MERCURY

ANNUAL SURVEY COVERING THE YEAR 1980

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TABLE OF CONTENTS

1. REVIEWS

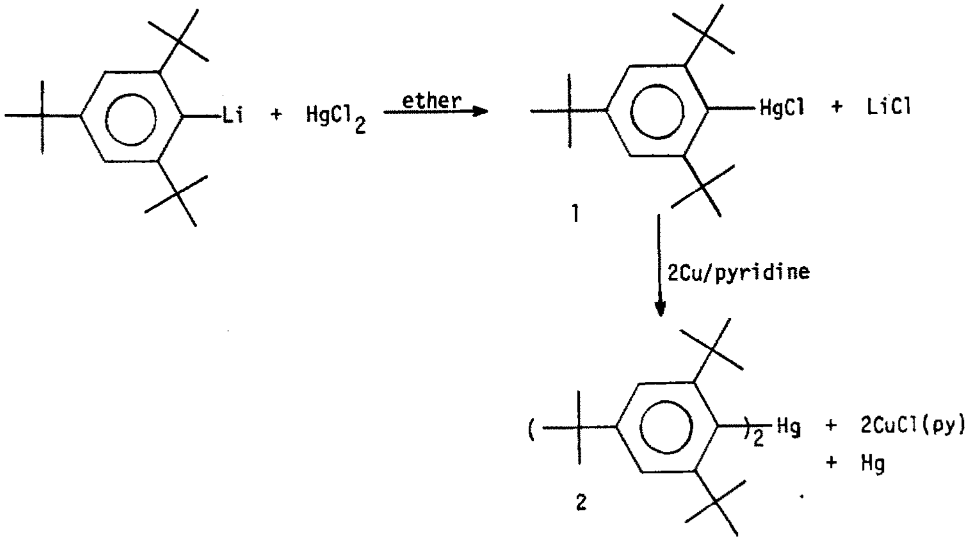
Reviews covering the following topics in organomercury chemistry have appeared:

- Chemistry of organometallic polymuclear compounds containing σ-bonded metals (1);
- $S_E1(N)$ mechanism in organic chemistry (2);
- Radioanalytic determination of mercury in the environment (3);
- σ,π-Conjugation in organomercury compounds (4);

2. PREPARATION OF ORGANOMERCURY COMPOUNDS

A. Organometallic Routes

The preparation of organomercury compounds from organolithium reagents continues to be a popular approach. For example; 2,4,6-tri(tert-butylphenyl)mercury chloride, **1**, has been prepared by the reaction of the corresponding lithium reagent with mercuric chloride (5). Symmetrization of this compound by treatment with metallic copper in pyridine gave bis[2,4,6-tri(tert-butylphenyl)]mercury, **2**.



In addition, bis[tris(trimethylsilyl)methyl]mercury, has also been prepared by this method (6).

Two studies involving the use of organotin compounds as precursers have been reported. K. A. Kocheshkov, et. al., (7) have studied the reaction of 5,5-dibutyl-5H-dibenzostannole with mercuric chloride, mercuric acetate, and acetoxy arylmercury compounds. The reactions, which are summarized in Scheme 1 may be carried out in either chloroform or methylene chloride and gives high purity compounds in good yield.

The reactions of $HgCl_2$ and $Hg(OAc)_2$ with $PhCH_2SnR_3$, (R= CH_3-, C_2H_5-, n-C_3H_7- and n-C_4H_8-), also have been reported (8). In cases where R= n-C_4H_8-, n-C_3H_7-, and C_2H_5-, product analysis indicates that $PhCH_2HgCl$ is produced in 90-98% yield.

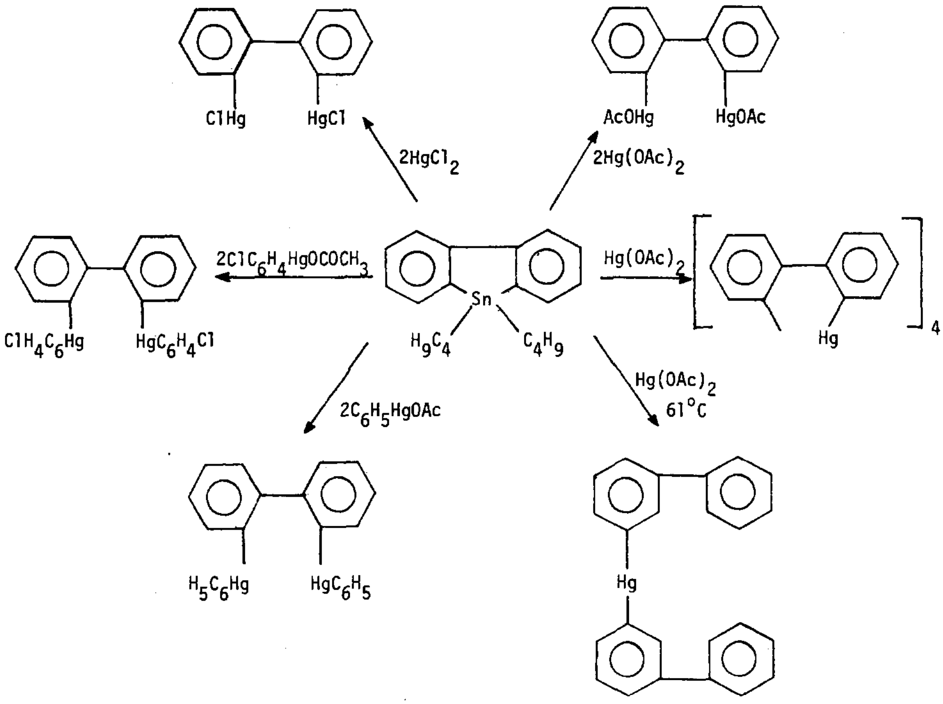
$$PhCH_2SnR_3 + HgX_2 \longrightarrow PhCH_2HgX + R_3SnX$$

R = n-C_4H_8-, n-C_3H_7-, C_2H_5-
X = Cl, OAc

On the other hand, in the reaction between $PhCH_2Sn(CH_3)_3$ and $HgCl_2$, no benzylmercury(II) was detected and only a small amount of CH_3HgCl was obtained.

$$PhCH_3Sn(CH_3)_3 + HgCl_2 \longrightarrow CH_3HgCl + PhCH_2Sn(CH_3)_3$$

Scheme 1 (7)



With one exception, the reactions all follow second order kinetics (rate constants are presented in Table 1). The following sequence for the reactivity of the R-Sn bonds toward mercury(II) salts, in methanol, was observed.

$$C_6H_5(1.4\mathrm{x}10^5) > CH_3(430) > PhCH_2(11) > C_2H_5(1) > n\text{-}C_3H_7(0.19) > n\text{-}C_4H_9(0.17)$$

The transfer of organic substituents from transition metals to mercury continues to receive attention. Samuels and Espenson (9) have examined the kinetics of the reaction of $RCr([15]\text{ane } N_4)(H_2O)^{2+}$ complexes with mercury(II) and methylmercury(II) ions in aqueous perchloric acid, as described by the two reactions below.

$$R\text{-}Cr([15]\text{and } N_4)H_2O^{2+} + Hg^{2+} \longrightarrow RHg^+ + (H_2O)_2Cr([15]\text{ane } N_4)^{3+}$$

R= CH_3, C_2H_5, n-C_3H_7, n-C_5H_{11},
i-C_3H_7, c-C_6H_{11}, 1-adamantyl,
benzyl

$$R\text{-}Cr([15\}\text{ane } N_4)H_2O^{2+} + CH_3Hg^+ \longrightarrow CH_3HgR + (H_2O)_2Cr([15]\text{ane } N_4)^{3+}$$

R=CH_3, CH_3CH_2, $CH_2C_6H_5$

TABLE 1

Second-order rate constants ($l\ mol^{-1}\ min^{-1}$) for the reaction of $PhCH_2SnR_3$ with $HgCl_2$ and $Hg(OAc)_2$ in methanol at 298 K (8)

R	$HgCl_2$[a]	$Hg(OAc)_2$[a,b]
Bu^n	0.460 ± 0.002	114 ± 5
Pr^n	0.392 ± 0.003	135 ± 13
Et	0.646 ± 0.002	220 ± 16
Me	35.9 ± 0.7	20000

[a] Runs carried out in triplicate. Errors given are estimated standard deviations.
[b] In the presence of 0.04m-acetic acid to suppress solvolysis

The reactions all follow a second-order rate expression, and are proposed to proceed by the S_E2 mechanism. Kinetic data for the reactions are summarized in Tables 2 and 3, respectively. The reaction rates decrease sharply as the size of R is increased and are some 10^2 - 10^3 larger for Hg^{2+} than for CH_3Hg^{2+}. The rates also do not appear to be greatly affected by change in the reactant species RHg^+.

Mixed cyclometallated compounds of platinum and palladium, **3**, react with $HgBr_2$ to give organomercury complexes, **4**, (10) and cyclopropyl(isobutyrato)-

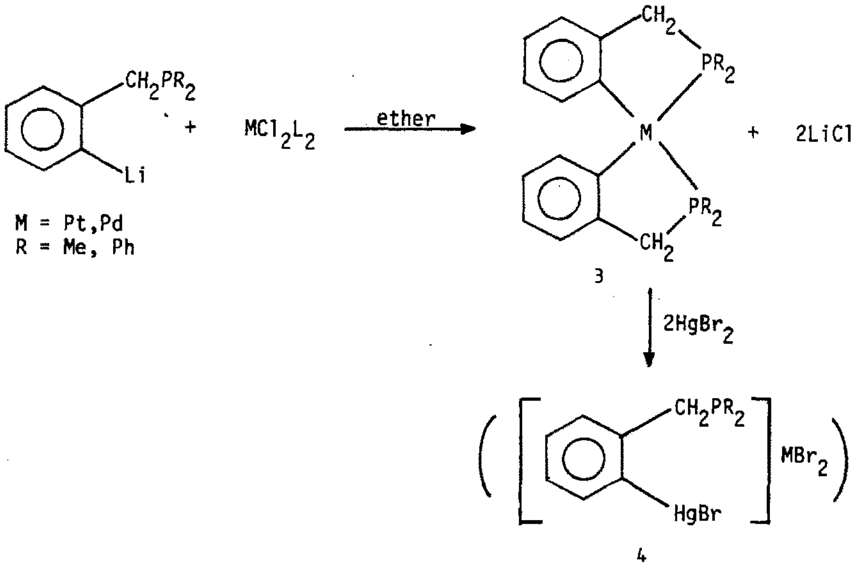


TABLE 2

Summary of Kinetic Data^{a,b}for Reactions of Mercury(II) Ion with R-Cr([15] and N_4)(H_2O^2) (9)

R	$10^2[Hg^{2*}]/M$	λ_{Hg}/M^{-1} $^{-1}$	ΔH^t/kJ mol^{-1}	ΔS^t/J $mol^{-1}K^{-1}$
$-CH_3$	0.047	$(3.1 \pm 0.2) \times 10^a$	30.2 ± 1.2	77 ± 4
$-CH_2CH_3$	1.2-11.7	$(2.53 \pm 0.03) \times 10^3$	48.8 ± 1.5	-45 ± 5
$-n-C_3H_7$	1.2-11.7	$(8.21 \pm 0.04) \times 10^1$	33.5 ± 2.1	-100 ± 7
$-n-C_4H_9$	2.3-11.7	$(4.88 \pm 0.17) \times 10^1$	29.7 ± 1.2	-114 ± 4
$-n-C_5H_{11}$	4.5-11.7	$(4.33 \pm 0.20) \times 10^1$	33.4 ± 1.6	-75 ± 5
$-CH_2C_6H_5$	1.17-11.7	$(1.14 \pm 0.03) \times 10^3$		
$-i-C_3H_7$[c]	216-432	$(4.3 \pm 0.4) \times 10^{-3}$		
$-c-C_6H_{11}$	216-432	$(1.6 \pm 0.4) \times 10^{-3}$		
-1-adamantyl[c]	216-432	$(3.1 \pm 0.1) \times 10^{-3}$		

[a] 25.0°C. [b] At μ=0.50 M,$[H^4]$=0.25 M, except as noted. [c] $[H^4]$=0.17 M,μ=1.46 M, maintained with $Ba(ClO_4)_2$.

mercury(II), **5**, is formed as a by-product of the synthesis of cyclopropyl(isobutyrato)-thallium(III), (11). This latter compound is prepared by an exchange reaction between bis(isobutyrato)mercury(II) and dicyclopropylisobutyratothallium(III) (11). Its structure is shown in Figure 1.

$$C_3H_5[(CH_3)_2CHCO_2]Tl + [(CH_3)_2CHCO_2]_2Hg \longrightarrow C_3H_5[(CH_3)_2CHCO_2]_2Tl + C_3H_5Hg[O_2CCH(CH_3)_2]$$

5

TABLE 3

Summary of kinetic data for reactions of methylmercury(II) ion with R-Cr([15] ane $N_4)(H_2O)^{2+}$ (9)

R	$10^3[CH_3Hg+]/M$	$k_{CH_3Hg}/M^{-1}s^{-1}$
$-CH_3$	1.04-8.93	$(1.63 \pm 0.02) \times 10^2$
$-CH_2CH_3$	0.94-7.43	9.9 ± 0.4
$-CH_2CH_3{}^b$		8.2^b
$-CH_2C_6H_5$	0.94-6.57	5.2 ± 0.1

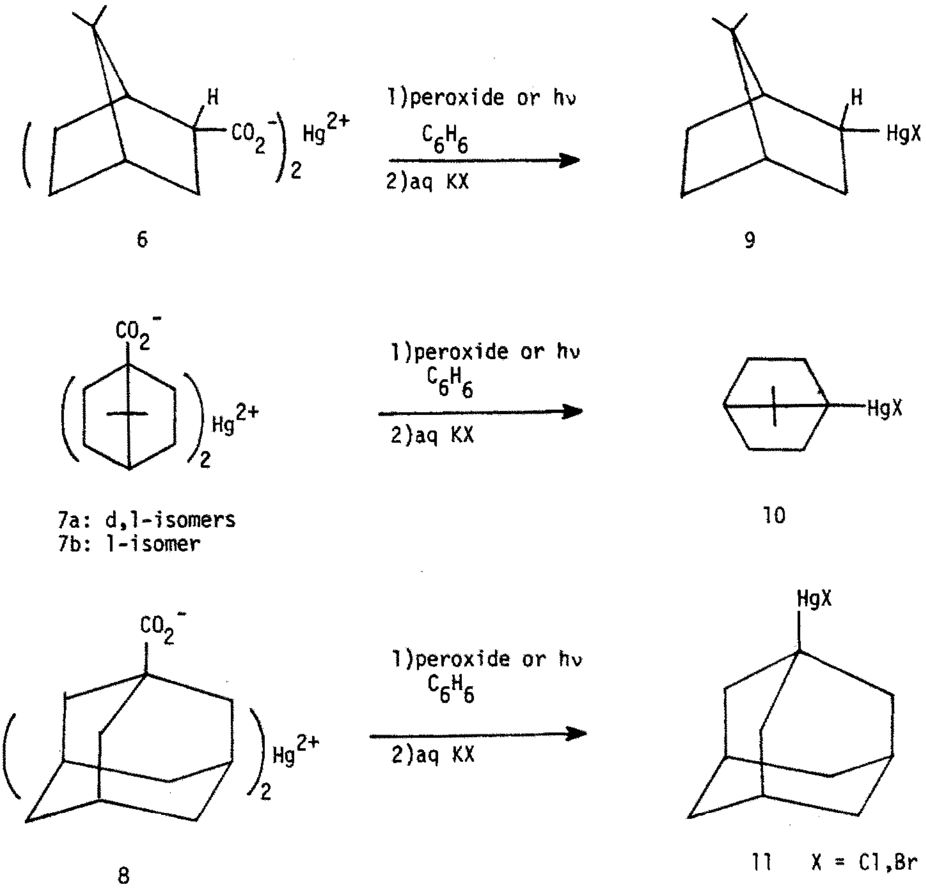
[a] At 25.0°C, $[H^+]$= 0.250 M, μ= 0.50 M.

[b] The reactint electrophile is $CH_3CH_2Hg^+$

The complete series of tetrakis(halomercuri)methanes, $C(HgX)_4$, (X= F, Cl, Br, and I), has been prepared by metathesis of $C(HgOAc)_4$ and aqueous HF and solutions of the halides (Cl^-, Br^-, and I^-), respectively (12).

B. Radical Processes

Mercuric endo-2-camphanecarboxylate, **6**, ketopinoate (d,l- and l-isomers),**7**, and 1-adamantoate, **8**, undergo initiated decarboxylation (13) under the action of either acylperoxides or UV-irradiation, to give the acylmercury derivatived,**9**, **10**,



and **11**, respectively, that were isolated as the halogenides in 65 - 92% yield. Decarboxylation of **6** proceeds with retention of configuration, however, decarboxylation of **7b** occurs without racemization to give an optically active product.

Cyclopentadienyl derivatives of tin(IV) and mercury(II) as well as alkylcyclopentadienyl derivatives of mercury(II) undergo photo-induced homolysis of the cyclopentadienyl-metal bonds to give the corresponding cyclopentadienyl and metalyl radicals (14).

$RC_5H_4M \longrightarrow RC_5H_4\bullet + M\bullet$

$R = H, D, Me, Et, Pr^i, or\ Bu^t$

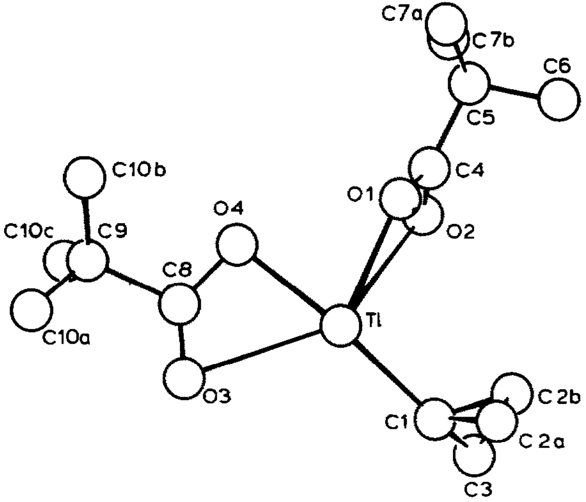
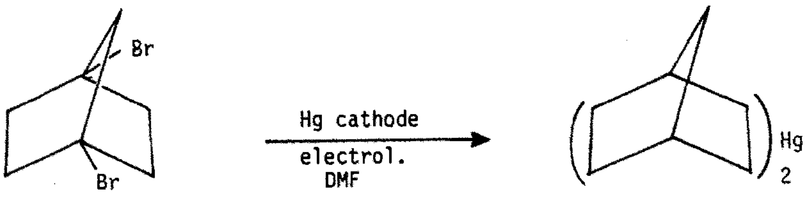


Figure 1. The molecular structure of dicycloproylisobutyratothallium(III) showing disorder in atoms C(2), C(7), and C(10). From F. Brady, K. Henrick and R. W. Matthews, J. Organometal. Chem., 165 (1979) 21.

