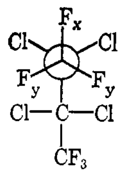

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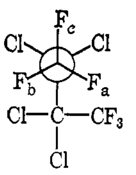

3

two fluorines in closest proximity to one another) suggests that the dominant effect may be one exerted through space rather than through the bonds.[7] The average long-range fluorine–fluorine coupling (8.6 Hz) measured in the ^{13}C satellites on the fluorine spectrum at room temperature suggests that all the other five-bond coupling constants are either small or cancel each other.

The present system seems to afford the first direct measurements of geminal fluorine–fluorine couplings in a trifluoromethyl group and also the first instance of nmr observation of slow rotation about a carbon–trifluoromethyl bond in a saturated compound. With respect to the geminal F–F coupling, Dyer[8] has been able to correlate such couplings in derivatives of the type $QCF_2C\equiv$ with the electronegativity (E_Q) of Q by the expression $J_{FF} \approx 5.4 \times 10^2/E_Q$. The small value of the geminal fluorine–fluorine couplings observed here supports this correlation.

Although a complete analysis of the changes in line shapes with temperature of the complex six-spin system afforded by **1d** is not within our present capability, if we neglect *all* couplings, E_a for the barrier to the rotation of the trifluoromethyl group seems to be about 8 kcal/mol for the *gauche* isomer and 6 kcal/mol for the *trans* isomer.[9] The barrier to rotation about the central carbon–carbon bond must be greater than 8 kcal/mol but cannot be accurately determined because of the small proportion of the *trans* conformation in the mixture and because of the similar coalescence temperatures associated with spectral changes arising from rotation about the central and exterior C–C bonds in the *gauche* isomer.

(7) S. Ng and C. H. Sederholm, *J. Chem. Phys.*, **40**, 2090 (1964). The calculated F–F internuclear distance between F_a and the nearest fluorine in the remote CF_3 group in **3** for the all-staggered conformation with tetrahedral angles and normal C–C and C–F bond distances is 1.69 Å, which is substantially less than the 2.9-Å fluorine–fluorine distance expected at the van der Waals minimum.

(8) J. Dyer, *Proc. Chem. Soc.*, 275 (1963).

(9) These values for the barrier to rotation about a CF_3–CCl_2C bond agree reasonably well with the 6-kcal barrier obtained for CF_3CCl_3 by E. Catalano and K. S. Pitzer, *J. Phys. Chem.*, **62**, 838, 873 (1958); but much less well with the (10.7–)13.2-kcal value reported for CF_3–CCl_3 (and similar very high figures for other chlorofluoroethanes) by N. W. Luft, *ibid.*, **59**, 92 (1955).

(10) National Science Foundation Predoctoral Fellow, 1965–1968.

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New Sulfur Chelate Chemistry

Sir:

Characterization of derivatives of the recently described difluorodithiophosphate anion,[1] $PS_2F_2^-$, has revealed a large class of metal chelates whose distinguishing features are relatively high volatility and unusual reactivity. Established examples of this class include the mono chelates of Cu(I), Ag(I), and Cu-$[P(C_6H_5)_3]_2^+$, the bis chelates of divalent Mn, Fe, Co, Ni, Pd, Zn, Cd, and Hg, and the tris chelates of trivalent Cr and Co.

Preparation was effected under water- and oxygen-free conditions through reaction of the metals or metal halides with the anhydrous acid $HSPSF_2$ and by reaction of $(S_2PF_2)_2$ with the metals, *e.g.*, mercury, as well as oxidation of bis chelates with the disulfide to give the tris chelates. All of these compounds have been compositionally identified by complete elemental analyses. A representative analysis follows. *Anal.* Calcd for $Fe(S_2PF_2)_2$: Fe, 17.3; S, 39.8; P, 19.2; F, 23.6. Found: Fe, 17.7; S, 39.9; P, 19.3; F, 23.6. Of the compounds carefully examined to date with respect to molecularity, all were found to be monomeric in such solvents as heptane, toluene, and 1,2-dichloroethane (vapor tension technique[2]). Such a definition of molecularity is consistent with the high solubility of the complexes in nonpolar solvents such as heptane. Furthermore, facile vaporization implies that no significant intermolecular association occurs in the solid state for most of the bis and tris transition metal chelates. Illustrative vapor tension data are $Co(PS_2F_2)_2$, 20 mm (95°), and $Ni(PS_2F_2)_2$, 13.5 mm (95°). The Mn(II) and post-transition derivatives appear to be much less covalent, a point consistent with their lower volatilities, *e.g.*, <1 mm (95°) for the cadmium chelate and the absence of strong charge-transfer bands so pronounced in the chromium, cobalt, and nickel derivatives.

