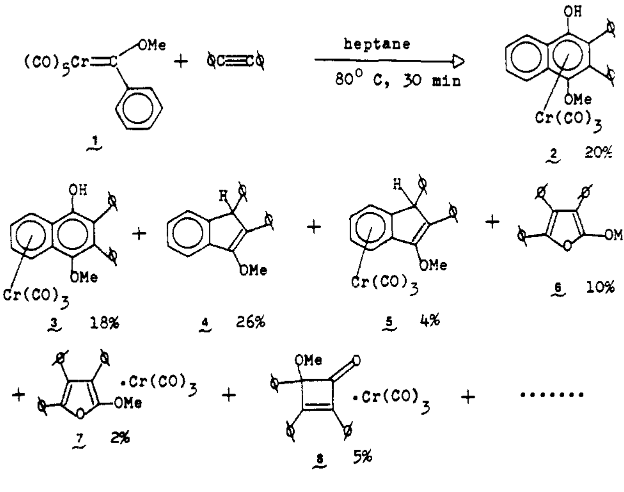
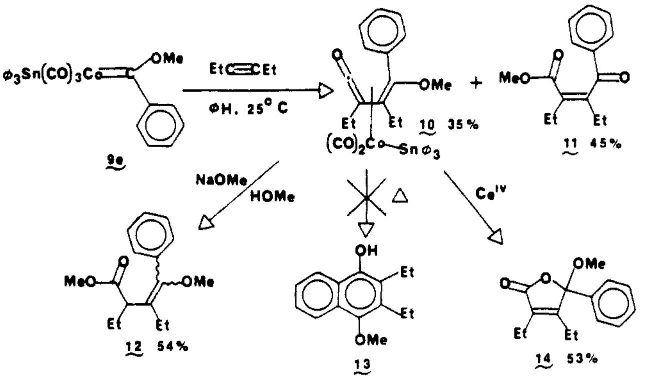
The report 8 years ago of the reaction of the chromium carbene complex **1** with diphenylacetylene in heptane (Scheme I) was the first to indicate the complexity of reactions of this type with regard to structural variations in the products and the sensitivity to reaction conditions.[3a] The reaction had previously been reported to give only the naphthol complex **2** in *n*-butyl ether.[3b] It has since been well established[4,5] that the benzannulated product (naphthol **2**) is the normal product of the reaction of chromium carbene complexes and that indenes,[4b,6] furans,[5b,7,8] and cyclobutenones[4b,5e,g,9] have only been observed on rare occasions and in low yields or as minor products. We report here that the reactions of (methoxyalkylidene)(triphenylstannyl)tricarbonylcobalt(0) complexes of the type **9** with alkynes occur with exclusive formation of 2-alkoxyfurans.

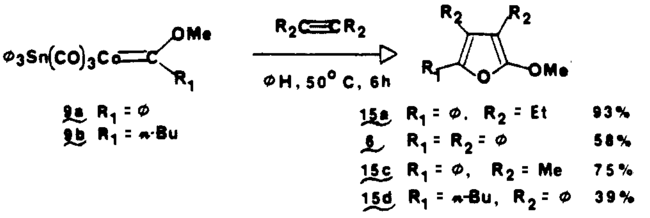
Scheme I



Scheme II



Tricarbonylcobalt carbene complexes of the type **9** have been previously prepared;[10] however, their reactivity with either olefins or acetylenes has not been previously reported. Complex **9a** was allowed to react with 1.2 equiv of diethylacetylene at room temperature in a deoxygenated benzene solution. After 48 h the η^4-vinylketene complex **10** and the γ-keto unsaturated ester **11** could be isolated after silica gel chromatography in air with a 1:1 mixture of benzene and hexanes as eluent. It has been suggested that η^4-vinylketene complexes are key intermediates in the reactions of chromium[4,8] and iron[5k] carbene complexes with acetylenes; however, until now such complexes have never been isolated from the reaction of a transition-metal carbene complex



[†] This work was presented at the 190th National Meeting of the American Chemical Society, Chicago, IL, Sept 8–13, 1985.

