C_4H_8O. *Anal.* Calcd: C, 65.56; H, 4.15; Sm, 26.49. Found: C, 65.04; H, 4.95; Sm, 27.02.

Magnetic susceptibility measurements of this compound by the Gouy method in the solid state and by the nmr method[9] in THF solution support a $4f^5$ electronic configuration as is observed in the "free" ion (μ_{eff} 298°K (solid) = 1.75 BM; $\mu_{eff}^{298°K}$ (THF solution) = 1.80 BM). This result is similar to that observed for the corresponding cyclopentadienide derivative[2a] and is not unexpected in view of the shielding of these 4f electrons by the outer $5s^25p^6$ electrons. Evidence for the assignment of a covalent bonding mode between the samarium and indenyl moiety, however, is found in the nmr spectrum[10] of the compound in THF-d_8. In addition to a complex band, centered at τ 3.02 of relative intensity 4 and assigned to the four protons of the aromatic six-membered ring, three other bands, each of relative intensity 1, are observed: τ 3.33 (doublet), 3.75 (double doublet), and 6.82 (doublet). Such an ABX pattern for the protons of the five-membered ring is similar to that reported by Cotton, *et al.*,[11] for the nonfluxional species (π-C_5H_5)Fe(CO)$_2$(1-In)[12] and supports a structure as in Figure 1. The indenyl group, in which there is an enhanced electron density at the C-1 position, would be expected to promote covalent bonding to the hard trivalent rare earth ions relative to the soft cyclopentadienyl group in which there is complete charge delocalization.

The nmr spectrum of a THF-d_8 solution of NaC_9H_7, in addition to two complex resonances, each of relative intensity 2, at τ 2.75 and 3.62, exhibits an A_2X pattern for the protons of the five-membered ring (τ 4.17 (doublet, relative intensity 2), 6.80 (triplet, relative intensity 1)). Such an A_2X pattern has been observed for π-bonded indenyl derivatives of iron and ruthenium[13] and would also be expected for the ionic bonding mode of the indenide group.

The presence of coordinated THF was demonstrated by the nmr spectrum of the compound in pyridine solution. The two characteristic THF bands, somewhat broadened as a result of the relatively weak paramagnetism of the Sm^{3+}, appear at τ 6.65 and 8.47. The coordinated THF is readily removed at 70° under vacuum (0.1 mm) as evidenced by the absence of these two peaks in the spectrum of a pyridine solution of the resulting dark red product. The lability of the THF is further shown by its replacement by 1,4-dioxane at room temperature by dissolution in that solvent and subsequent removal of the solvent at 0.1 mm. The nmr spectrum of this product in pyridine solution shows only a broadened signal at τ 6.42 due to 1,4-dioxane.

Further support of structure I is found in the electronic spectrum of the compound. Although the relatively weak f–f bands in the visible region (363, 375, and 402 mμ) are masked by an intense charge-transfer band at 248 mμ, the shift of this latter absorption from its position of 350 mμ for NaC_9H_7 supports a styrene-like structure.

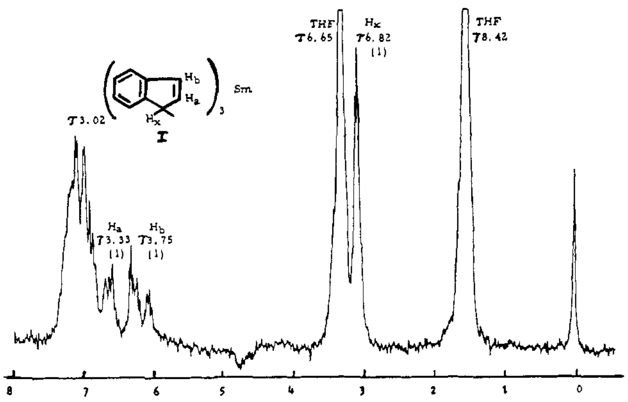

Figure 1. The nmr spectrum of $SmIn_3 \cdot THF$ in THF-d_8 at 25°.

The spectral data therefore indicate that the indenyl groups are covalently bound to the samarium, while the magnetic susceptibility measurements show the absence of spin pairing of the metal's 4f electrons. Since the 5d orbitals in the lanthanide ions are energetically similar to the 4f orbitals, the former may thus be available for bonding. The exact nature of the orbitals involved in the bonding is as yet uncertain. Hopefully, Mossbauer and single-crystal X-ray studies will provide such information.

The corresponding derivatives of La ($\mu_{eff}^{298°}$ = 0), Gd ($\mu_{eff}^{298°}$ = 7.89), Tb ($\mu_{eff}^{298°}$ = 9.43), Dy ($\mu_{eff}^{298°}$ = 9.95), and Yb ($\mu_{eff}^{298°}$ = 4.10) have also been prepared analytically pure. They are currently being characterized and will be the subject of a future report.

