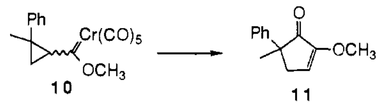
Scheme III



In one case, a reaction reminiscent of the Claisen rearrangement has been observed.[14c] Presumably, ring opening of the cyclopropane ring provides the necessary driving force to induce the Cope-like process is these systems.

We have explored the scope and limitations of this rearrangement with a variety of 2-alkenylcyclopropylcarbene–chromium complexes; the results are summarized in Table I. The reaction appears to be general for a wide variety of these types of complexes. Only in one case (entry E) does the reaction fail. Bicyclic carbene complex **12E** fails to rearrange, presumably because rearrangement requires the alkene and carbene complex functionalities to attain the cis relative configuration. This configuration is hard to attain because of steric interactions between the cyclohexyl ring and the carbene complex. In cases where R_2 = H, the reaction mixtures also contain some of the alkene isomerization product as an impurity.

In summary, we have explored rearrangements of cyclopropylcarbene–chromium complexes. These rearrangements reveal interesting similarities with classical electrocyclic reactions, and they may be one of the first examples where a $d\pi$–$p\pi$ bond participates in a Cope rearrangement. We are continuing to explore the mechanism, the scope, and the limitations of these novel rearrangement reactions.

Acknowledgment. We thank the Petroleum Research Fund, administered by the American Chemical Society, and the National Institutes of Health (Grant GM-40777) for financial support of this research. We are grateful for the assistance and discussion provided by Seniz U. Tumer and technical assistance provided by undergraduate assistants Charles Daitch and Steve Strong.

Supplementary Material Available: Spectra and procedures for the synthesis of the carbene complexes and for the reactions in Table I (28 pages). Ordering information is given on any current masthead page.

Heptadecanuclear Mixed Metal Iron Oxo–Hydroxo Complexes, $[Fe_{16}MO_{10}(OH)_{10}(O_2CPh)_{20}]$, M = Mn or Co, Structurally Comprised of Two Fragments Derived from $[Fe_{11}O_6(OH)_6(O_2CPh)_{15}]$

Wolfgang Micklitz and Stephen J. Lippard*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received April 10, 1989

Recent interest in polynuclear oxo–hydroxo complexes of iron and manganese has been stimulated by their occurrence in biology, prominent examples including ferritin[1] and photosystem II.[2] The hydrolytic polymerization of iron[3] is of particular importance in biomineralization[4] and corrosion.[5] Because of the difficulty in controlling hydrolytic chemistry above pH 1–2, examples of discrete soluble polyiron or -manganese oxo–hydroxo complexes are rare.[6] Structurally characterized species include M_3,[7] M_4,[8] M_6 (M = Fe, Mn),[9] Fe_8,[10] Mn_9,[11] Mn_{10},[12] Fe_{11},[13] and Mn_{12}[14] complexes, most of which were prepared since 1984. Despite this progress, there remains a need to understand the synthetic pathways by which such molecular aggregates form and to elu-

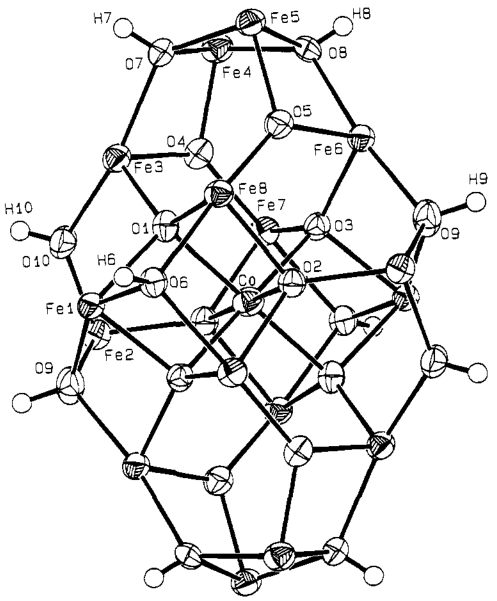


Figure 1. ORTEP drawing of the metal oxo–hydroxo core in **2**, showing the 50% probability thermal ellipsoids and atom labels for the metal and oxygen atoms. Hydrogens are presented as small spheres for clarity.

