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.

Acknowledgment. We are indebted to Dr. E. Whipple and Dr. P. Kasai at the Union Carbide Research Institute for the measurements of nmr.

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).

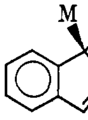
[5] F. A. Cotton and C. R. Reich, *J. Am. Chem. Soc.*, 91, 847 (1969).

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

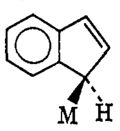
[7] F. A. Cotton, A. Musco, and G. Yagupsky, *ibid.*, **89**, 6136 (1967).

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

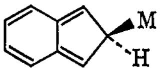
ably more stable than III, since the delocalization energy of the σ-xylylene π-electron structure is about 9 kcal/mol less than for the styrene-like π system found in I and II.[9] In the case of $(h^5\text{-}C_5H_5)(h^1\text{-}C_9H_7)(CO)_2Fe$,[7] the 2-indenyl structure is so unfavorable that it does not serve as a suitable transition state or intermediate for the interconversion of I and II at a rate sufficient to cause broadening of the nmr spectrum even at +70° (above which temperature the compound undergoes rapid decomposition).



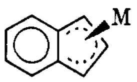
I



II



III



IV

However, it is also possible for an indenyl group to function as a donor of several electrons (up to five) thus forming some sort of π complex, as represented schematically by IV provided the metal atom possesses the requisite number of vacant, low-lying orbitals. In the limit a (1,2,3,8,9-*pentahapto*indenyl)metal type of linkage is possible, as found, for example, in bisindenyliron[10] (also called dibenzoferrocene). It is reasonable to suppose that with an appropriate metal a structure of type IV in which the metal has its primary interaction with the C(1), C(2), and C(3) carbon atoms, thereby leaving the benzenoid resonance largely unperturbed, might be fairly stable. Mercury could be an appropriate metal in this sense owing to its capability of expanding its coordination number from two (linear bonds using digonal, sp hybrids) to three or four by including one or both of its remaining 6p orbitals in the set used for bonding.

With specific reference to bisindenylmercury, the above considerations led us to foresee several possible results in the study of the nmr spectrum of that compound over a range of temperatures.

Case 1. If the mercury atom, like the $(h^5\text{-}C_5H_5)\text{-}Fe(CO)_2$ group, were limited to a two-electron, two-center (*i.e.*, σ interaction) with the indenyl group, we would observe a sharp spectrum containing the HAB pattern due to the hydrogen atoms of C(1), C(2), and C(3), respectively, as well as a sharp WXYZ pattern from the four aromatic protons, up to the highest temperatures of observation.

Case 2. If the mercury atom were to have a preferred coordination number of two, so that a bis(1-*monohapto*indenyl) structure would be the most stable structure, but at the same time have the possibility of expanding that coordination number without too great a promotion energy, the molecule could be fluxional, undergoing 1,3 shifts *via* a transition state of structure IV. In this case the limiting low-temperature spectrum would be of the HAB–WXYZ type described under case 1, but this would collapse at intermediate temperatures and eventually become an AA'B–XX'YY' type of spectrum.

Case 3. If the mercury were to prefer using all four of its valence-shell (6s and 6p) orbitals, the compound might have two rings bonded in the manner of IV permanently. Its nmr spectrum would then be of the AA'B–XX'YY' type at all temperatures.

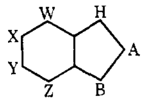
Case 4. Finally, there is the possibility that a structure with one 1-*monohapto* and one 1,2,3-*trihapto*- (or other *multihapto*-) indenyl ring might be preferred. Presumably at intermediate and/or higher temperatures the rings would interchange their roles rapidly giving rise to an AA'B–XX'YY' spectrum, while at low temperatures a complex superposition of the spectra of the two types of ring would be observed.

