shifted by -23 cm^{-1} from the dominant original band. Its formation kinetics establishes that this band is due to complexes of composition BBXHQ–Ar.[7] The most striking feature of the new band is that it is only monitored by red fluorescence. Blue fluorescence only observes the original band at 4178 Å of the bare molecule, disregarding the overwhelming presence of complexed molecules.

Fluorescence excitation of BBXHQ was also examined at higher resolution in pulsed expansions of He mixed with Ne, Ar, Kr, or Xe (Figure 1). Two bands are generally observed—by their red fluorescence only—for complexes BBXHQ–R with a single noble atom R. Through the dependence of their spectral position on the polarizability of R, the stronger band must be associated with the original excitation band for dual fluorescence at 4178 Å. It is therefore due to a complex formed by the molecule in its favored conformation shown in Figure 1.

Why does complexation with a single noble gas atom R effectively remove the blue fluorescence associated with the excited molecule prior to proton transfer? A possible explanation is the preferred stabilization of the excited tautomer by dipole-induced dipole interaction with R. This should lower the barrier for ESIPT. In cooperation with proton tunneling,[4] a relatively small stabilization would be needed for a strong enhancement of the transfer rate.

Regardless of interpretation, the observations reported here suggest that the relative short-wavelength fluorescence of BBXHQ in noble gas matrices may be quite reduced by comparison with the isolated molecule. Conversely, the dual character of fluorescence may be significantly more pronounced in a supersonic jet, for similar molecules[8] which have previously been studied in noble gas matrices.

Acknowledgment. Prof. U. Even for information on nozzle design and particularly Prof. F. P. Schäfer for his continued support.

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Crystal and Molecular Structure of $[(CH_3)_2N]_3S^+CF_3O^-$. Evidence for Negative Fluorine Hyperconjugation

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Perfluorinated alkoxide anions are well-known reactive intermediates[1] and have been the subject of limited theoretical study,[2] but except for the infrared vibrational frequencies of some Cs$^+$ and Rb$^+$ salts,[1f,3] no experimental structural data have been reported. We now report the first single-crystal X-ray structure of a perfluoroalkoxide salt, tris(dimethylamino)sulfonium (TAS) trifluoromethoxide, and we present our theoretical studies of the structure and bonding in CF_3O^- and related perfluoroalkoxides.

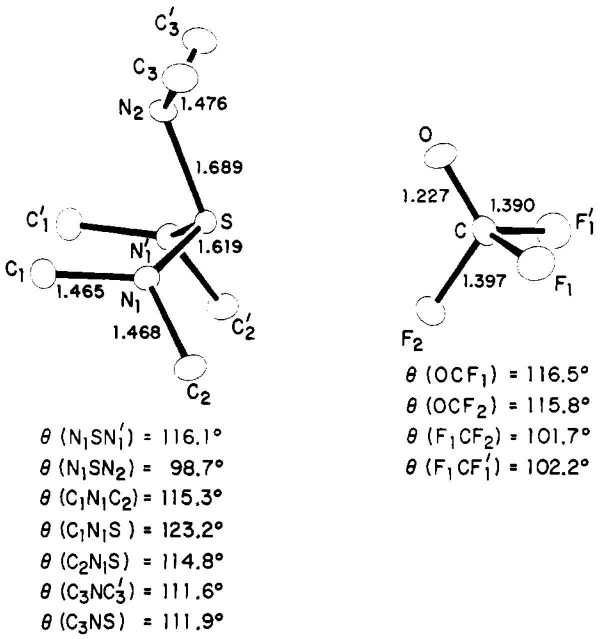

Figure 1. X-ray crystal structure of tris(dimethylamino)sulfonium trifluoromethoxide (**1**). Bond distances in Å. The mirror plane relates atoms bearing primed and unprimed labels.

