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A PMR INVESTIGATION OF THE SELF EXCHANGE OF BIS(TRIMETHYLSILYL)-, BIS(TRIMETHYLGERMYL)-, BIS(TRIMETHYLSTANNYL)-, BIS(METHYLDICHLOROSILYL)- AND (TRIMETHYLSILYL)PROPYNYLMERCURY

THEODORE F. SCHAAF AND JOHN P. OLIVER
135 Chemistry Building, Department of Chemistry, Wayne State University, Detroit, Michigan 48202 (U.S.A.)

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SUMMARY

PMR studies of the self-exchange of $(Me_3Si)_2Hg$ and of $(Me_3Ge)_2Hg$ have shown that these reactions proceed by a second order process with Arrhenius activation energies of 11.3 ± 0.4 and 11.1 ± 0.6 kcal/mole for the trimethylsilyl derivative in xylene and triethylamine respectively, and with 12.1 ± 0.4 kcal/mole for the trimethylgermyl derivative in toluene. Attempts to study the exchange of $(Me_3Si)_2Hg$ in 4-methylpyridine and tributylphosphine were unsuccessful because of irreversible decomposition reactions. Quantitative results for the self-exchange of $(Me_3Sn)_2Hg$ were unobtainable because of the rapid decomposition of this material above $-20°$, but the collapse of the $^{199}Hg{-}^{1}H$ satellites indicate that rapid exchange occurs. $(MeCl_2Si)_2Hg$ was shown not to undergo rapid self-exchange although it does undergo exchange with $(Me_3Si)_2Hg$ in less than 1 min. The rate of group exchange decreases in the order:

$$(Me_3Sn)_2Hg > (Me_3Ge)_2Hg > (Me_3Si)_2Hg > (MeCl_2Si)_2Hg > Me_2Hg.$$

The mixed compound $Me_3SiHg{-}C{\equiv}C{-}CH_3$ was shown to have rapid exchange of the propynyl group unlike bis(propynyl)mercury which does not undergo exchange readily.

INTRODUCTION

Fast exchange reactions of organometallic compounds have been a topic of considerable interest in the past few years[1]. These studies have largely concentrated on the methyl species, since they are particularly convenient for PMR investigations. The recent preparations of (organosilyl)-[2-5], (organogermyl)-[2,6] and (organostannyl)metal compounds[7] suitable for PMR studies considerably broadens the number and scope of fast exchange reactions which may be studied easily; however, very little has been reported on fast exchange reactions of Group IV-metal compounds. Lee and Sheldrick[8] found that the rate and activation energy for exchange of trimethylsilyl groups on tris(trimethylsilyl)thallium were almost identical to those reported for exchange of methyl groups in trimethylthallium[9]. Fast exchange of trimethylsilyl groups between $LiHg(SiMe_3)_3$ and bis(trimethylsilyl)mercury; and in the system $LiHg(SiMe_3)_3/Li_2Hg(SiMe_3)_4/LiSiMe_3$ has been observed[10]. Lee reported that the ^{199}Hg satellites of bis(trimethylsilyl)mercury were sharp at room temperature and suggest that this indicated a slow rate of exchange of trimethylsilyl groups under these conditions[11].

A number of recent papers deal specifically with rapid exchange reaction of organozinc and cadmium derivatives[12–14]. In contrast, exchange reactions of dialkylmercurials are very slow relative to other Group IIB dialkyls, and do not undergo fast exchange on the PMR time scale[1]. A typical case is the exchange of dimethylmercury with diphenylmercury which reaches equilibrium only after six hours at 150° or eighty hours at 100° [15].

With this information in hand, we became interested in studying the effect of changing the atom bound directly to the Group II metal on the rate of group exchange. The organo Group IV mercurials are the most accessable compounds which are suitable for this type of investigation. In this paper we report on the first of these studies which show fast intermolecular exchange reactions of organo-Group IV mercurials.

RESULTS AND DISCUSSION

The room temperature PMR spectra of bis(trimethylsilyl)mercury and bis(trimethylgermyl)mercury consist of a single sharp line flanked by sharp ^{199}Hg satellites, 16.8% (Table 1). As the temperature is raised the satellites broaden and collapse into the central resonance line. This indicates that exchange has become rapid on the PMR time scale.