Results

Preparation. The molecule bis(1-indenyl)mercury was prepared by the reaction of mercuric chloride with indenyllithium at about −78°. It is crucial that all solvents and reagents be purged of water and peroxides or the yield will be drastically reduced, often to none. The substance is a white solid, though it is often obtained with a pale yellow coloration. It is insoluble in common nonpolar organic solvents, but sparingly soluble in CH_2Cl_2, $CHCl_3$, and THF. The solid slowly decomposes on standing at 25°, and it decomposes rapidly at higher temperatures.

One previous attempt to prepare bis(indenyl)mercury has been recorded, but no product was isolated.[11] It is probable that failure in this case was due to a combination of at least the following two factors: (1) the use of insufficiently pure (*i.e.*, peroxide-containing) solvent and (2) failure to cool the reaction mixture in the early stages.

Low-Temperature Pmr Spectrum. The 60-MHz spectrum recorded at −41° (Figure 1) is the limiting low-temperature spectrum since further cooling caused no significant changes. This spectrum is very similar in its main features to that of the indenyl protons in $(h^5\text{-}C_5H_5)(h^1\text{-}C_9H_7)(CO)_2Fe$.[7] The complex multiplet of relative intensity 4 lying between τ 2.2 and 2.9 may be assigned to the aromatic protons, the WXYZ set shown in V. The proton bound to C(1), the carbon atom to which the Hg atom is also bound, gives a line well upfield, as is usual for such protons, at τ 6.19, with a relative intensity of 1. The A and B protons have very similar chemical shifts and are coupled to each other with $J_{AB} \approx 5.7$ Hz; neither is strongly coupled (<2 Hz) to the H proton. They therefore give rise to a relatively simple AB pattern centered at $\sim\tau$ 3.24. All features of the limiting low-temperature spectrum are thus in excellent accord with the bis(1-indenyl)-mercury structure. We can conceive of no other structure which accords with the observed spectrum and consider the bis(1-indenyl) structure to be conclusively proved.



V

As noted earlier, structures I and II are enantiomorphs. Consequently, bis(1-indenyl)mercury can exist in racemic (*dd,ll*) and *meso* forms. It was brought to our attention by Dr. H. Maltz that our limiting low-temperature spectrum shows no indication of such nonequivalent forms. Whether this is because the racemic or *meso* molecules are present in only negligible pro-

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[9] See footnotes 3 and 4 of ref 7.

[10] For the structure of this molecule see J. Trotter, *Acta Cryst.*, 11, 355 (1958).

[11] J. D'Ans, H. Zimmer, and M. v. Brauchitsch, *Ber.*, **88**, 1507 (1955).