The X-ray single-crystal diffraction analysis of $TAS^+CF_3O^-$ (**1**)[4] shows that the TAS cation and the CF_3O anion both lie on a crystallographic mirror plane[5] (Figure 1). The C–F bond lengths (1.390 (3), 1.397 (4) Å) are exceptionally long and the C–O bond length (1.227 (4) Å) is quite short compared with the corresponding gas-phase experimental values for CF_3OR (R = F, Cl, CF_3) derivatives (r(C—F) = 1.319–1.327 Å, r(C—O) = 1.365–1.395 Å).[7] In fact, the C—O bond length in **1** approaches that for the C=O bond in CF_2=O (1.171 Å).[8] Moreover, the FCF bond angles (101.7 (2)°, 102.2 (3)°) are extraordinarily small.[9]

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(4) The $TAS^+CF_3O^-$ salt (**1**) was prepared by adding COF_2 to a slurry of 11.0 g (39.5 mmol) of tris(dimethylamino)sulfonium difluorotrimethylsiliconate (TASF)[6] in 100 mL of anhydrous tetrahydrofuran at -75 °C until the exothermic reaction subsided. The mixture was warmed to 25 °C and filtered with the rigorous exclusion of moisture to give 8.81 g (88%) of **1**: mp 214–216 °C dec; IR (CH_2Cl_2) 1553 (ν_1), 805 (ν_2) cm^{-1}; ^{19}F NMR (CD_2Cl_2) δ -21.3 (br s, $w_{1/2}$ = 430 (23 °C), 110 Hz (-1 °C)); ^{1}H NMR (CD_2Cl_2) δ 2.88(s). Anal. C, H, N, F, S. Crystals for X-ray analysis were grown by slowly diffusing an 8:1 mixture of tetrahydrofuran/diethyl ether into a solution of **1** in 1,2-dichloroethane. The solvent mixture was then removed and replaced with tetrahydrofuran to afford crystals which were mounted in glass capillaries in an atmosphere of dry nitrogen.

(5) Crystal structure information: orthorhombic; space group *Pnma* (No. 62); a = 14.547 (2) Å, b = 11.125 (1) Å, c = 7.310 (1) Å, V = 1183 Å^3, Z = 4; T = -100 °C. Data collected on Syntex R3 diffractometer, graphite monochromator, Mo K$\bar{\alpha}$, λ = 0.71069 Å; 1643 reflections, 4.6° < 2θ < 55.0°; 895 unique reflections with $I > 3.0\sigma(I)$. Structure solved by direct methods (MULTAN); full-matrix, least-squares refinement. All hydrogens refined isotropically, other atoms, anisotropically. Final R = 0.036, R_w = 0.039 for 112 independent variables.

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(9) For CF_3OR (R = F, Cl, CF_3),[7] ∠FCF = 108.8–109.4°. The ∠FCF for the CF_3 group in saturated derivatives normally ranges from 108.1° to 109.5°.[7,10]

(10) Typke, V.; Dakkouri, M.; Oberhammer, H. *J. Mol. Struct.* **1978**, *44*, 85.

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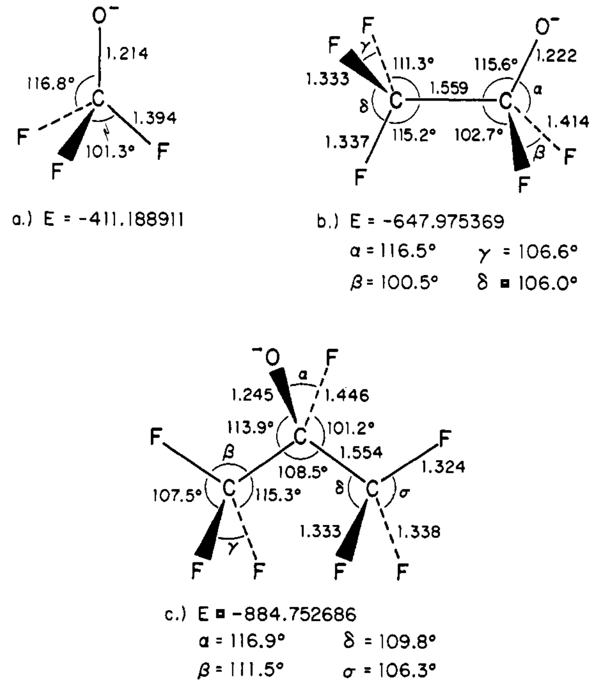
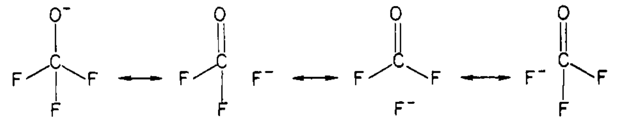


Figure 2. Calculated molecular structures (bond distances in Å) and total energies (au): (a) trifluoromethoxide anion; (b) pentafluoroethoxide anion; (c) heptafluoro-2-propoxide anion.

