Figure 2. The bipartite graph $K_{2,3}$ (a) in the Berry pseudorotation mechanism for ligand exchange in five-coordinate systems.

with the absurd ω value of zero. Thus neither the trigonal bipyramid nor the square pyramid represents a favorable *graph* for the coordination number 5.

The desired 1, 3, 1 eigenvalue pattern for coordination number 5 may be obtained by use of the $K_{2,3}$ bipartite graph shown in Figure 2a. The eigenvalues of this graph are $+6^{1/2}$, 0, 0, 0, and $-6^{1/2}$ (Figure 1e). The $K_{2,3}$ graph is planar, has the D_{3h} automorphism group, and can thus mimic the trigonal bipyramid. Indeed, it differs from the trigonal bipyramid only in that the equatorial–equatorial interactions are taken to be negligible relative to the equatorial–axial interactions. This is not unreasonable since the equatorial–equatorial bond angles are 120° whereas the equatorial–axial bond angles are only 90°. Furthermore, if a $K_{2,3}$ graph is visualized in three-dimensional space with vertices of like charge, minimization of its repulsion energy will cause the vertices to form a trigonal bipyramid.

By recognizing that the graph representing the energy minimum for a five-coordinate system is the $K_{2,3}$ bipartite graph of Figure 2a, we have accounted for the stereochemical nonrigidity of five-coordinate systems as compared to the relative rigidity of four- and six-coordinate systems. The $K_{2,3}$ graph has a very flexible shape and considerable freedom of motion without any change of the bond lengths. Moreover, the Berry pseudorotation mechanism[11,12] can be represented using $K_{2,3}$ graphs as in Figure 2. For example, flexing of the $K_{2,3}$ graph of Figure 2a such that new edges BC and BD are formed gives the square pyramid, Figure 2b. Rupture of the edges BA and BE of this square pyramid gives the new $K_{2,3}$ bipartite graph of Figure 2c, where C and D are now the vertices of order 3. Repetition of this process makes the five ligands in a five-coordinate system equivalent on an appropriate time scale.[13]

The situation is still different with coordination numbers 7 and 8, which require respective eigenvalue patterns of 1, 3, 3 and 1, 3, 4. These patterns are impossible[14] in a relatively symmetrical graph which can be inscribed in a sphere without its edges crossing, i.e., in a planar graph.[15] Only by taking a relatively unsymmetrical graph with at least two edge orbits and varying their relative weights can the appropriate eigenvalue patterns for the coordination numbers 7 and 8 be attained. Eigenvalue patterns obtained in this fortuitous manner represent unstable equilibria which should lead to inherently nonrigid stereochemical systems.

In summary, our analysis indicates the following possibilities for coordination numbers from 4 to 8 inclusive, when use is made of sp^{3}d^m ($0 \leq m \leq 4$) hybridization for the central atom: (1) structures for coordination numbers 4 and 6 should be relatively rigid and have a stable symmetry-determined equilibrium; (2) structures for coordination number 5 should be flexible and nonrigid and have a stable symmetry-determined equilibrium; (3) structures for coordination numbers 7 and 8 should be nonrigid and have an unstable equilibrium which is not determined by symmetry. We also note that the octahedron is the graph having the largest number of vertices which can be formed for sp^{3}d^m hybrids *and* that this graph has the appropriate eigenvalue pattern for an sp^{3}d^m system. These facts may account for the predominance and stability of the octahedron in many areas of coordination chemistry.

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The Radiofrequency Plasma as a Synthetic Method. Preparation of Tris(trifluoromethyl)bismuth

AIC60882K

Sir:

Recently we have reported[1] a new preparative route to organometallic compounds which are highly or fully substituted with CF_3 groups. The first successful synthesis of, e.g., $Te(CF_3)_2$, $Sn(CF_3)_4$, and $Ge(CF_3)_4$ from the metal halides and CF_3 radicals produced by the glow discharge of C_2F_6 indicates that the plasma technique may be of general utility for the preparation of other new compounds not readily accessible through standard thermal routes. The species produced in these low-pressure discharges are vibrationally and electronically excited, but almost in thermal equilibrium with the surroundings ($T_g \approx 40$ °C). Thus the trifluoromethyl radical is very reactive, but any molecules synthesized by interaction with a second substrate are formed at or near room temperature. Consequently, these products are less likely to undergo unimolecular decomposition than if produced by methods which employ higher temperatures.