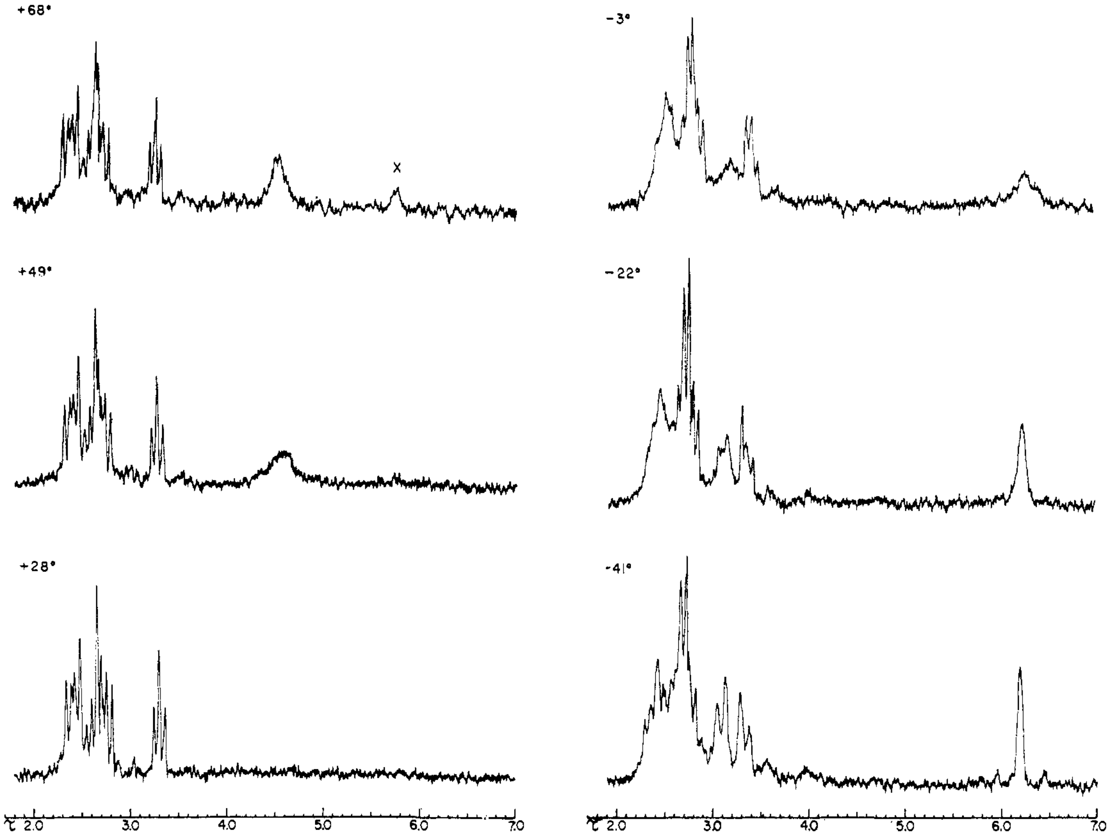

Figure 1. Proton magnetic resonance spectra (at 60 MHz) of bis(1-indenyl)mercury at various temperatures. An approximately 0.37 *M* solution in CCl_3D was used. The small peak marked X is due to an impurity resulting from thermal decomposition at the highest temperature.

portions or because the chemical shift differences between rings in the two types of molecule are unresolvable, we do not know.

There are two notable differences between this spectrum and the limiting spectra of $(h^5\text{-}C_5H_5)(h^1\text{-}C_5H_5)(CO)_2Fe$[8] and $(h^5\text{-}C_5H_5)(h^1\text{-}C_9H_7)(CO)_2Fe$.[7] First, there is no observable difference between J_{HA} and J_{HB}, and indeed both are very small (≤ 2 Hz) and unresolved, whereas in both of the former compounds there was a distinct difference in these two *J*'s. In the case of $(h^5\text{-}C_5H_5)(h^1\text{-}C_9H_7)(CO)_2Fe$ it was possible to show conclusively that $|J_{HA}| > |J_{HB}|$. The small magnitudes and lack of any distinct difference between $|J_{HA}|$ and $|J_{HB}|$ in $(h^1\text{-}C_9H_7)_2Hg$ are reminiscent of the situation in indene itself where Elleman and Manatt[12] found $J_{HA} = 2.02$ Hz and $J_{HB} = -1.98$ Hz. These couplings are likely to be a moderately sensitive function of the angles between each of the several C–H bonds and the ring plane, and at least one of these angles, namely that involving C(1)–H, may in turn be sensitive to the nature of the substituent on C(1), *viz.*, H, $(h^5\text{-}C_5H_5)(CO)_2Fe$, or $(h^1\text{-}C_9H_7)Hg$. Therefore, variation in the absolute and relative magnitudes of J_{HA} and J_{HB} with variation in substituent at C(1) is not unexpected. Conversely, however, it is plausible that compounds of indene and cyclopentadiene with the same substituent should exhibit parallel variations in J_{HA} and J_{HB}. It was on the basis of the latter assumption that the results for $(h^5\text{-}C_5H_5)(h^1\text{-}C_9H_7)(CO)_2Fe$ were invoked[7] to support the assignment which had earlier been put forward[8] for $(h^5\text{-}C_5H_5)(h^1\text{-}C_5H_5)(CO)_2Fe$.