Ab initio Hartree–Fock calculations were performed on CF_3O^-, $CF_3CF_2O^-$, and $(CF_3)_2CFO^-$ using the program HONDO.[11] The (9,5)/[3,2] double-ζ basis set of Dunning and Hay augmented by a set of d polarization functions on C and O[12] was used. The geometry of CF_3O^- was gradient optimized[13] in C_{3v} symmetry; C_s symmetry was employed for the other ions. The calculated structure for CF_3O^- (Figure 2) agrees well with both experiment and previous calculations,[2a–c] although the C–O bond length is somewhat too short as is expected with this polarized basis set.[14]

The force field for CF_3O^- was determined using gradient techniques[13] to verify the C_{3v} symmetry of the isolated ion. The observed C_{2v} symmetry in the crystal thus is presumably due to packing forces. The calculated frequencies for CF_3O^- are $\nu_1(A) = 1748$, $\nu_2(A) = 912$, $\nu_3(A) = 662$, $\nu_4(E) = 1077$, $\nu_5(E) = 643$, and $\nu_6(E) = 461\ cm^{-1}$, which reasonably agree with values calculated with a 3-21G basis set[2a] but are slightly higher than the matrix values and those for solid $Cs^+CF_3O^-$.[3]

The unusual molecular structure predicts CF_3O^- can be attributed largely to negative hyperconjugation (HCJ).[15] The role of HCJ can be estimated by comparing the electronic charge on F in CF_3O^- with that for model CF_3 compounds. From Mulliken population analyses, the charge on F (q_F) in a CF_3 group is normally between $-0.15e$ and $-0.20e$ for CF_3X derivatives.[16,17] For CF_3O^-, $q_F = -0.35e$ ($q_C = 0.64e$, $q_O = -0.59e$) which compares with $q_F = -0.15e$ in the isoelectronic molecule CF_4. Thus there is an additional charge of $-0.2e$ on each F in CF_3O^-. This excess charge implies that each of the hyperconjugative resonance structures **1b–d** contributes approximately 20% to the bonding in CF_3O^-. From the ab initio CO bond lengths of 1.307 Å in CF_3OH and 1.157 Å in $CF_2{=}O$,[16] and assuming 40% single- and 60% CO double-bond character in CF_3O^-, the C–O bond length in CF_3O^- calculates to be 1.217 Å, in excellent agreement with experiment. The observed 0.07–0.08 Å increase in the C–F bond length over the normal values in CF_3OR derivatives also is consistent with negative HCJ since an increase in CO bond order requires a simultaneous decrease in bond order of the C–F bonds.[21]



1a **1b** **1c** **1d**

Although the HCJ model predicts a somewhat reduced ∠FCF in CF_3O^- (∠FCF = 107.7° in $CF_2{=}O$)[8] compared with the normal values for CF_3 groups,[9] it does not account for the observed angle shrinkage of about 7°. The origin of the small ∠FCF in CF_3O^- is unclear.[22]

Electrostatic (polar) effects also are likely to be important to the bonding in CF_3O^-. The very electropositive O^- substituent on a CF_3 group will withdraw electron density from the C–F bonds, increase the p character in the carbon hybrid orbitals directed toward the fluorines, and consequently lengthen the C–F bonds and reduce the FCF bond angles. The magnitude of the electrostatic effect and its importance relative to HCJ, however, are difficult to ascertain.[24]

A comparison of the C_1–F bond lengths in the series CF_3O^-, $CF_3CF_2O^-$, and $(CF_3)_2CFO^-$ further reveals the importance of negative HCJ. The C_1–F bonds in $CF_3CF_2O^-$ and $(CF_3)_2CFO^-$ are respectively 0.02 and 0.05 Å longer than the C–F bond in CF_3O^- (Figure 2).[27] The alkoxide $(CF_3)_2CFO^-$ expectedly has

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(12) Dunning, T. H., Jr.; Hay, P. J. "Methods of Electronic Structure Theory"; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Chapter 1.