(1) The University of Chicago.

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(3) (a) Dötz, K. H. *J. Organomet. Chem.* **1977**, *140*, 177. (b) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 644.

(4) For reviews of the chemistry of these complexes, see: (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. "Transition Metal Carbene Complexes"; Verlag Chemie: Deerfield Beach, FL, 1984. (b) Wulff, W. D.; Tang, P. C.; Chan, K. S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron*, in press. (c) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (d) Casey, C. P. *React. Intermed.* (*Wiley*) **1985**, *5*, 3. (e) Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1. (f) Casey, C. P. In "Transition Metal Organometallics in Organ Synthesis"; Alper, H., Ed.; Acadmeic Press: New York, 1976; Vol. I. (g) Casey, C. P. *Organomet. Chem. Libr.* **1976**, *1*, 397–421.

(5) For recent references on the reactivity of Fischer carbene complexes with alkynes, see: (a) Yamashita, A. *J. Am. Chem. Soc.* **1985**, *107*, 5823. (b) Wulff, W. D.; Kaesler, R. W. *Organometallics* **1985**, *4*, 1461. (c) Wulff, W. D.; Kaesler, R. W.; Peterson, G. A.; Tang, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 1060. (d) Dötz, K. H.; Popall, M. *J. Organomet. Chem.* **1985**, *291*, C1. (e) Dötz, K. H.; Strum, W. *J. Organomet. Chem.* **1985**, *285*, 205. (f) Yamashita, A.; Scahill, T. A.; Chidester, C. G. *Tetrahedron Lett.* **1985**, 1159. (g) Yamashita, A.; Scahill, T. A.; Toy, A. *Tetrahedron Lett.* **1985**, 2969. (h) Katz, J. K.; Sivavec, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 737. (i) Parlier, A.; Rudler, H.; Platzer, N.; Fontanille, M.; Soum, A. *J. Organomet. Chem.* **1985**, *287*, C8. (j) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1984**, *106*, 7565. (k) Semmelhack, M. F.; Tamura, R.; Schnatter, W.; Springer, J. *J. Am. Chem. Soc.* **1984**, *106*, 5363. (l) Macomber, D. W. *Organometallics* **1984**, *3*, 1589. (m) Dötz, K. H.; Strum, W.; Popall, M.; Riedl, J. *J. Organomet. Chem.* **1984**, *277*, 267. (n) Wulff, W. D.; Chan, K. S.; Tang, P. C. *J. Org. Chem.* **1984**, *49*, 2293. (o) Tang, P. C.; Wulff, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 1132. (p) Wulff, W. D.; Tang, P. C. *J. Am. Chem. Soc.* **1984**, *106*, 434.

(6) (a) Dötz, K. H.; Dietz, R.; Kappenstein, D.; Neugebauer, D.; Schubert, V. *Chem. Ber.* **1979**, *112*, 3682. (b) Foley, H. C.; Strubinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 3064.

