splittings for the three d metal orbitals using ESCA[24] for the isolated tetracyanoplatinate(II) ions in $(Bu_4N)_2Pt(CN)_4$ in the solid state.[17] The results were not useful since a single broad band was observed which could not be deconvoluted into the expected three d levels.

The striking correspondence between the electronic spectra of **1** and **2** suggests in principle that **2** could become partially oxidized to form a highly conducting one-dimensional complex. The dipositive charge on the ion would make $Pt(CNCH_3)_4^{2+}$ more difficult to oxidize with respect to $Pt(CN)_4^{2-}$; however, a number of similar dications have been oxidized by halogen.[25-27] Bromine oxidation of **1**, in contrast to results for **2**, results in the formation of $Pt^{II}(CNCH_3)_3Br^+$,[18,28] presumably through an unstable Pt^{IV} intermediate, with no evidence for the formation of a partially oxidized phase of a stable Pt^{IV} complex. Furthermore, several platinum(IV) isocyanide complexes have been reported to be unstable with respect to dealkylation.[27] Thus, the electronic structure of an isolated complex cannot be used to predict the ability of the ion to undergo partial oxidation.

Both **1** and **2** have similar electronic structures but only the cyano complex has been partially oxidized. Strong band formation must occur in a solid in order to achieve partial oxidation and a metallic state. The formation of such a solid cannot be predicted on the basis of the symmetry and ordering of the electronic structure of the isolated building block of the solid. In order to achieve strong overlap of the d_{z^2}-like wave functions to form a band, the d_{z^2} orbital needs a large spatial extension. This is facilitated by the d^8 third-row transition metals. However, the 4+ charge difference should diminish the overlap of the a_{1g} wave functions between adjacent $Pt(CNCH_3)_4^{2+}$ ions, relative to the overlap of wave functions for those $Pt(CN)_4^{2-}$ ions, thereby decreasing the probability of formation of one-dimensional complexes. These observations are qualitatively borne out by noting[1,4] that the only highly conducting transition metal one-dimensional complexes are based on $5d^8$ Ir^I and Pt^{II} anions.[29-31]

Registry No. $Pt(CNCH_3)_4(PF_6)_2$, 38317-61-2.

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(19) Low-temperature glasses, i.e., EPA and 9:1 $MeOH:H_2O$, alter the spectra presumably through reaction with the alcohol.
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Perfluoro(alkylsilanes). 3. Fluorine–Fluorine Coupling Constants in Perfluoro(alkylsilanes) and Related Molecules

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Coupling constants between fluorine atoms in linear and cyclic fluorocarbons and their derivatives have been the subject of numerous investigations in the past 15 years. However, the path to understanding theoretical principles and recognizing molecular parameters which are most influential in determining magnitudes of such couplings has often not been a smooth one. Early workers[3,4] formulated correlations between $^3J_{FF}$ in fluoroethanes with substituent electronegativity without consideration of the relative signs of the coupling constants or of relative free energies of the various rotational conformers. Lack of recognition of magnetic nonequivalence in CF_2 groups[5] and controversy over "through space" interactions[6] have also retarded progress in this area to some extent.

More recently, a variety of workers have demonstrated the marked sensitivity of F–F couplings to stereochemical disposition, both in cyclic and acyclic systems. Long-range couplings have been more widely reported, and theoretical calculations of F–F couplings which include orbital and spin dipolar terms have appeared.[6b,c]

Perfluoroalkanes would seem to be reasonable prototypes for studies of F–F coupling constants; however, the high symmetry of these species can lead to highly complex spin systems. A good illustration is n-C_4F_{10}: the spin system was initially incorrectly assigned.[5] Harris and Woodman[7] subsequently analyzed the spectrum as an $[AA'X_3]_2$ system. The spectrum is of such complexity that, even with the use of ^{13}C satellite spectra as an aid to analysis, definitive values of all the F–F couplings in the molecule could not be obtained.

