A New Series of Organolanthanides: Ln(indenyl)$_3$[1a]

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Abstract: A new series of organolanthanides containing the indenyl group and having the general formula $Ln(C_9H_7)_3\cdot OC_4H_8$ (Ln = La, Sm, Gd, Tb, Dy, and Yb) has been prepared by the reaction of the corresponding anhydrous trichloride with sodium indenide in tetrahydrofuran solution. The magnetic properties of these derivatives have been studied, and in the cases of the diamagnetic La and the weakly paramagnetic Sm compounds proton nmr spectra have been recorded. Evidence is presented for a covalent bonding mode in the Sm derivative.

Although the coordination chemistry of the lanthanides has been an area of intense study,[2] only a rather limited amount of work has been reported in the field of organolanthanide chemistry. Indeed, the only reported organolanthanide compounds involve the cyclopentadienyl group, attempts to prepare alkyl and aryl derivatives having been unsuccessful.[3]

All of the trivalent derivatives of the type $Ln(C_5H_5)_3$[4] have been prepared with the exception of radioactive promethium. The divalent derivatives, $M(C_5H_5)_2$, have been isolated in the cases of Eu and Yb by the reaction of a liquid ammonia solution of the metal with cyclopentadiene.[4c] The divalent chemistry of these two lanthanides is well known and in fact is the basis of their isolation from the other lanthanides, for which the trivalent state is most stable, in an early separation method. In addition, mixed derivatives of the types $LnCl(C_5H_5)_2$[5] and $LnCl_2(C_5H_5)\cdot 3THF$[6] have also been prepared in the cases of the heavier lanthanides. These compounds are monomeric in THF, but the di(methylcyclopentadienyl)lanthanide chlorides of Gd, Eu, and Yb,[5] which have an enhanced solubility over the unsubstituted compounds in benzene, have been shown to be dimeric in that solvent. The postulated chloride bridges are apparently relatively weak since THF is a sufficiently strong base to effect the dissociation of the dimer through dissolution in that medium.

Although all of these compounds are quite reactive hydrolytically and oxidatively, substitution of the chloride in the $(C_5H_5)_2LnCl$ derivatives by phenoxide, formate, acetate, or benzoate ions produces compounds which are quite air stable.[5] The methoxide and amide analogs, however, closely resemble the parent chlorides.

An "ionic" bonding mode of the C_5H_5 group to the rare earth metal has been postulated for each of these compounds on the basis of their chemical reactivity and their magnetic moments, which are essentially those of the corresponding "free" ion.[7] However, recent electronic spectral studies of $Yb(C_5H_5)_3$[8] and $Tm(C_5H_5)_3$[9] by Fischer and Fischer suggest that the metal–ring bonding in these cases is not exclusively electrostatic. An unusually large nephelauxetic effect here indicates some 4f orbital interaction.

To date, however, no direct evidence has been reported for a covalent metal–carbon bond for the lanthanides. We have sought, therefore, to study the effect on the generally ionic bonding mode of the tripositive lanthanide ions by the use of the indenyl ligand which, unlike the resonance delocalized cyclopentadienyl system, has a localization of charge density at the C-1 position. By the reaction of the anhydrous lanthanide trichloride with sodium indenide in tetrahydrofuran solution, we have prepared the compounds $Ln(C_9H_7)_3\cdot THF$ where M = La, Sm, Gd, Tb, Dy, and Yb. These compounds have been characterized by elemental analysis and magnetic susceptibility measurements, and, in the cases of the diamagnetic La derivative and weakly paramagnetic Sm analog, by proton nmr spectroscopy. In the case of the Sm compound, by analogy with the nmr spectrum of a covalent indenyl compound reported by Cotton, *et al.*, a covalent bonding mode is postulated.

Experimental Section

Physical Measurements. Electronic spectra were measured with a Cary Model 14 spectrophotometer. Proton nmr spectra were obtained by means of a Varian A-60 and in the case of $Sm(C_9H_7)_3\cdot OC_4H_8$ by a Varian HR-60 spectrophotometer. All chemical shifts are reported relative to external tetramethylsilane.