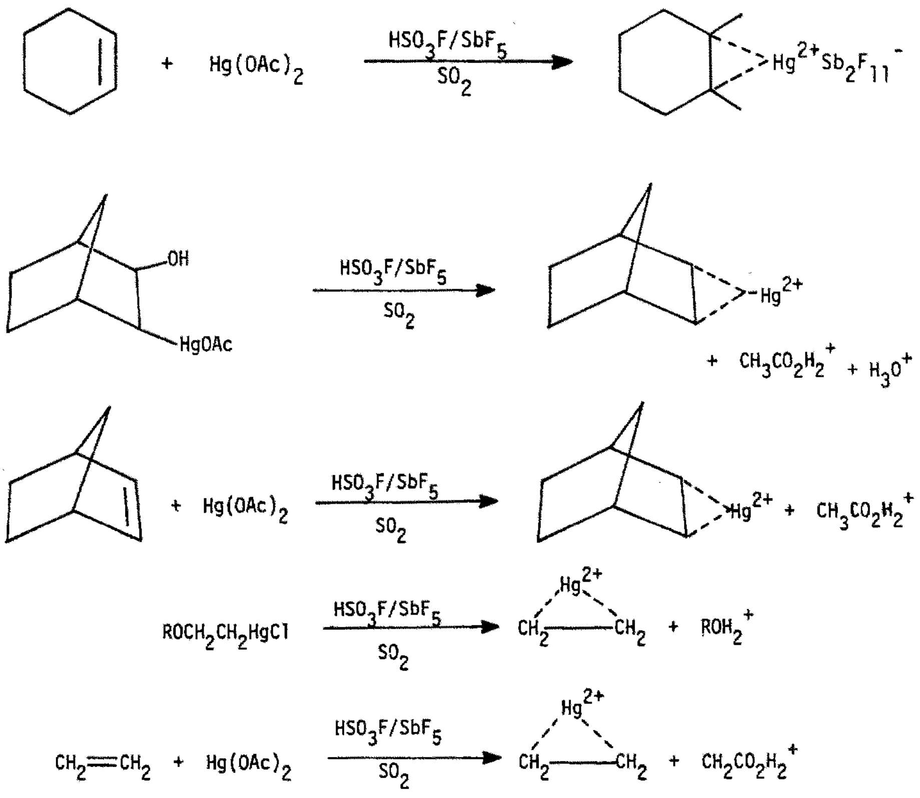
C. Miscellaneous

Methylhydrazine reacts with mercuric oxide in anhydrous ethylether to give a variety of products among which $(CH_3)_2Hg$ has been identified as a major constituent (15). This appears to be the first reported incident in which $(CH_3)_2Hg$ has been detected in HgO oxidation of methylhydrazine. $(CF_3)_2Hg$ is formed in the reactions of C_2F_6 with Hg, HgX_2, (X= Cl,Br,I), or HgO in a chemical plasma. The best yields are obtained with Hg and HgO (16).

The low temperature (-34°C) electrolytic reduction of 1,4-dibromonorbornane at mercury cathodes in dimethylformamide containing tetraalkylammonium perchlorates gives, in addition to bis(1-norbornyl)mercury, norborname and 1'-binorbornyl (17). These same three products, along with 1-iodonorbornane, and other minor products are formed during reduction of 1,4-diiodonorbornane. The intermediate in these reductions is suggested to be [2,2.1]propellane.



Olah and Garcia-Luna have prepared long-lived mercurinium ions of ethylene, cyclohexene, and norbornene in $FSO_3H/SbF_5/SO_2$. (18) Details concerning these ions may be found in section 10B.



3. MERCURATION OF UNSATURATED COMPOUNDS

A. Olefins and Polyenes

The reaction rates and activation parameters for the methoxymercuration of a series of styrene derivatives and related compounds have been reported (19). Product analysis shows that addition to the double bond usually involves attack of

TABLE 4 (19)

Second-order rate constants for the methoxymercuration of some styrenes and stilbenes in methanol at 25 C; comparison with the vinylferrocene system.

Compound	k_2 ($M^{-1}s^{-1}$)	k_{rel}	Compound	k_2 ($M^{-1}s^{-1}$)	k_{rel}
Styrene	10.4[a]	1	Vinylferrocene	230[a]	1
α-Methylstyrene	24.0	2.1	α-Methylvinylferrocene	910[a]	4.0
α-t-Butylstyrene	0.074	7.1×10^{-3}	α-t-Butylvinylferrocene	0.024[b]	1×10^{-4}
trans-β-Methylstyrene	0.020	1.9×10^{-3}	trans-β-Methylvinylferrocene	0.67	2.9×10^{-3}
cis-β-Methylstyrene	0.025	2.4×10^{-3}	β,β-Dimethylvinylferrocene	0.026[b]	1×10^{-2}
β,β-Dimethylstyrene	0.16	1.5×10^{-2}			
trans-Stilbene	1.6×10^{-4}	1.5×10^{-5}			
cis-Stilbene	2.9×10^{-4}	2.8×10^{-5}			
Allylbenzene	4.3[c]	0.4			

[a] Ref. 7. [b] Upper limit given by 10% of the ring substitution rate coefficients [7]. [c] $[PhCH_2CH{=}CH_2]$ 4.78 x 10^{-3} M, $[Hg(OAc)_2]$ 9.2 x 10^{-4} M.

the mercury exclusively at the carbon β to the phenyl group. However, in the case of trans-β-methylstyrene both orientations of addition were observed. The reactions involving styrenes follow second order kinetics and the behavior of both α- and β-alkyl substituted styrenes generally parallels that of the similarly substituted vinyl ferrocenes, [B. Floris and G. Illuminati, J. Organometal. Chem.168, 203, (1979)]. Rate constants and activation parameters for the compounds studied are presented in Tables 4 and 5, respectively.

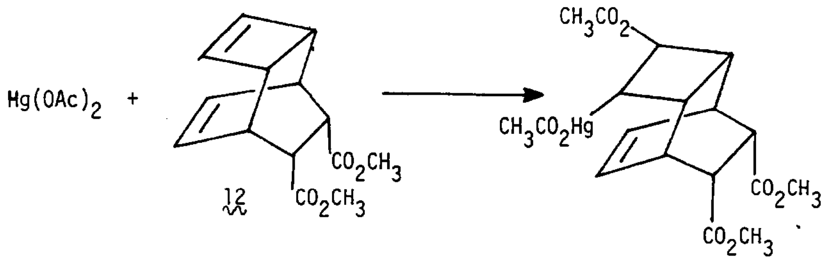
TABLE 5

Activation parameters for the methoxymercuration of some styrene and stilbenes (19)

Compound	E (kcal/mol)	$\Delta S^{\neq}$ (e.u.)
$PhCH{=}CH_2$	10.6 ± 0.5[a]	-20 ± 1.5[a]
$PhC(CH_3){=}CH$	29.2 ± 0.5	-23 ± 1.5
$PhC(t\text{-}Bu){=}CH_2$	11.5 ± 0.5	-27 ± 1.5
$PhCH{=}C(CH_3)_2$	10.3 ± 0.5	-30 ± 1.5
trans-$PhCH{=}CHCH_3$	14.1 ± 0.5	-21 ± 1.5
cis-$PhCH{=}CHCH_3$	15.0 ± 0.5	-17 ± 1.5
trans-PhCH=CHPh	14.1 ± 0.5	-30 ± 1.5
cis-PhCH=CHPh	11.7 ± 0.5	-37 ± 1.5

[a] From B. Floris and G. Illuminati, J. Organmetal. Chem., 168 (1979) 203.

Zefirov and coworkers (20) have re-examined the stereochemistry of the electrophilic addition of $Hg(OAc)_2$ to dimethyltricyclo[4,2,2,$0^{2,5}$]deca-3,7-diene-9,10-dicarboxylate, **12**. Contrary to previous suggestions, [T. Saski, et. al., J. Org. Chem., 39, 3569, (1974) ; G. Mehta and P. N. Pandey, J. Org. Chem., 40, 3631, (1975)] , oxymercuration of the diester, **12**, was found to occur via trans addition. Initial attack on the cyclobutene is directed from the endo- side in contrast to other electrophilic additions which have been shown to proceed from the exo- side. This unusual



mode of initial approach is suggested to be due to the coordination of the mercury ion to both double bonds. The structure of the addition product is shown in Figure 2.

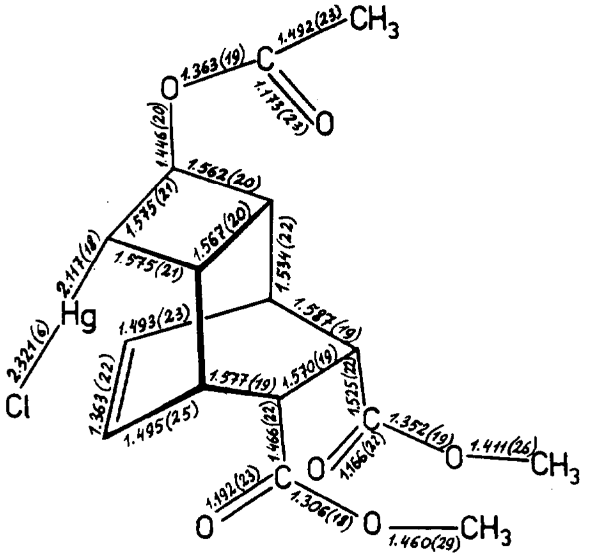
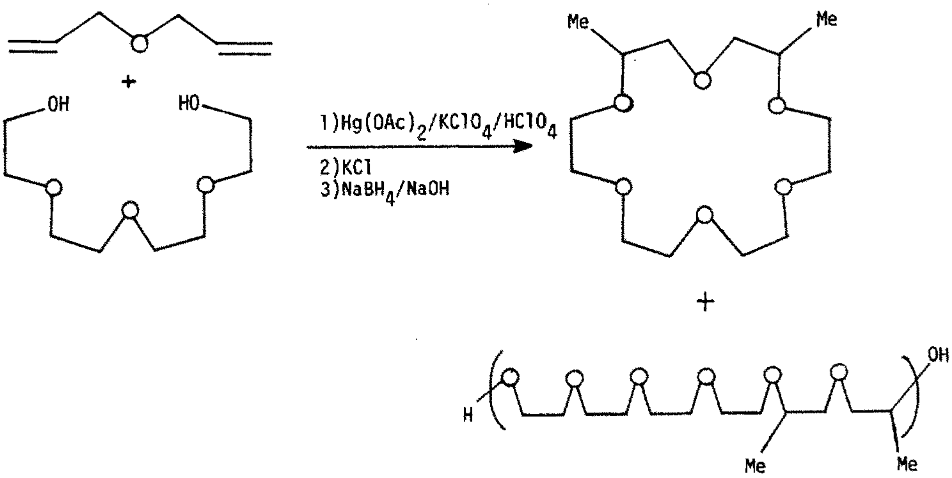
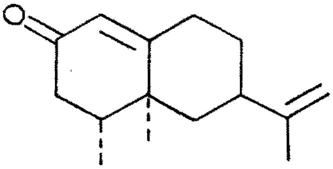


Figure 2. The molecular structure of dimethyl trans-3-endo-chloromercur-4-acetoxy-tricyclo[4,2,2,$0^{2,5}$]dec-7-eno-9,10-cis-endo-dicarboxylate. From N. S. Zefirov, A. S. Koz'min and v. N. Kirin, Tetradedron Let., 21 (1980) 1667.

The oxymercuration-demercuration technique has been successfully applied to the preparation of the previously unknown 2,6-dimethyl-18-crown-6 (21). The ether was prepared in 11% yield as shown below.



A facile stereoselective syntheses of (+)-nootkotene, **13**, has been achieved starting with (+)-nopinone, **14**, (22).



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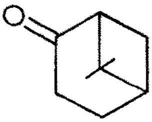

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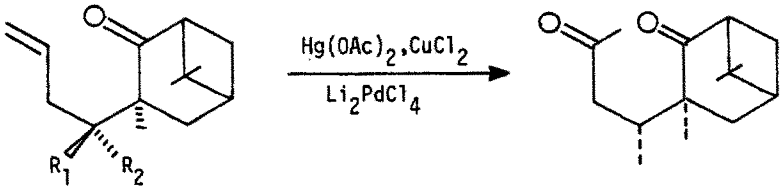
The approach used involved oxidative oxymercuration-demercuration to convert the allyl group of **15a** and **15b** to an acetonyl group to afford diene, **16**, Acidification of

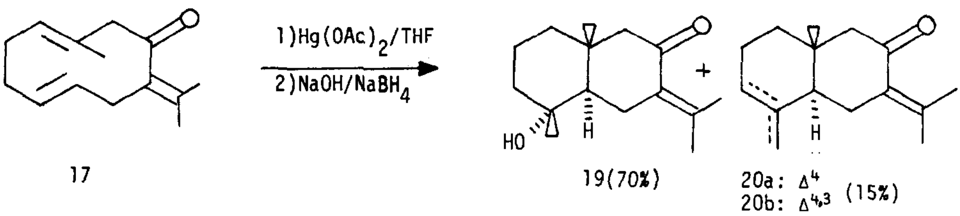


15a: (R_1= H, R_2= CH_3)
15b: (R_1= CH_3, R_2= H)

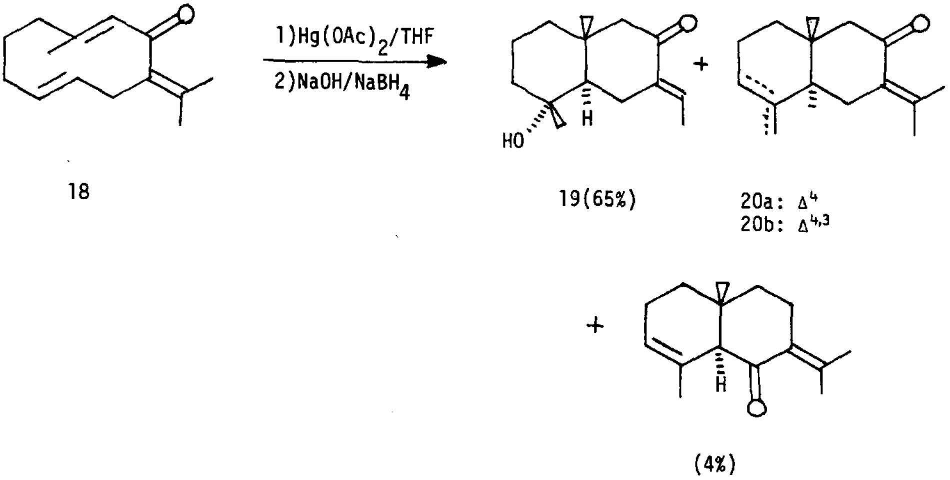
16

16 followed by regioselective dehydrochlorination of the resulting hydrochloride gave the desired (+)-nootkotene.

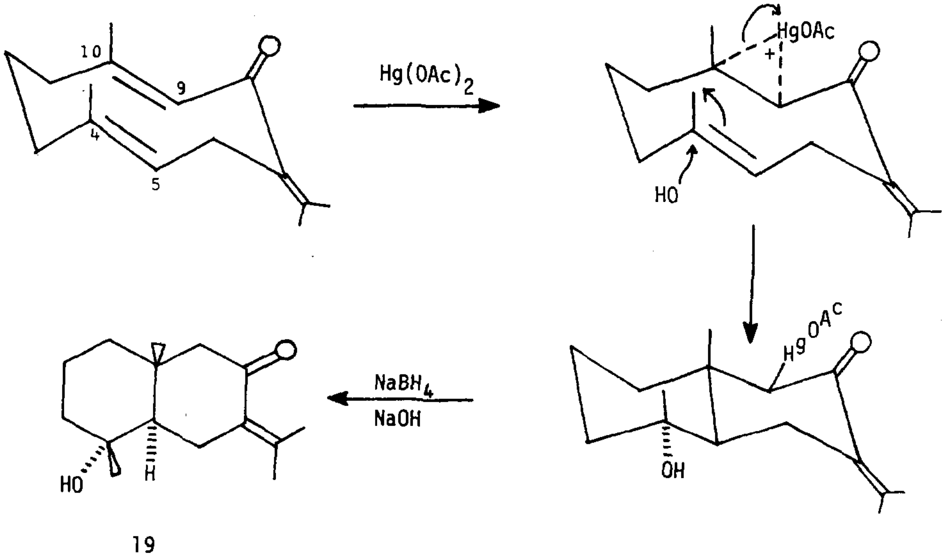
Germacrone, **17**, and Isogermacrone, **18**, undergo transanular cyclization by oxymercuration-demercuration to give trans-decaline derivatives **19**, **20a**, and **20b** (23).



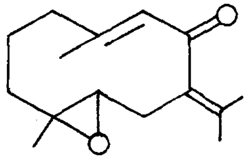
The cyclization of isogermacrone is both regio- and stereoselective and is suggested to occur by a concerted mechanism involving synchronous formation of carbon-metal and carbon-carbon bonds as shown is Scheme 2.



Scheme 2 (23)



Support for this suggestion is found in the fact that epoxidation of isogermacrone gives only the isogermacrone-4,5-epoxide, **21**.



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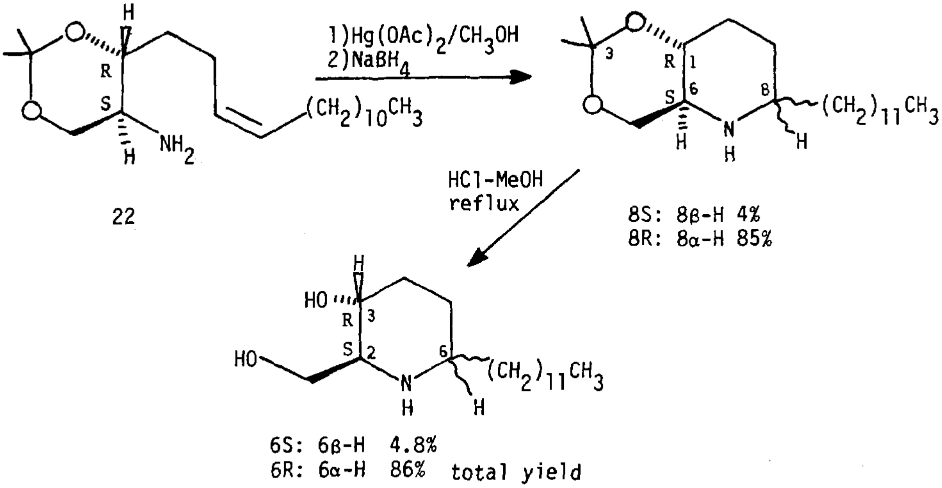
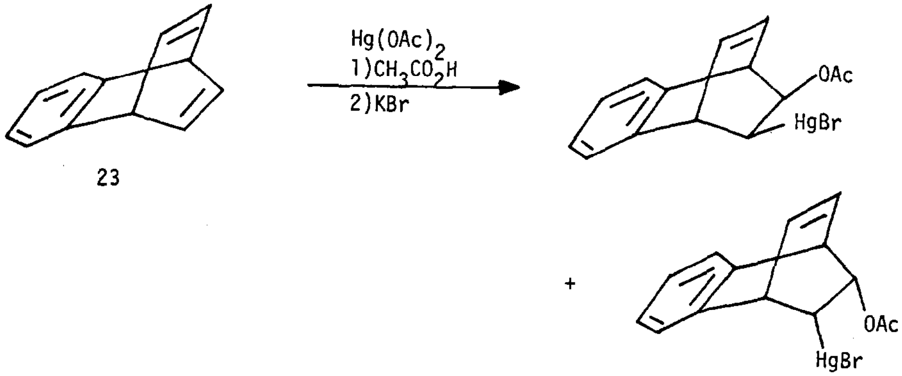
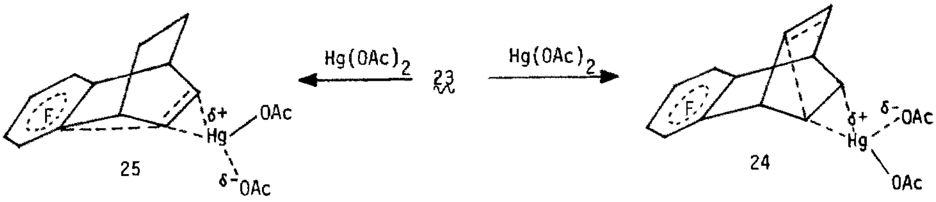
(-)-Deoxoprosopinine and (-)-deoxoprosophylline have been synthesized from L-serine by a route invloving the intramolecular aminomercuration of the chiral ε-unsaturated amine, **22**, shown below (24).