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Rearrangement Reactions of Secondary Carbonium Ions. Isopropyl Cation

Sir:

Examination of simple tertiary carbonium ions has yielded detailed information concerning rapid rearrangement reactions which they undergo and the energies of the corresponding transition states.[1,2] Species too high in energy are not kinetically attainable from tertiary ions. We therefore have sought to examine stable secondary carbonium ions which are expected to be 11–15 kcal higher in energy.[1]

Isopropyl cation cannot suffer the usual fate of secondary ions since it has no tertiary isomer. We have prepared it in SO_2ClF–SbF_5 solution from isopropyl chloride on a vacuum line in the same manner in which the *t*-amyl cation was prepared.[1] The nmr spectrum at low temperatures was similar to that previously reported[3] but displayed better resolution (Figures 1 and 2). The solutions were also more stable, decomposing rapidly only at temperatures above 50°, leading to the conclusion that the decomposition process in this case is dependent upon the presence of impurities. Over the range from 0 to 40° the spectrum

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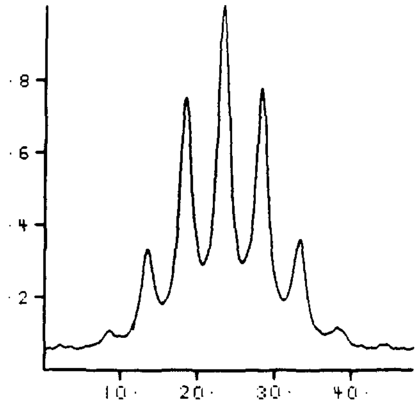

Figure 1. Experimental isopropyl cation septet at −11°.

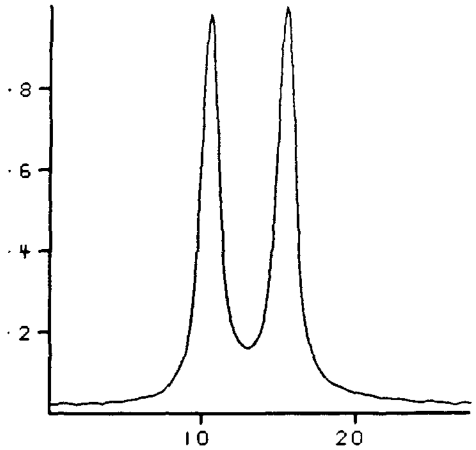

Figure 2. Experimental isopropyl cation doublet at −5°.

changed in a manner indicating interchange between the two types of protons present. The simplest mechanism for this interchange is reversible rearrangement to *n*-propyl cation. This mechanism leads to the matrix of transition probabilities[4]

$$\begin{vmatrix} \diagdown & ^{1}/_{4} & ^{1}/_{4} \\ ^{1}/_{12} & \diagdown & ^{5}/_{24} \\ ^{1}/_{12} & ^{5}/_{24} & \diagdown \end{vmatrix}$$

where the matrix elements are the probabilities that a proton at the *i*th frequency will go to the *j*th frequency when a single step of the reaction considered occurs. Site 1 is all of the lines of the downfield multiplet taken together, and sites 2 and 3 are the frequencies of the methyl doublet. For example, the matrix element $^{5}/_{24}$ arises from the product of factors $^{1}/_{2}$, $^{5}/_{6}$, and $^{1}/_{2}$ originating from the probabilities that a *different* proton returns from the center carbon of *n*-propyl than the one which migrated there, that the proton considered is one of the five methyl protons which did *not* interchange with the proton which had been in the center, and that the proton which exchanged places with the central proton had a *different* spin orientation, respectively. Broadening due to natural line width was introduced into the calculated spectra using the digitally recorded sharpest spectrum of the upfield doublet. The downfield half of the downfield peak and the upfield half of the upfield peak were combined, and a convolution[1,5] was performed on the calculated curve with this composite line shape. Calculated curves for the doublet agreed satisfactorily with the experimental spectra over the temperature range examined. We could not fit the observed spectra with mechanisms involving intermolecular hydrogen exchange with intermediate olefin formation. Olefin formation would also be expected to lead rapidly to the stable hexyl ions by addition of more cation. Fitting the rates obtained to the Arrhenius equation gave $E_a = 16.4 \pm 0.4$ kcal/mol and $\log A = 13.2 \pm 0.3$, where errors reported are standard deviations.

Using the proposed mechanism, the interpretation of the observed activation energy is the enthalpy difference between isopropyl and *n*-propyl ions plus E_a for the reverse reaction. In a similar way the 15.3-kcal/mol activation energy obtained from studying the rearrangement of *t*-amyl cation[1] was assigned to the energy difference between secondary and tertiary ions, plus E_a for the secondary–secondary Wagner–Meerwin shift rearrangement. From what is known, both the exothermic primary–secondary and degenerate secondary–secondary processes have low barriers. Therefore, within the uncertainties of the barriers for these rapid steps, it may be concluded that the energy difference between simple primary and secondary ions is approximately the same as that between secondary and tertiary ions.

A further process which might be considered is rearrangement of the intermediate *n*-propyl cation to protonated cyclopropane before return to isopropyl. Proton scrambling in protonated cyclopropanes is well documented, so complete mixing could result before return to *n*-propyl.[6,7] The protonated cyclopropane might be formed *via* *n*-propyl cation or conceivably directly from isopropyl by simultaneous ring closure and hydride shift. Complete proton scrambling *via* this mechanism predicts line shapes identical with those of the first mechanism proposed since the elements in the probability matrix are the same except that they are all multiplied by a factor of $^{12}/_{7}$. Alteration of the preexponential term in the Arrhenius equation by this factor would not be experimentally noticeable, and the activation energy would be unaffected.

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Rearrangement Reactions of Secondary Carbonium Ions. Protonated Cyclopropane Intermediates Formed from *sec*-Butyl Cation

Sir:

Protonated cyclopropane intermediates undergoing rapid rearrangements have been invoked in accounting

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[8] Fellow of the Alfred P. Sloan Foundation.

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