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(1) (a) Clegg, G. A.; Fitton, J. E.; Harrison, P. M.; Treffry, A. *Prog. Biophys. Mol. Biol.* **1980**, *36*, 53. (b) Crichton, R. R. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 57. (c) Theil, E. C. *Annu. Rev. Biochem.* **1987**, *56*, 289.

(2) (a) Dismukes, G. C. In *Manganese in Metabolism and Enzyme Function*; Schramm, V. L., Welder, F. C., Ed.; Academic Press: New York, 1986; pp 275–309. (b) Babcock, G. T. In *New Comprehensive Biochemistry: Photosynthesis*; Amesz, J., Ed.; Elsevier: Amsterdam, 1987; pp 125–158. (c) Brudvig, G. W. In *Metal Clusters in Proteins*; Que, L., Jr., Ed.; American Chemical Society: Washington, D.C., 1988; ACS Symp. Ser., No. 372, p 221.

(3) (a) Lippard, S. J. *Chem. Brit.* **1986**, *22*, 222. (b) Schneider, W. *Chimia* **1988**, *42*, 9.

(4) (a) Lowenstam, H. A. *Science* **1981**, *211*, 1126. (b) Mann, S.; Frankel, R. B.; Blakemore, R. P. *Nature (London)* **1984**, *310*, 405.

(5) Flynn, C. M. *Chem. Rev.* **1984**, *84*, 31.

(6) (a) Lippard, S. J. *Angew. Chem.* **1988**, *100*, 353. (b) Brudvig, G. W.; Crabtree, R. H. *Progr. Inorg. Chem.* **1989**, *37*, in press. (c) Christou, G.; Vincent, J. B., ref 2c, p 238.

(7) (a) Cannon, R. D.; White, R. P. *Progr. Inorg. Chem.* **1988**, *36*, 195 and references therein. (b) Gorun, S. M.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 4244. (c) Vincent, J. B.; Chang, H.-R.; Folting, K.; Huffman, J. C.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 5703. (d) Bhula, R.; Gainsford, G. J.; Weatherburn, D. C. *J. Am. Chem. Soc.* **1988**, *110*, 7550.

(8) (a) Wieghardt, K.; Bosek, U.; Gebert, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 328. (b) Stukan, R. A.; Ponomarev, V. I.; Nifontov, V. P.; Turtè, K. I.; Atovmyan, L. O. *J. Struct. Chem.* **1985**, *26*, 197. (c) McKee, V.; Shepard, W. B. *J. Chem. Soc., Chem. Commun.* **1985**, 158. (d) Jameson, D. L.; Xie, C.-L.; Hendrickson, D. N.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1987**, *109*, 740. (e) Armstrong, W. H.; Roth, M. E.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 6318. (f) Murch, B. P.; Bradley, F. C.; Boyle, P. D.; Que, L., Jr.; Papaefthymiou, V. *J. Am. Chem. Soc.* **1987**, *109*, 7993. (g) Vincent, J. B.; Christmas, C.; Huffman, J. C.; Christou, G.; Chang, H.-R.; Hendrickson, D. N. *J. Chem. Soc., Chem. Commun.* **1987**, 236. (h) Bashkin, J. S.; Chang, H.-R.; Streib, W. E.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1987**, *109*, 6502. (i) Gorun, S. M.; Lippard, S. J. *Inorg. Chem.* **1988**, *27*, 149. (j) Kulawiec, R. J.; Crabtree, R. H.; Brudvig, G. W.; Schulte, G. K. *Inorg. Chem.* **1988**, *27*, 1309. (k) McKee, V.; Tandon, S. S. *J. Chem. Soc., Chem. Commun.* **1988**, 1334. (l) Li, Q.; Vincent, J. B.; Libby, E.; Chang, H.-R.; Huffman, J. C.; Christou, G.; Hendrickson, D. N. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1731. (m) Vincent, J. B.; Christmas, C.; Chang, H.-R.; Li, Q.; Boyd, P. D. W.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1989**, *111*, 2086.