The fully substituted trifluoromethyl derivative of bismuth, $Bi(CF_3)_3$, which is currently unknown, provides a particularly interesting case; each of the group 5A trisubstituted analogues $N(CF_3)_3$,[2] $P(CF_3)_3$,[3] $As(CF_3)_3$,[4] and $Sb(CF_3)_3$[5] has been characterized and many have been prepared by a variety of methods. Representative reactions[5-7] which yield the trisubstituted derivatives of the lighter members of group 5 are shown in eq 1-3. However, in each case, either the corre-

$$E + CF_3I \rightarrow (CF_3)_3E + (CF_3)_2EI + CF_3EI_2 \quad (E = P, As, Sb) \quad (1)$$

$$(CF_3)_2E-E(CF_3)_2 + CF_3I \rightarrow (CF_3)_3E + (CF_3)_2EI \quad (E = P, As) \quad (2)$$

$$(CF_3)_nEI_{3-n} \rightarrow (CF_3)_3E + (CF_3)_2EI + CF_3EI_2 \quad (E = P, As, Sb) \quad (3)$$

sponding reaction of bismuth is reported to fail[7] or the required reagent is also unknown.

Additionally, in the related reaction of a metallic bismuth mirror with CF_3 radicals produced by the pyrolysis of hex-
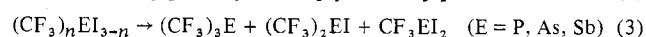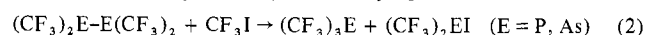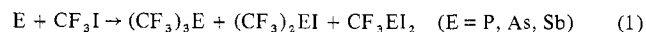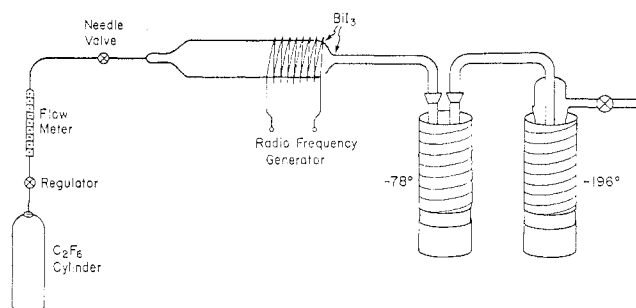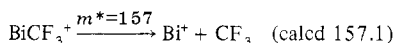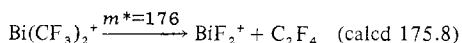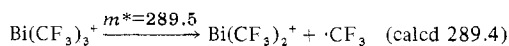
Figure 1. Diagram of the plasma apparatus.

afluoroacetone,[8] the metallic layer was removed but no bismuth-containing species were isolated. The preparation of $Bi(CF_3)_3$ by the plasma route thus appears to provide a critical test of the ability of the plasma system to generate compounds of limited thermal stability.

Experimental Section. In a typical experiment 18 g of BiI_3 was introduced into the reactor in the indicated region (see Figure 1) and the system was evacuated. Hexafluoroethane, after pressure reduction, was then admitted at a rate of 15 cm^3/min. During the course of the reaction the pressure was maintained at ca. 1 Torr. The Lepel radiofrequency generator, operating at 8.6 MHz, was adjusted to provide about 20 W of power to the load coil which was ample to maintain the discharge. The reaction was allowed to proceed for 100 h with periodic removal of the contents of the -196 °C trap. Upon completion of the experiment, the contents of the -78 °C trap were removed and, after fractionation, the appropriate portions of the two samples were combined and further separated by low-temperature distillation. Aliquots for the thermal decomposition studies were vacuum distilled into Pyrex tubes, sealed off with a torch, and placed in a water bath maintained at the appropriate temperature. Infrared (Beckman IR-20A 10-cm gas-phase cells), [19]FMR (Perkin-Elmer R20B), and mass (Hitachi RMU-6E) spectra were obtained by standard procedures.

