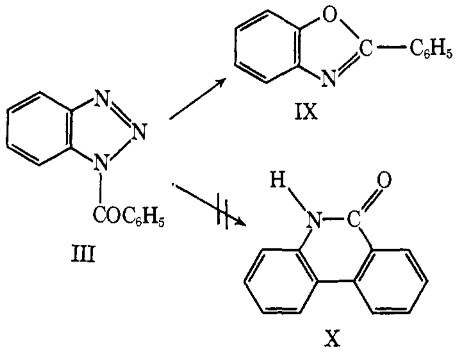
hr. After 12 hr no decrease in the total concentrations of I and IV was detected by comparison of the nmr integral for an unheated sample of starting soluton of III and IV. Thus, no significant yield losses to side reactions has occurred. Finally, the possibility of catalysis of the *trans*-acylation reaction by trace acylating agent in III or IV was examined.[7] A portion of the *o*-dichlorobenzene solution containing III (0.180 *M*) and IV (0.180 *M*) was treated with benzoyl chloride (0.005 g/ml), sealed in an nmr tube, and heated and analyzed as described above. The rate of *trans* acylation was found to be measurably retarded rather than being enhanced. The same result was found using *o*-xylene as solvent, thus indicating that the *trans*-acylation reaction does not result from catalysis by trace acylating agent.

The possibility that the thermal decomposition of N-acylbenzotriazoles might be of some preparative value was briefly examined. It was anticipated that benzoxazole (IX) and/or phenanthridone (X) might be formed from decomposition of III.[8] The decomposition of III was carried out either with samples in the melt in sealed tubes (350–400°) or in diphenyl ether solution (250°). In a typical experiment (0.1 *M* in diphenyl ether), an 11% yield of benzoxazole (IX) was isolated after 6 hr by means of liquid chromatography using Florisil.[9] No phenanthridone was detected (<1% by glpc) in the reaction mixture. A number of minor products whose presence was indicated were not isolated.



A more detailed investigation of the *trans*-acylation reaction discussed above is currently being made.

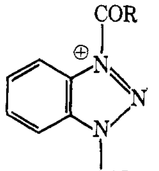
Acknowledgment. The assistance of Mr. R. S. Sudol and Mrs. J. H. Taylor in obtaining nmr spectra is appreciated.

Joe D. Druliner
Plastics Department, Experimental Station
E. I. du Pont de Nemours and Company
Wilmington, Delaware 19803

Received June 14, 1968

---

[7] A referee has suggested that trace acid chloride could cause *trans* acylation *via* an intermediate such as iii.



iii

[8] The thermal decomposition of N-phenylbenzotriazole provides a convenient synthesis of carbazole: C. D. Hurd, "Pyrolysis of Carbon Compounds," American Chemical Society Monograph Series, J. J. Little and Ives Co., New York, N. Y., 1929, p 639.

[9] (a) Identification of IX was made by comparison of spectroscopic data with those of authentic IX prepared by standard methods: F. F. Stephens and J. D. Bomer, *J. Chem. Soc.*, 2971 (1949). (b) The half-life for decomposition of III was approximately 2.5 hr at 250° in diphenyl ether.

Evidence for a Covalent Organolanthanide. Tris(indenyl)samarium–Tetrahydrofuran[1]

Sir:

The only organolanthanides reported previous to our current investigation have been those containing the cyclopentadienide group. All of the trivalent derivatives of the type $Ln(C_5H_5)_3$[2] have been prepared with the exception of that of radioactive promethium. In addition, mixed derivatives of the types $LnCl(C_5H_5)_2$[3] and $LnCl_2(C_5H_5)\cdot 3THF$[4] have also been isolated for several of the lanthanides.

The divalent compounds $Eu(C_5H_5)_2$ and $Yb(C_5H_5)_2$[2c] have also been reported. For all of these compounds an "ionic" bonding mode of the C_5H_5 group to the rare earth metal has been postulated on the basis of their chemical reactivity and their magnetic moments which are essentially those of the corresponding "free" ion.[5] However, recent electronic spectral studies have provided evidence for some f orbital interaction in the cases of $Yb(C_5H_5)_3$[6] and $Tm(C_5H_5)_3$.[7] This observation is of great theoretical significance in view of the generally held theory that the 4f orbitals are effectively shielded from interaction with external forces by the outer $5s^25p^6$ orbitals and that the bonding of the lanthanides is essentially ionic.[8]

Here we wish to report the preparation of the indenyl (In) derivatives of the trivalent rare earths and in particular evidence for a covalent bonding mode in the samarium compound, $SmIn_3\cdot THF$.