Table I. NMR Parameters[a] of Perfluoro(alkylsilanes) and Related Fluorocarbons

	δ_1[b]	δ_2	δ_3	δ_4	J_{12}[c]	J_{13}	J_{14}	J_{23}	J_{24}	J_{34}	$^1J_{\mathrm{SiF}}$
$CF_3CF_2SiF_3$ (I)[d,e]	86.5	134.4	150.2		−3.59	−2.81		+4.92			+275.3
$CF_3SiF_2SiF_3$ (II)[d]	69.8	142.4	123.3		+6.09	+1.91		+13.27			
$CF_3CF_2CF_2SiF_3$ (III)[d]	83.0	127.2	131.3	148.8	(+0.1 to +0.5)	+9.10	−1.76	0.62	−3.57	+4.82	+275.7
$SiF_3CF_2SiF_3$ (IV)[d]	150.5	146.6			+2.97	+1.66					+281.0
$CF_3CF_2CF_3$[f]	83.0	131.5			0.70	+7.3					
$SiF_3SiF_2SiF_3$[g]	127.1	139.6			+10.8	+3.61					+344.4 (SiF_3) +356.6 (SiF_2)
$CF_3CF_2CF_2CF_3$[h]	83.1	126.9			−0.2	+9.9	+2.0				

[a] Numbering of groups of fluorines is from left to right for the molecules as written. [b] Chemical shift in parts per million upfield from external $CFCl_3$. [c] F–F coupling constants in Hz. Values reported in this work are believed accurate to ±0.04 Hz. [d] This work. [e] Reference 9. [f] G. V. D. Tiers, *J. Phys. Chem.*, **66**, 945 (1962). [g] Reference 14. [h] Reference 7.

The recent synthesis of perfluoro compounds of carbon and silicon[8,9] has provided access to close structural analogues to the perfluoroalkanes whose lower symmetry, however, makes for simpler spectra which are more amenable to complete analysis. Moreover, comparison of absolute signs of F–F couplings in perfluoro(alkylsilanes) with those in analogous fluoroalkanes would allow exploration of possible systematic effects of "substitution" of silicon for carbon on the coupling constants. Such effects would provide new information on which to evaluate present or formulate new theories of F–F coupling and could be of considerable diagnostic value in characterization of new polyfluoro silicon compounds.

We present here NMR spectral analyses of the known[9] compound $CF_3CF_2SiF_3$ (I) and the new compounds $CF_3SiF_2SiF_3$ (II), $CF_3CF_2CF_2SiF_3$ (III), and $SiF_3CF_2SiF_3$ (IV), along with some correlations between values of $^3J_{FF}$ in these and related molecules.

Experimental Section

The air-sensitive compounds discussed in this study were manipulated in a grease-free glass high-vacuum system. CF_3SiF_3,[8] $CF_3CF_2SiF_3$,[9] and CF_3SiF_2X,[10] X = Cl, Br, and I, were prepared as previously described. n-$C_3F_7SiF_3$ was synthesized from n-$C_3F_7SiF_2I$, which was in turn generated from the reaction of SiF_2 with n-C_3F_7I. $CF_3Si_2F_5$ and $SiF_3CF_2SiF_3$ were obtained from iodosilane precursors which are formed in the reaction of SiF_2 with CF_3I.[11] Complete details of the syntheses and characterization of the latter three compounds will be provided elsewhere.

^{19}F NMR spectra were obtained on Varian Models DP-60 (modified for field-frequency lock, frequency sweep operation) at 56.4 MHz or XL-100-15 (94.1 MHz) spectrometers.[12] Relative signs of F–F couplings were determined by spin tickling double resonance techniques.[13,14]

Results and Discussion

NMR spectral parameters for $CF_3CF_2SiF_3$ (I), $CF_3SiF_2SiF_3$ (II), $CF_3CF_2CF_2SiF_3$ (III), and $SiF_3CF_2SiF_3$ (IV) are presented in Table I. Relative signs for all fluorine–fluorine coupling constants with the exception of $J_{CF_2CF_2}$ in III (vide infra) and the couplings in IV have been determined. Although the individual fluorines in the CF_2 groups in III are in principle magnetically nonequivalent, resulting in the spin system $A_3MM'RR'X_3$, the spectrum can be satisfactorily analyzed as being first order (that is, $A_3M_2R_2X_3$) since $|J_{MR} - J'_{MR}|$ is apparently $<<|J_{MM} \pm J_{RR}|$.[15] Confirmation of this situation stems from the fact that all resonances can be accurately computer simulated based on assumption of first-order interactions. The value for J_{23}(observed) in III is, however, in fact $|J_{23} + J'_{23}|$. Since J_{23}(observed) is quite small, the latter two couplings may both be small in magnitude, or may have sizable, nearly equal magnitudes and opposite signs. It was not possible to obtain individual values for these two couplings.

Absolute sign determinations for $^3J_{FF}$ are in principle possible for I, II, and III via determination of relative signs of J_{FF} and J_{SiF}. The latter is always >160 Hz in magnitude and is known to have a positive sign.[19] With these molecules, however, such a determination would require tickling experiments involving a directly observed ^{29}Si spectrum. Due to the complexity of the relevant ^{29}Si spectra and the silicon satellite spectra in the ^{19}F spectra, these experiments were not undertaken. Instead, signs of the various J_{FF} values can be put on an absolute basis according to the correlations discussed below.

