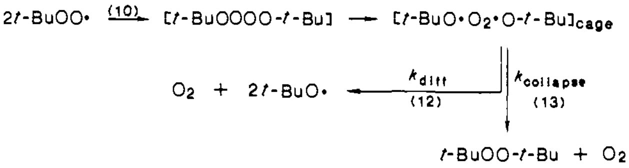
addition of 0.2 M *t*-BuOOH or H_2O_2 completely protects the hemin, affording *tert*-butyl alcohol, di-*tert*-butyl peroxide, and dioxygen from the hydroperoxide and dioxygen from hydrogen peroxide.[17] These products are diagnostic for hydroperoxy radical production, showing that the sequence of reactions for *t*-BuOOH is as shown below.[18]

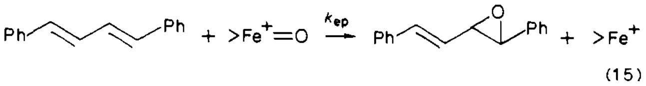
$$F_5PhIO + {>}Fe^+ \rightarrow {>}Fe^+{=}O + F_5PhI \qquad (8)$$

$$>Fe^+{=}O + t\text{-BuOOH} \longrightarrow t\text{-BuOO}\cdot + {>}Fe^+{-}OH \qquad (9)$$



$$t\text{-BuO}\cdot + t\text{-BuOOH} \rightarrow t\text{-BuOH} + t\text{-BuOO}\cdot \qquad (14)$$

To measure the rates of these reactions relative to rates of epoxidation, we have used a kinetic technique developed for relative epoxidation rates.[19] We follow the disappearance of the 348-nm peak of 1,4-diphenylbutadiene as an indication of epoxidation.



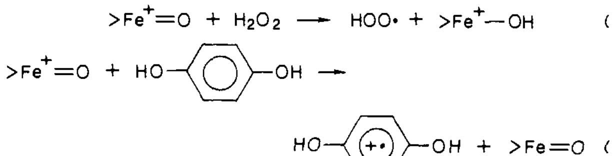
(15)

The pseudo-first-order rate constant is identical with that obtained by observing RIO disappearance.[16] However, addition of a second alkene, *t*-BuOOH or H_2O_2, results in a reduction of consumption of 1,4-diphenylbutadiene as seen in Figure 2. Kinetic analysis of this figure[19] reveals $k_9/k_{15} = 1.1$, the ratio of bimolecular rate constants for reactions of *t*-BuOOH and 1,4-diphenylbutadiene. By using the previously determined value[19] of k_{15}/k_{16} we calculate $k_9/k_{16} = 70$ and a similar ratio with hydrogen peroxide. This explains previous failures to observe epoxidation. From previous estimates of a minimum value[16c] of $k_{16} \geq 10^5$ M^{-1} s^{-1} we tentatively estimate that k_9 is near 10^7 M^{-1} s^{-1}. The catalase reaction is naturally efficient.

(16)

By using the same kinetic technique in deuteriated solvents (where hydroperoxides and hydroquinone are deuteriated) we observe the primary isotope effects for reactions 9, 17, and 18 to be 4.1, 3.1, and 1.3, respectively. These isotope effects suggest electron transfer for oxidation of hydroquinone[20] and hydrogen abstraction for reactions 9 and 17.

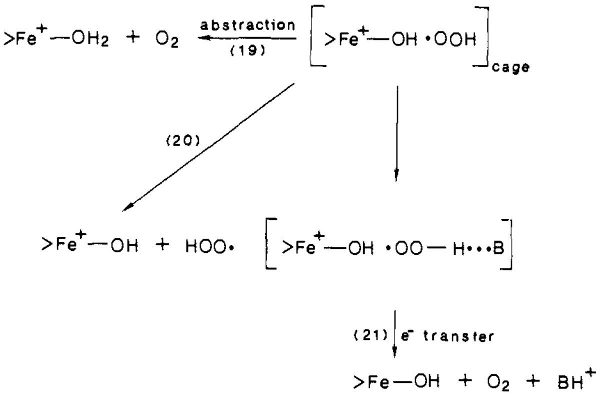
$$>Fe^+{=}O + H_2O_2 \rightarrow HOO\cdot + {>}Fe^+{-}OH \qquad (17)$$