(13) Pulay, P. "Applications of Electronic Structure Theory"; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Chapter 4.

(14) With a fully polarized basis set (d polarization functions on F added), r(C–O) = 1.220 Å, r(C–F) = 1.385 Å, and ∠FCF = 101.5° in CF_3O^-. Total $E = -411.215524$ au.

(15) Negative HCJ has been invoked to explain the IR spectral data for $Cs^+CF_3O^-$.[2a,3] For leading references on negative HCJ in carbanions, see: (a) Schleyer, P. v. R.; Kos, A. J. *Tetrahedron* **1983**, *39*, 1141. (b) Streitwieser, A., Jr.; Berke, C. M.; Schriver, G. W.; Grier, D.; Collins, J. B. *Tetrahedron,*, *Suppl.* **1981**, *37*, (1)345. (c) Sleigh, J. H.; Stephens, R.; Tatlow, J. C. *J. Chem. Soc., Chem. Commun.* **1979**, 921. (d) Sleigh, J. H.; Stephens, R.; Tatlow, J. C. *J. Fluorine Chem.* **1980**, *15*, 411. (e) Streitwieser, A., Jr.; Holtz, D.; Ziegler, G. R.; Stoffer, J. O.; Brokaw, M. L.; Guibe, F. *J. Am. Chem. Soc.* **1976**, *98*, 5229. (f) Stock, L. M.; Wasielewski, M. R. *Prog. Phys. Org. Chem.* **1981**, *13*, 253. (g) Holtz, D. *Prog. Phys. Org. Chem.* **1971**, *8*, 1. Evidence has also been offered for negative HCJ in the related CH_3O^- system: (h) DeFrees, D. J.; Bartmess, J. E.; Kim, J. K.; McIver, R. T., Jr.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 6451. (i) DeFrees, D. J.; Taagepera, M.; Levi, B. A.; Pollack, S. K.; Summerhays, K. D.; Taft, R. W.; Wolfsberg, M.; Hehre, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 5532. (j) Steigerwald, M. L.; Goddard, W. A., III; Evans, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 1994.

(16) Dixon, D. A., unpublished results, using same basis set as described in text.

(17) Ab initio (STO-3G)[18] and semiempirical calculations[10,19,20] give $q_F = -0.18e$ to $-0.22e$ for saturated CF_3X and $(CF_3)_2Y$ derivatives. It should be noted that the charge distributions obtained by Mulliken population analyses are used here only for comparative purposes. For criticism of this method, see, for example: (a) Streitwieser, A., Jr.; Williams, J. E., Jr.; Alexandratos, S.; McKelvey, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 4778. (b) Lüthi, H. P.; Ammeter, J. H.; Almlöf, J.; Faegri, K., Jr. *J. Chem. Phys.* **1982**, *77*, 2002.

(18) Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 2191.

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(20) Oberhammer, H. *J. Mol. Struct.* **1975**, *28*, 349.

(21) The C–F bond order in CF_3O^- is 0.8 from this model, but the corresponding bond length cannot be derived since the relationship between σ-CF bond order and bond length is unknown.

(22) The small bond angle is not unprecedented. The C–F bond length and ∠FCF in CF_3O^- are similar to those calculated for CF_3^-: r(C–F) = 1.417,[16] 1.434 Å;[23] ∠FCF = 99.5°,[16] 99.6°.[23]

(23) Marynick, D. S. *J. Mol. Struct.* **1982**, *87*, 161.