Magnetic susceptibilities of the solids were measured by the Gouy method using an Alpha Scientific Laboratory, Inc., Model 7500 electromagnet and Model Al-7500 power supply and current regulator and a Mettler analytical balance with a sensitivity of 0.05 mg. The standard employed was $HgCo(NCS)_4$. Susceptibilities in THF solution were measured by the nmr method.[10]

Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Materials. All operations were carried out under nitrogen by use of a manifold setup and standard Schlenk tubes. The anhydrous lanthanide trichlorides were prepared from the hydrated salts (Alfa Inorganics, Inc.) by refluxing with freshly distilled thionyl chloride.[11]

All the ethers were freshly distilled from $LiAlH_4$ and collected under nitrogen. Pyridine was distilled under nitrogen from barium oxide. Tetrahydrofuran-d_8 (Merck and Co., Inc.) was distilled

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(1) (a) Supported by the Petroleum Research Fund (administered by the American Chemical Society); (b) to whom requests for reprints should be made at the Department of Chemistry, Texas A&M University, College Station, Texas 77843.

(2) T. Moeller, D. F. Martin, L. C. Thompson, R. Ferrus, G. R. Feistel, and W. J. Randall, *Chem. Rev.*, **65**, 1 (1965).

(3) H. Gilman and R. G. Jones, *J. Org. Chem.*, **10**, 505 (1945).

(4) (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. Lorenz, *Z. Naturforsch., B*, **21**, 1 (1966).

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

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

(7) T. Moeller, "The Chemistry of the Lanthanides," Reinhold Publishing Corp., New York, N. Y., 1963, p 27.

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

(9) R. D. Fischer and H. Fischer, *ibid.*, **8**, 155, (1967).

(10) H. P. Fritz and K. E. Schwarzhans, *ibid.*, **1**, 208 (1964).

(11) T. Moeller, *Inorg. Syn.*, **5**, 153 (1957).

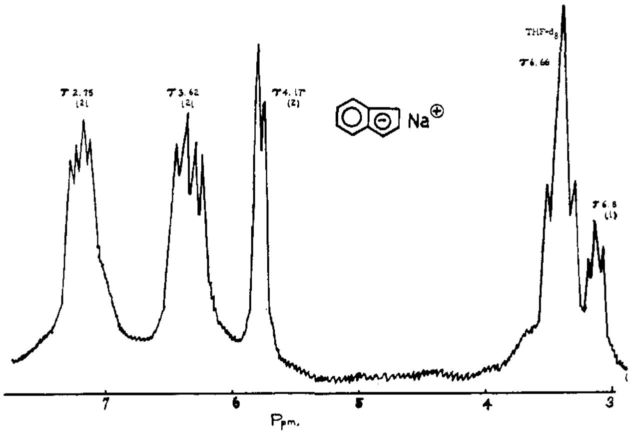

Figure 1. The proton nmr spectrum of NaC_9H_7 measured in THF-d_8 at 25°.

from LiD directly into an nmr tube fitted with a Schlenk top and containing the sample.

Tetrahydrofuran solutions of sodium indenide were prepared by heating 60 ml of freshly distilled indene (Eastman Organic Chemicals) and 200 ml of THF with 15 g of sodium under nitrogen at 75° for 2 days. The exact normality of such solutions, *ca.* 2 *N*, was determined by back titration with NaOH of 30 ml of 0.1 *N* HCl solution to which 1 ml of the sodium indenide solution had been added. The bright yellow solution is extremely air sensitive.

Preparation of the Triindenyl Compounds. All of the compounds were prepared in a manner similar to that described below in detail for the samarium derivative.

$Sm(C_9H_7)_3 \cdot OC_4H_8$. To a suspension of 3.5 g (13.6 mmoles) of $SmCl_3$ in 100 ml of THF at −78° in a flat bottom centrifuge tube fitted with a Schlenk top was added 21 ml of 1.98 *N* NaC_9H_7 solution (41.6 mmoles). The reaction solution immediately became bright orange and after a few minutes it was removed from the cold bath and allowed to come to room temperature. As room temperature was approached the solution turned to a deep wine red color. After further stirring for 3 hr the reaction solution was centrifuged and the red solution was decanted off into another Schlenk tube. The solid residue was then extracted twice with 100-ml portions of THF, both of which were added to the original solution. This combined solution was concentrated to *ca.* 21 ml and centrifuged. The supernatant liquid was decanted off and the deep-red air-sensitive product was recrystallized from THF, mp 185–200° (turned to black at ∼165–170°). *Anal.* Calcd for $Sm(C_9H_7)_3 \cdot OC_4H_8$: C, 65.56; H, 5.14; Sm, 26.49. Found: C, 65.04; H, 4.95; Sm, 27.02.