(18)

The rapid rate of hydrogen abstraction (9) suggests that the acid catalysis of this step conjectured from the catalase crystal structure[21] is unnecessary. The ionic and hydrogen-bonding groups on the distal side of the heme in catalase,[21] as in peroxidase,[22] are probably needed for the general acid catalysis of the first step,[22] already demonstrated in model compound studies.[6a,10]

We can therefore write the first and second steps in the model catalase reactions as reaction 2 followed by reaction 17. The third step in the catalase reaction might be cage abstraction, cage electron transfer, or diffusion followed by either of these. Details of this step are under study.



Acknowledgment. We are grateful to the National Science Foundation, Grant CHE 84-20612, for financial support.

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(16) (a) Traylor, T. G.; Marsters, J. C., Jr.; Nakano, T.; Dunlap, B. E. *J. Am. Chem. Soc.* **1985**, *107*, 5537. (b) Traylor, T. G.; Nakano, T.; Dunlap, B. E.; Traylor, P. S.; Dolphin, D. *Ibid.* **1986**, *108*, 2782. (c) Traylor, T. G.; Nakano, T.; Miksztal, A. R.; Dunlap, B. E. *Ibid.* **1987**, *109*, 3625.

(17) Determined by gas-liquid chromatography and gas analysis.

(18) (a) Factor, A.; Russell, C. A.; Traylor, T. G. *J. Am. Chem. Soc.* **1965**, *87*, 3692. (b) Hiatt, R.; Traylor, T. G. *Ibid.* **1965**, *87*, 3766. The reactions 10–14 are documented here and elsewhere.

(19) Traylor, T. G.; Xu, F. *J. Am. Chem. Soc.*, in press.

(20) We had previously determined $k_H/k_D = 1$ for phenol oxidation by a different method and presented other evidence for electron transfer.[6b]

(21) Fita, I.; Rossman, M. G. *J. Mol. Biol.* **1985**, *185*, 21.

(22) Poulos, T. L.; Kraut, J. *J. Biol. Chem.* **1980**, *255*, 8199.

A New Low-Temperature Route to Metal Polychalcogenides: Solid-State Synthesis of $K_4Ti_3S_{14}$, a Novel One-Dimensional Compound

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During the last few years a large number of new *molecular* sulfides have been reported.[1] These compounds are of interest as models for biologically and catalytically important sulfides.[1a,b] They exhibit a variety of polysulfide ligands (S_x^{2-}, x = 1,2...) and a number of sulfur-bonding modes.[1d] Concomitant with this work on molecular sulfides has been an increased activity in *nonmolecular* (i.e., extended structure) sulfides. This work has been fueled by the catalytic and electronic properties of these materials.[2] We report here a new synthetic approach that allows for the low-temperature synthesis of new low-dimensional polychalcogenides, a class of compounds that bridges the chemistry of the molecular and solid-state compounds.

Molten alkali metal polysulfides have previously been used as fluxes in the crystal growth of solid-state sulfides.[3-5] These previous reports have involved syntheses at high temperatures (>800 °C), and none of the compounds prepared contains polysulfide ions. We have used A_2Q/Q melts (A = alkali metal, Q = S or Se) for the synthesis at low temperatures of new low-

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(1) (a) Müller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934–955. (b) Müller, A. *Polyhedron*, **1986**, *5*, 323–340. (c) Harmer, M. A.; Halbert, T. R.; Pan, W. H.; Coyle, C. L.; Cohen, S. A.; Stiefel, E. I. *Polyhedron* **1986**, *5*, 341–347. (d) Coucouvanis, D.; Hadjikyriacou, A.; Draganjac, M.; Kanatzidis, M. G.; Ileperuma, O. *Polyhedron* **1986**, *5*, 349–356.

