responding β-amidocyclohexylmercurials.[4] Consequently, it would appear that the present combined procedure should be widely applicable to the conversion of olefins into the corresponding N-alkylamides.

The present results suggest that the solvomercuration–demercuration reaction may possess wide applicability for making reactions, previously achieved only with strong acids, possible under very mild reaction conditions. We continue to explore this possibility.

(9) National Science Foundation Fellow at Purdue University, 1967–1969.

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The Structures of Cyclopentadienylmercuric Halides and Dicyclopentadienylmercury

Sir:

We wish to report the first evidence that unequivocally establishes the predominant molecular configuration in solution of the cyclopentadienylmercury compounds CpHgX (X = Cl, Br, I, and Cp).[1] It has been inferred earlier[4] from certain similarities that exist between the infrared spectra of these compounds and cyclopentadiene itself, together with the fact that Cp_2Hg forms an adduct with maleic anhydride, that the Cp rings are σ-bonded to the mercury atom. On the other hand, nmr data published to date on these systems[4b,5-8] cannot be unequivocally interpreted in terms of either σ-Cp, π-allyl, or π-Cp (ferrocenyl) bonding. The debate concerning the relative merits of such forms of bonding can now, however, be resolved by considering the new data communicated here.

We have studied the nmr spectra of the above-mentioned CpHgX compounds in various ethereal solvents over the temperature range −140 to 120° and will illustrate our findings with spectra acquired on 0.03 *M* CpHgCl in perdeuteriotetrahydrofuran (THF-d_8) between −113 and 22° (Figure 1). All the spectra between −113 and −7° are consistent with CpHgCl being a fluxional[9] molecule with a nuclear configuration

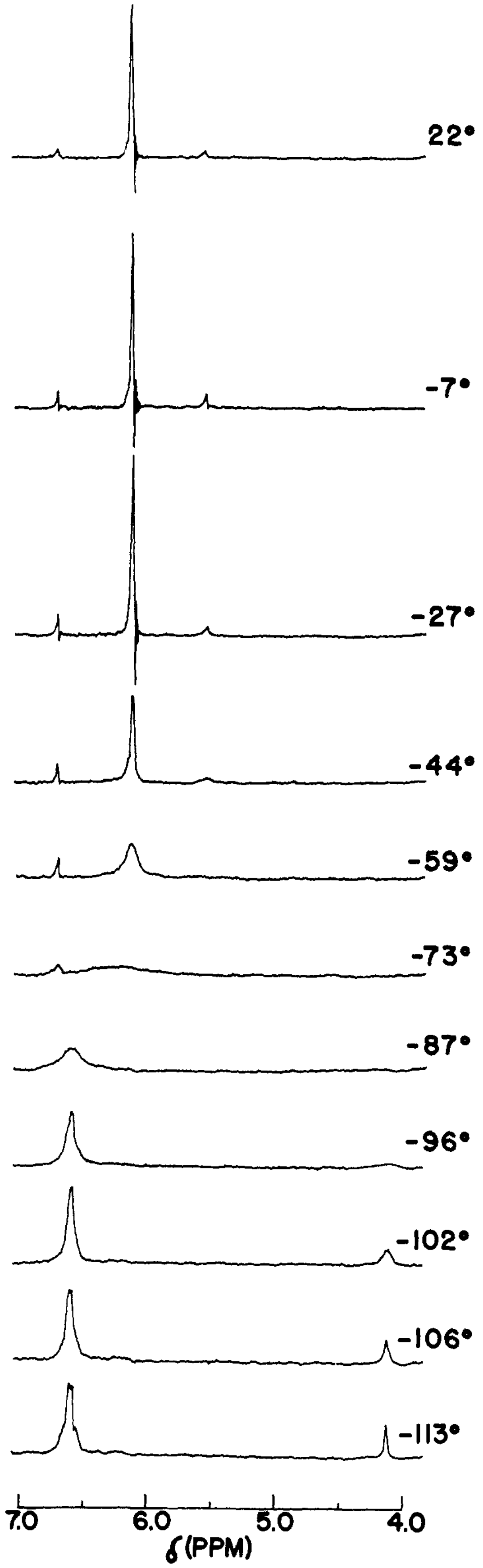

Figure 1. Temperature-dependent 100-MHz nmr spectra of 0.03 *M* CpHgCl in THF-d_8. The abscissa is calibrated in ppm downfield from internal tetramethylsilane.