(24) The increase in C–F bond lengths in CF_3X (X = F, Cl, Br, I, H) from 1.319 (X = F) to 1.334 Å (X = H) has been attributed solely to polar effects,[10,20] but this undoubtedly is oversimplified since resonance is known to be important in CF_4.[25,26] The FCF bond angles in CF_3X (X = Cl, Br, I, H) are nearly identical within experimental error, however.[10] Without a value for the effective electronegativity of O^-, the influence of polar effects on the structure of CF_3O^- remains moot.

(25) Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 289.

(26) Baird, N. C. *Can. J. Chem.* **1983**, *61*, 1567.

the longest C_1–F bond since only one fluorine hyperconjugative resonance structure is available to delocalize charge, whereas in $CF_3CF_2O^-$ and CF_3O^- there are two and three, respectively. The increase in C_1–F bond lengths, however, might simply reflect the well-known dependence of C–F bond length on the number of fluorines attached to the carbon atom.[7a,28] For CF_3–F, CF_3CF_2–F, and $(CF_3)_2CF$–F the calculated bond lengths are 1.306, 1.312, and 1.328 Å, respectively.[29] The C–F bond lengths in the perfluoroalkoxides show a much larger change than in the perfluoroalkanes, which clearly supports the importance of negative HCJ in the alkoxides.

Registry No. $(Me_2N)_3S^+CF_3O^-$, 96898-10-1; F_2CO, 353-50-4; $(Me_2N)_3S^+Me_3F_2Si^-$, 59218-87-0; CF_3O^-, 57178-38-8; $CF_3CF_2O^-$, 94295-10-0; $(CF_3)_2CFO^-$, 44967-50-2.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and structure amplitudes (5 pages). Ordering information is given on any current masthead page.

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(27) The TAS salts of $CF_3CF_2O^-$ and $(CF_3)_2CFO^-$ were easily prepared by adding $CF_3C(O)F$ and $(CF_3)_2C{=}O$, respectively, to TASF following the procedure to make **1**;[4] $TAS^+CF_3CF_2O^-$: mp 189–191 °C dec; ^{19}F NMR (CD_2Cl_2, −80 °C) δ −83.52 (s, CF_3), −34.56 (s, CF_2); $TAS^+(CF_3)_2CFO^-$: mp 129 °C dec; ^{19}F NMR (CD_2Cl_2, −30 °C) δ −81.24 (d, J = 4.5 Hz, CF_3), −71.17 (sept, J = 4.5 Hz, CF); δ (20 °C) −81.21 (s, CF_3), −69.30 (s, CF, $w_{1/2}$ = 12 Hz). Unfortunately we have not yet been able to obtain crystals of either salt suitable for X-ray analysis. Unlike their Rb^+ and Cs^+ salts, which rapidly decompose at or below 50 °C,[1f] the TAS^+ salts of $CF_3CF_2O^-$ and $(CF_3)_2CFO^-$ are both stable up to their respective melting points. Solution dynamic properties and synthetic use of TAS perfluoroalkoxides and related stable TAS perfluorocarbanions will be discussed in a forthcoming publication: Smart, B. E.; Middleton, W. J.; Farnham, W. B., unpublished results.

(28) Al-Ajdah, G. N. D.; Beagley, B.; Jones, M. O. *J. Mol. Struct.* **1980**, *65*, 271 and references cited therein.

(29) Ab initio (6-31G+ polarization functions on C) values: Van-Catledge, F. A.; Dixon, D. A. Experimental differences: $r(CF_3\text{–}F)^{10} - r(CF_3CF_2\text{–}F)^{30} \cong 0.007$ Å; $r(CF_2H\text{–}F)^{10} - r(CF_3CFH\text{–}F)^{31} \cong 0.009$ Å. No experimental $(CF_3)_2CX$–F bond lengths have been reported to date.

(30) Gallaher, K. L.; Yokozeki, A.; Bauer, S. H. *J. Phys. Chem.* **1974**, *78*, 2389.

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Changes in the Electronic Structure of Ni/TiO_x Composites as a Function of Reduction Temperature[†]

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Transition-metal catalysts are dispersed on high surface area oxide supports in order to obtain a large catalytic activity per metal atom. Many supports, such as SiO_2 and Al_2O_3, are considered to be inert; that is, these supports do not alter the intrinsic activity of the metal significantly but only serve to increase the surface area of the metal and prevent sintering. For some oxide supports, however, there is a strong interaction between the metal and the support.[1] In particular, TiO_2 can affect the activity of the supported metal depending on the conditions under which the metal-titanium dioxide composite is prepared. It is our goal to learn how to control the chemistry of supported metals by modifying the support composition and the composite preparation temperature.