(2) (a) Shenoy, G. K.; Dunlap, B. D.; Fradin, F. Y. *Ternary Superconductors*; Elsevier: North Holland, New York, 1981. (b) Whittingham, M. S. *Prog. Solid State Chem.* **1978**, *12*, 41–99. (c) Rouxel, J.; Brec, R. *Ann. Rev. Mater. Sci.* **1986**, *16*, 137–162. (d) Chianelli, R. R. *Catal. Rev. Sci. Eng.* **1984**, *26*(304), 361–393. (e) Topsøe, H.; Clausen, B. S. *Catal. Rev. Sci. Eng.* **1984**, *26*(324), 395–420.

(3) Scheel, H. J. *J. Cryst. Growth* **1974**, *24*, 669–673.

(4) Bronger, W.; Günther, O. *J. Less-Common Met.* **1972**, *27*, 73–79.

(5) Huster, J.; Bronger, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1974**, *29B*, 594–595.

0002-7863/87/1509-6202$01.50/0

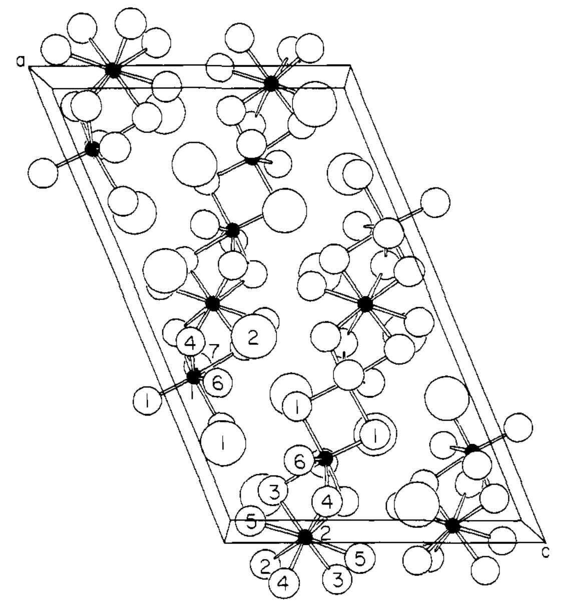


Figure 1. View of the unit cell of $K_4Ti_3S_{14}$. Small filled circles are Ti atoms, small open circles are S atoms, and large open circles are K atoms.

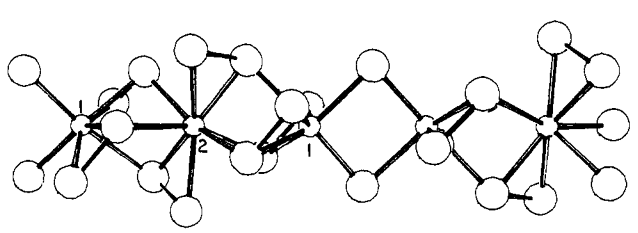


Figure 2. Sketch of the $^1_\infty[Ti_3(S_2)_6(S)_2{}^{4-}]$ chain in $K_4Ti_3S_{14}$.

dimensional solid-state materials. This approach appears to be of general utility;[6] we illustrate it here for the synthesis of a new one-dimensional polysulfide $K_4Ti_3S_{14}$. The reaction of Ti metal (0.023 g) with K_2S (0.107 g) and S powder (0.0932 g) in a sealed silica tube at 375 °C for 50 h leads to the formation of $K_4Ti_3S_{14}$. This compound forms as hexagonal-shaped needles within the K_2S/S melt. The excess melt is dissolved in distilled water. The resulting crystals are black to reflected light and dark burgundy to transmitted light. Crystals up to 1 mm in length are formed. These crystals are not soluble in organic solvents or in mineral acids. They are surprisingly stable during the water wash, as we found no spectroscopic or crystallographic evidence for oxide products.