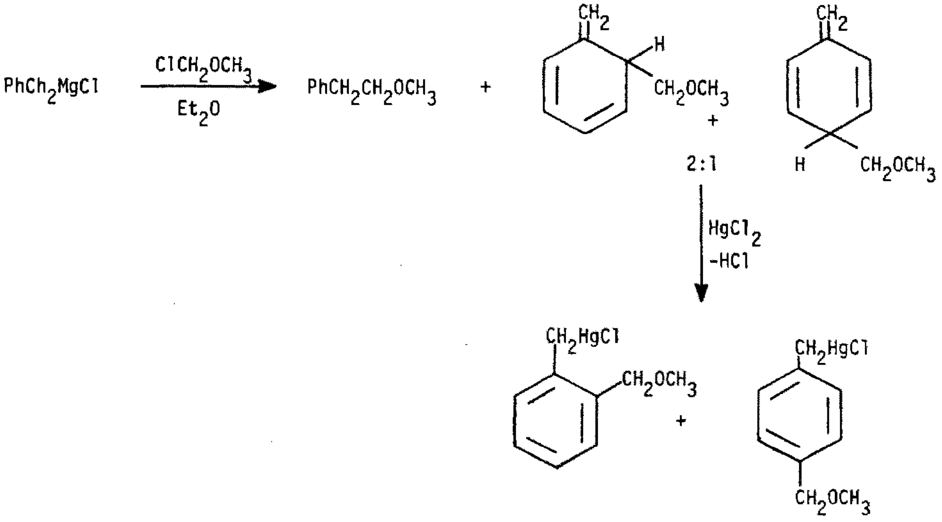
Alkene **23** reacts with mercuric acetate in acetic acid to afford two isomers, in a ratio of 2:3 (25).

These results are in agreement with the suggestion that π-participation of the 7,8 bond is more effective in stabilizing transition state **24** than is the fluorinated aromatic ring in stabilizing transition state **25**, as shown below.



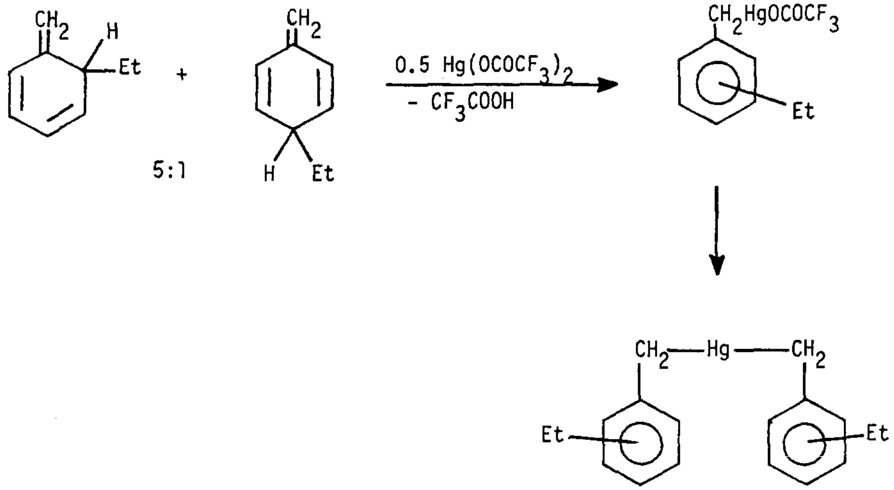
Reutov and coworkers (26) have shown that aromatization metalation of 1-methylene-6-methoxymethyl-2,4-cyclohexadiene and 1-methylene-4-methoxy-methyl-2,5-cyclohexadiene with $HgCl_2$ in ether affords the first members of a previously unknown class of compounds: namely o- and p-methoxymethylbenzylmercuric chloride.

In the presence of hydrochloric acid, p-methoxybenzylmercuric chloride exhibits a dual re- activity due to electrophilic attack both at oxygen and at the carbon-mercury bond. On the other hand, in the presence of excess mercuric chloride, p-methoxymethylbenzylmercuric chloride reacts with hydrochloric acid to give p-chloromethylbenzylmecuric chloride as shown in Scheme 3.

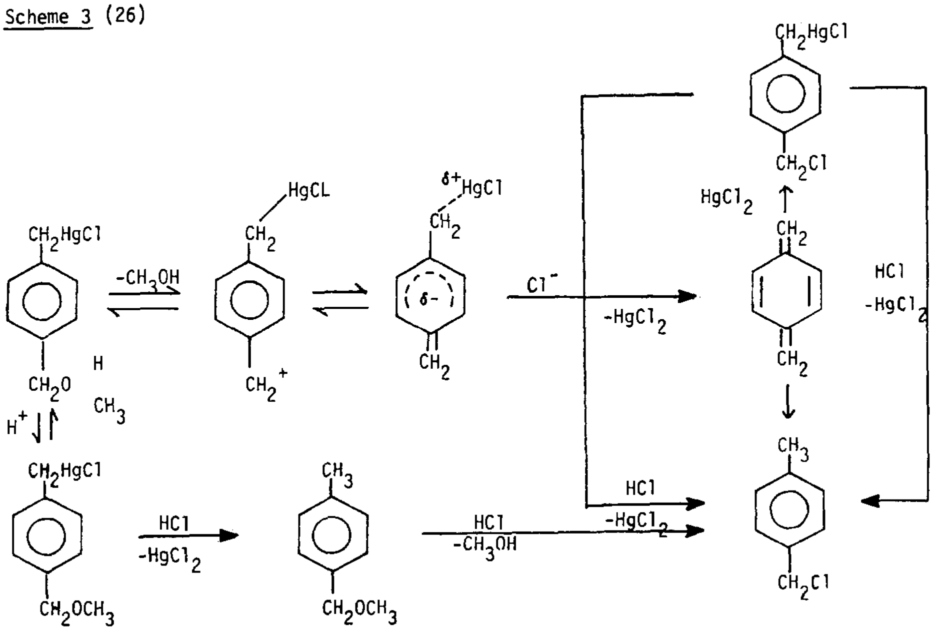


The aromatisational-mercuration, of 1-methylene-6-ethyl-2,4-cyclohexadiene and 1-methylene-4-ethyl-2,5-cyclohexadiene with several mercury(II) derivatives has been reported (27). Reaction of a 5:1 mixture of the trienes with a half equivalent of $Hg(O_2CCF_3)_2$ gave o- and p-di(ethylbenzyl)mercury.

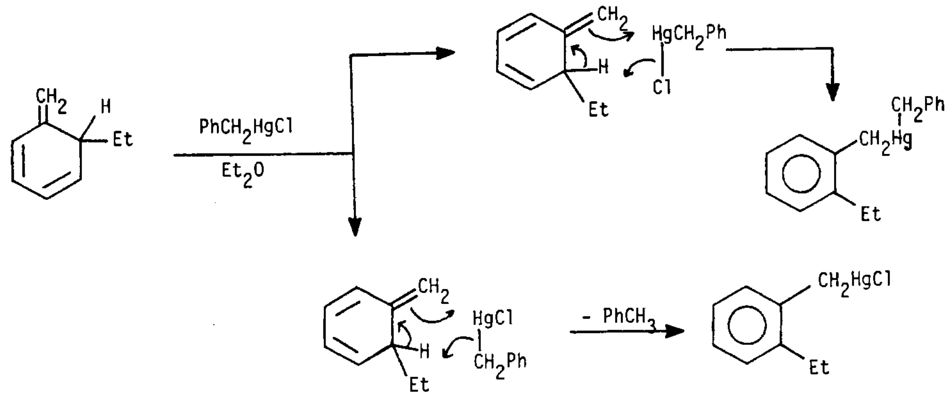
The reaction appears to proceed in two steps: the first step being aromatizational-mercuration of methylene-dihydrobenzene, to give o-$EtC_6H_4CH_2HgO_2CCF_3$, which then reacts with a second equivalent of triene to produce the product.



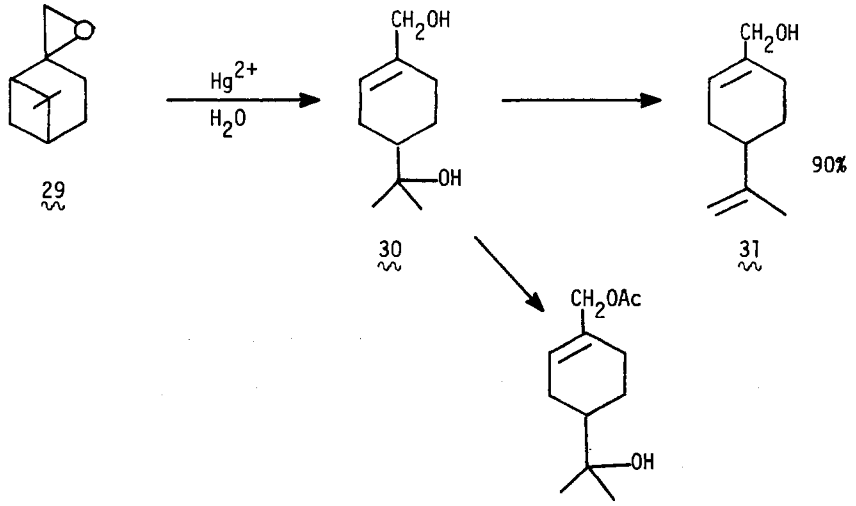
Scheme 3 (26)



What appears to be the first example of addition of an organomercury chloride to a carbon-carbon double bond was observed in the reaction between the trienes and $PhCH_2HgCl$ resulting in the formation of $EtC_6H_4CH_2HgCl$ and ethyldibenzylmercury.



Nucleophilic attack on the mercury(II) complex of pin-2(10)ene by water or alcohol gives the allylic organomercury(II) derivatives ,26, with a p-menthane skeleton (28). (Scheme 4).The intermediate **26** may be either reduced by hydride to p-menth-1(2)-en-8-ol, **27**, or can undergo an in situ S_E2' elimination to give p-menth-1(7)-en-8-ol, **28**, in 95% yield, which is believed to be formed by the mechanism outlined in Scheme 5. (-)-2,10-Epoxypinane, **29**, reacts under similar conditions to give p-menth-1(6)-ene- 7,8-diol, **30**, in virtually quantitative yield. In the presence of inorganic acids, **30**, affords p-mentha-1,8-dien-7-ol, **31**,in 90% yield.

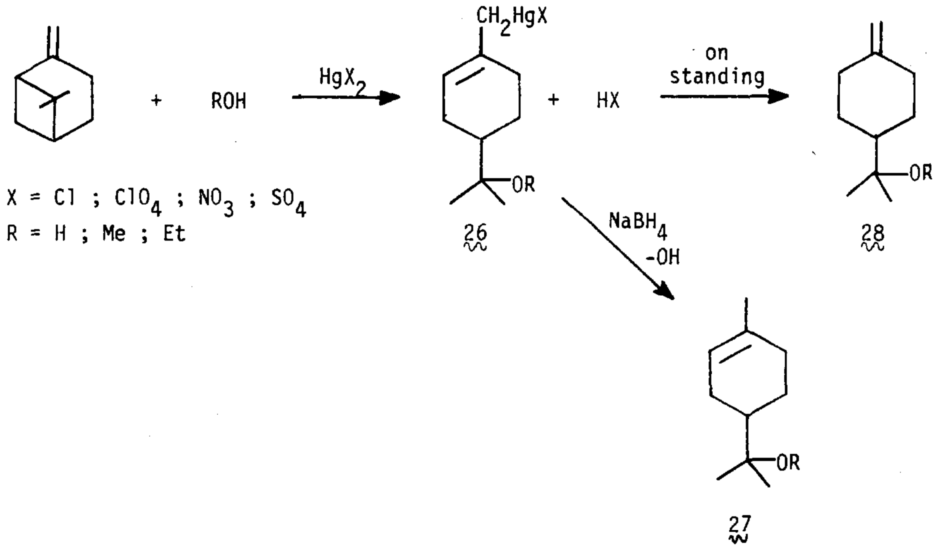


29

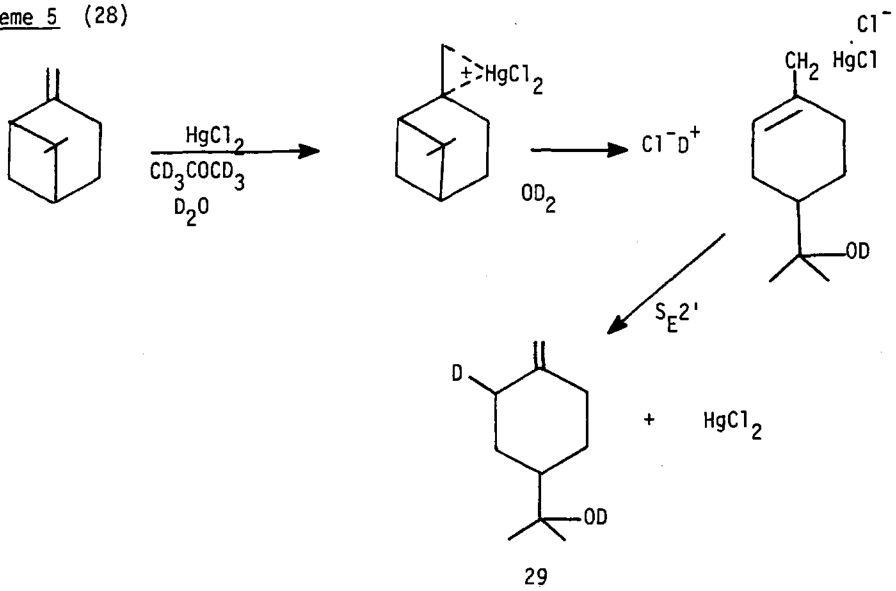
30

31

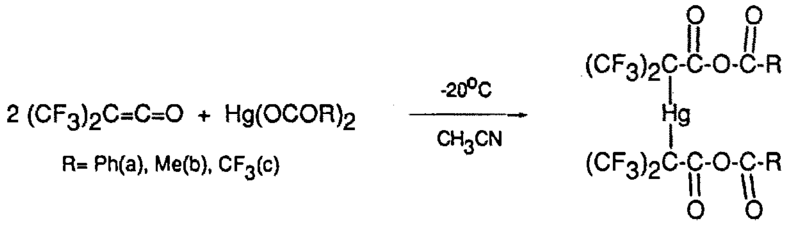
Scheme 4 (28)



Scheme 5 (28)

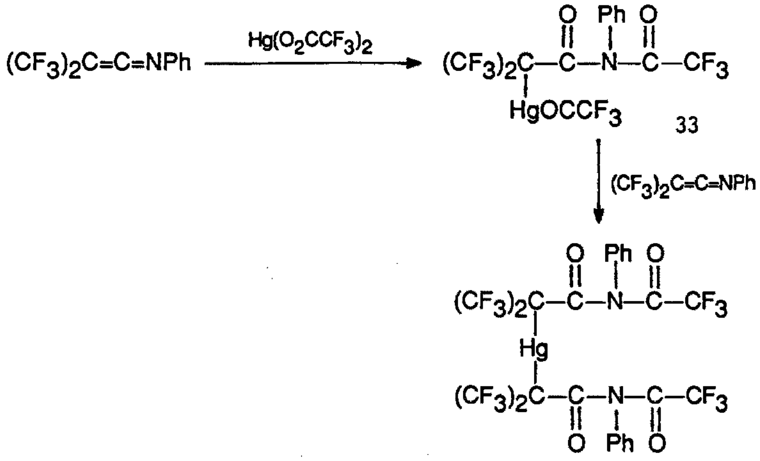


Mercury salts of carbocyclic acids, add to bis(trifluoromethyl)ketone to give mixed anhydrides of α-mercuriobishexafluoroisobutyric acid, **32**, (29).



32

The N-phenylimine of bis(trifluoromethyl)ketone reacts similarly to give the corresponding imide, **34**, with the asymmetric compound, **33**, being formed as an intermediate.



33

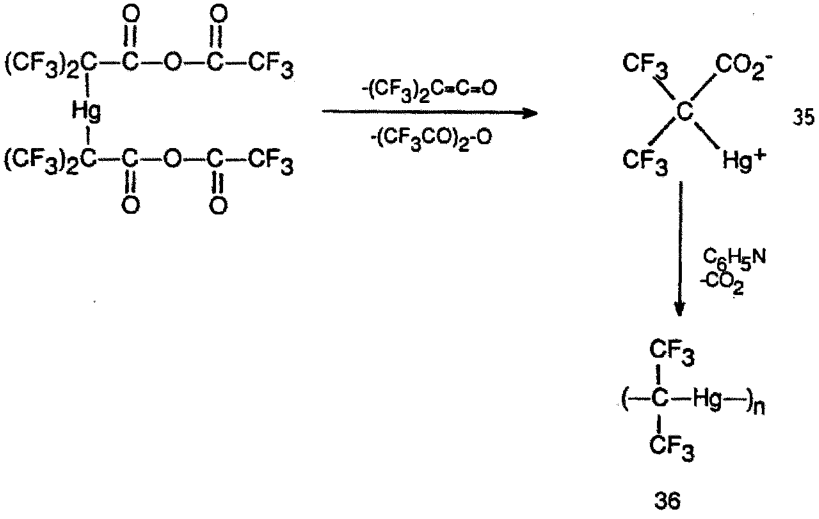
34

When R = CF_3, **32**, is readily decomposed to bis(trifluoromethyl)ketone, trifluoroacetic anhydride, and the internal salt of mercuriohexafluoroisobutene acid, **35**, which on decarboxylation in pyridine gives polymeric hexafluoroisopropylidene mercury, **36**.

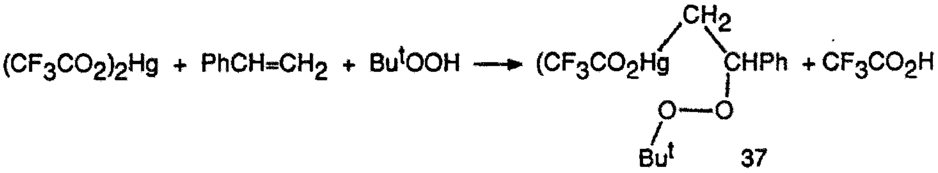
Benzylmercuric acetate and $NaBH_4$ react with ethylacrylate to give the addition product 4-phenylbutyric acid ester (30). Styrene and alkylbenzene react similarly, however, styrene is less electrophilic than ethylacrylate and alkylbenzene reacts only in pyridine with di-2-pyridylamine as a complexing reagent.

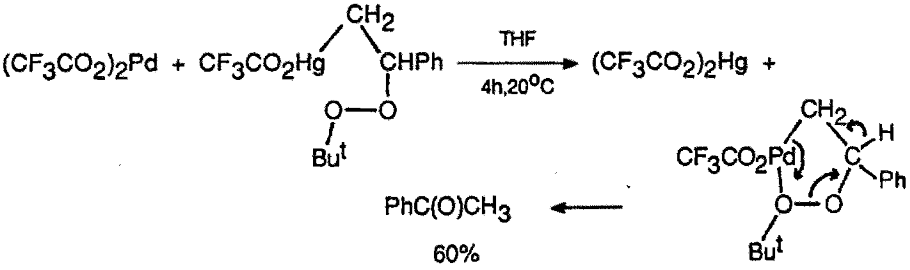
$$C_6H_5CH_2HgOAc + H_2C{=}CH\text{-}Y \xrightarrow{NaBH_4} C_6H_5CH_2CH_2CH_2Y$$

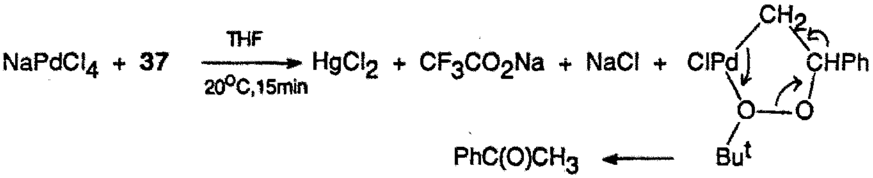
$Y = CO_2C_2H_5, C_6H_5, C_6H_4Cl, CH_2C_6H_5$



The t-butylperoxymercurial, **37**, reacts with palladium trifluoroacetate to afford acetophenone in 60% yield, (THF, 20°C,4h) (31).