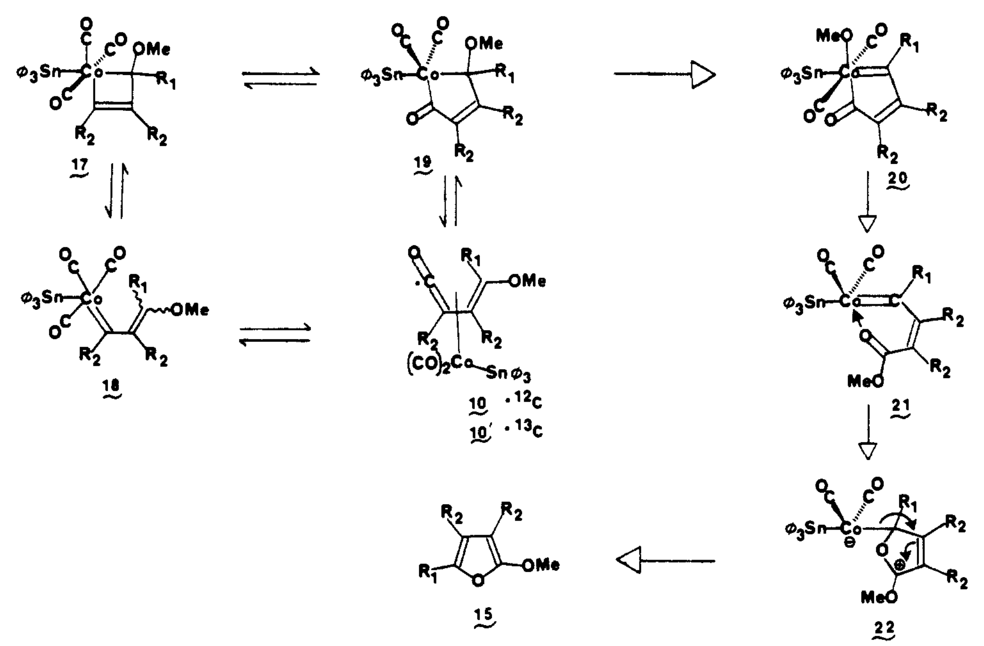
(7) Dötz, K. H.; Dietz, R.; Neugebauer, D. *Chem. Ber.* **1979**, *112*, 1486.

(8) Wulff, W. D.; McCallum, J. S., unpublished results.

(9) Dötz, K. H.; Dietz, R. *J. Organomet. Chem.* **1978**, *157*, C55.

(10) (a) Darensbourg, D. J.; Darensbourg, M. Y. *Inorg. Chem.* **1970**, *9*, 1691. (b) Carre, F.; Cerveau, G.; Colomer, E.; Corriu, R. J. P.; Young, J. C.; Ricard, L.; Weiss, R. *J. Organomet. Chem.* **1979**, *179*, 215.

Scheme III



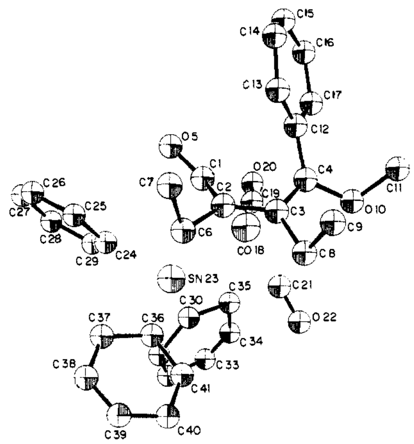
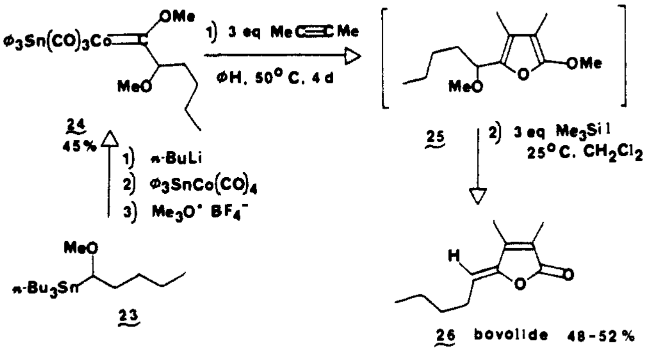


Figure 1. Computer-generated drawing of **10** derived from the X-ray coordinates with hydrogens omitted for clarity.

and an alkyne.[11] In contrast to the suggested behavior of the corresponding chromium vinylketene complexes, the cobalt complex **10** will not react with methanol.[5b,c,8,12] Treatment with sodium methoxide does produce the β-γ-unsaturated ester **12**.[13] Oxidative cleavage[11b] with cerium(IV) gives the lactone **14** (Scheme II).