(9) (a) Baikie, A. R. E.; Howes, A. J.; Hursthouse, M. B.; Quick, A. B.; Thornton, P. *J. Chem. Soc., Chem. Commun.* **1966**, *569*. (b) Batsanov, A. S.; Struchkov, Yu. T.; Timko, G. A. *Koord. Khim.* **1988**, *14*, 266. (c) Micklitz, W.; Lippard, S. J. *Inorg. Chem.* **1988**, *27*, 3067. (d) Micklitz, W.; Bott, S. G.; Bentsen, J. G.; Lippard, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 372.

(10) Wieghardt, K.; Pohl, K.; Jibril, I.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 77.

(11) Christmas, C.; Vincent, J. B.; Chang, H.-R.; Huffman, J. C.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1988**, *110*, 823.

(12) Hagen, K. S.; Armstrong, W. H.; Olmstead, M. M. *J. Am. Chem. Soc.* **1989**, *111*, 774.

(13) (a) Gorun, S. M.; Lippard, S. J. *Nature* **1986**, *319*, 666. (b) Gorun, S. M.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 3337.

(14) Boyd, P. D. W.; Li, Q.; Vincent, J. B.; Folting, K.; Chang, H.-R.; Streib, W. E.; Huffman, J. C.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1988**, *110*, 8537.

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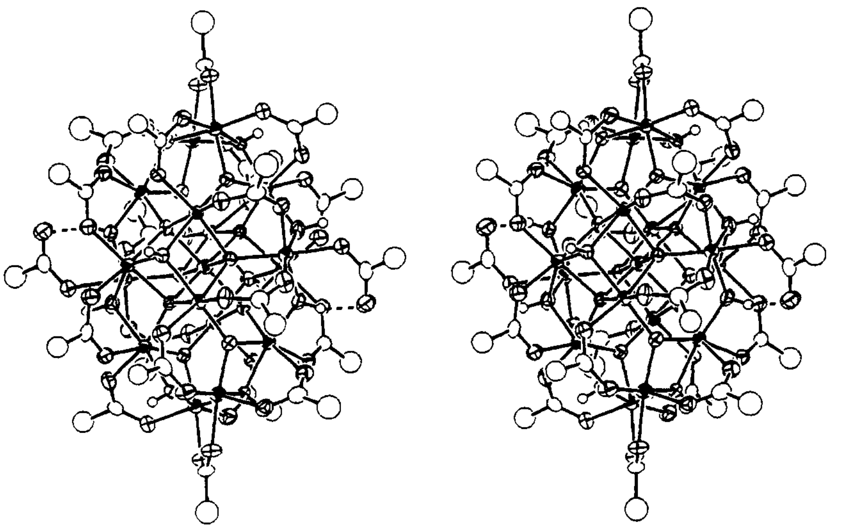


Figure 2. Stereo view of the structure of **2**. Phenyl rings are omitted for clarity and hydrogen bonds are drawn as dashed lines.

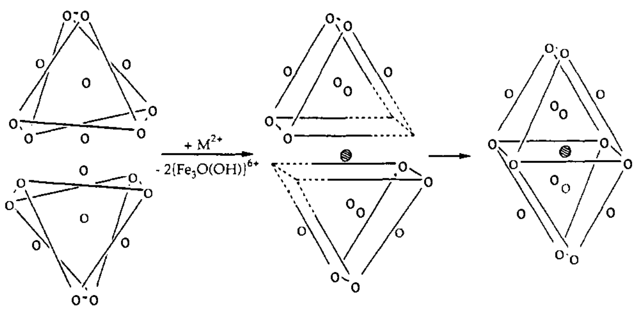
cidate the rules that dictate their formation.