TABLE 1

PMR PARAMETERS FOR (GROUP IV)–MERCURIALS

Compound	Chemical shift τ (ppm)	$J(^{199}Hg-E^{IV}-C-^1H)$ (Hz)
$(Me_3Si)_2Hg$	9.83^a	40.8^a
$(Me_3Ge)_2Hg$	9.60^b	37.0^b
$(Me_3Sn)_2Hg$	9.75^b	^{c}
$(MeCl_2Si)_2Hg$	9.35^b	28.0^b
$Me_3SiHg-C{\equiv}C-Me$	Me_3Si- 9.82^d	70.6^d
	$Me-C{\equiv}C-$ 8.31^d	$J(^{199}Hg-C-C-C-^1H)$ $13.2^{d,e}$

[a] In mixed xylenes containing about 24% ethylbenzene. [b] In toluene. [c] Not observed. [d] At −55°. [e] In 1,2-dimethoxyethane.

The rate of exchange and the kinetic parameter for these two exchange reactions in aromatic hydrocarbons were determined by observing their PMR spectra. The rate of exchange for both bis(trimethylsilyl)mercury and bis(trimethylgermyl)-mercury showed second order concentration dependence (Table 2) suggesting a bimolecular reaction path. The Arrhenius plot of ln k *vs.* $1/T$ for these systems is shown in Fig. 1. The values for the activation energies are summarized in Table 3 with other kinetic and activation parameters. The value of the rate constant at 25° was calculated from the Arrhenius equation.

TABLE 2

CONCENTRATION DEPENDENCE OF EXCHANGE IN BIS(TRIMETHYLSILYL)MERCURY AND BIS(TRIMETHYLGERMYL)-MERCURY

Concentration of $(Me_3E^{IV})_2Hg$ (moles/liter)	$1/\tau_{ex}$ (sec^{-1})	k_2 ($l \cdot moles^{-1} \cdot sec^{-1}$)
$E^{IV}=Si$; *in xylene*[a,b] *at* 392°K		
0.830	87.54	210.9
0.448	35.35	157.8
0.241	23.06	191.4
0.130	14.95	230.0
0.070	9.61	274.4
	average =	212.9
$E^{IV}=Ge$; *in toluene at* 383°K		
0.614	61.18	199.3
0.312	39.23	251.5
0.270	31.24	231.1
0.174	21.24	244.1
0.144	19.47	270.4
0.078	11.81	303.0
	Average =	249.0

Average = 212.9

[a] $k_2 = \dfrac{2/\tau_{ex}}{[Hg(E^{IV}Me_3)_2]}$. [b] Mixed xylenes containing 24% ethylbenzene.

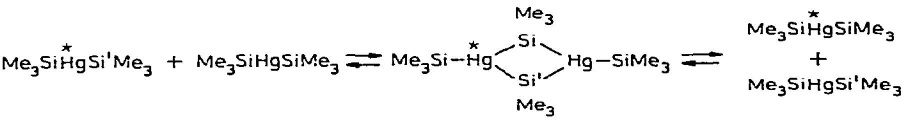
TABLE 3

KINETIC PARAMETERS FOR EXCHANGE OF TRIMETHYL-E^{IV} GROUPS ON BIS(TRIMETHYL-E^{IV})MERCURIALS AT 25°

Compound	Solvent	E_a[a] ($kcal/mole^{-1}$)	$\Delta H^{\ddagger}$ ($kcal/mole^{-1}$)	$\Delta S^{\ddagger}$ (e.u.)	k ($l \cdot mole^{-1} \cdot sec^{-1}$)
$(Me_3Si)_2Hg$	Xylene	11.3±0.3	10.7±0.5	−21.8±2.5	0.31
	Triethylamine	11.1±0.7	10.5±0.7	−22.8±4.0	0.17
$(Me_3Ge)_2Hg$	Toluene	12.1±0.3	11.5±0.5	−18.4±2.5	0.99

[a] Standard deviation from the least squares lines in fig. 1.