An X-ray diffraction analysis[14] of the vinylketene complex **10** reveals that cobalt is within bonding distance to all four carbons of the vinylketene moiety and that the phenyl group is syn to the ketene carbon (Figure 1). The corresponding chromium vinylketene complex with the this stereochemistry has been proposed[15] to cyclize to the naphthol **13**; however, thermolysis of the cobalt complex **10** does not give a trace of naphthol **13** but rather gives rise to the furan **15a**. The reaction of **9a** and diethylacetylene can be driven completely to furan **15a** in 93% isolated yield at 50 °C in 6 h.[16] These 2-alkoxyfurans are sensitive to air oxidation, particularly on silica gel, since attempted isolation gives only acyclic keto esters of the type **11**. The furans can be chromatographically isolated if the silica gel has been pretreated with triethylamine and the elution solvents have been purged with argon. In a direct comparison to the chromium carbene complex **1**, the cobalt complex **9a** will react with diphenylacetylene in *heptane* to give exclusively the furan **6** in 58% isolated yield.[16]

Scheme IV



The reaction of the cobalt complex **9a** with diethylacetylene was observed to be independent of acetylene concentration[17] (k_1 = (6.2 ± 0.5) × 10^{-6} s^{-1} at 22 °C) and is inhibited by carbon monoxide (3 atm); both of these observations have been made for the reaction of the chromium complex **1** and diphenylacetylene.[18] Drawing from proposed mechanisms for the reactions of the corresponding chromium complexes[15] the intermediacy of the cobaltacyclobutene **17**[19] can be envisioned from the formal [2 + 2] cycloaddition of **9** and an alkyne. Whether the carbon monoxide insertion occurs at **17** to **19** or **18** to **10**, it must be rever-

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(11) A few examples of η^4-vinylketenes complexes have been prepared by other methods. (a) Jens, K. J.; Weiss, E. *Chem. Ber.* **1984**, *117*, 2469. (b) Franck-Neumann, M. *Pure Appl. Chem.* **1983**, *55*, 1715. (c) Klimes, J.; Weiss, E. *Chem. Ber.* **1982**, *115*, 2606. (d) Klimes, J.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 205. (e) Mitsudo, T.; Sasaki, T.; Watanabe, Y.; Takegami, Y.; Nishigaki, S.; Nakatsu, K. *J. Chem. Soc., Chem. Commun.* **1978**, 252.

(12) Yamashita, A.; Scohill, T. A. *Tetrahedron Lett.* **1982**, 3765.

(13) Certain η^4-vinylketene complexes of iron are stable to methanol.[12b]

(14) Refer to supplementary material.

(15) For mechanistic discussions of the reactions of chromium complexes, see: (a) Fischer, H.; Mulhemeier, J.; Markl, R.; Dötz, K. H. *Chem. Ber.* **1982**, *115*, 1355. (b) Casey, C. P. In "Reactive Intermediates"; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1981; Vol. 2.

(16) (a) **15a**: 2.5 equiv of alkyne, isolated yield, 0.007 M in benzene. (b) **6**: 1.2 equiv of alkyne, isolated yield, 0.007 M in heptane. (c) **15c**: 2.5 equiv of alkyne, ^{1}H NMR yield, 0.007 M in benzene. (d) **15d**: 1.2 equiv of alkyne, ^{1}H NMR yield 0.01 M in benzene.

(17) A 10-fold change in the concentration of diethylacetylene was examined (0.3–3.0 equiv). k_1 = 8.4 ± 0.5 × 10^{-5} s^{-1} at 45 °C. It is not possible to exclude the possibility of an open coordination site created by a reversible CO insertion into the triphenyltin group.

(18) Dötz, K. H.; Fügen-Köster, B. *Chem. Ber.* **1980**, *113*, 1449.