$Gd(C_9H_7)_3 \cdot OC_4H_8$. The reaction mixture of $GdCl_3$ and NaC_9H_7 was stirred 50 hr at room temperature resulting in a dark green solution from which a pale green product was isolated. *Anal.* Calcd for $Gd(C_9H_7)_3 \cdot OC_4H_8$: C, 64.75; H, 5.09; Gd, 27.37. Found: C, 64.64; H, 4.94; Gd, 27.88.

$Tb(C_9H_7)_3 \cdot OC_4H_8$. The reaction mixture of $TbCl_3$ and Na_9CH_7 was stirred for 5 days at room temperature. A pale yellow product was isolated from the reaction mixture. *Anal.* Calcd for $Tb(C_9H_7)_3 \cdot OC_4H_8$: C, 64.56; H, 5.07; Tb, 27.58. Found: C, 64.17; H, 4.68; Tb, 27.15.

$Dy(C_9H_7)_3 \cdot OC_4H_8$. The reaction mixture of $DyCl_3$ and NaC_9H_7 was stirred for 2 days at room temperature and a pale tan solid was isolated. *Anal.* Calcd for $Dy(C_9H_7)_3 \cdot OC_4H_8$: C, 64.16; H, 5.39; Dy, 28.08. Found: C, 63.78; H, 5.53; Dy, 28.45.

$Yb(C_9H_7)_3 \cdot OC_4H_8$. A dark green product was isolated after reaction of $YbCl_3$ and NaC_9H_7 for 15 hr. *Anal.* Calcd for $Yb(C_9H_7)_3 \cdot OC_4H_8$: C, 63.02; H, 4.95; Yb, 29.32. Found: C, 62.77; H, 4.81; Yb, 29.57.

$La(C_9H_7)_3 \cdot OC_4H_8$. A very pale tan product was isolated after a reaction time of 15 hr. *Anal.* Calcd for $La(C_9H_7)_3 \cdot OC_4H_8$: C, 66.91; H, 5.25; La, 24.98. Found: C, 66.45; H, 5.21; La, 24.49.

Results and Discussion

All the analogs of this series of organolanthanides resemble the corresponding cyclopentadienide derivatives in their magnetochemistry. The values of their magnetic moments, together with those of the corresponding cyclopentadienides, and the "free" ion values are listed in Table I.

Table I. Magnetic Data of Organolanthanides

	μ_{298}^{eff}, BM		
	$Ln(C_9H_7)_3 \cdot OC_4H_8$	$Ln(C_5H_5)_3$[a]	Theoretical[b] (Van Vleck)
La^{3+}	0	0	0
Sm^{3+}	1.55	1.54	1.55–1.65
Gd^{3+}	7.89	7.98	7.94
Tb^{3+}	9.43	. . .	9.7
Dy^{3+}	9.95	10.0	10.6
Yb^{3+}	4.10	4.00	4.3

[a] References 4a and e. [b] Reference 7.

The solution values, as measured by the nmr method[10] in THF, are essentially the same as the solid-state values. The similarity of the magnetic moments of these indenyl derivatives with the free ion values is not unexpected in view of the shielding of the 4f orbitals from interaction with external forces by the outer $5s^25p^6$ orbitals. Indeed, with the exception of the recently reported antiferromagnetism in the case of $Eu(bipy)_4$,[12] no example of spin pairing of 4f electrons is reported. The magnetic data, however, can ultimately indicate only the extreme of covalent interaction, namely spin pairing.