The reaction of 1 equiv of $SmCl_3$ and 3 equiv of NaIn in THF media at room temperature under inert conditions resulted in the formation of a wine red solution. Removal of the NaCl formed by centrifugation and subsequent concentration of the red solution led to the isolation of an orange-red solid which was purified by recrystallization from tetrahydrofuran. This air- and moisture-sensitive compound, mp 185–200° (turned to black at 165–170°), has been formulated as $Sm(C_9H_7)_3\cdot$

---

[1] Supported by the Petroleum Research Fund, administered by the American Chemical Society.

[2] (a) J. M. Birmingham and G. Wilkinson, *J. Amer. Chem. Soc.*, **78**, 42 (1956); (b) S. Manastyrskyj and M. Dubeck, *Inorg. Chem.*, **3**, 1647 (1964); (c) E. O. Fischer and H. Fischer, *J. Organometal. Chem.*, **3**, 181, (1965); (d) A. F. Reid and P. C. Wailes, *Inorg. Chem.*, **5**, 1213 (1966); (e) M. Tsutsui, T. Takino, and D. Lorentz, *Z. Naturforsch.*, *B*, **21**, 1 (1966).

[3] R. E. Maginn, S. Manastyrskyj, and M. Dubeck, *J. Amer. Chem. Soc.*, **85**, 672 (1963).

[4] S. Manastyrskyj, R. E. Maginn, and M. Dubeck, *Inorg. Chem.*, **2**, 904 (1963).

[5] T. Moeller, "The Chemistry of the Lanthanides," Reinhold Publishing Corp., New York, N. Y., 1963, p 27.

[6] R. D. Fischer and H. Fischer, *J. Organometal. Chem.*, **4**, 412 (1965).

[7] R. D. Fischer and H. Fischer, *ibid.*, **8**, 155 (1967).

[8] (a) T. Moeller, D. F. Martin, L. C. Thompson, R. Ferrus, G. R. Feistel, and W. J. Randall, *Chem. Rev.*, **65**, 1(1965); (b) J. L. Burmeister, S. D. Patterson, and H. J. Gysling, Proceedings of the 10th International Conference on Coordination Chemistry, Tokyo, Japan, Sept 1967 p 356.

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.

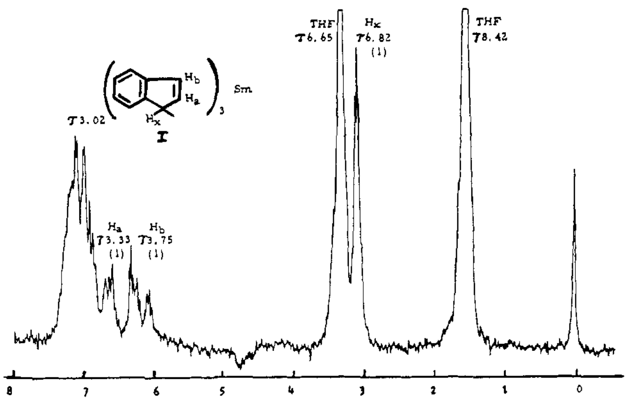


Figure 1. The nmr spectrum of $SmIn_3 \cdot THF$ in THF-d_8 at 25°.

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.

M. Tsutsui, H. J. Gysling
Department of Chemistry, New York University
Bronx, New York 10453

Received September 3, 1968

---

[9] H. P. Fritz and K. E. Schwarzhans, *J. Organometal. Chem.*, **1**, 208 (1964).

[10] All nmr data are reported relative to external tetramethylsilane as reference.

[11] F. A. Cotton, A. Musco, and G. Yagupsky, *J. Amer. Chem. Soc.*, **89**, 6136 (1967).

[12] H_A, τ 3.28 (double doublet); H_B, τ 3.47 (doublet); H_X, τ 6.03 (singlet) in $CDCl_3$ at 25°.

[13] J. H. Osiecki, C. J. Hoffman, and D. P. Hollis, *J. Organometal. Chem.*, **3**, 107 (1965).

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

---

[1] M. Saunders and E. L. Hagen, *J. Am. Chem. Soc.*, **90**, 2436 (1968).

[2] D. M. Brouwer, *Rec. Trav. Chim.*, **87**, 210 (1968).

[3] G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Am. Chem. Soc.*, **86**, 1360 (1964).