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(1) Cp_2Hg was prepared from CpTl and $HgCl_2$.[2] CpHgX compounds (X = Cl, Br, and I) were prepared from Cp_2Hg and the corresponding HgX_2.[3] Each compound was analyzed for all the elements C, H, Hg, and halogen. Excellent agreement between the analytical values and theory was obtained in each instance.

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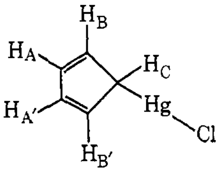
Table I

Compound	Solvent	σ-CpHgX (AA'BB'C)			$J(^{199}Hg\text{–}H)_{av}$,[c] Hz
		δ_{av}, ppm[a,b]	Av of $\delta_{A,A'}$ and $\delta_{B,B'}$, ppm[a]	δ_C, ppm[a]	
CpHgCl	THF-d_8	6.118	6.613	4.136	116[8b]
CpHgBr	THF	6.12	6.60	(4.20)[d]	116
CpHgI	THF	6.12	6.60	(4.20)[d]	114
Cp_2Hg	THF	5.95			71[6b,f]
Cp_2Hg	Dimethyl ether–THF[e]	5.89	~6.35		71

[a] All chemical shifts are downfield with respect to internal tetramethylsilane. [b] $\delta_{av} = {}^1/_5(2\delta_{A,A'} + 2\delta_{B,B'} + \delta_C)$. [c] Defined in text. [d] δ_C calculated using equation in footnote *b*. Use of highly concentrated samples or resorting to further experiments in THF-d_8 will allow the direct observation of proton C in this system. [e] The instantaneous structure of Cp_2Hg only begins to be noticed at the lowest temperature attainable (*ca.* −140°). In this mixed solvent system, the chemical shifts of the protons in Cp_2Hg are temperature dependent. [f] The appearance of ^{199}Hg satellite peaks in the nmr spectrum of Cp_2Hg [$J(^{199}Hg\text{–}H)_{av} \cong 66$ Hz in $CDCl_3$] was first reported by M. D. Rausch, Abstracts of Papers, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., March 31–April 5, 1963, p 21K; see also comments by M. D. Rausch in "Proceedings of The Robert A. Welch Foundation Conferences on Chemical Research. IX. Organometallic Compounds," W. O. Milligan, Ed., Houston, Texas, 1966, p 221.

of lowest free energy in which the Cp moiety is σ-bonded to the mercury atom (I).



(16.86% ^{199}Hg, $I = {}^1/_2$)

I

Fluxional behavior is observed because the means exists whereby the mercury atom has an equal probability of being attached in turn to each of the five carbon atoms in the Cp ring. In practice, at −113° the interconversion of one nuclear configuration into another equivalent configuration is slow enough that the instantaneous structure of CpHgCl is revealed in its nmr spectrum. The observed spectrum at −113° is a superposition of spectra of three magnetically nonequivalent molecules: 83.14% CpHgCl (AA'BB'C), 8.43% $Cp^{199}Hg(\alpha)Cl$ (AA'BB'CM), and 8.43% $Cp\text{-}^{199}Hg(\beta)Cl$ (AA'BB'CM) [the natural abundance of ^{199}Hg ($I = {}^1/_2$) atoms is 16.86%]. The findings are consistent with molecular configuration I. The chemical shifts of the cyclopentadienyl ring protons and the temperature dependence of the nmr spectra are similar to those reported for other σ-Cp organometallic compounds.[10] The AA'BB'C spectrum observed at −113° differs vastly from that expected for CpHgCl in the absence of valence tautomerism were it to possess a π-allyl structure.[11] A singlet occurs at 4.136 ppm (δ_C, CpHgCl; relative intensity = 1.0) with a half-height line width in the 100-MHz spectrum of only 3Hz, virtually all the remainder of the spectrum falling between 6.1 and 7.0 ppm (relative integrated intensity = 4.8). The bulk of the absorption in the latter region is centered about 6.613 ppm and is due to the vinylic protons in CpHgCl (preliminary spectral analysis yielding $\Delta\delta_{AB} \cong 0.06$ ppm). Suspected satellite absorptions due to $Cp^{199}HgCl$ between 6.1 and 7.0 ppm are confirmed by spectra taken at −113° on more concentrated solutions.[12]