The second order concentration dependence of these exchanges and the large negative entropies of activation suggest an electron deficient bridged transition state for the reactions:



(1)

The rate of exchange observed for bis(trimethylsilyl)mercury and bis(trimethylgermyl)mercury are similar with the germanium compound exchanging slightly faster. Both the entropy and enthalpies of activation are similar.

Since the exchange of methyl groups on dimethylcadmium is greatly accelerated by Lewis bases[14], the exchange of bis(trimethylsilyl)mercury was studied using triethylamine as solvent. The Arrhenius plot is shown in Fig. 1 and the kinetic parameters are listed in Table 3. The parameters are almost identical to the value in xylene. It may therefore be concluded that Lewis bases do not serve as a catalyst for this exchange.

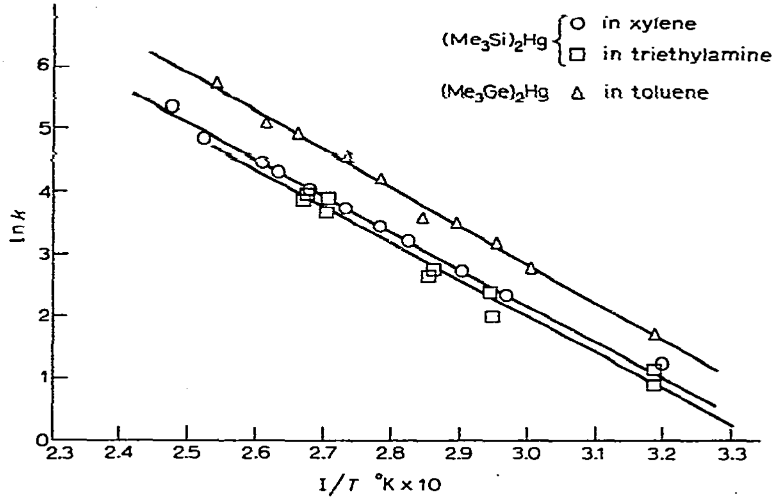
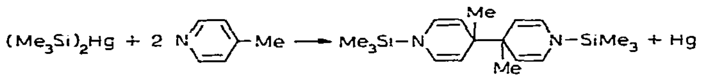


Fig. 1. The Arrhenius activation energies (ln k vs. $1/T$) for the self-exchange of $(Me_3Si)_2Hg$ in xylene ○; in triethylamine □ and for the self-exchange of $(Me_3Ge)_2Hg$ in toluene △. The energies determined from the least squares fits are 11.3±0.3, 11.1±0.7 and 12.1±0.3 kcal/mole respectively.

An attempt was made to study the exchange reaction of bis(trimethylsilyl)mercury in 4-methylpyridine. In this solvent the rate of exchange increases irreversibly with time. The presence of bis(trimethylsilyl)mercury was confirmed by the observation of ^{199}Hg satellites at low temperature. Subsequently. Becker and Neuman reported that bis(trimethylsilyl)mercury reacted with 4-methylpyridine by the following path[16]:



$$(Me_3Si)_2Hg + 2\ NC_5H_4\text{-}Me \longrightarrow Me_3Si\text{-}NC_5H_4(Me)\text{-}C_5H_4(Me)N\text{-}SiMe_3 + Hg \qquad (2)$$

(I)

The product of this reaction, however, neither catalyzes exchange of trimethylsilyl groups or exchanges trimethylsilyl groups with bis(trimethylsilyl)mercury as shown by the sharp lines and ^{199}Hg satellites in the PMR spectra of a mixture of (I) and bis(trimethylsilyl)mercury in toluene. Apparently some intermediate in reaction (2) catalyzes the exchange.

Similar behavior was observed when tributylphosphine was used as a solvent; however, the irreversible increase in rate was not large until the temperature was raised.