Temperature Dependence of Pmr Spectrum. The 60-MHz pmr spectra of bis(1-indenyl)mercury dissolved in CCl_3D at various temperatures are shown in Figure 1. The changes have all been shown to be reversible with temperature. It is immediately obvious that, provided rapid *inter*molecular exchanges are not occurring (and this will be demonstrated later), the molecule is fluxional. We therefore eliminate case 1 and case 3 described above. Further, as we have just shown, the limiting low-temperature spectrum is clearly that of the bis(1-*monohapto*indenyl)mercury structure, thus eliminating case 4.

The three major changes which take place as the temperature is raised are as follows. (1) The H resonance and one-half of the AB resonance collapse at the same rate, virtually disappearing around room temperature. At higher temperatures a new resonance of relative intensity 2 arises at a position ($\tau \approx 4.60$) which is the same (within experimental error and/or allowing for some small intrinsic dependence of chemical shifts on temperature) as the mean ($\tau \approx 4.68$) of the initial positions of the two separate resonances. Thermal decomposition of $(h^1\text{-}C_9H_7)_2Hg$ above about 70° is too rapid to permit us to observe the further narrowing of this merged resonance.[13a] (2) At the same time,

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[12] D. D. Elleman and S. L. Manatt, *J. Chem. Phys.*, 36, 2346 (1962).

[13] (a) Pmr samples prepared in the presence of air are considerably more stable than those from which oxygen is rigorously excluded. The sample used for Figure 1 also contained a trace of dihydroquinone, which improves stability. These observations are indicative of a free radical chain mechanism of decomposition. (b) Manatt and Elleman[12] have shown that in indene itself J_{HA} and J_{AB} have the same sign. Our results show that this is still true in $(C_9H_7)_2Hg$ since $|\pm 5.7 \pm J_{HA}|/2$ can equal $\sim|3.5|$ whereas $|\mp 5.7 \pm J_{HA}|/2$ cannot. Thus, the relative signs of two coupling constants can be deduced by studying the high-

the fine structure of the noncollapsing half of the AB resonance changes, and from about room temperature to +68° it approaches more and more closely a 1:2:1 triplet structure with a splitting (~3.5 Hz) which is, within experimental uncertainty, equal to the average[13b] of the splittings ($|J_{AB}| = 5.7$, $|J_{HA}| \leq 2$ Hz) in the low-temperature spectrum. (3) The multiplet due to the aromatic protons undergoes complex changes throughout the temperature range. These changes lead to sharpening and simplification and appear to be tending toward the development of a symmetrical XX′YY′ spectrum at higher temperatures.

The changes just summarized are susceptible of only one explanation, namely, that the point of attachment of a mercury atom to the indenyl group shifts back and forth from the C(1) to the C(3) position more and more rapidly as the temperature increases. In this way a time-average plane of symmetry is established so that the H and B environments, the W and Z environments, and the X and Y environments become nmr equivalent.

Rates and Activation Parameters. Since there are only two exchanging protons in this case, and their coupling to each other is very much less than their chemical shift difference, the Gutowsky–Holm[14] treatment may be applied with reasonable accuracy to determine the thermodynamic parameters of activation. In the slow exchange region the line width of the singlet at τ 6.2 was used. In the fast exchange (high-temperature) region the width of the resonance at τ 4.5 was used, with the assumption that this would have a width in the fast exchange limit (which could not be reached experimentally) equal to the average of the widths of the τ 3.15 and 6.2 resonances as observed in the −41° spectrum. Fitting a linear Arrhenius plot by the method of least squares to the two sets of points led to the activation parameters $E_a = 12.9 \pm 0.6$ kcal/mol and $\log A = 12.0 \pm 0.5$.