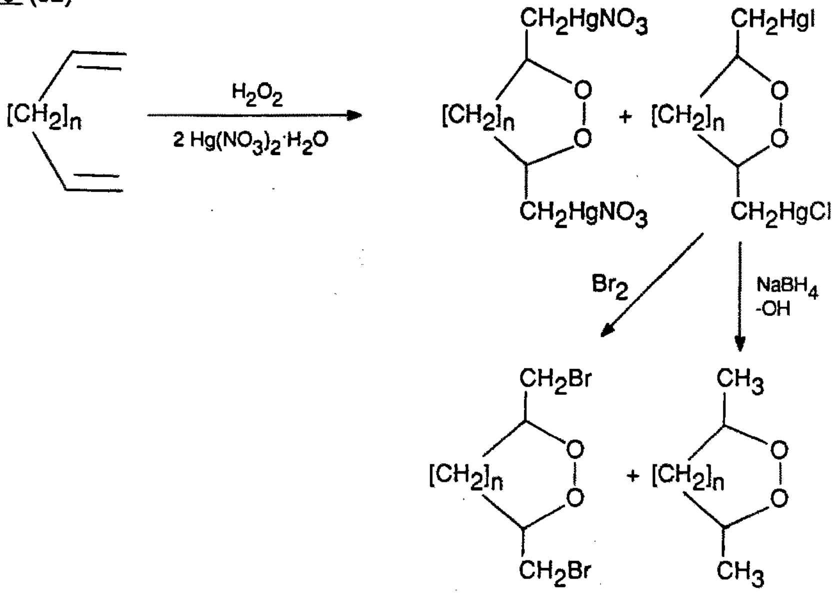




On the other hand, reaction with Na_2PdCl_4 under the same conditions gave acetophenone in a 95% yield in less than 25 minutes.

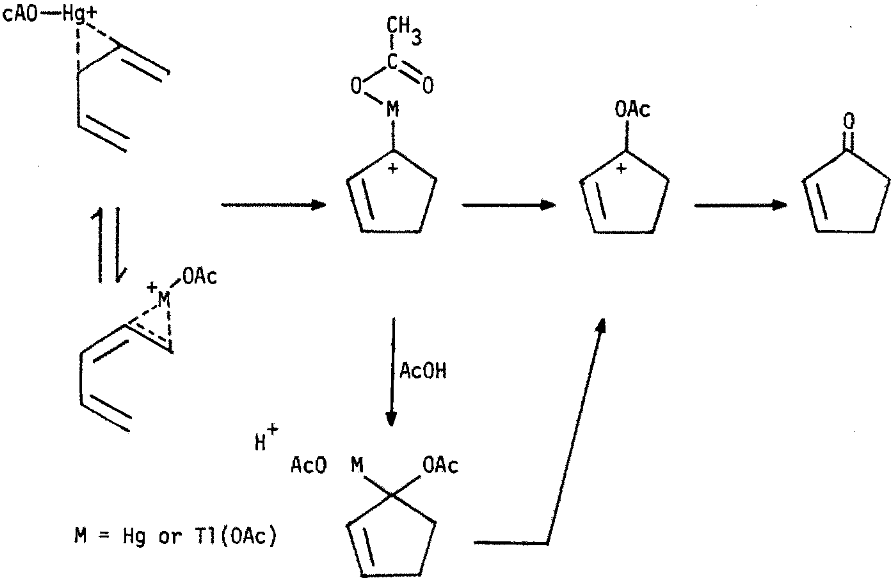
The scope of the cycloperoxy mercuration reaction , Scheme 6, has been further studied (32).

Scheme 6 (32)



Reactions with several non-conjugated dienes, penta-1,3-diene and 2,5-dimethyl-hexa-2,4-diene and with two alkenyl hydroperoxides have been investigated. By hydrogeno- and bromo-demercuration of the products, several new methyl- and

Scheme 7 (33)



M = Hg or Tl(OAc)

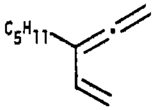
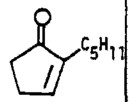
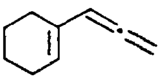
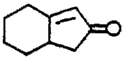
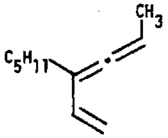
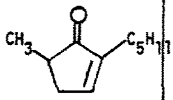
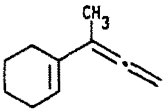
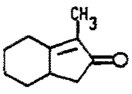
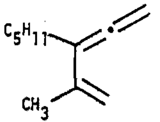
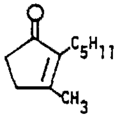
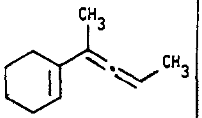
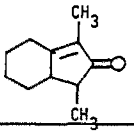
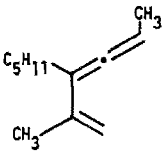
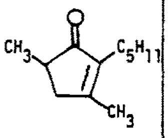
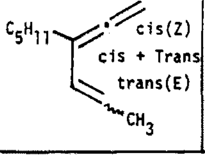
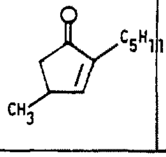
bromomethyl- substituted 1,2-dioxacyclopentanes and -hexanes have been prepared.

Substituted vinylallenes undergo acetoxymercuration and acetoxythallation to give cyclopentenones (33). Demetallation is particularly favorable and is spontaneous in acetic acid. Results of the reactions are summarized in Table 6 and a proposed mechanism in Scheme 7.

Chien and coworkers (34) report the successful nitromercuration of hydrophobic olefinic polymers using a modification of the method developed by Corey and Estreicher, [E.J. Corey and H. Estreicher, J. Am. Chem. Soc., 100, 6294 (1978)]. The procedure uses nonaqueous conditions, CH_2Cl_2, assisted by the phase transfer catalyst tetrabutylammonium bisulfate.

Table 6

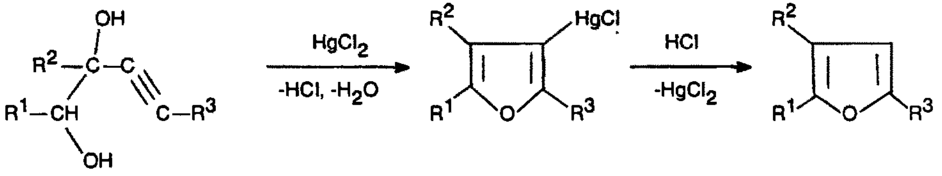
Acetoxymercuration of Vinylallenes

Vinylallene	Cyclopentenone	Yield	Vinylallene	Cyclopentenone	Yield
		70%			
		50%			75%
		54%			49%
		79%			
		50% 51% 78%			

Pal and Saxena (35) have developed an improved procedure for the separation of mono- and diolefins as their methoxy mercurated adducts by paper chromatography. The method depends upon an improved solvent system which allows a much cleaner separation.

B. Acetylenes

Acetylenic diols, **38**, react with $HgCl_2$ in alcoholic solution to give the corresponding substituted furans, **40**, in 60 - 85% yield (36). Good yields of the 3-(chloromercurio)furans, **39**, are obtained in the cold, however, at the boiling point of the alcohol, dimerization occurs and the substituted furans are obtained directly.



38 a-h

39 a- h

40 a-h

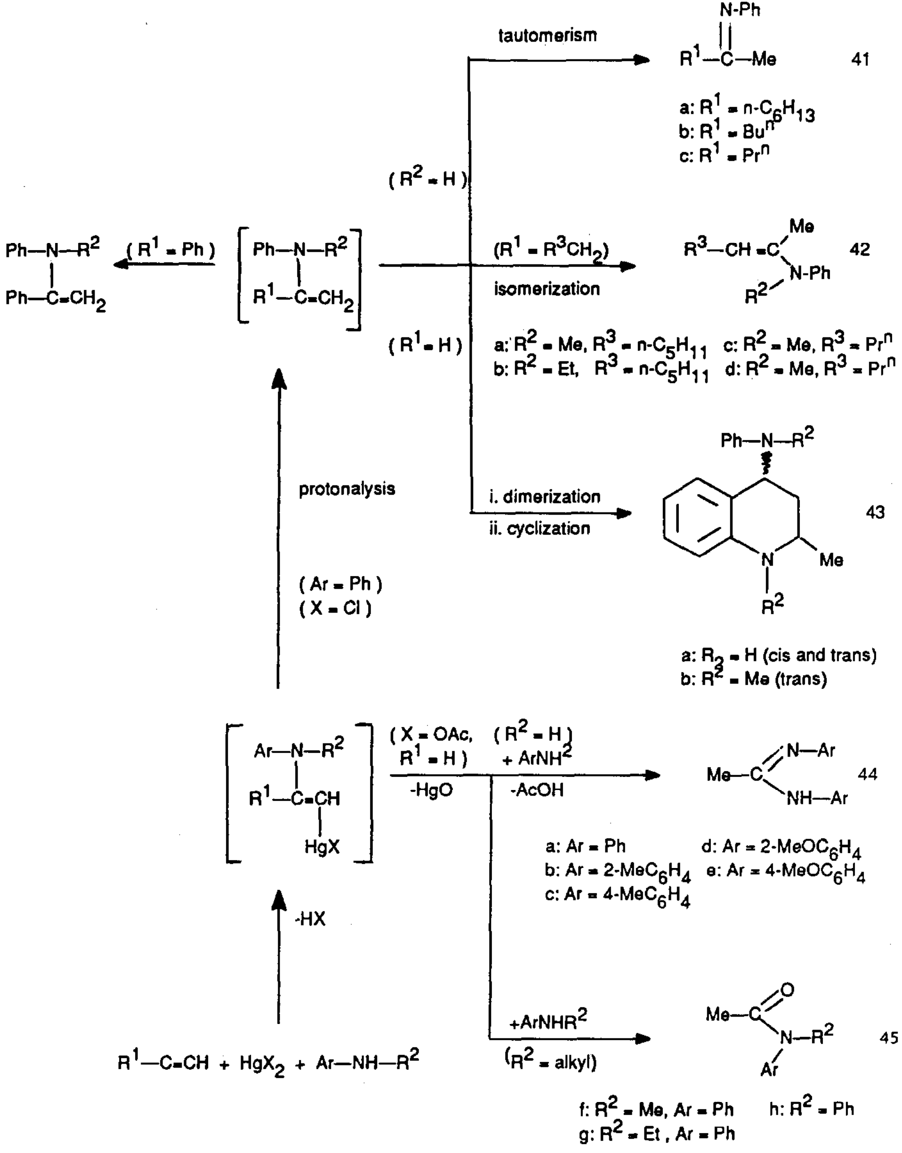
a: R^1=R^2=R^3= CH_3
b: R^1=R^2= CH_3, R^3=C_4H_9
c: R^1=R^2+ CH_3, R^3=p=C_6H_4Cl
d: R^1=R^2=C_4H_{11}, R^3=C_6H_5

e: R^1=R^2=C_7H_{13}, R^3=C_6H_5
f: R^1=R^2=C_7H_{13}, $R^3C_6H_5$
g: R^1=R^2=$(CH_2)_5$, R^3=C_6H_5
h: R^1=R^2=$(CH_2)_{10}$, R^3=C_6H_5

The addition of aromatic amines to terminal acetylenes in the presence of catalytic amounts of $HgCl_2$ gives imines, enamines, and 1,2,3,4-tetrahydroquinoline derivatives as outlined in Scheme 8 (37). The imines, **41**, are produced by the room-temperature addition of aniline to monoalkylacetylenes in the presence of $HgCl_2$, in a ratio of (1:20:100 ; $HgCl_2$: alkyne : amino). Enamines, **42**, are obtained as a mixture of Z- and E-isomers, from the reaction of secondary aromatic amines with monoacetylenes using a $HgCl_2$; alkyne : amine ratio of 1:20:100 to give 2-methyltetrahydroquinoline derivatives, **43**. Mercury(II)acetate may also be used but it shows considerably less catalytic activity. In this case, depending upon the molar ratio of amine to mercury(II) acetate, the main processes are the non-catalytic formation of sybstituted acetamidines, **44**, and/or sugstituted acetamides, **45**.

Diisopropyl[1-alkyoxy-2-(chloromercurio)-1-alkenyl]phosphonates, **46a-g**, have

Scheme 8 (37)



been prepared by the reaction of 1-alkynylethers with (i-PrO)$_3$PHgCl$_2$ (38) in virtually quantitative yield.

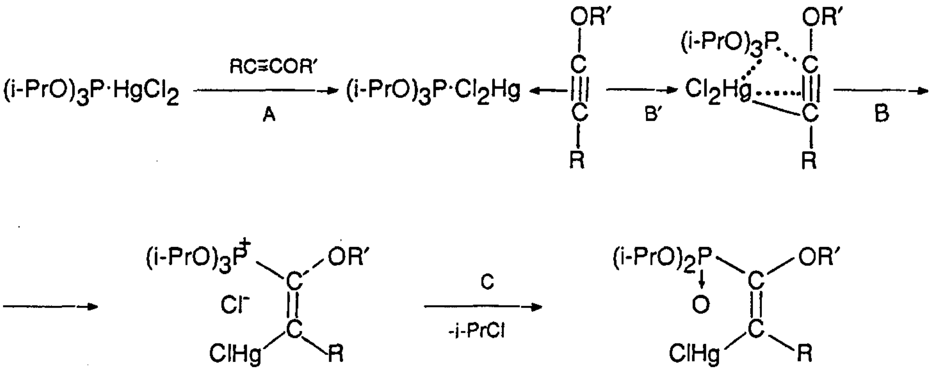
$$(i\text{-PrO})_3P\cdot HgCl_2 + RC{\equiv}COR' \xrightarrow[C_6H_6\ \text{or THF}]{-i\text{-PrOCl}} (i\text{-PrO})_3P(O)C(OR'){=}C(R)HgCl$$

46a - g

46 a: R=H ; R'=C_5H_5 d: R=C_2H_5 ; R'=CH_3
b: R=H ; C_4H_9 e: R=i-Pr ; R'=CH_3
c: R=R'=CH_3 f: R=CH_3 ; R'=C_2H_5

Addition of the acetylene is suggested to occur as in Scheme 9.

Scheme 9 (38)



The 2-mercurated (1-alkoxy-1-alkenyl)phosphonates were also obtained in the reaction between 1-chloro-2-(chloromercurio)-1-alkenyl esters, **47**, and triisopropylphosphite.

$$\mathrm{ClHgC(R){=}C(Cl)OR' + (i\text{-}PrO)_3P \longrightarrow (i\text{-}PrO)_2P(O)C(OR')C{=}(R)HgCl}$$

47 a: R=H ; R′=C_2H_5
b: R=H ; R′=C_4H_9
c: R=R′=CH_3

This reaction is believed to proceed via the initial elimination of mercuric chloride to give the alkyl-1-alkynyl ether and (i-PrO)$_3$P·HgCl$_2$ which then undergoes subsequent conjugate addition to the alkyl-1-alkynyl ether in accordance with Scheme 9.

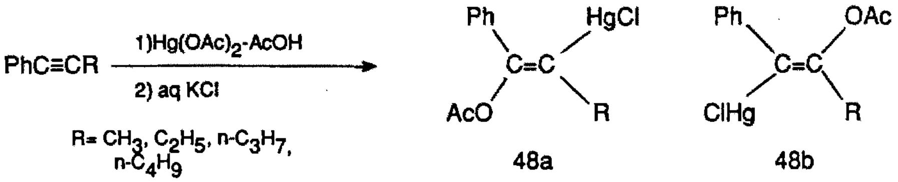
$$\mathrm{ClHgC(R){=}C(Cl)OR' + (i\text{-}PrO)_3P \longrightarrow (i\text{-}PrO)_3P{\cdot}HgCl_2 + \underset{\substack{\downarrow \\ \text{Scheme 9}}}{RC{=}COR'}}$$

In the presence of water, alcohol, or an amine the phosponates, **46a-g** decompose to give chloro(diiospropoxyphosphinyl)mercury, and are readily symmetrized in the presence of triphenylphosphine.

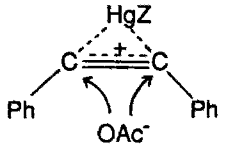
$$2\ (i\text{-}PrO)_2P(O)C(OR')=C(R)HgCl\ +\ Ph_3P \rightarrow Hg[C(R)=C(OR')P(O)(OPr\text{-}i)_2]_2$$

$$\begin{array}{ll} \text{46 h: } R=H\ ;\ R'=C_2H_5 & \qquad\qquad +\ Ph_3P\cdot HgCl_2 \\ \text{i: } R=R'=CH_3 & \end{array}$$

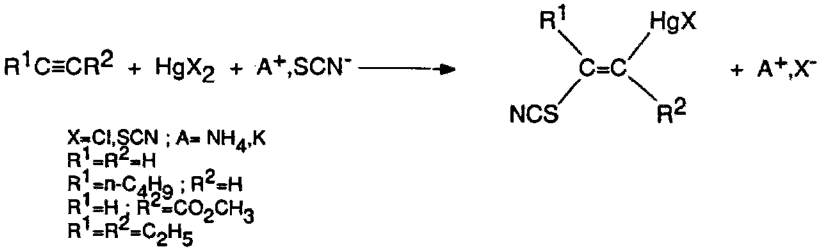
Acetoxymercuration of alkylphenylacetylenes, (PhC=CR, R= CH_3, C_2H_5, n-C_3H_7, n-C_4H_9) in acetic acid at 20 - 60°C proceeds by trans-addition to afford a regioisomeric mixture of two vinylmercury(II) compounds **48a** and **48b** (39) in 44 - 96% yield.



Increasing the chain length of the alkyl group results in increasing attack at the carbon α to the alkyl group and consequently an increase in the amount of **48a** formed. in the case where R = i-C_3H_9, **48a** is the only product, while no acetoxy mercuration occurs when R = t-C_4H_9. The reaction is suggested to involve intermediate formation of a bridged mercurinium ion in which the phenyl and alkyl groups are bent toward the side of attack.