Previously, we described the synthesis of tetranuclear $\{Fe_4O_2\}^{8+}$ [8c,e] and hexanuclear $\{Fe_6O_2(OH)_2\}^{12+}$ or $\{Fe_6O_2(O_2)\}^{12+}$ [9b,c] iron oxo aggregates by simple dimerization of $\{Fe_2O\}^{4+}$ and $\{Fe_3O\}^{7+}$ building blocks, respectively. Except for $\{Fe_6O_2(O_2)\}^{12+}$, these units all readily convert to $[Fe_{11}O_6(OH)_6(O_2CPh)_{15}]$[13] by pathways yet unknown. Here we report the synthesis and structural characterization of two remarkable new molecules, $[Fe_{16}MO_{10}(OH)_{10}(O_2CPh)_{20}]$ (M = Mn (**1**) and Co (**2**)) formally comprised of two fused Fe_{11} molecules encapsulating a divalent metal ion.

To a slurry of basic iron(III) benzoate[15] (0.60 g, 0.5 mmol) in 40 mL of CH_3CN and 1.0 mL of H_2O was added solid $MCl_2 \cdot nH_2O$ (0.10 g: M = Mn, n = 4, 0.51 mmol; M = Co, n = 6, 0.42 mmol) and the mixture was heated to 80 °C for 15 min. The cooled, clear solution was then passed through a cake of $MgSO_4$ and the brown (M = Mn) or green (M = Co) filtrate was allowed to concentrate slowly in air. Within 48 h, dark brown crystals of CH_3CN solvates of **1** and **2** formed in 8–12% yield. The crystals, which rapidly lose solvent when exposed to air, proved suitable for X-ray diffraction analysis.[16] Vacuum-dried samples of **1** and **2** were also analyzed for elemental composition and by spectroscopic and magnetic measurements.[17,18]

Compounds **1** and **2** contain identical $\{Fe_{16}MO_{10}(OH)_{10}\}^{20+}$ cores in which, barring disorder, the central atom can be assigned to the unique heterometal M situated on a crystallography required center of symmetry (Figure 1, M = Co). Charge balance requires 16 Fe(III) ions and a heterometal ion in the +2 oxidation state, consistent with the absence of a notable Jahn-Teller distortion of Mn in **1**. The metals are bridged by four types of oxo and hydroxo ligands, μ_4-O, planar μ_3-O, and μ_2- and μ_3-OH. Six μ_4-oxide atoms are bound to the central heterometal, the $(M-O)_{av}$ distance being 2.033 (9) Å. Most Fe–O bonds range from 1.87 (1) to 2.16 (1) Å, following the order Fe–μ_3-O < μ_2-OH < μ_4-O < μ_3-OH. Exceptionally long distances are found for Fe(1)–O(9′) and Fe(1)–O(6), 2.339 (15) (av. **1**,**2**) and 2.32 (2) Å (**1**), respectively. An interesting structural feature of **1** and **2** is the presence of two corner-sharing $\{\{Fe_3O_3(OH)\}_2M\}^{6+}$ cubes. Although structures containing iron–chalcogen cubes are well documented in the case of sulfur,[19] selenium,[20] and tellurium,[21] no example of an iron oxo–hydroxo cube has been reported so far. In contrast, structures with manganese oxo cubes are known.[8j-l,14] The octahedral coordination spheres of the iron atoms are completed by 20 $PhCOO^-$ goups, 18 of which are bidentate and bridging while 2 are monodentate (Figure 2, M = Co). The two structures differ only in the hydrogen bonding of the monodentate benzoates, which occurs to μ_3–OH (H(9)) in **1** and μ_2-OH (H(10)) in **2**.

Scheme I



The structures may be formally constructed by fusion of two twisted, pentacapped trigonal prisms of $[Fe_{11}O_6(OH)_6(O_2CPh)_{15}]$ along a distorted rectangular face, as illustrated in Scheme I, where circles represent metal atoms. In the first step two $\{Fe_3O(OH)(O_2CPh)_5\}^+$ units, similar to that of basic iron(III) carboxylates,[7a] are removed. The resulting $\{Fe_8O_5(OH)_5(O_2CPh)_{10}\}^-$ fragments combine in the presence of a divalent metal ion, forming an octacapped, body-centered octahedron. As a consequence, an array of oxo-centered MFe_3 tetrahedra is formed, a motif long known for basic beryllium[22] or zinc[23] acetate and more recently

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(15) Weinland, R. F.; Herz, A. *Ber. deutsch. chem. Ges.* **1912**, *45*, 2662.