An attempt was made to study the rate of exchange of trimethylstannyl groups in bis(trimethylstannyl)mercury. This compound is very difficult to work with since it undergoes facile decomposition to hexamethyldistannane and metallic mercury above −20° or under the influence of light[7]. It is also nearly impossible to obtain low temperature PMR spectra due to the low solubility of the compound at reduced temperature. We were able, however, to observe a PMR resonance at 9.75 τ (40°) which we assign to bis(trimethylstannyl)mercury. As the sample ages at this temperature the resonance due to this peak decreases while that for hexamethyldistannane increases. Observations are complicated because the two resonances lie close together and hexamethyldistannane is always present in large amount under these conditions. We were not able to observe any ^{199}Hg or ^{117}Sn and ^{119}Sn satellites for bis(trimethylstannyl)mercury. It is possible that the tin satellites are obscured by the tin satellites of hexamethyldistannane. The ^{199}Hg satellites would be expected to have a J value of from 25 to 40 Hz from comparison with the analogous silicon and germanium compounds. Since ^{199}Hg satellites are not observed, we may conclude that exchange of trimethylstannyl groups is very rapid in bis(trimethylstannyl)mercury. The possibility that low concentration of decomposition intermediate, such as a trimethylstannyl radical catalyzes this exchange cannot be completely excluded but it does appear that the uncatalyzed self-exchange is rapid for this compound.

The PMR spectra of bis(methyldichlorosilyl)mercury shows sharp ^{199}Hg satellites even in concentrated samples at high temperatures. The second order rate constant for exchange of methyldichlorosilyl groups at 116° in toluene is less than $k < 0.166\ \text{l} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$. However, exchange in bis(methyldichlorosilyl)mercury is probably faster than exchange of methyl groups in dimethylmercury. Dimethylmercury scrambles with bis(trimethylsilyl)mercury to form methyl(trimethylsilyl)mercury. This reaction takes weeks to reach equilibrium at room temperature[17]. Bis(methyldichlorosilyl)mercury also reacts with bis(trimethylsilyl)mercury to form a mixed species. This reaction reaches equilibrium in a minute or less. The relative rates of these scrambling reaction strongly imply that the rate of exchange of methyldichlorosilyl groups in bis(methyldichlorosilyl)mercury is substantially faster than the rate of exchange of methyl groups in dimethylmercury.

Exchange in 1-propynyl(trimethylsilyl)mercury was investigated. This compound undergoes moderately fast decomposition at room temperature, which makes isolation difficult[17]. The compound was prepared *in situ* by the reaction of bis(trimethylsilyl)mercury and dipropynylmercury in 1,2-dimethoxyethane (DME) solvent. Excess bis(trimethylsilyl)mercury was always used so that this species was present in large amount in the samples. The equilibrium concentration for the mixed species is large, but some dipropynylmercury was also present.

Two mercury proton coupling constants can be observed in propynyl(trimethylsilyl)mercury; $^3J(^{199}\text{Hg–Si–C–}^1\text{H})$ to the trimethylsilyl protons, and $^4J(^{199}\text{Hg–C–C–C–}^1\text{H})$ to the propynyl methyl protons. However, the coupling to the propynyl methyl protons is observed only at low temperatures, showing that the propynyl group is undergoing rapid exchange at room temperature. This represents a marked contrast to dipropynylmercury where the satellites are sharp and exchange is slow at 35° in DME or pyridine.

The $^3J(^{199}\text{Hg–Si–C–}^1\text{H})$ satellites of bis(trimethylsilyl)mercury and propynyl(trimethylsilyl)mercury are relatively sharp at room temperature, but broaden at higher temperatures. The relative broadening is considerably larger for the bis(trimethylsilyl)mercury satellites. A complete analysis of this broadening is very difficult because of the number of species present in solution, and the many exchange reactions which can occur.

The broadening of the mercury satellites of bis(trimethylsilyl)mercury can be satisfactorily accounted for by exchange of trimethylsilyl groups between bis(trimethylsilyl)mercury molecules, reaction (1). Assuming all the broadening of these satellites is due to reaction (1), a second order rate constant of 9.03 $l \cdot mole^{-1} \cdot sec^{-1}$ was calculated at 61°. This is similar to the rate of exchange determined at this temperature in xylene, 10.31 $l \cdot mole^{-1} \cdot sec^{-1}$.