The reactivity of these new chelates varies with the metal electronic configuration and coordination number. Least reactive are the six-coordinate complexes exemplified by the relatively inert chromium(III) derivative. The cobalt(II) chelate is readily oxidized in air to the tris derivative. The generally high reactivity of the tetrahedral chelates required all manipulations to be effected in either a high-vacuum system or an efficient drybox.

Nuclear magnetic resonance studies show the nickel and palladium compounds to be diamagnetic and accordingly square planar. Susceptibility measurements by nmr technique revealed moments at 30° of 3.8, 5.9, 5.2, and 6.2 BM for Cr(III), Mn(II), Fe(II), and Co(II), respectively. These values were reproduced within 0.1 to 0.2 BM in solvents ranging from heptane to dichloromethane. The moments are consonant with octahedral chromium and tetrahedral manganese and iron. On the other hand, the value of 6.2 BM for a tetrahedral[3] cobalt complex is inexplicable. Solution Gouy measurements yielded a value of 5.1 BM which is still high but consistent with a very weak ligand field.

F^{19} nmr data for the diamagnetic species show that the PF spin-spin coupling varies significantly from values of 1189 cps for the Cu(I) derivative to 1316 cps for the square-planar palladium species.[4] Similarly,

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(1) H. W. Roesky, F. N. Tebbe, and E. L. Muetterties, *J. Am. Chem. Soc.*, **89**, 1272 (1967).

(2) With the more reactive bis chelates, considerable difficulty was encountered in obtaining reproducible data because of oxidation and hydrolysis reactions; apparent molecular weights increased with time.

(3) There is no indication of association of this chelate, and the interaction of such a complex with heptane is implausible. Hence, we do not suspect a six-coordinate cobalt in such solutions of $Co(S_2PF_2)_2$.

(4) Variations in the PF coupling constants may reflect changes in the FPF angle. The J_{PF} values of the apparently more ionic derivatives approach that of $HSPSF_2$ (1214 cps).

there is a substantial variation in the chemical shifts. A few representative values are +3.9 for Co(III), 8.2 for Ni(II), and 12.9 for Cd(II) (ppm, with reference to $CFCl_3$). These are to be compared with the value of 15.8 for the anhydrous acid. Cobalt-fluorine coupling is evident in the spectrum of the Co(III) derivative; however, the relatively large line width precluded assignment of a meaningful value to the $Co^{59}F^{19}$ coupling. Long-range FF or PF coupling (~5 cps) was evident in the palladium compound.

Singularly, $Mn(S_2PF_2)_2$ in warm benzene solution absorbs oxygen with a change in color from a very light yellow characteristic of tetrahedral Mn(II) to a deep red. A nitrogen purge of the warm solution does not regenerate the original Mn(II) complex. There is some degradation of the ligand, but the decomposition reaction has not been completely defined. Most of the bis chelates react readily with donor molecules to yield five- and six-coordinate complexes. Of particular note is the reaction of $Co(S_2PF_2)_2$ with nitric oxide. There is a fast process which leads to the formation of $(NO)_2CoS_2PF_2$ and $(S_2PF_2)_2$. In a concurrent reaction the bis chelate is oxidized by the disulfide, $(S_2PF_2)_2$, to form the trisdithiophosphato derivative of Co(III). The tris chelate is also attacked by nitric oxide although the reaction is slow, and this attack leads to the formation of the nitrosyl derivative as well as the disulfide. The nitrosyl derivative is diamagnetic and volatile (bp 64° (12 mm)). Nitrosyl stretching frequencies are at 1797 and 1869 cm^{-1}. The position of the nitrosyl bands suggests function of the nitrosyl ligand as NO^+ implicating the relatively unusual *formal* −1 oxidation state for cobalt.

Full experimental details, as well as a more complete chemical characterization, of these unusual chelates will be presented shortly. We wish to acknowledge the assistance of Mr. D. Hall and Dr. M. O'Connor in the Gouy measurements.