(16) Crystal data for **1**·9CH_3CN ($C_{158}H_{137}N_9O_{60}Fe_{16}Mn$, M_r = 4070.3) at 298 K: space group $P\bar{1}$, a = 17.636 (1) Å b = 17.693 (1) Å, c = 18.254 (1) Å, α = 115.308 (6)°, β = 102.489 (6)°, γ = 99.371 (6)°, V = 4813 Å^3, Z = 1; R = 0.0931, R_w = 0.0928. Crystal data for **2**·17CH_3CN ($C_{174}H_{161}N_{17}O_{60}Fe_{16}Co$, M_r = 4402.7) at 298 K: space group $P\bar{1}$, a = 16.9237 (9) Å, b = 17.531 (1) Å, c = 18.144 (1) Å, α = 105.365 (5)°, β = 99.501 (4)°, γ = 104.705 (5)°, V = 4863 Å^3, Z = 1; R = 0.0636, R_w = 0.0678. Full details will be reported elsewhere.

(17) **1**: Anal. ($C_{140}H_{110}O_{60}Fe_{16}Mn$) found (Calcd) C, 45.45 (45.44); H, 3.05 (3.00); Mn, 1.56 (1.48); Fe 23.68 (24.14); IR (KBr, cm^{-1}) 3592, 3559 (ν_s, OH), 1599, 1544 (ν_{as}, COO), 1421 (ν_s, COO); electronic spectrum in CH_3CN (λ_{max}, nm) 264 (sh), 296 (sh), 358, 464 (sh); X-band ESR, frozen solution (45 K), g = 2.0, $A = 8.9 \times 10^{-3}$ cm^{-1}; magnetic susceptibility, solid state [T (K) μ_{eff}/molecule, B.M.] (300) 13.07, (200), 11.95 (100) 10,56, (50) 9.25, (10) 6.04, (1.65) 3.97.

(18) **2**: Anal. ($C_{140}H_{110}O_{60}Fe_{16}Co$) Found (Calcd) C, 44.49 (45.39); H, 2.82 (2.99); IR (KBr, cm^{-1}) 3596, 3565 (ν_s, OH), 1598, 1544 (ν_{as}, COO), 1421 (ν_s, COO); electronic spectrum in CH_3CN (λ_{max}, nm) 264 (sh), 296 (sh), 360, 464 (sh); X-band ESR, solid state (45 K) g = 4.4.

(19) Berg, J. M.; Holm, R. H. In *Iron–Sulfur Proteins*; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1982; Chapter 1. (b) Münck, E.; Papaefthymiou, V.; Surerus, K. K.; Girerd, J.-J., ref 2c, p 302. (c) Averill, B. A., ref 2c, p 258.

(20) Bobrik, M. A.; Laskowski, E. J.; Johnson, R. W.; Gillum, W. O.; Berg, J. M.; Hodgson, K. O.; Holm, R. H. *Inorg. Chem.* **1978**, *17*, 1402.

(21) Simon, W.; Wilk, A.; Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1009.

(22) Bragg, W. H. *Nature (London)* **1923**, *111*, 532.

(23) (a) Auger, V.; Robin, I. *C. R. Hebd. Seances Acad. Sci.* **1924**, *178*, 1546. (b) Wyatt, J. *Bull. Soc. Fr. Mineral* **1926**, *49*, 148.

found in Co[24] and Mn[9a] carboxylates, but rarely observed for Fe.[25] Low-temperature ESR studies[17,18] of **1** in frozen pyridine solution and of solid **2** reveal characteristic features of Mn(II) and Co(II), respectively. Integration of the ESR signal confirms that **1** contains 1.0 ± 0.1 Mn atoms per molecule. The μ_{eff} vs T plot for **1** indicates antiferromagnetic exchange coupling and a ground state with $S_T \leq 1$.

