TABLE II

ELECTRONIC SPECTRA FOR AMINE COMPLEXES

Complex	Solvent	Absorption bands, cm^{-1}
$[Ni(ligand)_6](ClO_4)_2$[a]	Mull	10,300
		12,800 sh
		17,000
		27,700
$[Ni(C_{18}H_{39}N)_6](ClO_4)_2$	Mull	10,300–10,700
		12,900 sh
		17,100
		27,800
$[Ni(n\text{-}C_4H_9NH_2)_6](ClO_4)_2$	n-$C_4H_9NH_2$	10,100 (5.3)[b]
		12,800 sh
		16,700 (7.4)
		27,200 (12.8)

[a] For all ligands except *n*-octadecylamine. [b] Molar absorptivities.

atoms,[6] and they contain ionic noncoordinated perchlorate.[7]

Two features arise from this work: (A) the chain length of the coordinating amine plays an insignificant role in deterring complex formation,[8] and (B) branching, although still a critical steric factor for isobutylamine, ceases to prevent complex formation with isopentylamine and beyond.

Acknowledgment.—Support of this work by a Research Corp.–Frederick Gardner Cottrell grant is gratefully acknowledged.

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Correspondence

The Raman Spectrum of $IF_6^+AsF_6^-$ in Hydrogen Fluoride Solution

Sir:

The vibrational spectrum of solid $IF_6^+AsF_6^-$ has previously been reported by us.[1] For IF_6^+ an unusual assignment of ν_2 (E_g) having a higher frequency value than ν_1 (A_1) was required to account for the observed intensities. Subsequently, Hardwick and Leroi proposed[2] a reversal of our original assignment based upon Urey–Bradley force field calculations. However, a comparison with the known spectra of a series of isoelectronic ions and molecules supported our original assignment.[3]

We have now resolved this controversy by recording the Raman spectrum of $IF_6^+AsF_6^-$ in HF solution. Since only ν_1 (A_1) should be polarized, it should be easy to distinguish between ν_1 (A_1) and ν_2 (E_g). As can be seen from Figure 1, the 711-cm^{-1} band is clearly polarized whereas the one at 732 cm^{-1} is depolarized, thus confirming our original assignment. Polarization characteristics are given qualitatively rather than quantitatively owing to internal reflections from the metal walls of the cylindrical sample container.

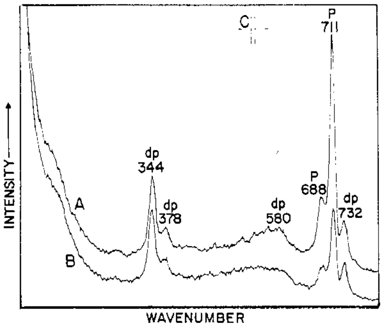

Figure 1.—Raman spectrum of $IF_6^+AsF_6^-$ in HF solution: traces A and B, incident polarization perpendicular and parallel, respectively; C indicates spectral slit width.

Comparison of the spectrum shown in Figure 1 with that[1] of solid $IF_6^+AsF_6^-$ shows a remarkable difference. In HF solution the bands due to AsF_6^- have suffered a considerable loss in relative intensity and also have become quite broad. This effect might be caused by interactions such as hydrogen bonding with the HF solvent. The fact that only AsF_6^- shows a pronounced change might be due to the acidic solvent HF interacting with the Lewis base, AsF_6^-, more readily than with the Lewis acid, IF_6^+. This parallels to some extent the general observation made for F^{19} nmr measurements on complex fluorides in HF solution. These show that rapid fluorine exchange occurs preferentially with the anions and not with the cations.[4]

Technique.—The preparation of $IF_6^+AsF_6^-$ has previously been described.[1] Hydrogen fluoride (from The Matheson Co.) was electrolytically dried.[5] The Raman spectrum was recorded using a Coherent Radiation Laboratories Model 52 Ar ion laser as a source of 1.3 W of exiting light at 5145 Å. The scattered light was analyzed with a Spex 1400 double monochromator, a photomultiplier cooled to about −25°, and a dc ammeter. Polarization measurements were carried out using a Model 310 polarization rotator from Spectra-Physics. A stainless steel cell with Teflon O rings and sapphire windows was used as a sample container. The design of this cell was similar to that of Gasner and Claassen.[6]

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[2] J. L. Hardwick and G. E. Leroi, *ibid.*, **7**, 1683 (1968).

[3] K. O. Christe and W. Sawodny, *ibid.*, **7**, 1685 (1968).