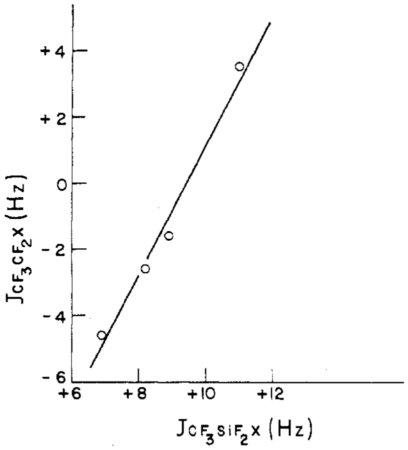
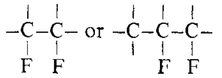


Figure 1. Plot of $^3J_{FF}$ in C_2F_5X vs. that in CF_3SiF_2X, X = F, Cl, Br, I. Data for C_2F_5X were taken from ref 17; data for CF_3SiF_2X were taken from ref 10.

Correlations. Correlations between $^3J_{FF}$ in fluoroethanes and substituent electronegativities were among the first to be formulated in ^{19}F NMR.[3,4,16] Unfortunately, these early contributions were compromised by failure of some workers to recognize the possibility of sign inversion and/or consequences of unequal free energies of various rotational conformers. Nevertheless, subsequent work by Cavalli[17] has demonstrated that for strict structural analogues such as



$$-\underset{\mathrm{F}}{\underset{|}{\overset{|}{\mathrm{C}}}}-\underset{\mathrm{F}}{\underset{|}{\overset{|}{\mathrm{C}}}}-\ \text{or}\ -\underset{|}{\overset{|}{\mathrm{C}}}-\underset{\mathrm{F}}{\underset{|}{\overset{|}{\mathrm{C}}}}-\underset{\mathrm{F}}{\underset{|}{\overset{|}{\mathrm{C}}}}-$$

$^3J_{FF}$ correlates well with substituent electronegativity.

We find that $^3J_{FF}$ in the series CF_3SiF_2X and Si_2F_5X (X = halogen) exhibit parallel behavior to that observed for C_2F_5X as a function of X provided the sign of the coupling in the former two series is *opposite* to that of the pentafluoroethyl species (the exception for the latter is the positive sign for C_2F_6). Figures 1 and 2 are plots of $^3J_{FF}$ in C_2F_5X vs. that in CF_3SiF_2X and Si_2F_5X, respectively. The value for Si_2F_6 has been absolutely determined[14] to be positive, and thus provides a benchmark for the Si_2F_5X values.

The relative signs obtained for I, II, and III can be put on an absolute basis with the use of these and other correlations. The following arguments can be advanced.

1. $^4J_{FF}$ in n-C_3F_7 species falls in a narrow range of 8 to 10 Hz for a wide variety of compounds (exceptions are X = H or transition metal). The sign of this coupling is known to

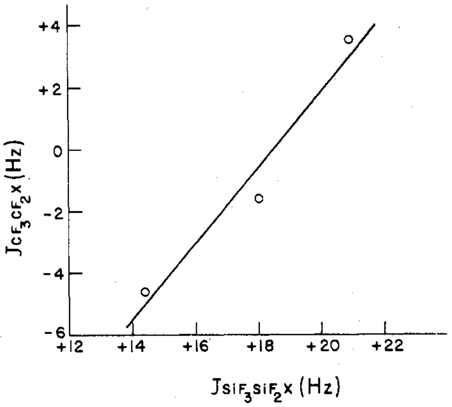


Figure 2. Plot of $^3J_{FF}$ in C_2F_5X vs. that in Si_2F_5X, X = F, Cl, I (Si_2F_5Br has not been reported). The value for Si_2F_6 is from ref 14; the value for Si_2F_5I is from ref 11; the value for Si_2F_5Cl is based on a private communication from F. E. Brinckman and T. D. Coyle.

be positive for X = Br and I and, since $|J_{13}|$ in III is 9.1 Hz, it seems justifiable to assign the sign as positive in III.

2. The dependence of $^3J_{FF}$ in CF_3SiF_2X on the nature of X (Figure 1) strongly suggests a positive value for this coupling. The related couplings J_{23} in I, J_{12} in II, J_{34} in III, and J_{12} in IV should be positive as well. Such a finding is consistent with the absolute assignments for III just discussed.