Concentration Independence. As a means of determining whether the changes in the pmr spectrum which occur between −41 and +68° (Figure 1) are in fact due to an intramolecular process, the dependence of the spectrum upon concentration at room temperature was examined. Figure 2 shows two spectra each run at probe temperature (~25°) on solutions which differ by a factor of 8 in concentration. For a bimolecular process the rates should differ by a factor of 64, but there is, in fact, no noticeable difference between the two spectra. Based on the previously determined rates we can estimate that the 25° spectrum at $^1/_{64}$th the rate characteristic of the upper trace (which is for a saturated solution) should be similar in appearance to the trace given by the saturated solution at −20°. Figure 1 shows that at this temperature the peaks for the H and B protons are still very prominent, and the triplet structure of the A resonance is still very unsymmetrical. It is thus quite evident that the process responsible for the averaging is not bimolecular.[15]

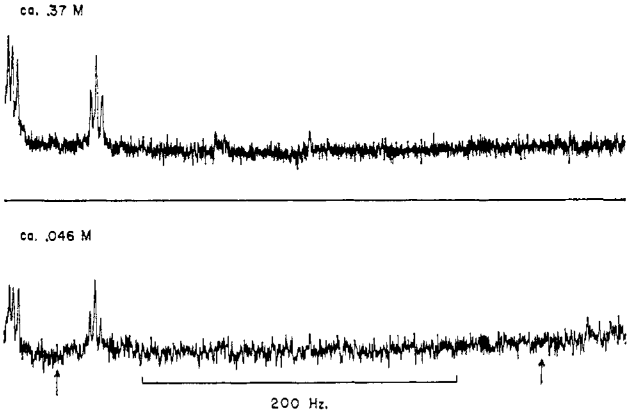

Figure 2. Proton magnetic resonance spectra (at 100 MHz) of bis(1-indenyl)mercury at 25° in CCl_3D as a function of concentration. The upper trace was recorded with a saturated solution (~0.37 M), while the lower trace was obtained after dilution by a factor of 8. The lower trace is computer-averaged from 18 sweeps. Arrows indicate the expected positions of the H and B proton resonances.

Discussion

The results reported here for bis(1-indenyl)mercury complete the line of argument which was begun in the study[7] of $(h^5\text{-}C_5H_5)(h^1\text{-}C_9H_7)(CO)_2Fe$. The metal atom in the $(h^5\text{-}C_5H_5)(CO)_2Fe$ group has all its valence-shell orbitals engaged in bonding except for one, which contains a single electron. It has only the possibility of interacting with univalent radicals, R· (such as Cl·, C_nH_{2n+1}·, or 1-indenyl), to form a simple two-center, two-electron bond. The position of this bond can move from one atom to another on R only if these atoms are adjacent and the pathway carries through a transition state or intermediate in which only two electrons are involved in the Fe–R interaction. This situation obtains in $(h^5\text{-}C_5H_5)(h^1\text{-}C_5C_5)(CO)_2Fe$, and the point of attachment to the $(h^1\text{-}C_5H_5)$ ring shifts rapidly. In the case of $(h^5\text{-}C_5H_5)(h^1\text{-}C_9H_7)(CO)_2Fe$ no shifting can occur because, on the one hand, the intermediate of structural type III is too unstable while, on the other, the kind of greater-than-two-electron interaction involved in a transition state represented by IV is impossible for the $(h^5\text{-}C_5H_5)(CO)_2Fe$ group.

Conversely, when the metal-containing moiety has empty low-lying valence-shell orbitals, which can be used in a transition state such as IV, the rapid interconversion of I and II *via* IV should be feasible. The mercury atom in $(h^1\text{-}C_9H_7)_2Hg$ has a linear, two-coordinate C–Hg–C ground-state structure; the additional orbitals needed to form a transition state with multicenter bonding (*i.e.*, one like IV) are most likely the two additional 6p orbitals, although the participation of outer-d orbitals (5d) cannot be ruled out. Indeed, where such outer-d orbitals are sufficiently low in energy, they alone may be adequate to permit the attainment of a transition state suitable for rapid 1,3 shifts. The exploration of this possibility is being carried out by others in this laboratory.[16]

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temperature spectrum of a fluxional molecule. We know of only one previous instance[13c] in which this type of argument has been utilized. (c) M. Saunders and E. L. Hagen, *J. Am. Chem. Soc.*, **90**, 2436 (1968).