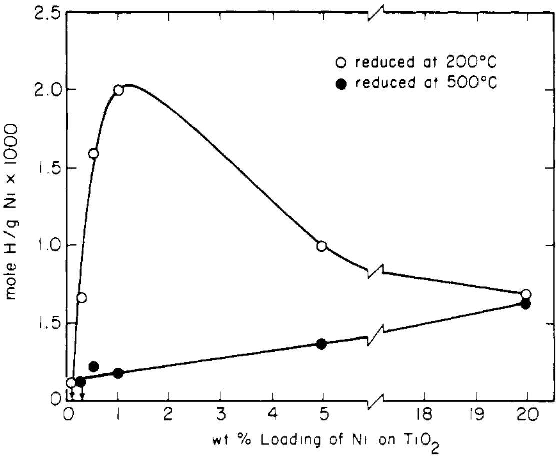

Figure 1. Dependence of H_2 chemisorption at room temperature on the weight percent of Ni supported on TiO_2.

Typically, transition metals are dispersed on oxide supports by impregnation of the support with a metal salt and subsequent reduction to the metal in flowing hydrogen. The catalytic activity and chemisorption properties of group 8–10 metals supported on TiO_2 depend on the reduction temperature used to prepare the catalyst. In particular, the chemisorption of H_2 and CO at 295 K decreases sharply as the reduction temperature is increased from 473 to 773 K. This supression of chemisorption can be attributed to (1) the migration of TiO_x species from the support onto the metal particles, thereby decreasing the number of metal sites exposed for chemisorption,[2] (2) an electronic effect, due to charge transfer from the reduced support to the metal,[3] or (3) the formation of a new metastable Ni–Ti–O phase. We have studied the magnetic properties of Ni/TiO_2 and have shown that an electronic change occurs as a function of reduction temperature.

We chose to study nickel supported on TiO_2 because the magnetic properties of the nickel provide an excellent probe of changes in the electronic properties of the Ni/TiO_2 composites. Nickel is ferromagnetic below its Curie temperature of 627 K with a saturation magnetization M_s = 57.50 emu/g at absolute zero.[4] By measuring the saturation magnetization of the Ni/TiO_2 samples, the amount of Ni present as bulk metal can be determined. TiO_2, on the other hand, is an insulator and is diamagnetic. It can be reduced, however, in hydrogen to a series of paramagnetic phases known as the Magneli phases of formula Ti_nO_{2n-1} for $n \geqslant 3$.[5] Whereas this reduction does not occur for pure TiO_2 below ~1000 K, it occurs at much lower temperatures in the presence of metal impurities.[6] These Magneli phases are all paramagnetic due to the presence of Ti^{3+} species.[7] By measuring the paramagnetic moment of the Ni/TiO_2 samples it is possible to determine the degree of support (TiO_2) reduction. Therefore, in a single magnetic measurement one can determine both changes in the electronic properties of the nickel and the degree of reduction of the support.

Samples of Ni/TiO_2 were prepared from TiO_2 (Cerac, 99.9% pure) which was 15–20% rutile and 80–85% anatase with a surface area of 51 m^2/g. Samples with nickel loadings from 0.1% to 20% by weight were prepared by incipient wetness techniques using

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[†] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

(1) (a) Tauster, S. J.; Fung, S. C.; Garten, R. C. *J. Am. Chem. Soc.* **1978**, *100*, 170. (b) Tauster, S. J.; Fung, S. C. *J. Catal.* **1978**, *55*, 29. (c) Tauster, S. J.; Fung, S. C.; Baker, R. T.; Horsley, J. A. *Science (Washington, D.C.)* **1981**, *211*, 1221.

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(6) Wyss, R. *Ann. Chim. (Paris)* **1948**, *3*, 215.

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