(19) Calabrese, J. C.; Roe, D. C.; Thorn, D. L.; Tulip, T. H. *Organometallics* **1984**, *3*, 1223.

sible,[11d] since exposure of the vinylketene complex **10** to 3 atm of ^{13}C-labeled carbon monoxide at ambient temperatures resulted in incorporation of the label at the ketene carbon (**10′**).[20] At this point we can only suggest a mechanism for the furan formation which involves a migration of methoxy to the metal (**19** → **20**),[5k] reductive elimination of methoxy and acyl (**20** → **21**), and addition of the ester carbonyl to the carbene carbon (**21** → **22**).[11c] Further studies on this mechanism will be reported later[8] (Scheme III).

The synthetic utility of the reaction of cobalt carbene complexes with acetylenes is illustrated by the synthesis of bovolide, a naturally occurring butenolide isolated from several sources,[21] which was first characterized as a component of butter flavor (Scheme IV).[22] The α-methoxy-*n*-pentyl complex **24** was prepared by the standard Fischer synthesis from the organolithium generated from the α-stannyl ether **23** and triphenyltin cobalt tetracarbonyl.[10,23] The cobalt carbene complex **24** was heated with 3 equiv of 2-butyne in benzene under an inert atmosphere. The crude reaction mixture was then treated with 3 equiv of trimethylsilyl iodide[24] to give bovolide in 48–52% yield.

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Supplementary Material Available: Spectral and physical data for all new compounds and the details of the X-ray analysis of compound **10** (8 pages). Ordering information is given on any current masthead page.

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(20) Oxidation of 10′ with cerium(IV) ammonium nitrate gives the lactone 14 which is 75% enriched with ^{13}C (mass spectrum) at the carbonyl carbon.

(21) (a) Patterson, G. *Prog. Chem. Org. Nat. Prod.* **1978**, *35*, 133–198. (b) Takahashi, K.; Someya, T.; Muraki, S.; Yoshida, T. *Agric. Biol. Chem.* **1980**, *44*, 1535. (c) Wahlberg, I.; Karlsson, K.; Austin, D. J.; Junker, N.; Roeraade, J.; Enzell, C. R. *Phytochemistry* **1977**, *16*, 1217. (d) Demole, E.; Berthet, D. *Helv. Chim. Acta* **1972**, *55*, 1866.

(22) (a) Lardelli, G.; Dijkstra, G.; Harbus, P. D.; Bondingh, J. *Recl. Trav. Chim. Pays-Bas.* **1966**, *85*, 43.

(23) Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481.

(24) Schmidt, A. H. *Aldrichimica Acta* **1981**, *14*, 31.

Demonstration of Contact Induced Ion Exchange in Zeolites

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Zeolites are of considerable practical importance and current interest because of their sorptive and catalytic properties.[1] They are framework aluminosilicate species, usually highly crystalline in nature, with well-defined pore and channel structures.[2] The structures can be considered as formally being derived from crystalline silica by the replacement of SiO_2 units by AlO_2 units and have a general formula $M_x^+(AlO_2)_x(SiO_2)_y$. Because of the difference in nuclear charge between Al and Si, a single positive charge (usually present as metal cations in the cavities) must be present for each aluminum moiety in the structure. The framework structures confer a size and shape selectivity toward sorbed organic molecules and catalytic activity results when the cationic charges are protonic in nature (H_3O^+ etc.).

In general, the nature of the cations present in a given zeolite exerts a very considerable influence on the physical and physicochemical properties of the system. Thus, the lattice dimensions may change as, for example, in the case of zeolite X where the lattice parameter of the cubic unit cell varies from 24.99 Å for the Na$^+$ salt to 24.88 Å for the Li$^+$ salt. The free space in the cavity is controlled by the variation in ionic radius of the cations. Thus, for zeolite A, which is commonly used as a "molecular sieve", when the cation is K$^+$ molecules of diameters up to 3 Å may be sorbed, when the cation is Ca^{2+} molecules of diameters up to 5 Å may be sorbed. In addition, certain metal ions may confer a very specific catalytic activity on the system by acting as the central metal atom in an organometallic complex in various chemical conversions.