(14) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(15) The possibility of a two-step dissociation–recombination mechanism, probably involving a mixture of intra- and intermolecular exchanges, but following a rate law first order in $(C_9H_7)_2Hg$, is not directly disproved by the evidence at hand. We believe it will be generally recognized, however, that such a process is highly unlikely and have ruled it out. Direct evidence against (or for) it could be obtained from the presence (or absence) of satellite lines due to ^{199}Hg···H couplings, in the fast exchange limit. Unfortunately, thermal instability denies us the opportunity to reach this limit; the line width of the merged resonance at +68° is still too large to allow observation of the satellites which we believe to be present.

(16) Professor A. Davison and coworkers, private communications.

The results of our study of $(h^1\text{-}C_9H_7)_2Hg$ provide a basis for some comments on other fluxional molecules containing $(h^1\text{-}C_5H_5)$ or $(h^1\text{-}C_9H_7)$ groups. Interestingly, we can now adduce direct evidence against the validity, but an indirect argument for the ultimate correctness, of the assignment of 1,3 shifts as proposed for $(C_2H_5)_3PCu(h^1\text{-}C_5H_5)$ by Whitesides and Fleming.[6]

The conclusion that 1,3 shifts occur in $(C_2H_5)_3PCu(h^1\text{-}C_5H_5)$ follows automatically from their assignment of the AA′BB′ olefinic resonance in the low-temperature spectrum of that compound. A reversal of assignment necessitates a change in one's conclusion about the predominant shift (to 1,2) and, conversely, each of the two possible assumptions about the dominant kind of shift process demands, strictly, that one of the two possible assignments be made.

The basis for the assignment of Whitesides and Fleming was simply that for a series of $M\text{–}C_5H_5$ compounds they expected the spectral position (chemical shift) of the B protons (which are separated by four bonds from the metal atom) to be substantially constant while the position of the A protons (which are separated by only three bonds from the metal atom) would be more variable. It can now be demonstrated that this is an unsafe assumption. For $(h^5\text{-}C_5H_5)(CO)_2Fe(h^1\text{-}C_9H_7)$ and $Hg(h^1\text{-}C_9H_7)_2$ we have found the following chemical shifts (in τ), all at 60 MHz in CCl_3D solution.

Compound	A proton	B proton
$(h^5\text{-}C_5H_5)(CO)_2Fe(h^1\text{-}C_9H_7)$	3.28	3.47
$Hg(h^1\text{-}C_9H_7)_2$	3.32	3.09

Clearly, the position of the B protons varies greatly, while the A protons have a substantially constant position.

The reason why the facts here are contrary to the expectation expressed by Whitesides and Fleming is that the chemical shifts of both A and B protons are affected significantly (perhaps predominantly) by the diamagnetic anisotropies of the $h^5\text{-}C_5H_5$, CO, and C_9H_7 groups, in a manner which cannot be simply predicted. In other words, the shifts do not depend simply upon the inductive influence of a metal acting solely through and being attenuated by the electron pairs of intervening chemical bonds.[17] The change from $(h^5\text{-}C_5H_5)(CO)_2Fe$ to $(C_2H_5)_3PCu$ is such that constancy in the position of the B resonance of the $h^1\text{-}C_5H_5$ group *cannot be assumed*, although it is possible. We must conclude therefore that *on the experimental evidence per se*, there is no basis for choosing between 1,2 shifts and 1,3 shifts to describe the rearrangement pathway in $(C_2H_5)_3PCu(h^1\text{-}C_5H_5)$.

However, since Cu^I (like Hg^{II}) in a linear, two-coordinate complex has additional valence-shell orbitals (4p orbitals for Cu^I) it may (like Hg^{II}) be able to participate in a transition state like that represented by IV and thereby permit 1,3 shifts to constitute the main rearrangement pathway. Thus, the conclusion of Whitesides and Fleming may be correct but proof is lacking.