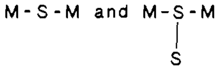
A view of the unit cell of $K_4Ti_3S_{14}$ is given in Figure 1.[7] The structure is composed of one-dimensional chains that run along the [201] direction. These chains (Figure 2) contain two crystallographically unique Ti atoms; Ti(1) is coordinated to seven S atoms while Ti(2) is coordinated to eight. Atom Ti(2) shares three S atoms with two Ti(1) atoms (Ti(1) - Ti(2) = 3.340 (3) Å). Each Ti(1) atom is bound to a second Ti(1) atom through two bridging S atoms (Ti(1) - Ti(1) = 3.314 (3) Å). The three S atoms that bridge atoms Ti(1) and Ti(2) are each a part of an $S_2{}^{2-}$ unit (d_{av} = 2.069 (3) Å) while the S atoms that link Ti(1)-Ti(1) do not form S-S pairs. When the disulfide ions are taken into account, $K_4Ti_3S_{14}$ contains Ti^{IV} and may be described as $K_4[Ti_3(S_2)_6(S)_2]$.

The Ti-S distances (d = 2.283 (2) - 2.652 (2) Å) are in the same range as those found in TiS_3 (d = 2.358 (4) - 2.855 (6) Å), and the S-S distances in $K_4Ti_3S_{14}$ (d = 2.065 (2) - 2.071 (2) Å) are in good agreement with that found in TiS_3 (d = 2.038 (7) Å).[8] The coordination geometries around the Ti atoms are unusual. In most titanium sulfides the Ti atoms possess octahedral coordination, with the exception of TiS_3 where the metal is in a bicapped trigonal prism of S atoms.[8,9] While atom Ti(2) in $K_4Ti_3S_{14}$ is also eight coordinate, its environment is not easily described in terms of a simple coordination polyhedron. This complicated geometry may result from the numerous S-S pairs. The coordination about atom Ti(1) can be described as a distorted pentagonal bipyramid where the pentagon contains two S-S pairs.

The structure of $K_4Ti_3S_{14}$ is truly one-dimensional as each chain is isolated from all others by surrounding K atoms. One-dimensional behavior and considerable chalcogen-chalcogen bonding are also observed in Nb_2Se_9, which is composed of chains of Nb-centered polyhedra.[10] Infinite linear-chain compounds have also been postulated in the solution chemistry of the compounds $(PPh_4)[M'MS_4]$, where M' = Fe, Cu, or Ag and M = Mo or W.[11] These compounds are thought to contain chains of edge-shared MS_4 and $M'S_4$ tetrahedra.

The solution chemistry of metal sulfides has focused largely on molybdenum and tungsten. For these metals, tetrahedral, square-pyramidal, and octahedral coordination geometries prevail.[1a] One interesting example of higher metal coordination is $[Mo_3S_{13}]^{2-}$ where the Mo is bound to seven sulfur atoms.[12] This compound is similar in composition to $K_4Ti_3S_{14}$ ($[Ti_3(S_2)_6(S)_2]^{4-}$ versus $[Mo_3(S_2)_6(S)]^{2-}$), but the molybdenum compound forms as a three-metal cluster, whereas the Ti compound forms in infinite chains.

By analogy with TiS_2 and TiS_3,[13] the infrared spectrum of $K_4Ti_3S_{14}$ in Nujol shows an S-S stretch at 500 cm^{-1} and a number of Ti-S bands below 450 cm^{-1} (410 cm^{-1} s, 375 cm^{-1} m, 370 cm^{-1} w, 360 cm^{-1} w, 290 cm^{-1} w, 275 cm^{-1} w, 265 cm^{-1} w). The large number of M-S bands is attributable to two types of M-S linkages



$$\text{M-S-M} \quad \text{and} \quad \text{M-}\underset{\displaystyle \text{S}}{\underset{|}{\text{S}}}\text{-M}$$

Similar bands are observed in $[Mo_3S_{13}]^{2-}$.[12a]

New one-dimensional materials, such as $K_4Ti_3S_{14}$ and $Na_2Ti_2Se_8$,[6] provide a bridge between two- and three-dimensional solid-state structures on the one hand and molecular structures on the other. Moreover, they afford the potential for cation exchange by low-temperature methods as well as dissolution in highly polar solvents[14] and thus should display a variety of interesting solid-state and solution properties.