In this paper, we demonstrate that exchange of these important cationic species can occur *between* different zeolite crystals based only on a simple physical contact between the crystallites. The structural changes accompanying the exchange have been monitored by powder XRD and ^{29}Si MAS NMR[3] studies which, because they are sensitive to long- and short-range ordering effects, respectively, complement each other and give a complete description of the structures. Zeolite A has been chosen for this work as it has a well-defined structure and XRD pattern and gives a single sharp absorption in its ^{29}Si MAS NMR spectrum.

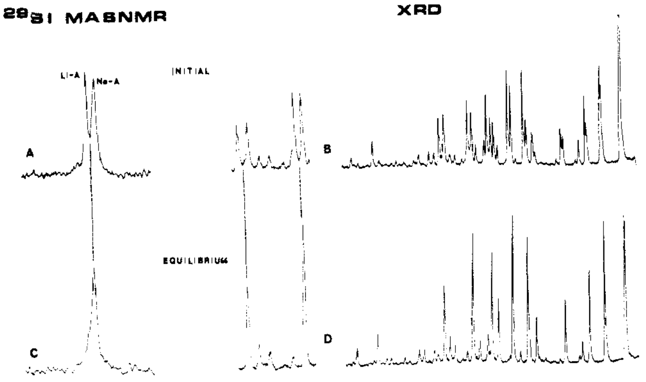

Figure 1. ^{29}Si MAS NMR spectra, obtained at 79.5 MHz, of a mixture of Li$^+$A and Na$^+$A: (A) immediately after mixing and (C) at equilibrium as well as the corresponding powder XRD patterns (B) and (D).

Figure 1A shows the ^{29}Si MAS NMR spectrum of a mixture of crystals of Li$^+$A and Na$^+$A prepared separately (the Na$^+$A species ion exchanged thoroughly to the Li$^+$A form) and then mixed for 10 s in a "wigglebug" (as described in ref 4), the spectrum being recorded immediately after mixing. Figure 1B shows the corresponding powder XRD pattern. Since the replacement of Li$^+$ for Na$^+$ causes a shrinkage in the unit cell dimension, clear and predictable changes in the position of the absorptions in the X-ray diffraction pattern are observed. The XRD pattern of the mixture (Figure 1B) shows the superposition of the two patterns giving a "doublet" splitting of many of the peaks and indicating clearly that the sample consists of a simple physical mixture of the two sets of crystallites. This is confirmed by the ^{29}Si MAS NMR spectrum of the same sample (Figure 1A) which shows two sharp resonances at δ -85.1 and -88.9 due to there being *two* local silicon environments which do not exchange rapidly on the NMR time scale. This is again in agreement with there being two types of crystallites present as rapid diffusion within

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[†] Chemistry Department, University of Northern Illinois, DeKalb, IL (now deceased).

(1) (a) Barrer, R. M. "Zeolites and Clay Minerals"; Academic Press: London, 1978. (b) Rabo, J. A., Ed. *ACS Monogr.* **1976**, *171*.

(2) (a) Breck, D. W. "Zeolite Molecular Sieves"; Wiley: New York, 1974. (b) Meier, W. M.; Olson, D. H. "Atlas of Zeolite Structure Types"; Structure Commission of the International Zeolite Association, 1978.

(3) (a) Lippmaa, E.; Mägi, M.; Samoson, A.; Tarmak, M.; Engelhardt, G. *J. Am. Chem. Soc.* **1981**, *103*, 4992. (b) Fyfe, C. A.; Thomas, J. M.; Klinowski, J.; Gobbi, G. C. *Angew. Chem.* **1983**, *22*, 259.

0002-7863/86/1508-0522$01.50/0