Because of the large paramagnetism of most of the trivalent lanthanides, structural elucidation by nmr spectroscopy was precluded. However, in the cases of the diamagnetic La and weakly paramagnetic Sm derivatives, spectra were successfully recorded. The proton nmr spectrum of a THF-d_8 solution of sodium indenide (Figure 1) exhibits, in addition to the two resonances, each of relative intensity 2, at τ 2.75 and 3.62 due to the protons of the six-membered ring, an A_2X pattern for the three protons of the side ring (τ 4.17 doublet, relative intensity 2; τ 6.80 triplet, relative intensity 1). The solid compound $NaC_9H_7 \cdot (OC_4H_8)_2$ was isolated by concentration of a THF solution and recrystallization of the pale yellow solid so obtained from THF followed by drying at room temperature (0.1 mm) for 1 hr. The formulation of the solid as the bistetrahydrofuranate was based on the relative intensities of 3:8 for the H_H resonance (τ 7.35) compared to each of the two THF signals (τ 7.01 and 9.02) observed in pyridine solution. Such an A_2X pattern has been observed for π-bonded indenyl compounds of $Fe^{13,14}$ and Ru^{13} and would also be expected for the ionic bonding mode of the indenide group. Table II lists this nmr data.

The nmr spectrum of $Sm(C_9H_7)_3 \cdot OC_4H_8$ in THF-d_8 (Figure 2) provides evidence for the assignment of a covalent bonding mode between the Sm and indenyl moiety. 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; τ 3.75, double doublet; τ 6.82, doublet). Such an ABX pattern for the protons of the five-membered ring is similar to that reported by Cotton,

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(12) G. R. Feistel and T. P. Mathai, *J. Amer. Chem. Soc.*, 90, 2988 (1968).

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

(14) R. B. King and M. B. Bisnette, *Inorg. Chem.*, 3, 796 (1964).

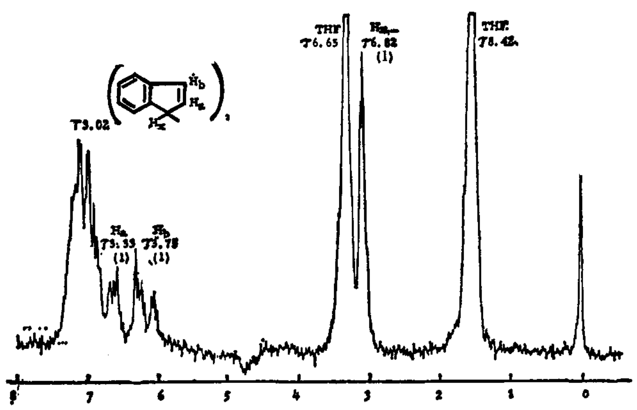


Figure 2. The nmr spectrum of $Sm(C_9H_7)_3 \cdot OC_4H_8$ in THF-d_8 at 25°.

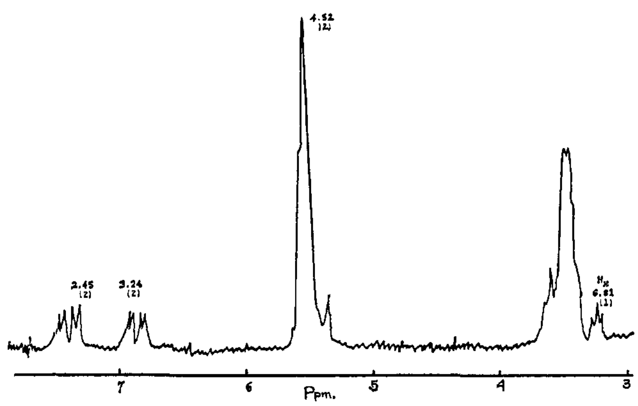
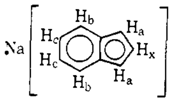
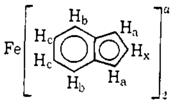
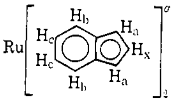
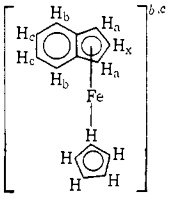


Figure 3. $LaIn_3 \cdot THF$ in THF-d_8 at 25°.

et al., for the nonfluxional[15] species $(\pi\text{-}C_5H_5)Fe(CO)_2$-(1-indenyl).[16,17] Here a combination of spin decoupling and deuteration experiments were performed to unambiguously assign the A, B, and X resonances.