The synthetic technique described takes advantage of low-melting eutectics in the A_2Q/Q systems and allows for low-temperature (<400 °C) synthesis where polysulfide ligands are more stable. This approach to new transition-metal ternary chalco-

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(6) The compound $Na_2Ti_2Se_8$ has been prepared in an analogous manner, and its structure has been determined by single-crystal X-ray methods. It is composed of infinite chains of the type $^1_\infty[Ti_2(Se_2)_3(Se)_2{}^{2-}]$ and is again a compound of Ti^{IV}. Other materials that are currently under investigation include one in the Na/Nb/S system and another in the Cs/Fe/Se system. Both of these latter substances have been obtained in crystalline form, and X-ray structural studies are in progress. (Kang, D.; Ibers, J. A., unpublished results.)

(7) $K_4Ti_3S_{14}$: monoclinic, C_{2h}^6-$C2/c$ with four formula units in a cell of dimensions a = 20.91 (2), b = 7.916 (8), c = 12.84 (1) Å, β = 112.20 (3)°, V = 1967 Å^3 at -160 °C. A total of 2285 independent reflections were collected out to 2θ (Mo Kα) = 55°. Complete anisotropic refinement (96 variables) has resulted in $R(F^2)$ of 0.057 and $R(F)$ for the 1711 reflections having $F_o{}^2 > 3\sigma(F_o{}^2)$ of 0.036.

(8) (a) Jeannin, Y.; Benard, J. *Compt. Rend.* **1958**, *246*, 614-617. (b) Furuseth, S.; Brattas, L.; Kjekshus, A. *Acta Chem. Scand.* **1975**, *A29*, 623-631.

(9) (a) Hahn, H.; Harder, B. *Z. Anorg. Allg. Chem.* **1956**, *288*, 257-259. (b) Huster, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 775. (c) Hahn, H.; Harder, B. *Z. Anorg. Allg. Chem.* **1956**, *288*, 241-256.

(10) (a) Meerschaut, A.; Guemas, L.; Berger, R.; Rouxel, J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 1747-1750. (b) Sunshine, S. A.; Ibers, J. A. *Acta Crystallogr.* **1987**, *C43*, 1019-1022.

(11) (a) Müller, A.; Hellmann, W.; Schneider, J.; Schimanski, U.; Demmer, U.; Trautwein, A.; Bender, U. *Inorg. Chim. Acta* **1982**, *65*, L41-L42. (b) Müller, A.; Hellmann, W. *Spectrochim. Acta* **1985**, *41A*, 359-366.

(12) (a) Müller, A.; Sarkar, S.; Bhattacharyya, R. G.; Pohl, S.; Dartmann, M. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 535. (b) Müller, A.; Pohl, S.; Dartmann, M.; Cohen, J. P.; Bennett, J. M.; Kirchner, R. M. *Z. Naturforsch. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *34B*, 434-436.

(13) (a) Chianelli, R. R.; Dines, M. B. *Inorg. Chem.* **1978**, *17*, 2758-2762. (b) Perrin, C.; Perrin, A.; Prigent, J. *Bull. Soc. Chim. Fr.* **1972**, *8*, 3086-3091.

(14) Tarascon, J. M.; DiSalvo, F. J.; Chen, C. H.; Carroll, P. J.; Walsh, M.; Rupp, L. *J. Solid State Chem.* **1985**, *58*, 290-300.

genides is readily extended to Q = Te and A = alkaline earths.

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Supplementary Material Available: A table of atomic and thermal parameters (1 page). Ordering information is given on any current masthead page.