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Organogallium Compounds. V. The Gallium–Carbon–Gallium Bridge Bond in Trivinylgallium[1,2]

Sir:

The trialkyl compounds of group III have been studied intensively in order to characterize electron-deficient bridge bonds and the exchange phenomena associated with them. In contrast, little is known about the corresponding vinyl systems: $B(C_2H_3)_3$ is monomeric,[3] uncoordinated $Al(C_2H_3)_3$ polymerizes too readily to study,[4] the synthesis of $In(C_2H_3)_3$ has not been reported,[5] and attempts to prepare $Tl(C_2H_3)_3$ have failed.[6] $Ga(C_2H_3)_3$ and the three isomeric propenyl derivatives have been isolated and shown to be dimeric in noncoordinating solvents,[7] unlike the saturated alkyl derivatives which are known to be monomeric.[8]

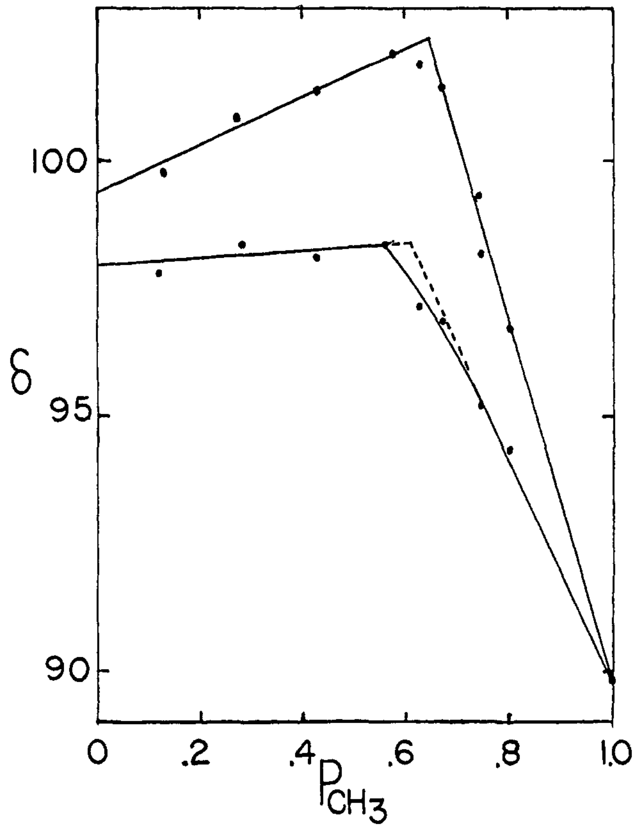

Figure 1. The chemical shift (in cps, 60 MHz) upfield from cyclopentane of the methyl protons *vs.* the mole ratio $(CH_3)/((CH_3) + (C_2H_3))$. The lower curve was obtained at +40°, while the upper one was obtained at −50°.

A structure similar[9] to that of $Al_2(CH_3)_6$ has been proposed for $Ga_2(C_2H_3)_6$ in which the vinyl groups occupy both bridge and terminal positions.[7a] Attempts to directly observe the groups in these positions by low-temperature nmr studies (−100°, 100 MHz) have failed since a single sharp vinyl spectrum is observed under all conditions. This implies the vinyl groups are still undergoing rapid exchange.

In order to gain further insight into the nature of the vinyl bridge bond, we undertook a study of the $Ga(CH_3)_3$–$Ga(C_2H_3)_3$ system. Rapid exchange between all sites also occurs in this system. Only a single methyl resonance and a single vinyl spectrum were observed for all relative $CH_3:C_2H_3$ ratios and all temperatures; however, marked changes occur in the spectrum with variation of these parameters. Figure 1 shows the effect of relative concentration and temperature on the methyl resonance while Figure 2 portrays these effects on chemical shifts, obtained from exact analyses of the vinyl spectrum, of the proton *trans* to the metal. Iden-

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(1) Presented in part at the 3rd International Symposium on Organometallic Chemistry, Munich, Aug 1967.

(2) Supported in part by National Science Foundation Grant GP 6762.

(3) T. D. Parsons, M. B. Silverman, and D. M. Ritter, *J. Am. Chem. Soc.*, **79**, 5091 (1957); F. E. Brinckman and F. G. A. Stone, *ibid.*, **82**, 6218 (1960).

(4) B. Bartocha, A. J. Bilbo, D. E. Bublitz, and M. Y. Gray, *Z. Naturforsch.*, **14b**, 357 (1961).

(5) $In(C_2H_3)_3$ has been synthesized in this laboratory and will be reported at a later date.

(6) J. P. Maher and D. F. Evans, *J. Chem. Soc.*, 5534 (1963).

(7) (a) J. P. Oliver and L. G. Stevens, *J. Inorg. Nucl. Chem.*, **24**, 953 (1962); (b) D. Moy, J. P. Oliver, and M. T. Emerson, *J. Am. Chem. Soc.*, **86**, 371 (1964).

(8) M. Muller and A. L. Otermat, *Inorg. Chem.*, **4**, 296 (1965).

(9) R. G. Vranka and E. L. Amma, *J. Am. Chem. Soc.*, **89**, 3121 (1967); P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, **21**, 986 (1953).