At higher temperatures, predictable sharp singlet character develops (Figure 1, −44° spectrum) in the form of both a low-field $Cp^{199}Hg(\beta)Cl$ absorption and a principal CpHgCl absorption,[10] prior to very noticeable high-field $Cp^{199}Hg(\alpha)Cl$ absorption appearing. By analogy to diallylmercury,[13] allyl fluoride,[14] and allyl phosphorus compounds,[15] presumably $J(^{199}Hg\text{–}H_C)$ is large and greater than $J(^{199}Hg\text{–}H_B)$ in I, the smallest mercury-proton coupling being $J(^{199}Hg\text{–}H_A)$. Consequently, the differences in proton chemical shifts in $Cp^{199}Hg(\beta)Cl$ are appreciably smaller than those encountered in $Cp^{199}Hg(\alpha)Cl$. The proton resonances in the Hg(β) compound thus coalesce at a lower temperature than those of the Hg(α) compound. Ultimately, at −7° three sharp singlets are observed (δ_{av}, $Cp^{199}Hg(\beta)Cl$) = 6.698 ppm, (δ_{av}, CpHgCl) = 6.118 ppm, and (δ_{av}, $Cp^{199}Hg(\alpha)Cl$) = 5.538 ppm. From these chemical shift values it is obvious that, for CpHgCl in THF, $J(^{199}Hg\text{–}H)_{av}$ = 116 Hz, where $J(^{199}Hg\text{–}H)_{av} = {}^1/_5[2J(^{199}Hg\text{–}H_{A,A'}) + 2J(^{199}Hg\text{–}H_{B,B'}) + J(^{199}Hg\text{–}H_C)]$.

In an analogous fashion, we have observed fluxional character associated with a predominance of σ-Cp–Hg bonding in THF solutions of CpHgBr, CpHgI, and Cp_2Hg (Table I). It has been found that the less electronegative the second substituent on the mercury atom, the more facile the intramolecular "ring-whizzing" of the mercury atom about the Cp ring, *viz.*, Cp_2Hg > CpHgI > CpHgBr > CpHgCl.

Between 25 and −98°, the half-height line width of the main peak in the 100-MHz spectrum of a Cp_2Hg solution in THF increases only from 1.1 to 1.6 Hz. Nevertheless, below −100° in dimethyl ether–THF, this peak rapidly broadens, and the spectra closely resemble those of CpHgCl at temperatures less than *ca.*

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(11) (a) M. L. H. Green and P. L. I. Nagy, *Advan. Organometal. Chem.*, **2**, 332 (1964); (b) M. I. Bruce, M. Cooke, and M. Green, *Angew. Chem. Intern. Ed. Engl.*, **7**, 639 (1968); (c) F. A. Cotton and C. R. Reich, *J. Amer. Chem. Soc.*, **91**, 847 (1969).

(12) Evidence available suggests that all $Cp^{199}HgCl$ proton resonances, except for the upfield satellite of proton C, lie between 6.1 and 7.0 ppm, since were this the case, the calculated integrated intensity within this range, when compared to the peak at 4.132 ppm, would be 4.9, in good agreement with the measured value of 4.8.

(13) In diallylmercury $J(^{199}Hg\text{–}H\alpha) \cong 145$ Hz: P. West, unpublished data.

(14) A. A. Bothner-By, S. Castellano, and H. Günther, *J. Amer. Chem. Soc.*, **87**, 2439 (1965).

(15) V. Mark, "Mechanisms of Molecular Migrations," Vol. II, B. S. Thyagarajan, Ed., Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1969, p 359.