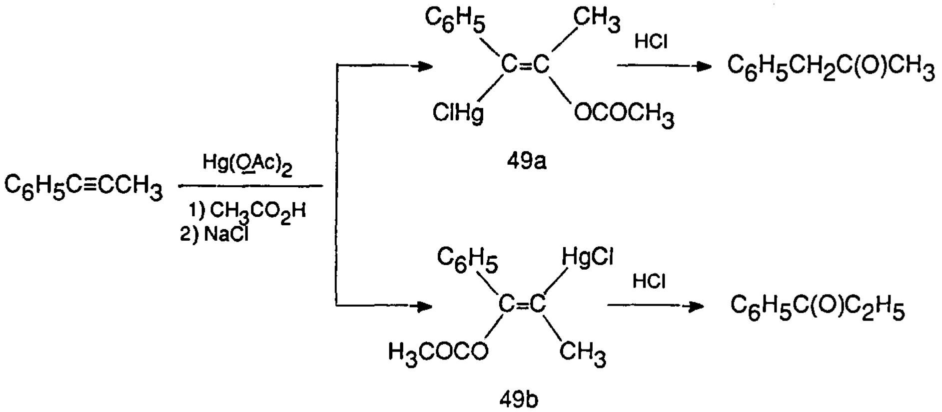


Alkynes react with mercury(II) salts, HgX_2, (X=Cl, SCN) in the presence of SCN^- to give β-isothiocyanatoalkenyl derivatives, $R^1C(HgX)=C(SCN)R^2$. (40)

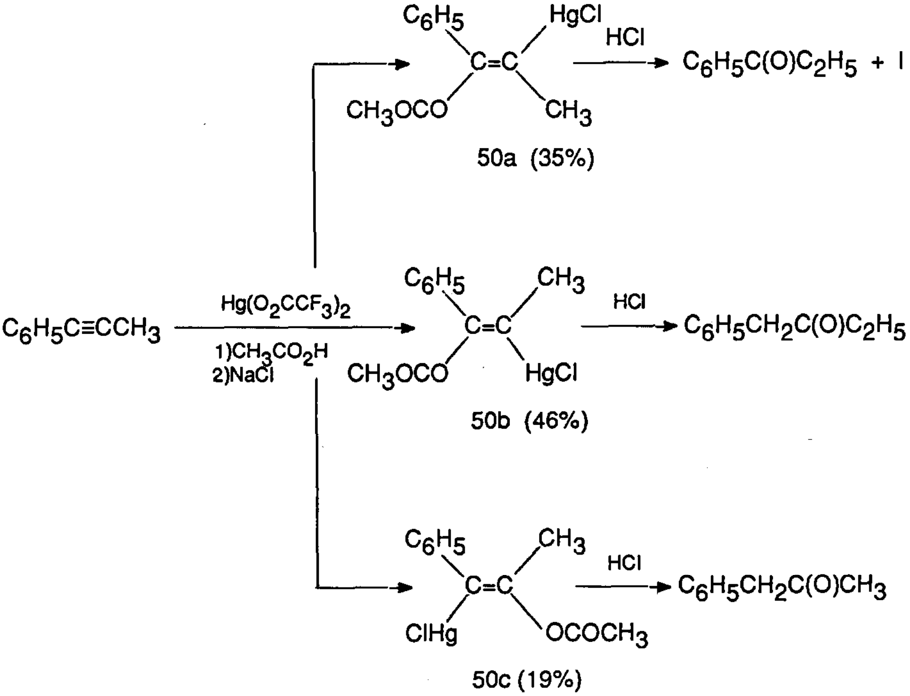


For R^1=R^2= C_2H_5, the SCN group is bound to carbon through nitrogen and through sulfur in the other cases. The reaction follows Markovnikov's rule with anti-addition.

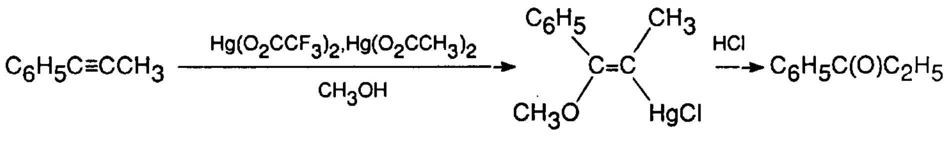
Mercuration of methylphenylacetylene in acetic acid gives two isomers, **49a**, and **49b**, in a ratio of 40 : 60 (41).



With mercury trifluoroacetate the direction of addition changes and the reaction results mainly in the addition of the solvent to the carbon attached to the phenyl group (81%) to afford a mixture of the isomers, **50a**, **50b**, and **50c**.

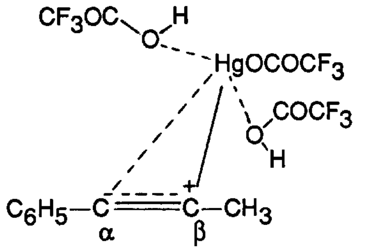


On the other hand, reaction with mercuric acetate and trifluoroacetate in methanol leads to only one product,**51**.

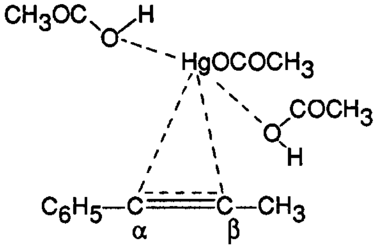


51

These results are explained by the formation of an unsymmetrical intermediate, **52**, which is close in structure to the β-mercurium ion, in the reaction with mercuric trifluoroacetate. The products are then formed by attack at the electron-deficient center by nucleophiles from the inner coordination sphere.



52



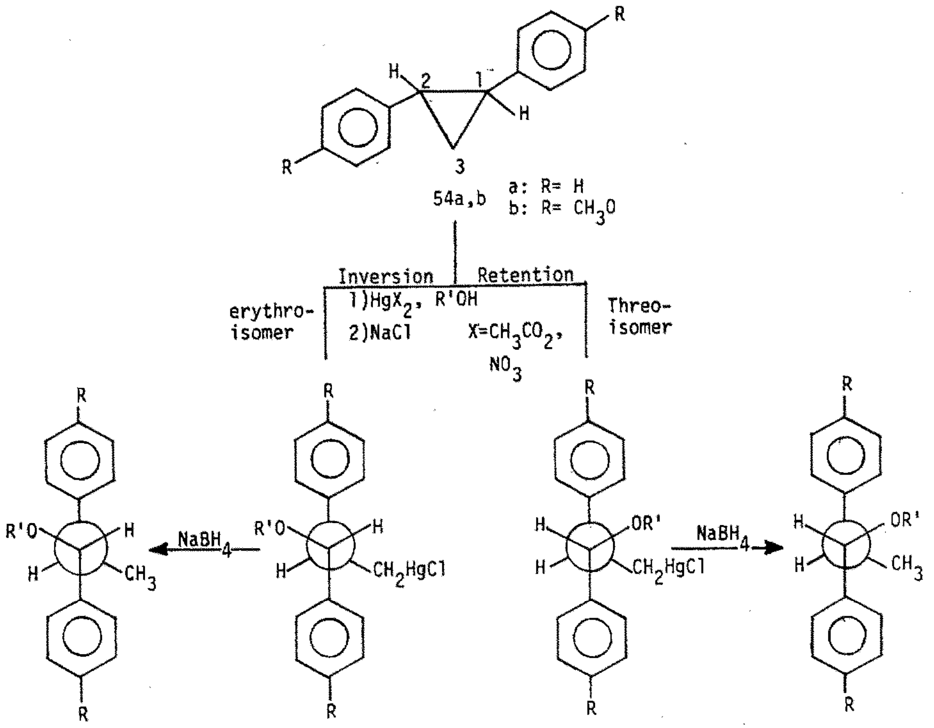
53

With mercuric acetate, however, the decrease in the electron-withdrawing character of the acetate group compared to trifluoroacetate results in the formation of a more symmetric intermediate, **53**, but full equivalence of the bonds is not observed.

C. Cyclopropanes and Cyclopropenes

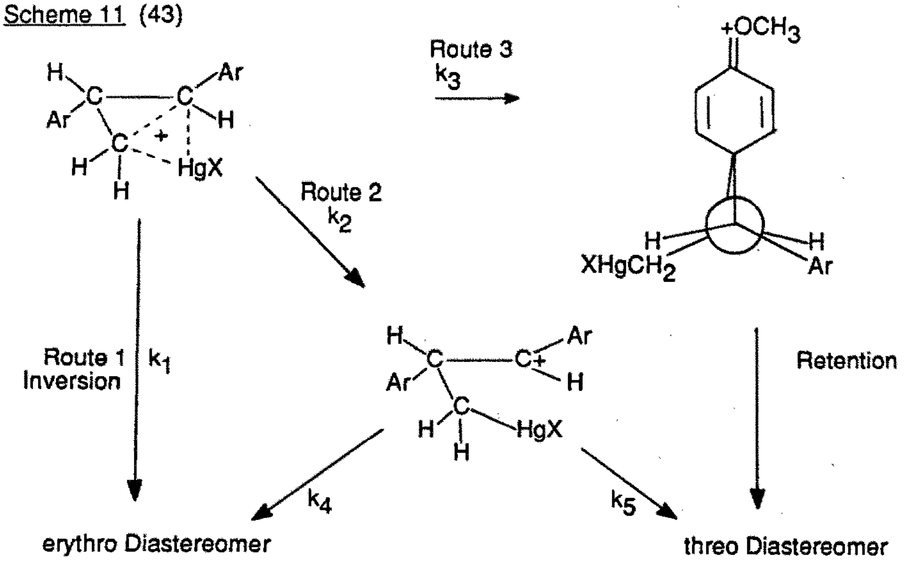
Reaction of the trans-1,2-diphenylcyclopropanes **54a** and **54b** with $Hg(OAc)_2$ or $Hg(NO_3)_2$ gives diastereomeric 1,2-diphenylpropanole derivatives as outlined in Scheme 10. (42)

Scheme 10 (42)



The ratio of erythro and threo diastereomers depends both on solvent properties and on the nature of substituents. Formation of the diastereomers is suggested to occur as outlined in Scheme 11.

Scheme 11 (43)



The "Mercury Method" [B. Grese and J. Meixner, Angew. Chem., Int. Ed. Engl. 18, (1974) 154] has been used to measure the rates of addition of a cyclohexyl radical to alkenes and alkynes (Table 7) (43).

D. Aromatic Compounds

Deacon and O'Conoghue (44) have shown that with short reaction times and a suitable choice of conditions, mercuration of 4-methoxybenzoic acid in trifluoroacetic acid can lead to 2,5-, 2,3,5- or 2,3,4,5-mercuration in the presence of CF_3SO_3H. However, reaction in the absence of CF_3SO_3H affords 3-, 3,5-, or 2,3,5-mercuration. Some ipso-mercuration was observed but was not of major significance. Increasing the CF_3SO_3H : CF_3CO_3H ratio to 1 : 1 (v/v) with a mercuric salt : arene ratio of 6 : 1 lead to 2,3,4,5-tetrabromoanisole following bromodemercuration.

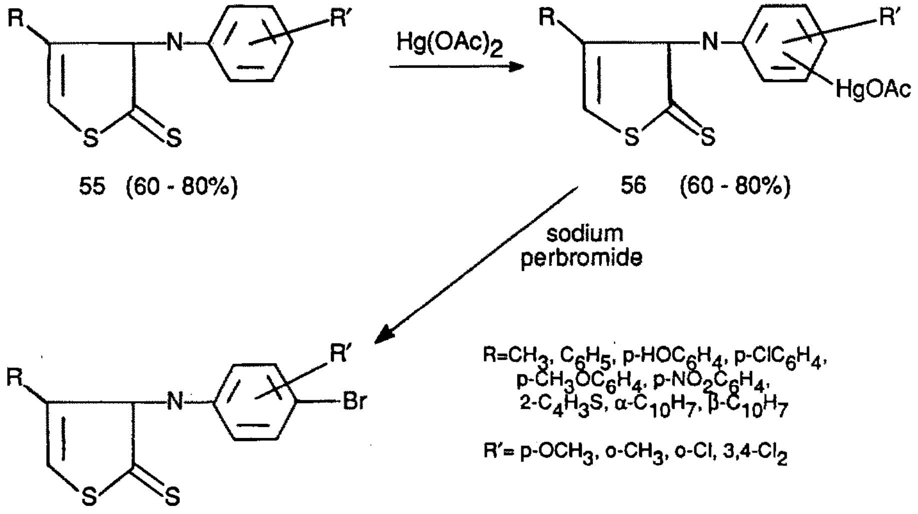
TABLE 7
Rel. addition rates of a cyclohexyl radical (k_{rad}) and of diazomethane (k_{cycl}) with alkenes and alkynes at 298 K. (43)

	k_{rad}	$k_{cycl}{}^a$
$H_2C{=}CHCO_2C_2H_5$	6.7	2520
$H_2C{=}CCH_3CO_2C_2H_5$	5.0	116
$HC{=}CCO_2CH_3$	2.1	1120
$H_2C{=}CHC_6H_5$	1.0	1.0
$HC{=}CC_6H_5$	0.25	0.061
$C_6H_5CH{=}CHCO_2C_2H_5$	0.44	5.9
$C_6H_5C{=}CCO_2C_2H_5$	0.20	8.9
$CH_3CH{=}CHCO_2C_2H_5$	0.067	14

a) Data from [J. Gekttner, R. Huisgenard, R. Sustmann, Tetrahedron lett., 1977, 881]

Spectroscopic studies of the mercuration of a series of aromatic derivatives (45) by mercury(II) trifluoroacetate in trifluoroacetic acid have revealed the presence of a rapidly formed intermediate π-complex. For benzene the complex has a formation constant of K= 8.2 l/mol at 25^{o}C and the rate constant (complex to products) is K_2= 3.5 x 10^{-3} s^{-1}. The free energy of formation of the intermediate is nearly zero [benzene: ΔH_0= -1.7 kcal mol^{-1}, ΔS_0= -1.2 cal $K^{-1}mol^{-1}$; toluene : ΔH_0= -2.1 kcal mol^{-1} , ΔS_0= -3.8 cal K^{-1} mol^{-1}] and only small kinetic isotope effects were found for the complex-forming step [benzene, 1.5 ; toluene, 0.93].

Mahapatra and coworkers (46) have reported the synthesis of several new 3-aryl-4-sybstituted-2-thio-Δ^4-thiazolines,4 , by condensation of ketones with arylammonium dithiocarbamates.



55 (60 - 80%)

56 (60 - 80%)

$R=CH_3, C_6H_5, p\text{-}HOC_6H_4, p\text{-}ClC_6H_4, p\text{-}CH_3OC_6H_4, p\text{-}NO_2C_6H_4, 2\text{-}C_4H_3S, \alpha\text{-}C_{10}H_7, \beta\text{-}C_{10}H_7$

$R' = p\text{-}OCH_3, o\text{-}CH_3, o\text{-}Cl, 3,4\text{-}Cl_2$

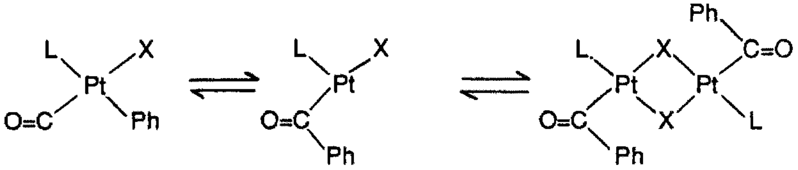
57

The thiazolines, **55**, can be mercurated by one equivalent of mercuric acetate to afford the monoacetoxymercury compounds, **56**, in which the acetoxymercury group substitutes preferrentially para-. Treatment of , **56**, (R= C_6H_5 ; R'= H) with sodium perbromide gives ,**57**,. Both **55** and **56** exhibit fungicidal activity against Pyricularia oryzae (Cav.) and bactericidal activity against Staphyaureus and Esch. coli. Aromatic astatine compounds can be prepared in high yield under mild conditions by reaction of astatine with arylmercuric chlorides in methylene chloride using iodine as a carrier(47)and treatment of metal porphyrin complexes bearing peripherally un-substituted positions with mercuric acetate affords the corresponding mercurated derivatives (48). This observation has been exploited in the preparation of coproporphyrin III tetramethyl ester, harderoporphyrin trimethyl ester and isoharderoporphyrin trimethyl ester.

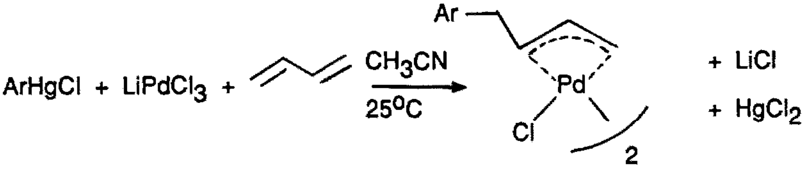
4. THE USE OF ORGANOMERCURY COMPOUNDS IS SYNTHESIS:

A. Synthesis of Organometallic Compounds

The reaction of diphenylmercury with cis-[$PtCl_2(CO)L$], (L= PEt_3, PMe_2Ph, $PMePh_2$, PPh_3, or $P(C_6H_{11})_3$) yields benzoylplatinum complexes, [$Pt_2(\mu\text{-}Cl)_2(COPh)_2L_2$], that are in equilibrium with [PtCl(Ph)(CO)L] in chloroform (49). NMR studies indicate that the carbonyl derivative [PtX(Ph)(CO)L] is formed first and then undergoes carbonyl insertion to give the benzoyl complexes. When L=$P(C_6H_5Me\text{-}o)_3$ $AsMePh_2$ or $AsPh_3$ only the [PtCl(Ph)(CO)L] complexes are formed.



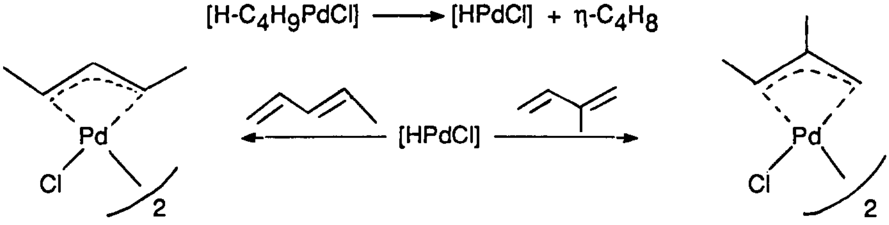
π-Allyl Palladium complexes have been prepared by treating dienes with arylmercuric chloride and lithium chloropalladate at room temperature (50).



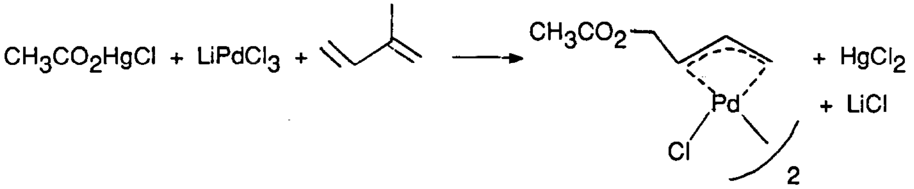
3-(Chloromercuri)benzaldehyde and 2,4-dimethoxyphenyl mercuric chloride also react with $LiPdCl_4$ and isoprene to form the expected adducts, however, the yields were only about 20%. If Alkylmercurials having at least one sp^3 bonded hydrogen β to the mercury are used, the intermediate allylpalladium chloride appears to undergo rapid β-hydride elimination to give the olefin and hydridopalladium chloride which reacts with the diene to form the π-allylic palladium chloride dimers.

$$\eta\text{-}C_4H_9HgCl + LiPdCl_3 \longrightarrow [\eta\text{-}C_4H_9PdCl] + HCl + LiCl$$

$$[H\text{-}C_4H_9PdCl] \longrightarrow [HPdCl] + \eta\text{-}C_4H_8$$

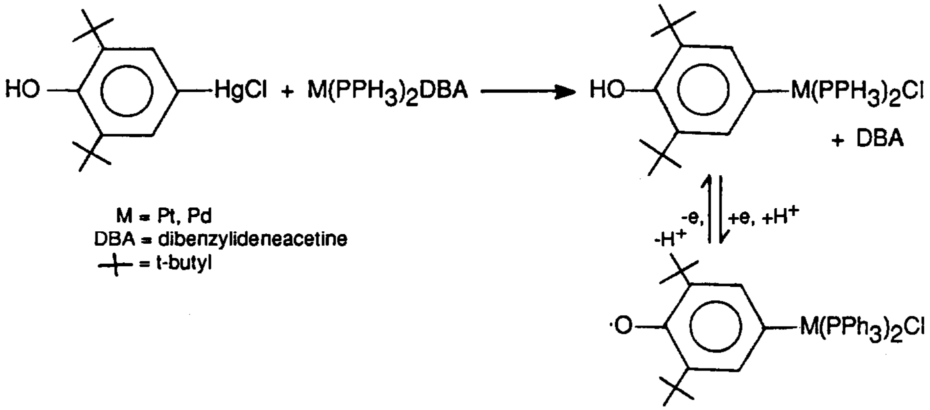


Carbomethoxymercuric chloride affords carbomethoxy- substituted π-allylic complexes.