One would expect that the indenyl group, in which there is an enhanced electron density at the C-1 position, would promote covalent bonding to the hard[18] trivalent rare earth ions relative to the "softer"[19] cyclopentadienyl group in which there is complete charge delocalization. The similarity of the nmr spectrum of the side ring protons of the Sm compound with the corresponding pattern for the covalent compound $(\pi\text{-}C_5H_5)Fe(CO)$(1-indenyl) supports an analogous bonding mode for the indenyl group in the former case. In contrast, the ionic bonding mode is characterized by an A_2X pattern for the protons of the five-membered ring.

Table II. Proton Nmr Data (cps) for Some Ionic and π-Bonded Indenyl Derivatives

Compound	τ (H_a)	τ (H_x)	τ (H_b)	τ (H_c)	τ (J_{AX})
	4.17 doublet	6.80 triplet	3.62	2.75	2.5
 [a]	5.39 doublet	5.95 triplet	3.09	3.09	2.5
 [a]	5.11 doublet	5.41 triplet	3.39	3.34	2.5
 [b,c]	5.25 doublet	6.11 triplet	3.22	2.59	2.5

[a] Reference 13. [b] Reference 14. [c] The signal due to the protons of the C_5H_5 group appears at τ 6.38.

Because of the similarity in analytical results for the compounds $Sm(C_9H_7)_3 \cdot n$THF (n = 0, 1, 2, 3), the formulation of the samarium derivative was confirmed by integrating the resonances arising from H_X and coordinated THF in pyridine solution. The intensity ratio 3:4 for the H_X resonance relative to each of the two THF resonances supports the formulation of the compound as the monotetrahydrofuranate.

The removal of the coordinated THF is readily effected by heating at 70° under vacuum (0.1 mm) for 1 hr as evidenced by the absence of the two THF signals in the nmr spectrum of a pyridine solution of the resulting deep red product. This behavior is similar to that of the cyclopentadienyl derivatives which have been isolated by sublimation at relatively high temperatures and have the general formula $Ln(C_5H_5)_3$.[4a–c] However, dissolution in THF followed by removal of the solvent and extraction with pentane for several days results in the isolation of the monotetrahydrofuranate.[20] The europium tricyclopentadienide which cannot be isolated by sublimation because of its thermal instability is first isolated as the monotetrahydrofuranate by a preparation similar to that employed here, and the coordinated THF can be removed by pumping this compound at 70° (0.1 mm).[4e]

The lability of the THF is further shown by its replacement by *p*-dioxane at room temperature by dissolution in that solvent and subsequent removal of the solvent at 0.1 mm. The nmr spectrum of the resulting solid in pyridine solution shows only a broadened signal at τ 6.42 due to *p*-dioxane. Triphenylphosphine can similarly replace the THF if the monotetrahydrofuranate is heated with an equimolar amount of the ligand in benzene at 60°.

Further support for the structure shown in Figure 2 is found in the electronic spectrum of the compound in hexane solution. Although the relatively weak f → f transitions in the visible region (363, 375, and 402 mμ), which are observed in 0.1 *M* solution of the trichloride, are masked by an intense charge-transfer band at 248 mμ, the shift of the latter absorption from its position of 350 mμ for NaC_9H_7 supports a styrene-like chromophore.

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(15) S. J. Lippard, *Trans. N. Y. Acad. Sci.*, **29**, 917 (1967).

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

(17) The corresponding resonances in a $CDCl_3$ solution of $(\pi\text{-}C_5H_5)Fe(CO)_2$(1-indenyl) appear at τ 3.28, double doublet (H_A); τ 3.47, doublet (H_B); and τ 6.03, singlet (H_X).

(18) J. L. Burmeister, S. D. Patterson, and H. J. Gysling, Proceedings of the 10th International Congress on Coordination Chemistry, Tokyo, Japan, Sept 1967, p 356.

(19) R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).

(20) E. O. Fischer and H. Fischer, *J. Organometal. Chem.*, **6**, 141 (1966).

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, Mössbauer and single-crystal X-ray studies will provide such information.

The nmr spectrum of $La(C_9H_7)_3 \cdot OC_4H_8$ in THF-d_8 solution resembles the ionic sodium derivative (Figure 3). Two low-field double doublets at τ 2.64 and 3.24, each of relative intensity 2, are assigned to the protons of the six-membered ring. The singlet at τ 4.52 has a relative intensity of 2. The reason for its failure to split into the expected doublet as observed in NaC_9H_7 is unknown. It does, however, show a slight shoulder on the low-field side. The triplet of relative intensity 1 at τ 6.81 is assigned to H_X. The possibility of an interpretation of the spectrum as an ABX pattern with degenerate H_A and H_B signals, however, remains a possibility.