A Diffuse Reflectance FTIR Spectroscopic (DRIFTS) Investigation of Carbon-Supported Metal Carbonyl Clusters

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For the first time, as far as we can determine, an infrared (IR) spectroscopic technique has been successfully applied to characterize metal carbonyl clusters and CO chemisorbed on metal particles that are dispersed on carbon. Amorphous carbons that have been subjected to medium-to-high temperatures are routinely opaque to IR radiation thereby preventing the use of conventional IR techniques,[1-4] although high-frequency bands of physisorbed toluene on carbon black have recently been reported.[5] Using Diffuse Reflectance IR Fourier Transform Spectroscopy (DRIFTS) incorporating a modified controlled environment cell,[6] we have obtained IR spectra for $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$ impregnated on a 1400 m^2/g carbon black, we have quantitatively followed the decomposition of these clusters at different temperatures by DRIFTS, and we have recorded spectra of CO adsorbed on the small reduced metal crystallites that remain after decomposition.[7] We would like to report here two sets of IR spectra illustrating the agreement of these results with previously reported spectra and demonstrating the applicability of DRIFTS to study carbons and carbon-supported catalysts.

The catalysts were prepared anaerobically with use of standard Schlenk techniques and an incipient wetness impregnation of Black Pearls 2000 (Cabot Corp.) with $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ in dried, degassed THF and $Os_3(CO)_{12}$ in CH_2Cl_2.[7] This carbon black was treated in H_2 at 1223 K for 12 h to remove sulfur and oxygen from the surface. The optimal diluent was found to be CaF_2, and a carbon:CaF_2 dilution weight ratio of 1:200 was used.[7]

Spectra were collected on a Mattson Instruments Sirius 100 FTIR spectrometer with use of a substantially modified version of an HVC-DRP (Harrick) closed environment DRIFTS cell in conjunction with a praying mantis assembly (Harrick DRA-2CS). The assembly was modified to allow height adjustment of the powder sample from outside the spectrometer cavity so that the energy throughput could readily be maximized.[6] The fully decarbonylated samples obtained after reduction in H_2 at 673 K for 16 h and He flushing were used to obtain background spectra. The background interferograms for both the supported carbonyls and adsorbed CO spectra were obtained by averaging 10000 scans while the sample inteferograms were obtained by averaging 1000 scans for the supported carbonyls and 10000 scans for the adsorbed CO spectra. The FTIR parameters were set for a resolution of 4 cm^{-1}. Data manipulation consisted of base line correcting the absorbance spectra and then transforming the base line corrected absorbance spectra into diffuse reflectance spectra (Kubelka-Munk units), thereby eliminating the possibility of spectral inversion due to the mathematical form of the Kubelka-Munk function. Agreement between absorbance and diffuse reflectance spectra was excellent.

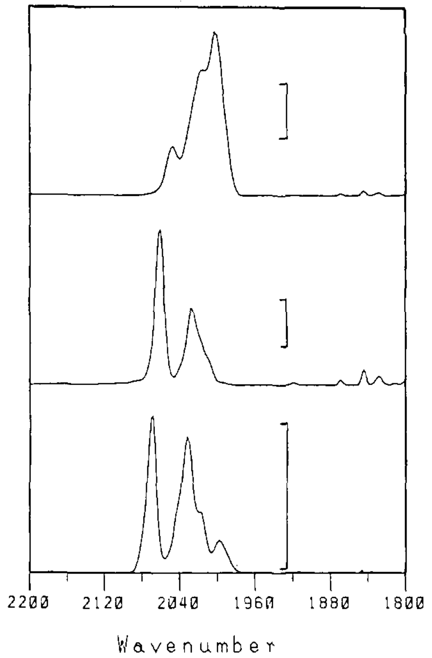

Figure 1. DRIFTS spectra of carbon-supported carbonyls under flowing He at 300 K: (A, top) $Fe_3(CO)_{12}/C$ (15 wt % Fe) with frequencies at 2047, 2018, 2000, 1990 (s) cm^{-1}; (B, middle) $Ru_3(CO)_{12}/C$ (10 wt % Ru) with frequencies at 2060, 2027, and 2010 (s) cm^{-1}; (C, bottom) $Os_3(CO)_{12}/C$ (10 wt % Os) with frequencies at 2068, 2031, 2015 (s), and 2002 cm^{-1}. (Scale = 0.0002 Kubelka-Munk units.)