In conclusion, formal fusion of two $[Fe_{11}O_6(OH)_6(O_2CPh)_{15}]$ fragments in the presence of a divalent heterometal has yielded the largest soluble polyiron oxo-hydroxo compounds to date. Further growth of the polymetal oxo-hydroxo core of **1** and **2** can be envisioned by repeating the steps outlined in Scheme I. This process allows the derivation of a general formula, $M_nFe_{5n+11}O_{4n+6}(OH)_{4n+6}(O_2CPh)_{5n+15}$, $n = 0, 1, 2$, etc., predicting the stoichiometry of higher members of this series. Attempts to synthesize such compounds, and to relate them to biological and mineralogical iron, are currently in progress.

Acknowledgment. This work was supported by grants from the National Institute of General Medical Sciences and the National Science Foundation. W.M. is grateful for a NATO Research Fellowship (DAAD). We also thank R. L. Rardin and Drs. J. G. Bentsen and S. G. Bott for assistance.

Supplementary Material Available: Table of atomic positional and thermal parameters for **2**·$17CH_3CN$ (10 pages). Ordering information is given on any current masthead page.

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(24) Blake, A. B. *J. Chem. Soc., Chem. Commun.* **1966**, 569.

(25) Wasfi, S. H.; Rheingold, A. L.; Kokoszka, G. F.; Goldstein, A. S. *Inorg. Chem.* **1987**, *26*, 2934.

Organolithic Macromolecular Materials Derived from Vinyl-Functionalized Spherosilicates: Novel Potentially Microporous Solids

Pradyot A. Agaskar

Department of Chemistry
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061

Received April 5, 1989

Organolithic macromolecular materials (OMM's) are substances containing both silicate and organic components, with a definite chemical relationship between the two.[1,2] The structure of the organic component is well defined but that of the silicate component is usually undefined. One way of achieving some degree of control over the structure of the latter is to use a variant of the Lentz trimethylsilylation technique[3] to attach organosilicon moieties to the free $\equiv SiO^-$ groups of a silicate of known structure. The structure of the silicate component of the materials thus obtained is similar to the structure of the silicate used as the starting material.[4] One of the limitations of this method, when applied to the synthesis of macromolecular materials, is that the silicate structures are not entirely stable under the reaction conditions and hence the resultant material is not structurally well defined.

An alternative route has allowed us to synthesize an OMM that contains spherosilicate moieties $[Si_{10}O_{25}]$, with well-defined pentagonal prismatic structures, that are cross-linked at the vertices by organosilicon moieties whose structure is $(Si(CH_3)_2CH_2CH_2Si(CH_3)_2C_6H_4O_{0.5})_2$. The repeating unit of this OMM is actually the tetravalent unit $O_{3/2}SiOSi(CH_3)_2CH_2CH_2Si(CH_3)_2C_6H_4O_{1/2}$. However, the OMM has a more ordered structure than is suggested by this formula because the synthesis is begun with a polyreactive oligomer of known structure.

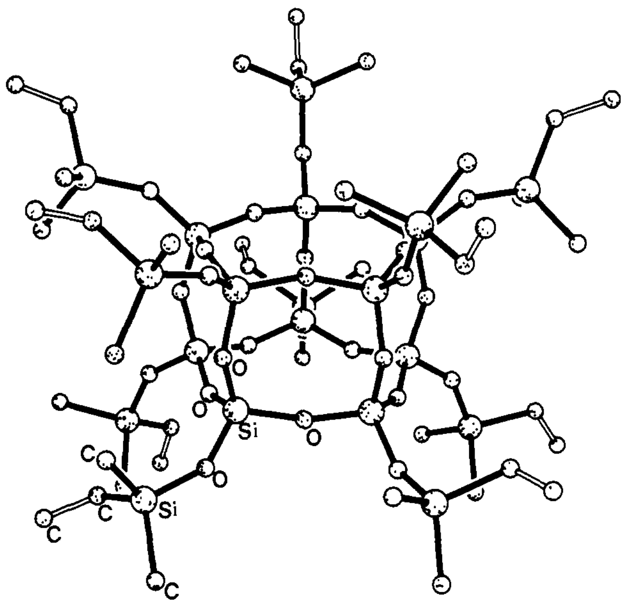

Figure 1. Ball-and-stick representation of the structure of $[Si_{20}O_{25}](Si(CH_3)_2(CHCH_2))_{10}$.