On the plasma vacuum line, tris(trifluoromethyl)bismuth was found in both the -78 °C trap and the -196 °C trap. Under static vacuum, the compound slowly passes through a trap maintained at -45 °C and is held in a -63 °C trap. $Bi(CF_3)_3$, 0.79 g, 6% conversion, 32% yield,[9] was then purified by low-temperature distillation (-55 °C). This compound is a colorless liquid, which fumes when exposed to air. At room temperature, it is hydrolyzed by base with the evolution of 3 equiv of fluoroform. In sealed 3-mm tubes, decomposition to deposit metallic bismuth occurs at 100 °C with a half-life of approximately 15 min. At 180 °C thermal decomposition occurs in seconds. The [19]FMR spectrum of the compound sealed in a 4-mm tube consists of a singlet at -45.9 ppm (downfield) from external trifluoroacetic acid.

With the spectrometer cooled to room temperature the positive ion mass spectrum at 70 eV contains the following peaks [m/e, assignment, (intensity)]: 416, $Bi(CF_3)_3$, (6.8%); 397, $Bi(CF_3)_2CF_2$, (1.6%); 347, $Bi(CF_3)_2$, (62.0%); 328, $Bi(CF_3)CF_2$, (0.7%); 297, $BiCF_4$, (17.1%); 278, $BiCF_3$, (14.5%); 259, $BiCF_2$, (4.8%); 247, BiF_2, (28.5%); 228, BiF, (11.6%); 209, Bi, (100.0%); 69, CF_3, (32.5%); 50, CF_2, (2.7%). The existance of the molecular ion in the spectrum indicates that ionization occurs by the loss of one of the lone pair electrons from the bismuth atom. The observed metastable ions are ascribed to the following decompositions

$$Bi(CF_3)_3^+ \xrightarrow{m^*=289.5} Bi(CF_3)_2^+ + \cdot CF_3 \quad (calcd\ 289.4)$$

$$Bi(CF_3)_2^+ \xrightarrow{m^*=176} BiF_2^+ + C_2F_4 \quad (calcd\ 175.8)$$

$$BiCF_3^+ \xrightarrow{m^*=157} Bi^+ + CF_3 \quad (calcd\ 157.1)$$

The infrared spectrum contains absorptions at 2135 (vw), 1235 (m), 1180 (vs), 1140 (s), 1120 (s), 1060 (vs), 1032 (w), and 718 (m) cm^{-1}. The appearance of the spectrum between 1000 and 1300 cm^{-1} is very similar to that of the corresponding arsine, $As(CF_3)_3$,[10] but the entire envelope is slightly red-shifted. It should be noted that authentic $Bi(CF_3)_3$ is significantly more volatile than the material obtained in the earlier experiment;[8] furthermore the band shapes, intensities, and energies of the infrared spectrum of our sample are exactly as expected in light of the spectra of the known lighter group 5 trisubstituted analogues.

Results and Discussion. The thermal stability experiments reported above clearly show why the earlier attempts to prepare $Bi(CF_3)_3$ resulted in failure. The desired product is not thermally stable at the temperatures required for its formation by these methods. Thus ligand-exchange reactions of methyl(trifluoromethyl)bismuthines (cf. eq 3) do not proceed[7] to yield the trisubstituted product at temperatures less than 100 °C even with very long reaction times. The reaction of metallic Bi with CF_3I as well as the attempted thermal decarboxylation of $(CF_3COO)_3Bi$ requires temperatures of at least 200 °C before the reactions proceed at a measurable rate, yet the desired product, $Bi(CF_3)_3$, is capable of only fleeting existence under these conditions. In the Paneth reaction,[8] in which CF_3 radicals were generated by the pyrolysis of hexafluoroacetone, the temperature is not reported but appears to be several hundred degrees, again too high to allow the isolation of the compounds. In conclusion, it appears that the plasma method for the preparation of trifluoromethyl-substituted compounds affords the only currently available route to several marginally stable species which lack the thermodynamic stability to survive preparation by more classical methods.

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Comments on the Observation of Carbon-13 Hyperfine Interaction in the Electron Spin Resonance Spectra of Bis(diethyldithiocarbamato)copper(II)

AIC70083H

Sir:

Recently, the observation of different sets of satellite lines, in the ESR spectra of $^{63}Cu(dtc)_2$ I, diluted in a single crystal