The difference in bonding modes of the La and Sm indenyls might be attributed to the lanthanide contraction. The smaller Sm ion being "harder"[19] would be expected to promote charge localization in the indenyl system. Mössbauer data, to be presented in a later paper, will hopefully give more information on the bonding in these indenyl derivatives.

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Stereochemically Nonrigid Organometallic Molecules. XXII.[1] A Fluxional Indenylmercury Compound[2]

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Abstract: The compound bis(indenyl)mercury has been prepared and its pmr spectrum studied as a function of temperature from −41 to +68°. At the lowest temperatures a spectrum indicative of a bis(1-*monohapto*indenyl)-mercury molecule is observed. As the temperature is raised this spectrum changes in a manner indicative of increasingly rapid occurrence of some process which exchanges the environments of the 1 and 3 protons of the indenyl groups. Concentration independence of the spectrum in the temperature range of intermediate exchange rate rules out a second-order intermolecular exchange. It is therefore suggested that the process is an intramolecular one with an activated state (or very short-lived intermediate) in which the mercury atom lies over the face of the five-membered ring forming a kind of delocalized bond to three or more of the carbon atoms. Mercury is able to participate in such a transition state by utilizing additional 6p orbitals of its valence shell, whereas the iron atom of $(h^5\text{-}C_5H_5)(h^1\text{-}C_9H_7)(CO)_2Fe$ has no comparable orbitals available and, therefore, this latter molecule is not fluxional, as previously reported. Data reported here on chemical shifts for 1-indenyl compounds vitiate the argument used to assign the spectrum of $(C_2H_5)_3PCu(h^1\text{-}C_5H_5)$, and hence the question of whether 1,2 or 1,3 shifts predominate in that case is very much open. Similarly, the proposal that 1,2 shifts predominate in $(C_5H_5)_2Hg$ is also shown to lack proof.

In a number of previous studies of fluxional organometallic molecules[4,5] containing conjugated cyclic olefinic molecules (*e.g.*, C_8H_8) or radicals (*e.g.*, C_5H_5, C_7H_7) bonded to a metal atom, it has been shown that, with the possible exception[6] of $C_5H_5CuP(C_2H_5)_3$, which we shall discuss later, the rearrangement pathways seem always to consist of a sequence of 1,2 shifts of the metal atom(s) relative to the ring, accompanied, of course, by concerted shifts of the π electrons of the ring.

In a previous study[7] from this laboratory advantage was taken of the special properties of the indenyl group in order to confirm the assignment[8] of the limiting nmr spectrum and the rearrangement pathway in the case of $(h^5\text{-}C_5H_5)(h^1\text{-}C_5H_5)(CO)_2Fe$. Since the principles on which this work was based would be applicable in other cases as well, efforts to prepare and study indenyl derivatives of other metals have been made. We describe here the preparation and nmr study of bis(1-*monohapto*indenyl)mercury, which is a new compound.

Before describing the results of the nmr study and their significance, the considerations essential to the design of the experiment will be presented.

The three structures involving a *monohapto*indenyl-metal system are shown as I, II, and III. Structures I and II are chemically equivalent (though enantiomorphous), and it is safe to assume that they are consider-

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[1] Part XXI: J. L. Calderon, F. A. Cotton, and P. Legzdins, *J. Am. Chem. Soc.*, **91**, 2528 (1969).

[2] This work was supported in part by the National Science Foundation under Grant No. GP-7034X and by a grant from the Petroleum Research Fund, administered by the American Chemical Society, to whom grateful acknowledgment is made.

[3] National Science Foundation Predoctoral Fellow, 1966–1969.

[4] F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968).

[5] F. A. Cotton and C. R. Reich, *J. Am. Chem. Soc.*, **91**, 847 (1969).

[6] G. M. Whitesides and J. S. Fleming, *ibid.*, **89**, 2855 (1967).

[7] F. A. Cotton, A. Musco, and G. Yagupsky, *ibid.*, **89**, 6136 (1967).

[8] M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *ibid.*, **88**, 4371 (1966).