This material can be expected to be microporous because "geometric factors limit the density with which corner-linked "polyhedra" can fill space".[5] This principle has been the basis on which several approaches have been made to the synthesis of purely inorganic,[5] purely organic,[6] and also organometallic[7] microporous materials.

The synthesis of the OMM begins with a hydridospherosiloxane, $H_{10}Si_{10}O_{15}$ (**1**), which is obtained from a mixture of $(HSiO_{1.5})_n$ species prepared by a scarce-water hydrolysis of $HSiCl_3$[8,9] and can be converted to a vinyl-functionalized spherosilicate, $[Si_{10}O_{25}](Si(CH_3)_2(CHCH_2))_{10}$ (**2**), whose structure is shown in Figure 1. This conversion of **1** to **2** is effected by using the reagent $(CH_3)_3NO{\cdot}ClSi(CH_3)_2(CHCH_2)$.[10]

Compound **2**, which is a polyreactive oligomer, is then allowed to react with a stoichiometric amount of the bifunctional compound $(HSi(CH_3)_2C_6H_4O_{0.5})_2$ (**3**) in the presence of a catalyst, $PtCl_2(C_6H_5CN)_2$.[11] The long rigid central portion of **3** increases the likelihood that the two terminal $\equiv SiH$ groups will react with the $\equiv SiCH{=}CH_2$ groups on separate spherosilicate cores.[12] The resultant solid is a hard, clear, resilient, thermally stable[13] material that absorbs >50% by weight of tetrahydrofuran (THF). ^{13}C CP/MAS and ^{29}Si CP/MAS spectra of the solvent-swollen solid[14]

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(1) Wilson, A. D.; Crisp, S. *Organolithic Macromolecular Materials*; Applied Science Publishers Ltd.: London, 1977; pp 3-4.

(2) Schmidt, H. *ACS Symp. Ser.* **1988**, *No. 360*, 333-344.

(3) Lentz, C. W. *Inorg. Chem.* **1964**, *3*, 574-579.

(4) Frazier, S. E.; Bedford, J. A.; Hower, J.; Kenney, M. E. *Inorg. Chem.* **1967**, *6*, 1693-1696.

(5) Day, V. W.; Klemperer, W. G.; Mainz, V. V.; Millar, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 8262-8264.

(6) Maiti, D.; Maiti, M. M. *Macromolecules* **1987**, *20*, 1159-1161.

(7) Feher, F. J. *Abstracts of the 8th International Symposium on Organosilicon Chemistry*, St. Louis, MO, 1987, p 230.

(8) Frye, C. L.; Collins, W. T. *J. Am. Chem. Soc.* **1970**, *92*, 5586-5588.

(9) Agaskar, P. A.; Day, V. W.; Klemperer, W. G. *J. Am. Chem. Soc.* **1987**, *109*, 5554-5554.

(10) Agaskar, P. A. *Synth. React. Inorg. Met.-Org. Chem.*, submitted.

(11) $PtCl_2(C_6H_5CN)_2$ was used as a solution in THF (250 μg of Pt/mL). Typical reaction procedure is as follows: **2** (0.204 g) + **3** (0.2 mL) + catalyst solution (0.25 mL); reaction time 2 days, under N_2; solvent allowed to evaporate slowly and the large chunks of solid material washed with several milliliters of THF.

(12) Two adjacent vertices of a spherosilicate unit cannot be cross-linked because they are too close to each other. Alternate pairs of vertices could be cross-linked but steric interference of bulky $\equiv Si(CH_3)_2(CHCH_2)$ substituents on intervening vertices makes this unlikely.

(13) Density (Hg displacement, 1 atm of pressure) 1.01 g/mL. TGA measurements (30-800 °C, 20 °C/min) show a 5% loss in weight by 110 °C (solvent desorption) and then no change in weight till the temperature reaches 350 °C.

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