The complex obtained depends to a large measure on the nature of the diene. Dienes that are not conjugated with ester groups react exclusively to place the aryl or carbomethoxy group on the terminal carbon of the least substituted double bond of the diene. Hence, the order of reactivity of the diene double bonds toward phenyl palladium chloride is $CH_2{=}CHR > CH_2{=}CH_2 > RCH{=}CHR$.

Interaction of Pd^0 and Pt^0 complexes with 4-hydroxy-3,5-di-t-butylphenylmercuric chloride gives the corresponding C-bonded transition metal derivatives (51) that upon oxidation give highly stable organometallic radicals.



M = Pt, Pd
DBA = dibenzylideneacetine
—┼— = t-butyl

Krause and Morrison (52) have prepared $[(\eta^5\text{-}C_5H_4C(CF_3)_2CH(CN)_2]Fe(\eta\text{-}C_5H_5)$ by the reaction of the olefin $(CN)_2C{=}C(CF_3)_2$ with chloromercuriferrocene followed by hydrolysis during the workup.

The formation of CF_3SnBr_3 and $(CF_3)_2SnBr_2$ from the reaction between $(CF_3)_2Hg$ and $SnBR_4$ has been studied at three temperatures (54). The trifluoromethyl tin bromides are easily formed, however, the decomposition of more fully substituted compounds, (e.g., $(CF_3)_3SnBr$), is almost instantaneous and therefore severely limits the temperature range that can be utilized in the reaction. The methylated compounds $CF_3Sn(CH_3)_3$ and $(CF_3)_2Sn(CH_3)_2$ are also formed in high yield.

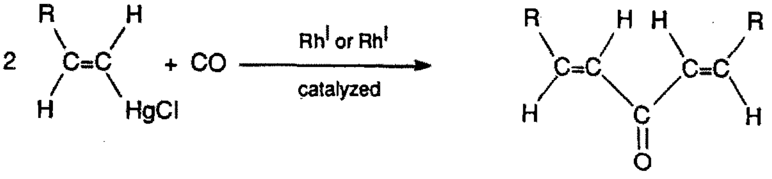
Bis(trifluoromethyl)cadmium glyme, (glyme= $CH_3OCH_2CH_2OCH_3$), has been prepared from the reaction of an excess of $(CF_3)_2Hg$ with $(CH_3)_2Cd$ in dry glyme, (54), and appears to be one of the best reagents currently available for preparing perfluoromethyl organometallic derivatives.

Bis(pyridine)bis(trifluoromethyl)zinc has been similarly prepared by reacting $(CH_3)_2Zn$ and $(CF_3)_2Hg$ in a 1:2 ratio in pyridine (55). The presence of pyridine is essential because in the absence of pridine no exchange occurs between $Hg(CF_3)_2$ and $Zn(CH_3)_2$ in CH_2Cl_2 even up to $100^{o}C$.

$$(CH_3)_2Zn + 2\,(CF_3)_2Hg \longrightarrow (CF_3)_2Zn\cdot 2\text{pyridine}$$

B. Applications in Organic Synthesis

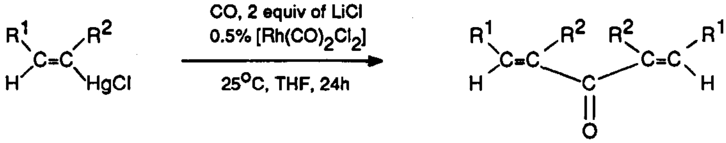
Symmetrical divinyl ketones have been synthesized by rhodium(I) and rhodium(II) catalyzed carbonylation of vinyl mercurials (Table 8) (56).



The reaction is highly stereospecific, proceeds with complete retention of configuration and is suggested to proceed as outlined below.

TABLE 8

Synthesis of Symmetrical Divinyl Ketones (56)



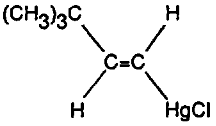
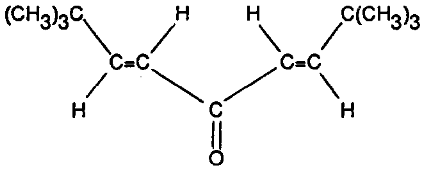
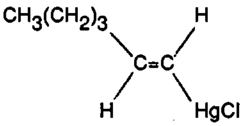
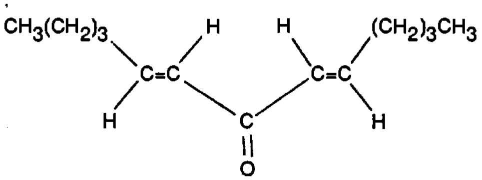
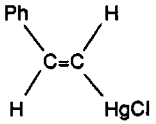
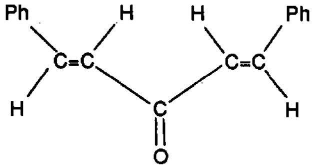
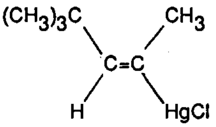
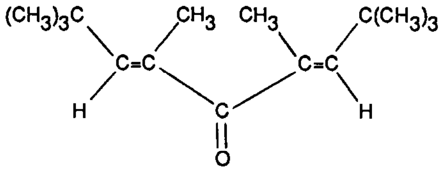
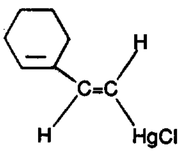
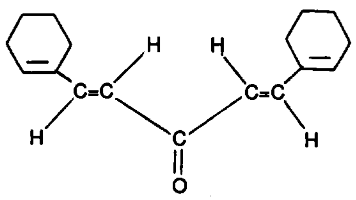
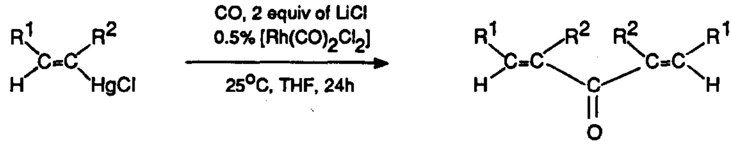
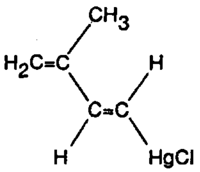
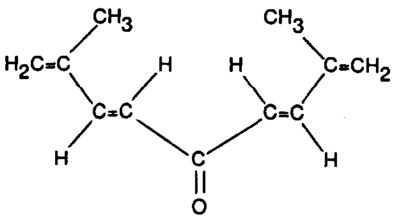
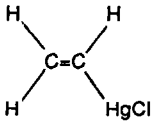
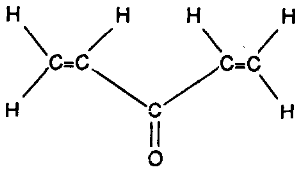
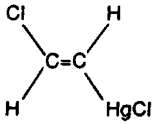
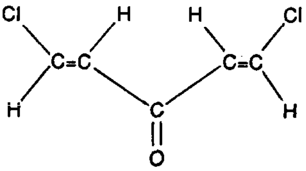
vinylmercurial	divinyl ketone	(%)Yield[a]
		96(78)
		94(78)
		64 (47)[b]
		96(78)
		100[c]

TABLE 8(Cont.)

Synthesis of Symmetrical Divinyl Ketones (56)



vinylmercurial	divinyl ketone	(%)Yield[a]
		41[c,d]
		89[e]
		d

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[a] Crude isolated yield (purified yield). [b] Reaction time of 4 days. [c] Attempted pruification resulted in decomposition. [d] Purity of organomercurial is questionable or unknown. [e] GC yield.

Proposed reaction scheme

$$\mathrm{RhCl + RCH{=}CHHgCl \rightarrow RCH{=}CHRhCl(HgCl)}$$

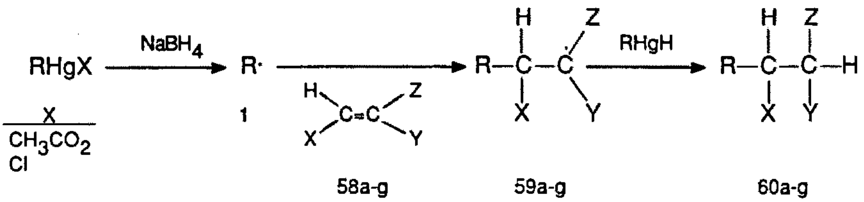
$$\mathrm{RCH{=}CHRCl(HCl) + Co \rightarrow RCH{=}CHC(O)RhCl(HgCl)}$$

$$\mathrm{RCH{=}CHC(O)RhCl(HgCl) + RCH{=}CHHgCl \rightarrow RCH{=}CHC(O)Rh(CH{=}CHR)HgCl + HgCl_2}$$

$$\mathrm{RCH{=}CHC(O)Rh(CH{=}CHR)(HgCl) \rightarrow RCH{=}CHC(O)CH{=}CHR + RCl + Hg}$$

Good to excellent yields of diarylketones also are obtained from arylmercurials.

Giese, Kretzschmar and Meixner (61) have used the "mercury method" to study the rates of addition of n-$C_6H_{13}\cdot$, c-$C_6H_{11}\cdot$, and t-$C_4H_9\cdot$ radicals to alkenes **58a-g**



58a-g 59a-g 60a-g

X
CH_3CO_2
Cl

R
n-C_6H_{13}
c-C_6H_{11}
t-C_4H_9

	X	Y	Z
a	H	H	CO_2CH_3
b	H	H	CN
c	$CO_2C_2H_5$	H	$CO_2C_2H_5$
d	O=C—O—C=O		CH_3
e	H	Cl	CN
f	CN	H	CN
g	O=C—O—C=O		H

Table 9

Relative rate constants(k_{rel}) for the addition of alkyl-radicals 1a-c to the alkenes 58a-g at 295K in methylene chloride (av. error ±10%) (57)

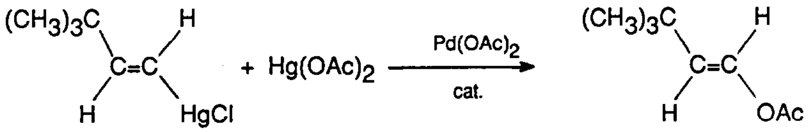
Alkene	n-C_6H_{13}·	$k_{rel}{}^a$ c-C_6H_{11}·	t-C_4H_9·
a	=1	=1	=1
b	2.9	3.6	5.2
c	5.0	4.5	3.0
d	7.6	21	33
e	19	30	45
f	20	47	90
g	30	110	234

a) The values show the relative rate constants for the vinyl carbon atom attacked. For the anlanes 58a, 58b, 58d and 58e the least substituted carbon atom is preferentially attacked.

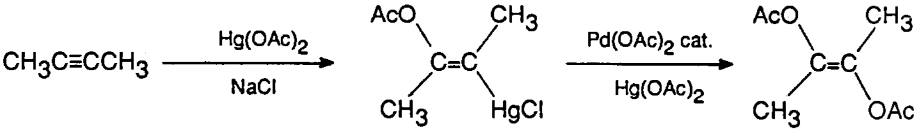
The relative rate constants (Table 9) suggest that alkyl radicals are nucleophiles and that their selectivity increases in the order primary < secondary < tertiary.

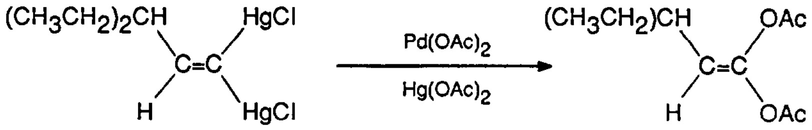
It is also shown, that in the absence of significant steric effects, the reactivities and selectivities can be explained by simple frontier molecular orbital theory.

The room temperature reaction of vinyl mercurials and mercury carboxylates, in the presence of catalytic amounts of palladium acetate, provides a novel stereospecific route to a variety of enol carboxylates (58). The reaction proceeds smoothly and affords high yields of the corresponding enol acetate in greater that 99% stereospecificity (Table 10).



Ene diacetates (Table 11) also are readily prepared from the corresponding β-acetoxyvinylmercurials and dimercurials.





Enol esters of other carboxylic acids may be prepared by using the appropriate mercuric carboxylate, [$Hg(O_2CCH_2CH_2CH_3)_2$, $Hg(O_2CC_6H_5)_2$], however, large amounts of $Pd(OAc)_2$ are required to obtain high yields of the products. Mixed ene-diesters are prepared by mercuration-esterification of internal acetylenes and with one exception, PhC≡CPh, appear to be formed with complete retention of configuration.The mechanism for the reaction is not known however two possible mechanistic schemes are proposed.

TABLE 10

Synthesis of Enol Esters (58)

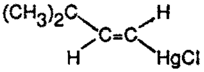
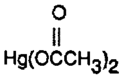
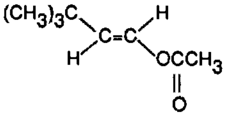
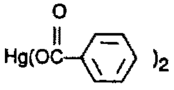
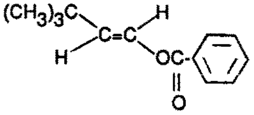
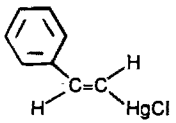
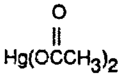
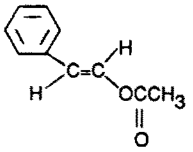
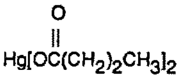
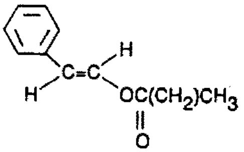
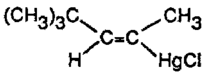
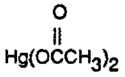
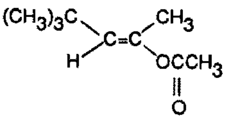
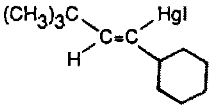
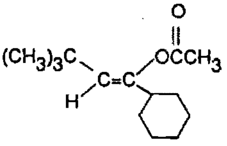
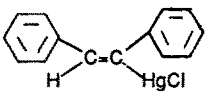
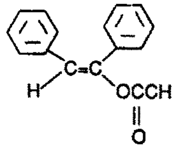
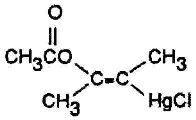
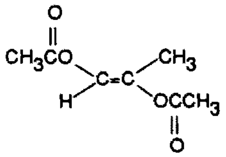
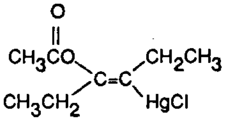
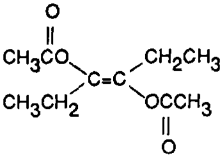
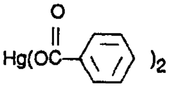
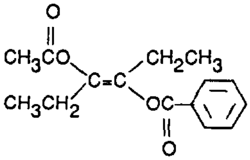
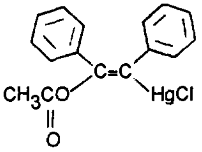
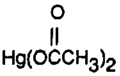
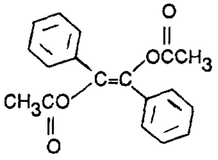
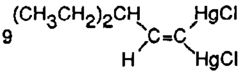
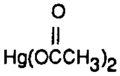
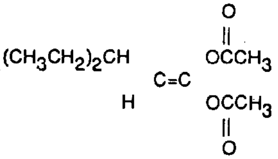
entry	vinylmercurial	mercuric carboxylate	enol ester	%Pd(OAc)$_2$ catalyst	time, h	%yield
1		 $\mathrm{Hg}(\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3})_2$		0.5 1 5	48 12 24 48 24	77 70 75 77(42) 77
				5 16 22	48 48 48	45[b] (50) 71[c]
2		 $\mathrm{Hg}(\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3})_2$		1	48	100(72)
		 $\mathrm{Hg}[\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}(\mathrm{CH_2})_2\mathrm{CH_3}]_2$		4 13	48 48	50(47) 72
3		 $\mathrm{Hg}(\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3})_2$		1 5	48 24	77(58) 97
4				15	48	(68)
5				1	48	(87)
6				1 5 10	96 48 48	36 60(35) 60

TABLE 10 (Cont.)

Synthesis of Enol Esters (58)

entry	vinylmercurial	mercuric carboxylate	enol ester	%Pd(OAc)$_2$ catalyst	time, h	%yield
7				10 18	48 48	80 86
				17	48	(31)
8		 $Hg(\overset{O}{\overset{\parallel}{OC}}CH_3)_2$		100	64 (70°C)	26
9		 $Hg(\overset{O}{\overset{\parallel}{OC}}CH_3)_2$		6	48	(89)

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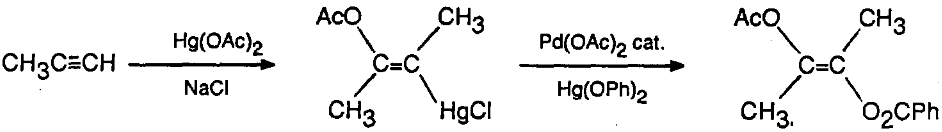
[a] Yield determined by gas-liquid phase chromatography (GLC) using an internal standard; isolated yield in parentheses. [b] ~4% yield of trans-1-acetoxy-3,3-dimethyl-1-butene. [c] ~15 yield of trans-1-acetoxy-3,3-dimethyl-1-butene.



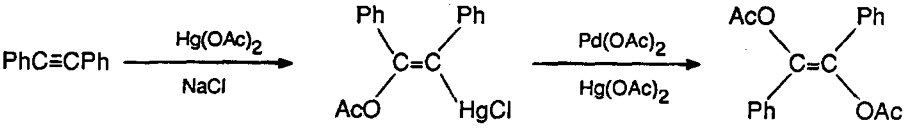
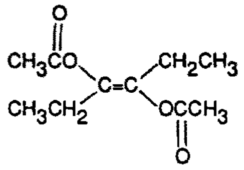
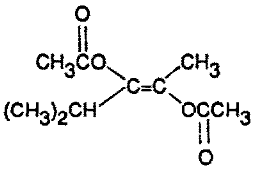
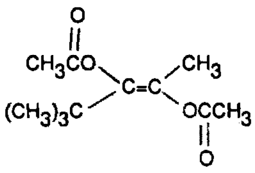
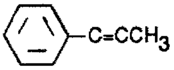
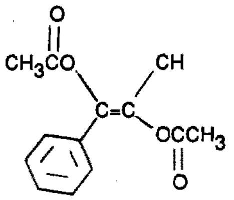
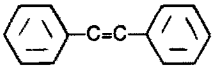
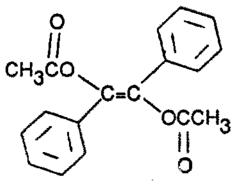


TABLE 11

Direct Synthesis of Ene Diacetates (58)

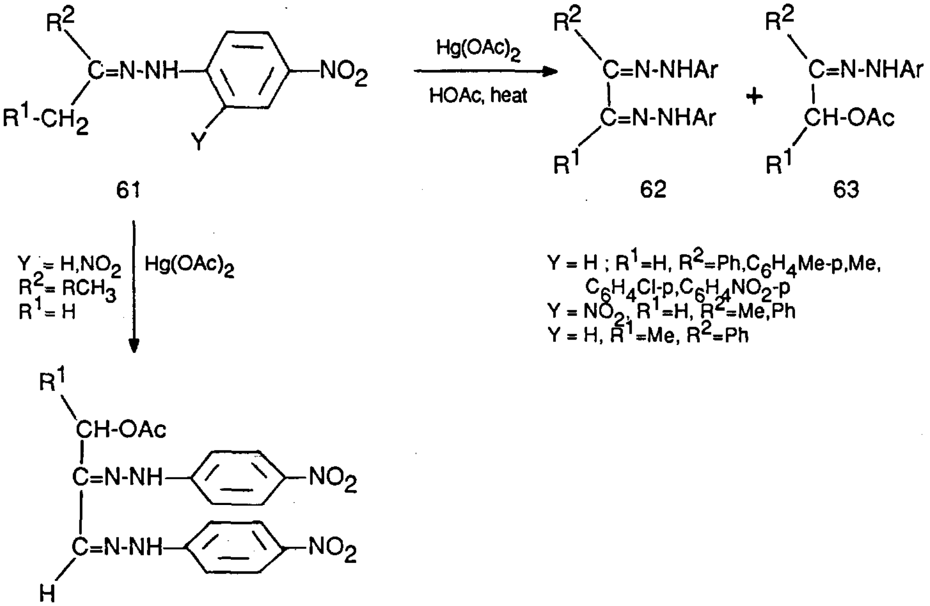
entry	acetylene	product	mercuration	%Pd(OAc)$_2$	%yield
1	$CH_3CH_2C{\equiv}CCH_2CH_3$		20h, 0°C 3h,25°C	12	80-86
2	$(CH_3)_2CHC{\equiv}CCH_3$		24h,25°C	15	40-45
3	$(CH_3)_3CCH{\equiv}CCH_3$		17h,25°C	15	7
4			70h,25°C	16 18	(85) 69
5			2-3h,95°C	10-17	(5-8)

---

[a] Isolated yield; GLC yield in parentheses.