The IR spectra of the supported carbonyls at 300 K are shown in Figure 1. The observed frequencies for $Ru_3(CO)_{12}$ (2060, 2027 and 2010 cm^{-1}) agree well with reported values of 2059–2064, 2026–2033, and 2012–2018 cm^{-1} for the cluster in solution[8-11] and the cluster supported on dehydroxylated SiO_2.[9,12,13] The observed frequencies for $Os_3(CO)_{12}$ (2068, 2031, 2015, and 2002 cm^{-1}), agree well with reported values (2065–2068, 2033–2037, 2014–2020, and 2000–2003 cm^{-1}) for the cluster in solution[14-17] and on dehydroxylated SiO_2.[18-20] This indicates that both $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ remain intact on the carbon following impregnation, as the familiar interaction with hydroxyl groups on oxide supports is avoided,[13,17,18] and it illustrates a major advantage of using carbon as a support for these compounds. The $Fe_3(CO)_{12}/C$ sample shows peaks at 2047, 2018, 2000, and 1990 (s) cm^{-1}. The peaks at 2047 and 2018 cm^{-1} are characteristic of $Fe_3(CO)_{12}$ in solution,[21-23] while frequencies for $Fe(CO)_5$ are

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(1) Kmetko, E. A. *Phys. Rev.* **1951**, *82*, 456.
(2) Smith, D. M.; Griffin, J. J.; Goldberg, E. D. *Anal. Chem.* **1975**, *47*, 233.
(3) Palmer, D. J. *J. Colloid Interface Sci.* **1971**, *37*, 132.
(4) Delhaes, P.; Carmona, F. *Chem. Phys. Carbon* **1981**, *17*, 89.
(5) Saperstein, D. D. *J. Phys. Chem.* **1986**, *90*, 3883.
(6) Venter, J. J.; Vannice, M. A., submitted for publication.
(7) Venter, J. J.; Vannice, M. A., to be submitted for publication.
(8) Poliakoff, M.; Turner, J. J. *J. Chem. Soc.* **1971**, A654.
(9) Schay, Z.; Lazar, K.; Mink, J.; Guczi, L. *J. Catal.* **1984**, *87*, 179.
(10) Dalla Betta, R. A. *J. Phys. Chem.* **1975**, *79*, 23.
(11) Goodwin, J. G.; Naccache, C. *J. Mol. Catal.* **1982**, *14*, 259.
(12) Robertson, J.; Webb, G. *Proc. R. Soc. London* **1974**, *A341*, 383.
(13) Kuznetsov, V. L.; Bell, A. T.; Yermakov, Y. I. *J. Catal.* **1980**, *65*, 374.
(14) Barth, R.; Gates, B. C.; Zhao, Y.; Knozinger, H.; Hulse, J. *J. Catal.* **1983**, *82*, 147.
(15) Crawford, J. E.; Melson, G. A.; Makovsky, L. E.; Brown, F. R. *J. Catal.* **1983**, *83*, 454.
(16) Watson, P. L.; Schrader, G. L. *J. Mol. Catal.* **1980**, *9*, 129.
(17) Psaro, R.; Dossi, C.; Ogo, R. *J. Mol. Catal.* **1983**, *21*, 331.
(18) Psaro, R.; Ugo, R.; Zanderighi, G. M.; Besson, B.; Smith, A. K.; Basset, J. M. *J. Organomet. Chem.* **1981**, *213*, 215.
(19) Smith, A. K.; Besson, B.; Basset, J. M.; Psaro, R.; Fusi, A.; Ugo, R. *J. Organomet. Chem.* **1980**, *192*, C31.
(20) Li, X. J.; Gates, B. C. *J. Catal.* **1983**, *84*, 1983.
(21) Effa, J. B. N.; Lieto, J.; Aung, J. P. *Inorg. Chim. Acta* **1982**, *65*, L105.

0002-7863/87/1509-6204$01.50/0