The maximum rate of trimethylsilyl group exchange in propynyl(trimethylsilyl)mercury, reaction (3), was calculated to be 1.49 $l \cdot mole^{-1} \cdot sec^{-1}$. The actual rate

$$Me_3Si^*HgC{\equiv}CMe + Me_3SiHg^*C{\equiv}CMe \longrightarrow Me_3Si^*Hg^*C{\equiv}CMe + Me_3SiHgC{\equiv}CMe \quad (3)$$

of reaction (3) may be much lower due to contributions to the broadening of the $J(^{199}Hg\text{-}Si\text{-}C\text{-}^1H)$ satellites of $Me_3SiHgC{\equiv}CMe$ by other exchange reactions. From the preceding, it may be concluded that trimethylsilyl groups on propynyl(trimethylsilyl)mercury are exchanged more slowly than the trimethylsilyl group on bis(trimethylsilyl)mercury.

The results of this investigation may be summarized by saying that the rate of exchange of the various mercurials follows the order:

$$(Me_3Sn)_2Hg? > (Me_3Ge)_2Hg > (Me_3Si)_2Hg > (MeCl_2Si)_2Hg > Me_2Hg\,.$$

This is similar to the order expected for the Group IV atom–mercury bond strengths. Literature bond energy data are available for dimethylmercury and bis(trimethylsilyl)mercury: $D_1 = 51^{18}$ and 13.6 kcal/mole[19], respectively. Bis(trimethylgermyl)mercury shows equal or slightly lower thermal stability than bis(trimethylsilyl)mercury, which indicates similar bond strength. Bis(trimethylstannyl)mercury is very much less thermally stable than the other compounds and probably has a much weaker bond. No data are available for $(MeCl_2Si)_2Hg$, but it is not unreasonable to expect the electronegative chlorine atoms to strengthen the mercury–silicon bond.

This inverse behaviour, of the rate of exchange of the Group IV–mercury derivatives with the Group IV–mercury ground state bond energy, leads to the postulate that the major factor determining the differences in activation energies in these systems is the ground state energy of the mercury derivative and not the bridging ability of the $-ER_3$ moiety. This also implies that the stability of the bridged transition states are closer in energy to one another than are the ground state energies. Unfortunately, the more general question regarding the relative bridging abilities of the congeners of carbon is still to be answered.

It seems likely that the bond strength of most metal–Group IV element bonds, $M\text{-}E^{IV}$ will decrease in the order $E^{IV} = C > Si > Ge > Sn > Pb$, and that bimolecular exchange involving these silicon–, germanium–, tin–, and lead–metal bonds will be more rapid than the analogous exchanges involving organic groups where the activation energy for formation of the bridged transition state is strongly influenced by the nature of the substituent. In cases where this process requires little of no energy, *i.e.*, diffusion controlled reactions, no relationship between bond energy and rate of reaction will be found*.

EXPERIMENTAL

All manipulations in this study were performed using standard high vacuum techniques or under an argon or nitrogen atmosphere, dried by sodium/potassium alloy. All solvents were dried over sodium/potassium alloy, distilled before use, and degassed on the vacuum line. PMR samples were run on a Varian A-60A spectrometer with standard variable temperature accessories. Temperatures were calibrated by the method of Van Geet[20].

Concentrations were determined by serial dilution of a standard solution for the bis(trimethylsilyl)mercury system and by integrating against an internal standard for the other systems.

Bis(trimethylsilyl)mercury[21] and bis(trimethylgermyl)mercury[6] were prepared by published procedures and sublimed before use. The decomposition of these compounds at higher temperatures to mercury and hexamethyldisilane or hexamethyldigermane was minor and did not interfere with the observations.

Bis(methyldichlorosilyl)mercury was prepared by a modification of a published procedure[3]. Excess methyldichlorosilane and bis(tert-butyl)mercury were sealed in a tube. After the tube stood in laboratory light for two hours a grayish precipitate formed filling the tube occluding all of the liquid. The precipitated bis(methyldichlorosilyl)mercury was recrystallized from methylene chloride. The unsymmetrical propynyl(trimethylsilyl)mercury was synthesized *in situ* by sealing an NMR tube containing 1,2-dimethyoxyethane, bis(trimethylsilyl)mercury, dipropynylmercury and the standard. After the tube stood at room temperature for several hours, significant quantities of propynyl(trimethylsilyl)mercury could be observed. This compound decomposes, probably to propynyltrimethylsilane and mercury[17], but this decomposition did not materially affect the observations, except for making the concentrations somewhat unreliable.