−44° (Figure 1). Such observations indicate a decrease in the fluxional character of Cp_2Hg at these very low temperatures.

A further observation noted during these studies is that, at any particular concentration, the extent to which intermolecular exchange of Cp groups takes place increases in the CpHg**X** series in the order **X** = Cp < Cl < Br < I. Factors such as steric size of **X** and the nature of both the Cp–Hg and Hg–**X** bonds no doubt largely control the over-all rates of Cp group migration. Satellite broadening in the 22° spectrum of Figure 1 is due to intermolecular exchange of Cp groups in the CpHgCl–THF system.[16]

Computer-simulated nmr spectra have been obtained which closely resemble all the experimentally measured spectra, such as those shown in Figure 1. At this stage, however, unambiguous assignments cannot be made to the ^{199}Hg–H spin–spin coupling constants and, therefore, a definite conclusion is not possible at the moment regarding the role played by 1,2 and/or 1,3 shifts of the mercury atom around the Cp ring.

The physical properties of cyclopentadienylmercury compounds in different solvents are currently under investigation, as are the effects of various mono- and bidentate ligands. A full report on the nmr spectra of these and related organomercurials will be published soon.

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(16) We have observed this phenomenon proceeding in a reversible manner up to 120° in a solution of CpHgCl in diethylene glycol–methyl *t*-butyl ether (bp 185°), appreciable thermal stability being demonstrated up to this temperature.

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Intramolecular Photoreduction of Alkyl α-Diketones[1]

Sir:

Biacetyl (**1**) has often been employed as a probe for the mechanism of photoreactions in solution.[2-10] On the other hand, until recently[11,12] very little quantitative data[2,3] on the solution photochemistry of biacetyl and its derivatives had been published. The ability of **1** and other α-diketones[13] to phosphoresce with moderate efficiency ($\Phi_P \cong 0.1$) in fluid solution is exceptional and contrasts with the general lack of phosphorescence from fluid solutions of monoketonic compounds.[14] This unusual resistance of biacetyl triplets to radiationless deactivation has not been satisfactorily explained. The fact that (a) **1** has a relatively low triplet energy (E_3 = 56 kcal/mol)[4] and (b) **1** abstracts hydrogen atoms with a rate constant which is very small[2,11,12] relative to alkyl and aryl ketones[15] perhaps gives some hint to the origin of the stability of triplet **1** toward thermal deactivation, since it has been proposed that chemical[16a] or physical[16b] quenching may indeed limit the lifetime of many triplet states in solution.

α-Diketones undergo primary photochemical hydrogen abstraction,[11,17] addition to alkenes,[18] and, possibly, α cleavage.[19] The intramolecular hydrogen abstraction of alkyl α-diketones, possessing a γ carbon bearing a hydrogen atom, yields 2-hydroxycyclobutanones.[17a,b,20] We report here our studies of the rates for intramolecular abstraction of primary, secondary, and tertiary hydrogens for α-diketones **2**, **4**, and **6**, respectively, and compare our data with the intensely studied type II abstraction of branched alkyl ketones.[15,21]

Irradiation of 0.15 *M* benzene solutions of **2**, **4**, and **6** with 4350-Å light results in smooth, and essentially quantitative, formation of the cyclobutanones **3**, **5**, and **7**, respectively.[22] Each reaction is quenched by pyrene (E_3 = 48 kcal/mol),[23] a compound which is expected to be a diffusion-control quencher of triplets **2**, **4**, and **6** ($E_3 \cong$ 56 kcal/mol).[4] The Stern–Volmer plots (in benzene, acetonitrile, and *t*-butyl acohol), for quenching of the photorearrangements indicated in eq 1, are linear. The slopes of these plots may thus be equated to $k_q\tau$ where k_q is the bimolecular rate constant for quenching of α-diketone triplets by pyrene and τ is the α-diketone triplet lifetime. Table I lists $k_q\tau$ values, $1/\tau$ values (calculated from the assumption that $k_q = 5 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ in benzene),[24] and quan-

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