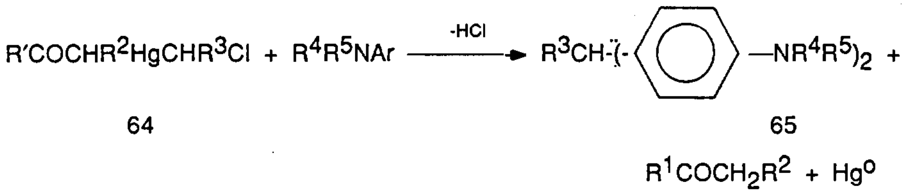
A new method has been described for the facile alkylation of uracilnucleotides (59). Treatment of the unprotected nucleotide with mercuric acetate followed by the addition of styrene or a substituted styrene and lithium tetrachloropalladate gives C-5-trans-styryl derivatives. The coupling reactions proceed in moderate to good yield and can be run in protic solvents. They are not adversely affected by the presence of the sugar hydroxyls or a phosphate group and are compatible with nitro, amino and azido substitution of the styrene phenyl ring. The reaction has been applied to the C-5-alkylation of pyrimidine nucleotides and nucleosides using 2′-deoxyuridine-5′-phospohate.

Reaction of p-nitrophenyl hydrazones of acetophenones and aliphatic ketones, **61**, with one equivalent of $Hg(OAc)_2$ in hot acetic acid gave 1,2-bis-hydrazones, **62**, as the main product, however, in some cases α-acetoxy derivatives, **63**, also were formed (60).Electron-donating substituents on the methine phenyl ring favor hydrazine transfer while electron-withdrawing groups favor α-acetoxylation. Similar reactions involving hydrozino-transfers to methyl groups were observed with the 4-nitro- phenylhydrazines of acetone, propiophenone, methylethylketone, methylbenzyl- ketone as well as with 2,4-dinitrophenylhydrazones of acetone and acetophenone. The proposed mechanism is shown in scheme 10.



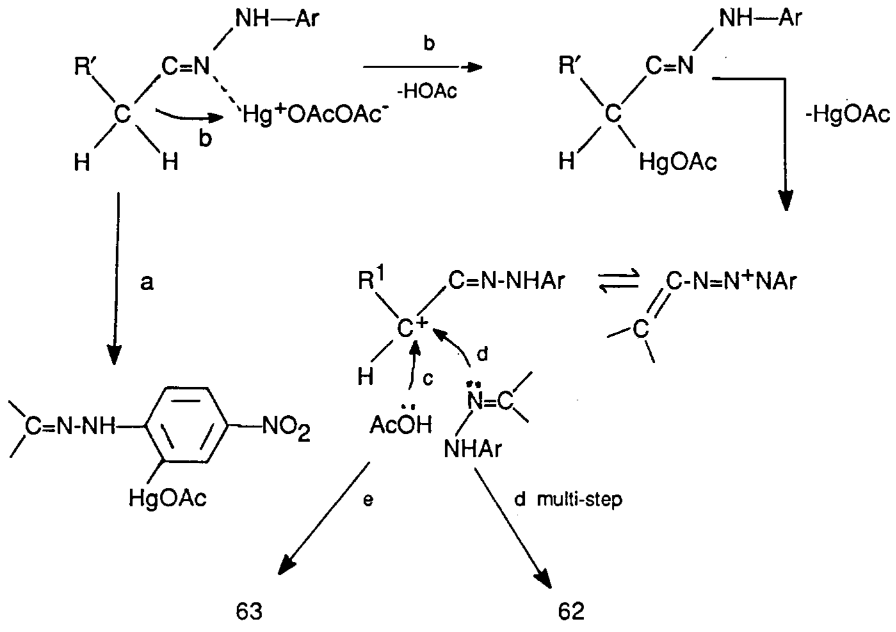
Y = H ; R^1=H, R^2=Ph,C_6H_4Me-p,Me, C_6H_4Cl-p,$C_6H_4NO_2$-p
Y = NO_2, R^1=H, R^2=Me,Ph
Y = H, R^1=Me, R^2=Ph

α,α-Diarylalkane derivatives have been prepared from monochloroalkylmercury(II) compounds via a non-carbenoid alkylidene transfer reaction which takes place selectively on the aromatic ring (61). Reaction of the monochloroalkylmercurials **64** with aromatic amines in a ratio of 1:4 gave bis(4-aminophenyl)alkanes, **65**.



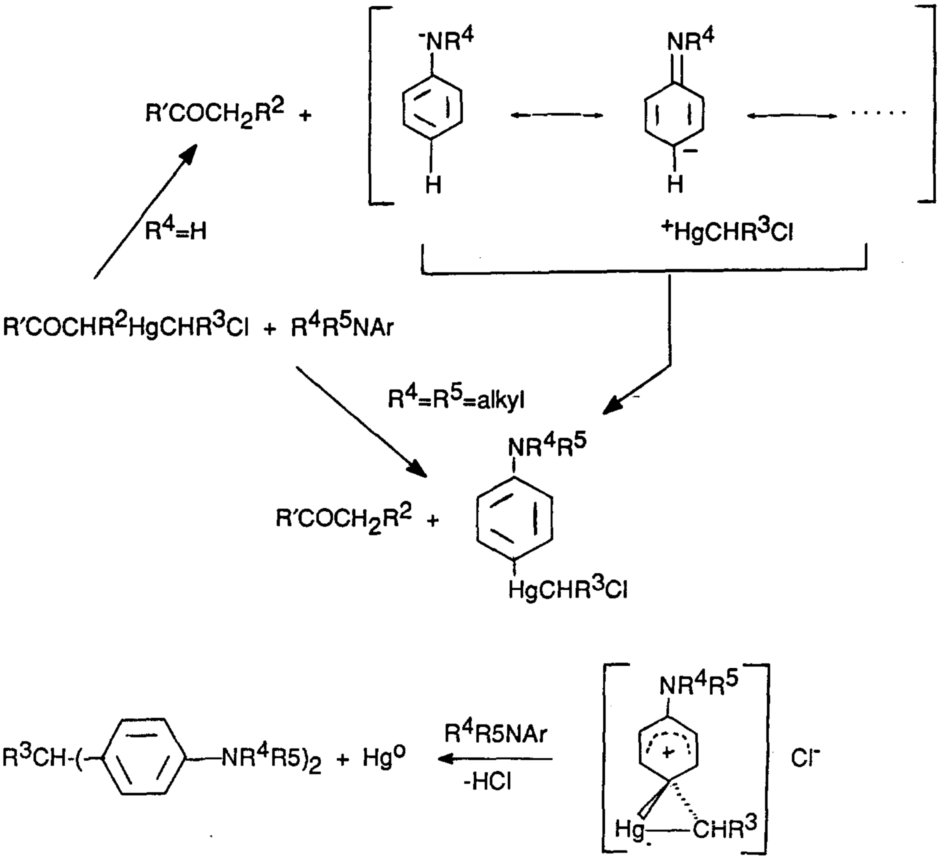
Scheme 10

Proposed mechanism: (60)

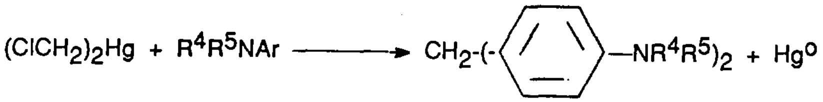


Bis(chloromethylmercury reacts with amines to give diamines, **66**, and elemental

Scheme 11 (61)



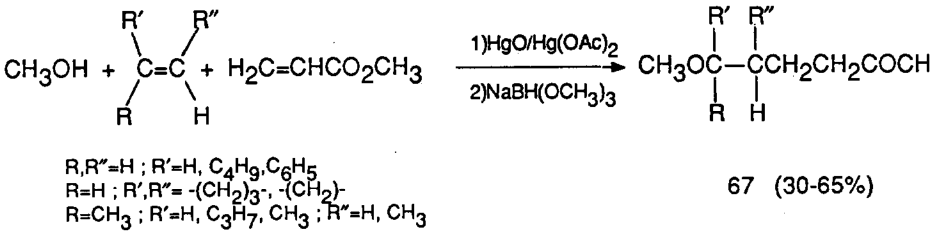
mercury , however, N-methylation products of the amines and **66** were also isolated. The course of the reaction is explained according to Scheme 11.



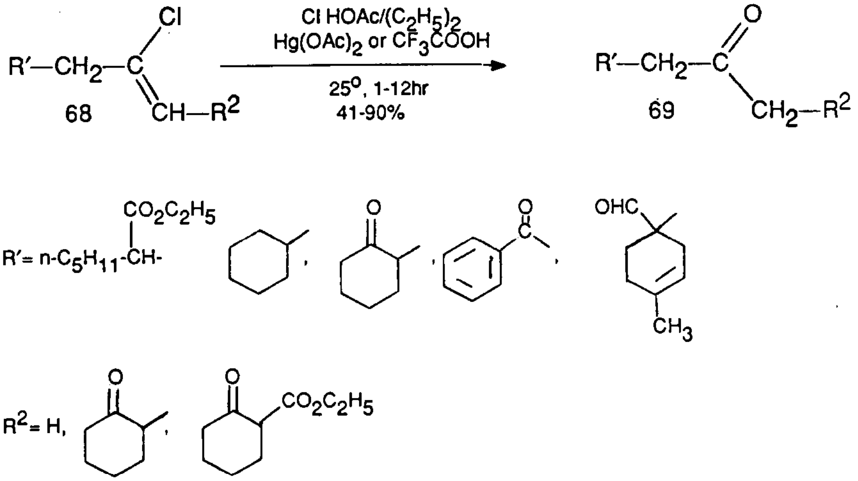
66

\+ products of N-methylation

Methoxy mercuration/demercuration reactions of alkenes in the presence of acrylic ester gave **67** in a carbon-carbon bond formation reaction in yields of 30-60% (62).



67 (30-65%)



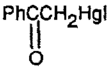
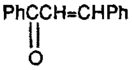
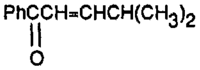
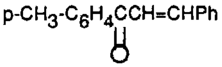
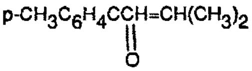
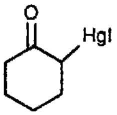
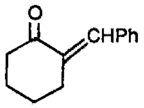
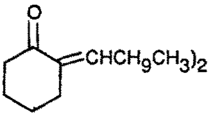
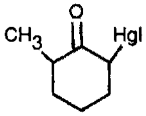
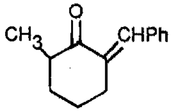
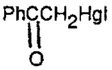
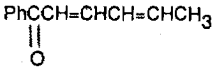
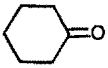
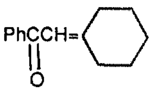
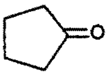
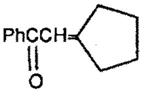
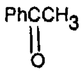
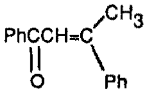
Vinylchlorides, **68**, may be readily transformed to ketones, **69**, with Hg(OAc)$_2$ in trifluoroacetic acid or in acetic acid/boron trifluoride etherate (63). The reaction proceeds under mild conditions and affords moderate to excellent yields of the ketones.

The reaction of α-iodomercuric ketones with nickel carbonyl in the presence of aldehydes or ketones afforded α,β-unsaturated ketones in good yield (64)(Table 12).

$$\mathrm{RC(O)CH_2HgI + R'CHO \xrightarrow[\text{DMF}]{\text{Ni(CO)}_4} RC(O)CH{=}CHR'}$$

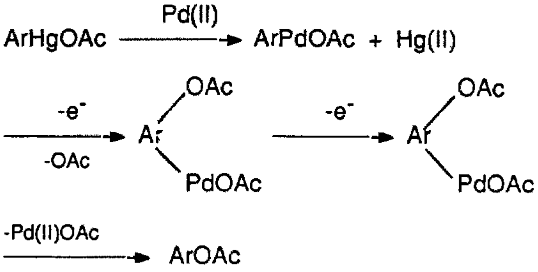
Acetylacetates may be prepared by anodic oxidation of arylmercury(II) compounds in the presence of palladium(II) acetate in HOAc/NaOAc (65). The distribution of the aryl acetate isomers obtained is essentially the same as that of the starting arylmercury(II)

TABLE 12
The Reaction of α-Iodomercuric Ketones with $Ni(CO)_4$ in the Presence of Aldehydes or Ketones. (64)

run	RHgI	Aldehyde or Ketone	Product	Yield(%)*
1	 $\mathrm{Ph}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH_2HgI}$	PhCHO	 $\mathrm{Ph}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH{=}CHPh}$	80
2		$(CH_3)_2CHCHO$	 $\mathrm{Ph}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH{=}CHCH(CH_3)_2}$	92
3	$p\text{-}CH_3\text{-}C_6H_4CCH_2HgI$	PhCHO	 $p\text{-}\mathrm{CH_3\text{-}C_6H_4}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH{=}CHPh}$	73
4		$(CH_3)_2CHCHO$	 $p\text{-}\mathrm{CH_3C_6H_4C}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{H{=}CH(CH_3)_2}$	80
5		PhCHO		80
6		$(CH_3)_2CHCHO$		85
7		PhCHO		75
8	 $\mathrm{Ph}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH_2HgI}$	$CH_3CH{=}CHCHO$	 $\mathrm{Ph}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH{=}CHCH{=}CHCH_3}$	50
9				20(90)**
10				30**
11		 $\mathrm{Ph}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH_3}$		40**

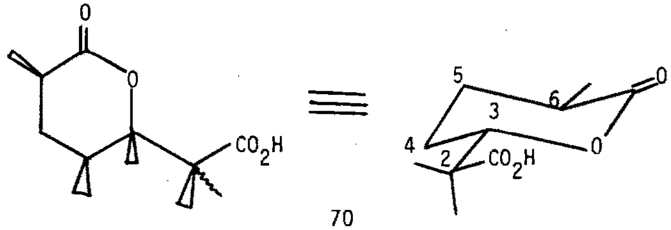
* Based on organomercuric halide used. ** Conducted at 75°C

isomers. The reaction requires the presence of both the palladium(II) acetate and an oxidizing agent and is suggested to proceed as follows:

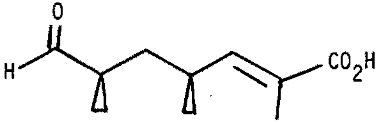


Scheme 12 (66)

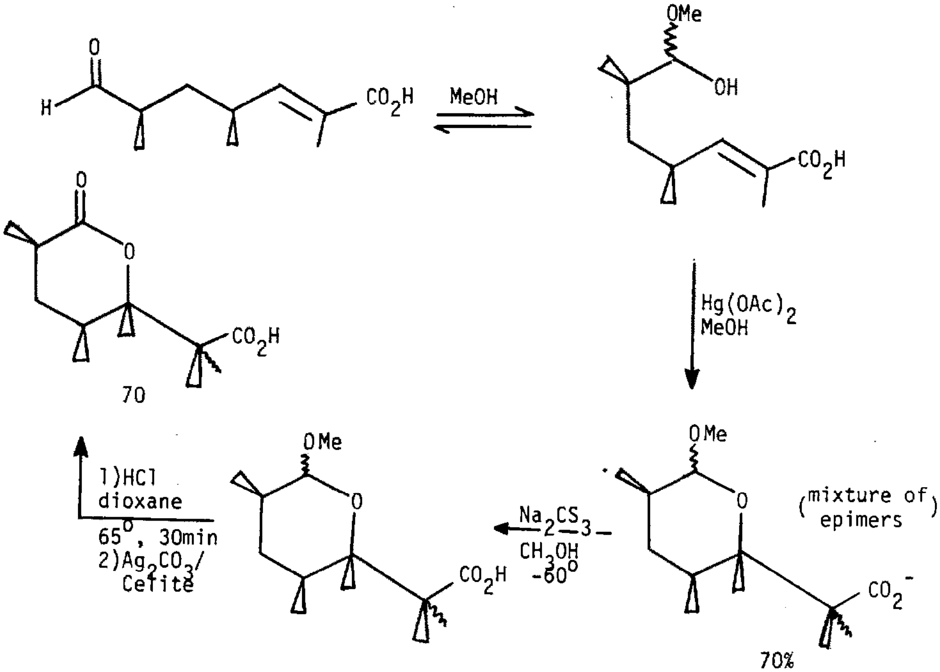
Synthesis of Racemic Prelog-Djerassi
Lactone



70



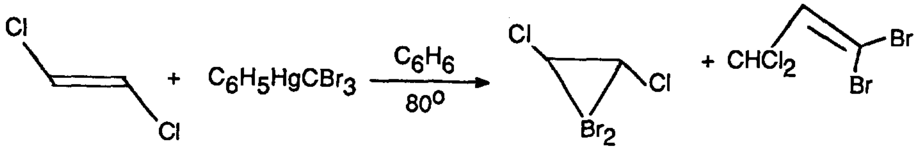
71



The total synthesis of racemic Prelog-Djerassi lastone, **70**, has been achieved (66) using the mercuric ion induced cyclization of aldehyde acid , **71**, to control the stereochemistry at C-2 and C-3 as presented in Scheme 12.