The preparation and handling of bis(trimethylstannyl)mercury caused considerable difficulty due to its thermal and light sensitivity. After preparing the compound in a separate vessel and unsuccessfully attempting to transfer it under nitrogen in the cold to NMR tubes, it was decided that the best method would be to prepare the compound in the NMR tube in which it would be run. The method of preparation was that of Neuman and Blaukat[7]. A weighed sample of bis(tert-butyl)mercury was sublimed into an NMR tube. Excess trimethylstannane was distilled in and the NMR tube was placed in a carbon tetrachloride slush, −23°, for six or seven hours. After this time, the tube, still at −23°, was pumped out on the vacuum line. A red solid had formed. Toluene was distilled into the tube, and after about one hour it was pumped out as before. The solvent and the standard were then distilled into the tube.

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* The only other quantitative study of exhange of a higher Group IV metal system, found that the rates of exchange and activation energies for exchange and trimethylsilyl groups on tris(trimethylsilyl)thallium and the exchange of methyl groups on trimethylthallium were very similar. Both of these exchange reactions are bimolecular with activation enthalpies in toluene of 6.3 and 7.0 kcal/mole^{-1}, respectively[8,9]. In this case the enthalpies are of the order of those for diffusion-controlled reactions.

Neuman and Blaukat[7] reported that the reaction gave 75% yield after three hours at −20°. We always found that the reaction was incomplete with considerable bis(tert-butyl)mercury remaining. No mixed species, tert-butyl(trimethylstannyl)mercury, could be observed and we concluded that this species must react much more rapidly with trimethylstannane than did bis(tert-butyl)mercury.

Red bis(trimethylstannyl)mercury gives a yellow solution when dissolved in toluene or 1,2-dimethoxyethane. Bis(trimethylstannyl)mercury is fairly soluble in these solvents at room temperature, but when the temperature was lowered, red solid invariably precipitated from solution. Spectra of bis(trimethylstannyl)mercury were obtained by working rapidly at room temperature. Under these conditions most of the bis(trimethylstannyl)mercury decomposes to mercury and hexamethyldistannane, which complicated observation since the chemical shift of these compounds is very similar, $\Delta\delta$ 0.025 ppm in toluene and about 0.05 ppm in 1,2-dimethoxyethane.

INTERPRETATION OF PMR DATA

Two methods were used to obtain pre-exchange lifetimes, τ. In one method, a three site computer program written by Dr. K. L. Henold employed the McConnell modification to the Bloch equations to generate theoretical spectra using an estimated lifetime[13]. The estimated τ value was varied until the best fit was obtained with the experimental spectrum. This program contains a potentially serious deficiency, since it does not treat exchange of groups from one satellite site to the other satellite site. Fortunately the satellites are small relative to the central peak, so the assumption is not serious and the program fit the spectra very satisfactorily. Another assumption involved the neglect of ^{29}Si- and ^{13}C-satellites. This is minor and is not expected to effect the results significantly. This method was used to obtain the great majority of τ values for the exchange of bis(trimethylsilyl)mercury in xylene and of the bis(trimethylgermyl)mercury.

The slow exchange approximation was used to obtain τ values in a small number of cases in the bis(trimethylsilyl)mercury/xylene, and in the bis(trimethylgermyl)mercury systems when the $1/\tau$ values were very small, and for all the values for the bis(trimethylsilyl)mercury/triethylamine system.

The lifetimes determined for any magnetic site τ_i were converted to pre-exchange lifetimes τ_{ex} of any group by the relationship:

$$1/\tau_{ex} = (1/\tau_i)\cdot[1/(1\text{–fraction of groups on the } i\text{th site})].$$

This correlation is necessary to take into account exchange of groups between sites which are magnetically equivalent.

Care must be taken in converting lifetimes to rates for systems containing more than one exchangeable group. The following simple expression was used:

$$\text{Rate of exchange} = (1/\tau_{ex})\cdot n\cdot[X_nM]$$

where n number of group X attached to moiety M can undergo exchange.

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