There have recently appeared several studies of the low-temperature pmr spectra of $(C_5H_5)_2Hg$.[19,20] Maslowsky and Nakamoto report that at −70° in SO_2 $(C_5H_5)_2Hg$ gives a spectrum indicative of slowly *shifting* $h^1\text{-}C_5H_5$ rings. Their proposal that 1,2 shifts occur (based on the unsymmetrical shape of the AA′BB′ signal) rests upon a direct deduction from Whitesides and Fleming's assignment for $(C_2H_5)_3PCu(h^1\text{-}C_5H_5)$ and is therefore inconclusive. Indeed, *if* the relative positions of the A and B resonances in $(C_5H_5)_2Hg$ are taken to be the same as those in $(C_9H_7)_2Hg$, we must conclude that 1,3 shifts are occurring. We are not, however, espousing that conclusion because we have no firm faith in the premise.

Nesmeyanov, *et al.*, conclude that $(C_5H_5)_2Hg$ actually has a $(h^5\text{-}C_5H_5)_2Hg$ structure apparently because ^{199}Hg–H coupling produces observable satellites in the room-temperature pmr spectrum. Though the conclusion *might* be correct, the argument (as we understand it) is not.

It is clear that much more thorough studies of cyclopentadienyl and indenyl compounds of the borderline metals such as mercury and copper are required in order to elucidate their structures, bonding, and fluxional behavior.

Experimental Section

Preparation. Commercial butyllithium (0.042 mole) in hexane was used to metalate 5.4 g (0.047 mole) of indene in 140 ml of ether. The ether was freshly distilled from sodium-benzophenone. To the stirred solution of indenyllithium, which had been cooled to −78° (using an acetone–CO_2 bath) under nitrogen, 6.05 g (0.0223 mole) of mercury(II) chloride in 60 ml of tetrahydrofuran was added dropwise over a period of 1.5 hr. The THF was also freshly distilled from sodium-benzophenone. The reaction mixture was allowed to stir for an additional 0.25 hr and was then treated with 100 ml of ether and 100 ml of pentane, both precooled to −78°. This mixture was kept overnight (~16 hr) at −78°, and the supernatant liquid was then siphoned from the reaction flask, leaving a pale yellow solid. This solid, still at −78°, was washed with two 80-ml portions of precooled ether, the ether being siphoned after each washing. Then 150 ml of methanol was added, the reaction flask was removed from the Dry Ice–acetone bath, and immediately 250 ml of water (at 25°) was added with rapid stirring. After 0.25 hr of stirring, the flocculent precipitate was suction filtered and washed with 300 ml of water and then with 60 ml of ether. The pale yellow to pale gray solid was sucked dry and then collected and dried further under high vacuum.

Additional purification was achieved by extracting this crude product in air with 80 ml of 4:1 methylene chloride–hexane and filtering under nitrogen into a flask at −78°. The methylene chloride was then slowly removed under high vacuum at low temperature until the volume of the solution was reduced by about one-third. The supernatant was then carefully removed with a syringe at −78°, and the pale yellow to white product was washed with several portions of pentane and dried under high vacuum at 0° in the dark: yield, 1.1 g (12%) of pale yellow to white solid.

Anal. Calcd for $C_{18}H_{14}Hg$: C, 50.16; H, 3.28. Found: C, 49.8; H, 3.04.

Pmr Spectra. Spectra at 60 HMz were obtained with a Varian Associates A-60 nuclear magnetic resonance spectrometer. Temperature control was achieved with a V-6040 variable-temperature controller, and peak separations in methanol and ethylene glycol samples were used to calibrate the temperature. The 100-MHz spectra were recorded with a Varian HA-100 spectrometer equipped with a C-1024 time-averaging computer.

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[17] For a very striking example of the effects of diamagnetic anisotropies see the nmr[18] and structural[1] data on $(C_5H_5)_3(NO)Mo$.

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