3. On the basis of the $^3J_{FF}$ correlations with substituent electronegativity in C_2F_5X formulated by Cavalli,[17] that coupling (J_{12}) in I should be negative, and that in III near zero (the corresponding coupling in C_3F_8 is 0.7 Hz). J_{12} in I is assigned as negative. J_{12} in III is indeed small, but is positive; to our knowledge this is only the second instance of such a positive sign in C_2F_5X species; the other is C_2F_6.[18]

4. The positive signs indicated for $^3J_{FF}$ in both CF_3SiF_2X and Si_2F_5X species (Figures 1 and 2) require J_{12} and J_{23} in II to have the same sign, as observed.

A final correlation becomes apparent as the number of couplings considered increases; when a three-bond coupling involving fluorine bonded to carbon is compared to the corresponding coupling in which the carbon has been replaced by silicon (e.g., $CF_3CF_2SiF_3$ vs. $CF_3SiF_2SiF_3$) the coupling constant is invariably larger in an algebraic sense in the molecule containing the additional silicon. Considering the structural and functional variety of the molecules whose couplings are reported here, a rather good correlation exists between $^3J_{FCCF}$ and $^3J_{FCSiF}$ (or between $^3J_{FCSiF}$ and $^3J_{FSiSiF}$). The correlation is presented graphically in Figure 3.

From the data presented here, it appears that (at least for $^3J_{FF}$) the influence of substituents on coupling in silicon-"substituted" fluoroalkanes (and fluoroalkylsilanes) is similar to those of the parent molecules. However, another systematic effect, more or less invariant with substituent, causes displacement on substituting silicon for carbon by approximately +6 to +10 Hz.

On the simplest level of interpretation, one might have forecast a *decrease* in $^3J_{FF}$ on such a substitution, given the uniform increase in J_{FF} as the electronegativity of X increases and the presumed lower group electronegativity of SiF_3 (or SiF_2R) than CF_3. Such simple inductive arguments relate to mutual polarization of s orbital components of valence orbitals in the Fermi contact term. The failure of this prediction to account for the increase in J_{FF} on substitution of silicon for carbon may indicate the relatively greater importance of the often neglected spin dipolar and orbital terms. Relatively low lying excited states could also contribute to the Fermi contact term, although a specific contribution from Si–Si bonds is not apparent.

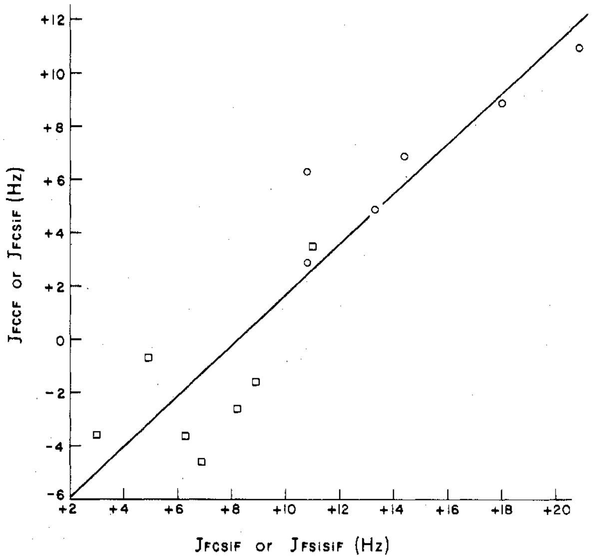


Figure 3. Plot of $^3J_{FF}$ in "carbon-rich" fragments (FCCF or FCSiF) vs. that in silicon-substituted analogues (FCSiF or FSiSiF, respectively): (□) FCCF → FCSiF; (○) FCSiF → FSiSiF.

Theoretical reckoning with values for $^3J_{FF}$ in such systems as these is a difficult proposition. All three contributing terms are sensitive to the dihedral angle between the coupled fluorines, often undergoing sign inversions.[6b,c] The contact and orbital terms are usually the largest contributors but are often of opposite sign in the more stable rotational conformers; the resultant J_{total} then can be smaller in magnitude than its component parts and calculational deficiencies are somewhat exaggerated. Although an accounting for the correlations discussed here may have to await further refinements of theoretical treatments, we suggest that these correlations will be of diagnostic value to future workers in the field of silicon–fluorine chemistry.

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Registry No. I, 354-89-2; II, 59435-37-9; III, 423-42-7; IV, 59433-74-8; Si_2F_5Cl, 59433-75-9.

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