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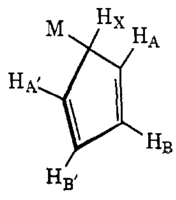
The Interpretation of a Spin-Tickling Experiment on (*Monohapto*cyclopentadienyl)-(methyl)(dichloro)silane

Sir:

It is now well known that *monohapto*cyclopentadienyl-metal and metalloid moieties are usually fluxional,[1] and many investigations[2–12] have been conducted to elucidate the rearrangement pathways in these and the related *monohapto*(1-indenyl)metal systems.

In the first mechanistic study of a fluxional *monohapto*cyclopentadienylmetal molecule[2] it was proposed that the rearrangement pathway in $(h^5\text{-}C_5H_5)Fe(CO)_2(h^1\text{-}C_5H_5)$ consists wholly or predominantly of 1,2 shifts. The line of argument, which need not be reviewed here, has as its crucial step the correct assignment of the two parts of the AA′BB′ multiplet due to the olefinic protons in the limiting low-temperature pmr spectrum. While absolutely direct, rigorous proof for that assignment which leads to the conclusion that 1,2 rather than 1,3 shifts are predominant has not been given, an indirect case which we consider to be virtually irrefutable has been built up for several of the transition metal compounds by a variety of data.[3–7]

The principal criteria,[12a] which are quite independent of one another, for the assignment of the AA′BB′ multiplet leading to 1,2 shifts in $(h^5\text{-}C_5H_5)Fe(Ru)(CO)_2(h^1\text{-}C_5H_5)$ are (1) comparison of relative chemical shifts with those in the analogous h^1-1-indenyl compound, where the assignment has been rigorously established by deuteration and multiple resonance experiments,[3,13] (2) correlation of the observed fine structure due to spin–spin coupling with empirically established ranges for magnitudes and signs of such couplings,[4] and (3) inference from the relative sensitivities of the two kinds of olefinic protons in the $h^1\text{-}C_5H_5$ ring of $(C_5H_5)_3MoNO$ to the effects of diamagnetic anisotropies.[5–7] It turns out that for the iron, ruthenium, and molybdenum molecules just discussed, as well as for $(h^5\text{-}C_5H_5)Cr(NO)_2(h^1\text{-}C_5H_5)$,[3] the portion of the AA′BB′ multiplet lying at *lower* field is due to the A protons, as defined in I. However, it was clearly demonstrated[8] that the relative values of the chemical shifts for A and B protons are sensitive to the nature of the group to which the $h^1\text{-}C_5H_5$ or h^1-(1-indenyl) group is attached and that no *general* argument for the constancy of these relative values or even for the constancy of one of them is likely to be tenable or safe.



I

Davison and Rakita[10–12] have studied *monohapto*cyclopentadienyl- and *monohapto*(1-indenyl) derivatives of $(CH_3)_3Si$, $(CH_3)_3Ge$, and $(CH_3)_3Sn$. Employing only the first of the aforementioned criteria, they adopted an assignment for the AA′BB′ multiplet in the $(CH_3)_3M(h^1\text{-}C_5H_5)$ compounds which led to 1,2 shifts. This assignment placed the A protons at *higher* field than the B protons, in contrast to the situation with the transition metal compounds just mentioned. However, as noted in the preceding paragraph, such a reversal is entirely credible and constitutes no cause whatever to doubt Davison and Rakita's conclusion that 1,2 shifts prevail in the nontransition metal (and metalloidal) as well as in the transition metal derivatives. Nevertheless, it rests on only one line of indirect argument.

The recent challenge to the conclusion of 1,2 shifts put forward by Sergeyev, Avramenko, and Ustynyuk[14] on the basis of a spin-tickling experiment[15] on $CH_3Cl_2Si(h^1\text{-}C_5H_5)$ therefore deserved careful scrutiny. These workers report very well-defined experimental results, from which they deduced an assignment opposite to Davison and Rakita's and then, necessarily, a 1,3-shift pathway. We report here that we have scrutinized their interpretation of their spin-tickling experiment and conclude that they are in error. We find that their results nicely confirm 1,2 shifts by confirming Davison and Rakita's assignment.

Sergeyev, Avramenko, and Ustynyuk first performed an analysis of the pmr spectrum to obtain the magnitudes and *relative* signs[16] of the coupling constants in the AA′BB′ system and the magnitudes of J_{AX} and J_{BX}. This analysis showed that these two constants

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(12a) NOTE ADDED IN PROOF.—Very recently another type of evidence has been provided for the assignment which leads to 1,2 shifts: C. H. Campbell and M. L. H. Green, *J. Chem. Soc.*, 1318 (1970).

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