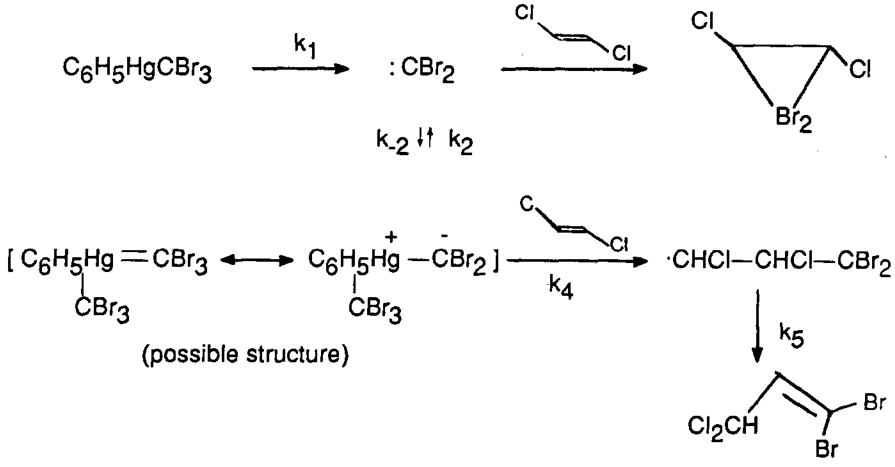
C. α-Halomethylmercury Compounds

Lambert, Mueller and Gaspar (67) have shown that trans-dichloroethene reacts with phenyl (tribromomethyl)mercury to give the stereospecifically formed cyclopropane and propene in approximately equivalent amounts. A similar result was obtained with the cis- and trans-dibromoethenes. The two products are formed

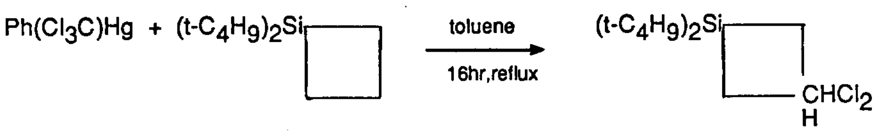


from two distinct intermediates. The cyclopropane is formed from the free carbene and the propene from a metal-carbene complex formed by the direct reaction of merecury(II) with dibromocarbene (Scheme 13).

Scheme 13 (67)



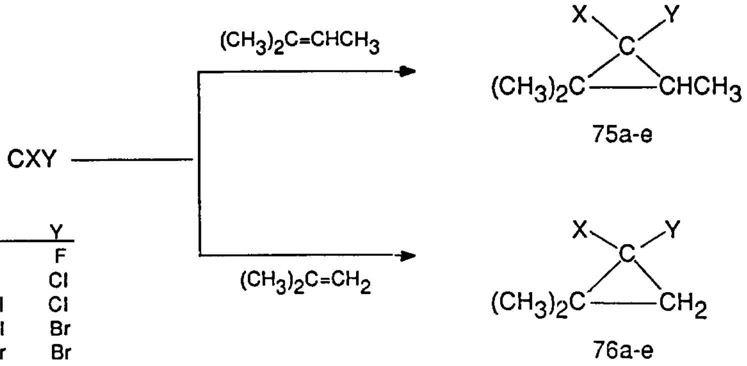
Trichloromethylphenylmercury(II) reacts with 1,1-Di-t-butyl-1-silacyclobutane, **72**, to give 1,1-Di-t-butyl-3-dichloromethyl-1-silacyclobutane, **73**, in 21% yield (68).



72

73 (21%)

Giese,Lee and Meister (69) have studied the relative selectivities of the dihalocarbenes **74a-e** CXY (XY= FF ; FCl ; ClCl ; ClBr ; BrBr) in a competitive reaction between 2-methyl-2-butene and 2-methylpropene to give the cyclopropanes **75a-e** and **76a-e**.



75a-e

76a-e

		X	Y
	a	F	F
	b	F	Cl
74	c	Cl	Cl
	d	Cl	Br
	e	Br	Br

The selectivity of the carbenes, prepared from the corresponding phenyl(trihalomethyl)mercury compound, 77, increased in the order

$$CBr < CClBr < CCl_2 < CFCl < CF_2$$

at 293K . At 393K the order is reversed:

$$CF_2 < CFCl < CCl_2 < CClBr < CBr_2$$

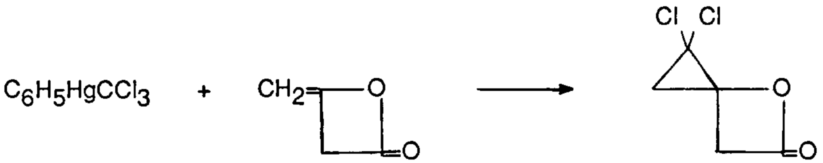
and at 360K (isoselective temperature) the carbenes react with equal selectivity.

$$C_6H_5HgCXYZ \xrightarrow{\Delta T} CXY + C_6H_5HgZ$$

77

	X	Y	Z
a	F	F	F
b	F	Cl	Cl
c	Cl	Cl	Br
d	Cl	Br	Br
e	Br	Br	Br

Refluxing Diketene with phenyl(trichloromethyl)mercury gave 1,1-dichloro-5-oxo-4-oxaspiro[2.3]hexane, **78**, in 75% yield.(70).

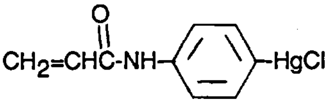


78

The dichlorocarbene precursor Hg(CCl_3)Ph reacts with $Co_2(CO)_8$ at 60°C in hexane to give [Co_3(CCl)$(CO)_9$] in 49% yield (71). Reaction at 30°C, where appreciable thermal decomposition of Hg(CCl)Ph to HgPhCl and CCl_2 occurs , gave a similar yield of $Co(CO)_8$. Two possible mechanistic pathways for the reaction are outlined in Scheme 14. Reaction of OsHCl(Co)$(PPh_3)_3$ and $Hg(CCL_3)_2$ gave the orange crystalline compound $OsCl_2(CCl_2)$(Co)(PPh_3) in >80% yield (72).

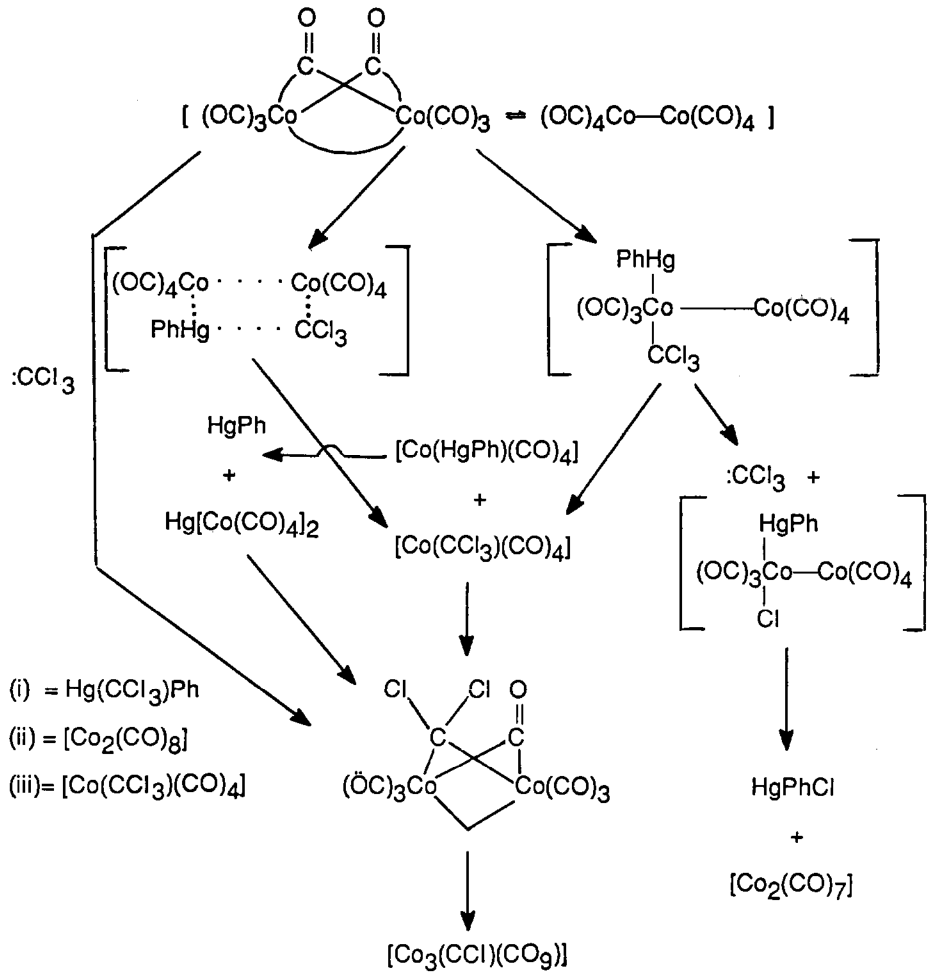
5. ORGANOFUNCTIONAL ORGANOMERCURY COMPOUNDS:

Reeve and Johnson (73) have synthesized p-acrylamidophenylmercury chloride , **79**, by direct coupling of acrylyl chloride to p-aminophenylmercuric acetate in dimethyl formamide.

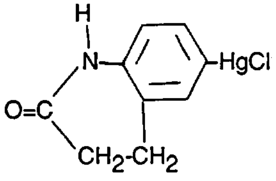


79

Scheme 14 (71)



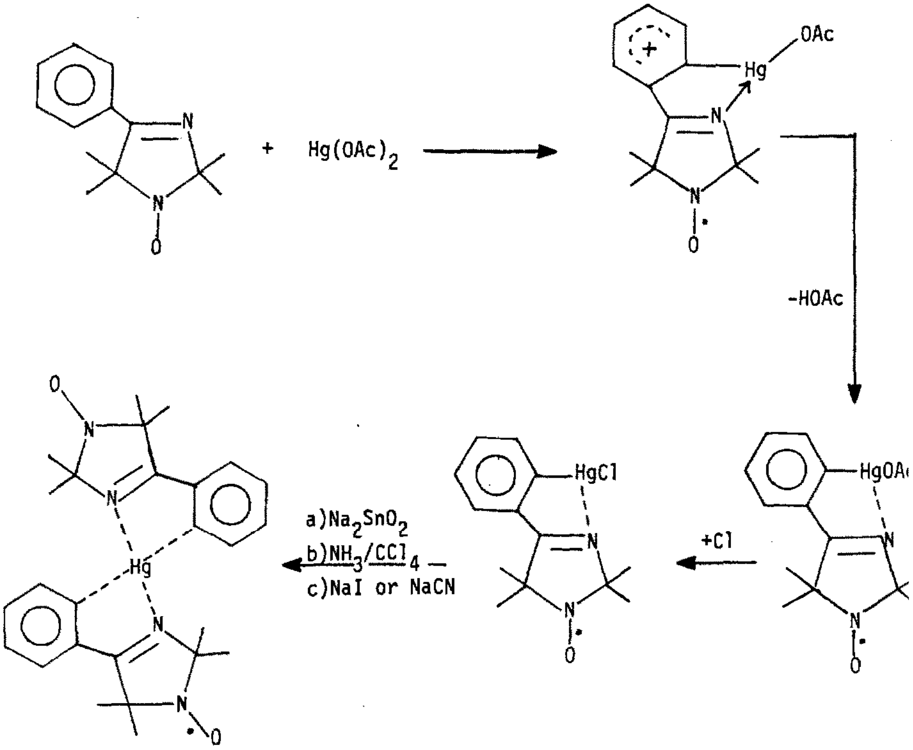
The mass spectrum of **79** exhibits fragment ions at m/e 369 and 355 that are believed to arise from compound **80** which is a secondary product of the synthesis.



80

A. B. Shapior and coworkers (74) have prepared an organomercury imidazoline nitroxylbiradical, **81**, as outlined in Scheme 15. The ESR spectrum of , **81**, shows a quintet (a_N is 14.2 gauss in benzene, J>>a). It is suggested that independence of the line intensities with solvent polarity and temperature, in the range -20 to +80°C, indicates that the spin-spin exchange in the biradical takes place through a system of C-Hg bonds. The x-ray structure of the radical is presented in Figure 3 .

Scheme 14 (71)



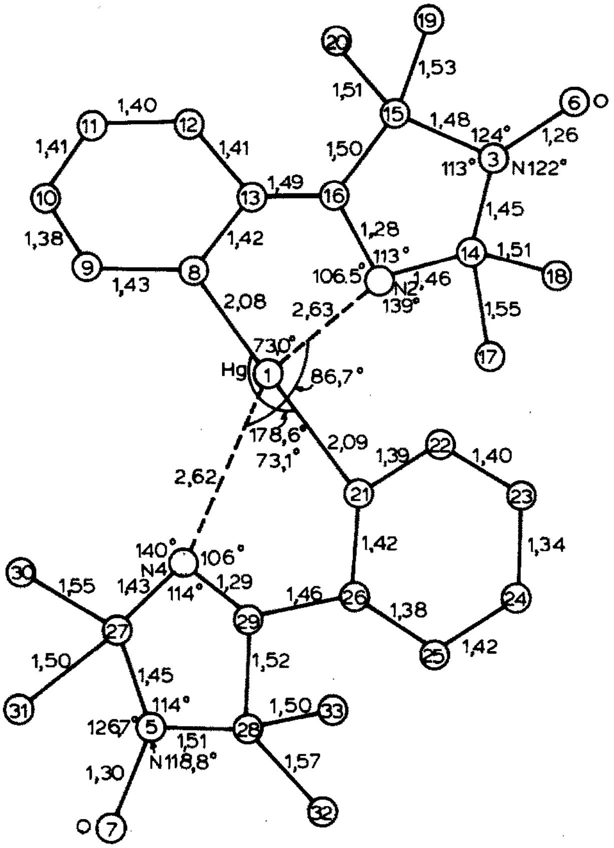


Figure 3. Bond lenghts in Å and valence angles (in degrees) in the mercury-organic biradical. From A. B. Shapiro, L. B. Volodarskii, O. N. Krasochka, L. O. Atovmyan, and E. G. Razantsev, Doklady Akad. Nauk SSSR, 248, 1135 (1979). (Reproduced with Permission from Plenum Publishung Corporation copyright 1979)

6. MERCURY -CARBON BOND REACTIONS:

1-Alkenyl mercury halides readily undergo photostimulated free-radical chain substitution reactions (75)

TABLE 13 (75)

Photostimulated Reaction of Vinylmercurials

vinylmercurial	reactant	conditions[a]	products	%yield[b]
(E)-Me$_3$CCH=CHHgCl	n-BuSSBu-n	PhH,17 h	(E)-Mc,CCH=CHSBu-n	100
(E)-Me$_3$CCH=CHHgCl	PhSSPh	PhH,6 h	(E)-Me,CCH=CHSPh	100
(E)-Me$_3$CCH=CHHgCl	PhSeSePh	PhH,2 h	(E)-Me,CCH=CHSePh	95
(E)-Me$_3$CCH=CHHgCl	PhTeTePh	PhH,18 h	(E)-Mc$_3$CCH=CHTePh	89
(E)-Me$_3$CCH=CHHgCl	PhSO$_2$Cl	PhH,4 h[c]	(E)-Me$_3$CCH=CHSO$_2$Ph	84
(E)-Me,CCH=CHHgCl	(EtO)$_2$POK	Me$_2$SO,29 h	(E)-Me$_3$CCH=CHP(O)(OEt)$_2$	76
(E)-Me$_3$CCH=CHHgCl	PhP(OBu)OK	Me$_2$SO,3.5 h	(E)-Me$_3$CCH=CHP(O)(OBu)Ph	84
(E)-Me$_3$CCH=CHHgCl	p-McPhSO$_2$Na	t-BuOH/H$_2$O,31 h	(E)-Me$_3$CCH=CHSO$_2$PhMe-p	81[d]
(E)-Me$_3$CCH=CHHgCl	n-PrSO$_2$Na	Me$_2$SO/t-BuOH/H$_2$O,30 h	(E)-Me$_3$CCH=CHSO$_2$Pr-n	75[d]
(E)-Me$_3$CCH=CHHgCl	PhSH	PhH,NaHCO$_3$,17 h	(E)-Me$_3$CCH=CHSPh	99
(E)-Me$_3$CCH=CHHgCl	t-BuSH	PhH,NaHCO$_3$,15 h	(E)-Me$_3$CCH=CHSCMe$_3$	100
(E)-Me$_3$CCH=CHHgCl	PhCH$_2$SH	PhH,NaHCO$_3$,5 h	(E)-Me$_3$CCH=CHSCH$_2$Ph	64
(Z)-HOCH$_2$C(Cl)=CHHgCl	PhSH	PhH,NaHCO$_3$,5.25	HOCH$_2$C(Cl)=CHSPh	61
CH$_2$=CHHgCl	PhSH	PhH,NaHCO$_3$,3 h	CH$_2$=CHSPh	100
(E)-EtC(OAc)=C(Et)HgCl	PhSH	PhH,NaHCO$_3$,11 h	EtC(OAc)=C(Et)SPh	92
(E)-Me$_3$CCH=CHHgOAc	PhSH	PhH,17 h	(E)-Me$_3$CCH=CHSPh	100
(E)-Me$_3$CCH=CHHgOAc	PhCH$_2$SH	PhH,18 h	(E)-Me$_3$CCH=CHSCH$_2$Ph	97
(Ph)$_2$CH=CHHgBr	McSSMe	PhH,8 h	(Ph)$_2$CH=CHSMe	100
(Ph)$_2$CH=CHHgBr	p-MePhSO$_2$Na	DMSO,40 h	(Ph)$_2$CH=CHSO$_2$PhMe-p	61
(Ph)$_2$CH=CHHgBr	Me$_2$CHI	PhH,2 h[c]	(Ph)$_2$CH=CHCH(Me)$_2$	50
(E)-Me$_3$CCH=CHHgSPh		PhH,3 h	(E)-Me$_3$CCH=CHSPh	99
(E)-Me$_3$CCH=CHHgSBu-n		PhH,6 h	(E)-Me$_3$CCH=CHSBu-n	100

$(Ph)_2C{=}CHHgSPh$		PhH,15 h	$(Ph)_2C{=}CHSPh$	100
$(Ph)_2C{=}C(CH_3)HgSPh$		PhH,6 h	$(Ph)_2C{=}C(CH_3)SPh$	100
(E)-PhCH=CHHgSPh		PhH,6 h	PhCH=CHSPh,E:Z=10:1	100
(E)-n-PrCH=CHHgSPh		PhH,4 h	n-PrCH=CHSPh,E:Z=1.2:1	100
(E)-nPrCH=CHHgCl	$(EtO)_2POK$	Me,SO,11 h	n-PrCH=CHP(=O)$(OEt)_2$,E:Z=10:1	56
(E)-n-PrCH=CHHgCl	p-MePhSO_2Na	Me_2SO/t-BuOH/H_2O,22 h	n-PrCH=CHSO_2PhMe-p,E:Z=6:1	71[d]
(E)-PhCH=CHHgCl	p-MePhSO_2Na	Me_2SO/t-BuOH,19 h	(E)-PhCH=CHSO_2PhMe-p,E:Z>20:1	81[d]
(E)-PhCH=CHHgCl	n-BuSH	PhH,NaHCO_3,3 h	(E)-PhCH=CHSBu-n	100
(E)-PhCH=CHHgCl	PhSeSePh	PhH,2h	(E)-PhCH=CHSePh	90
$CH_2{=}CHHgCl$	PhSeSePh	PhH,2h	$CH_2{=}CHSePh$	91
$CH_2{=}CHSn(Bu\text{-}n)_3$	PhSSPh	PhH,4h	$CH_2{=}CHSPh$	∿100

---

[a] Reactants were irradiated with a 275-W sunlamp approximately 6 in. from the Pyrex reaction flask. The sunlamp maintained a temperature of approximately 35-56°C. The mercurials (3 mmol) in 10-50 mL of solvent were reacted with a stoichiometric amount of the disulfide or $PhSO_2Cl$, a 10-20% excess of the anions or free thiols, and a 10-fold excess of Me_2CHI. The exclusion of molecular oxygen is essential. [b] Appropriate ^1H NMR,IR, and high-resolution mass spectra were obtained for all products. Satisfactory elemental analyses were obtained for all new compounds except for $Me_3CCH{=}CHTePh$ (oxidatively reactive), $HOCH_2C(Cl){=}CHSPh$ (unstable), and n-PrCH=CHP(O) $(OEt)_2$, for which an NMR yield is reported. The only previously reported 1-alkenylmercury mercaptide is $CH_2{=}CHHgSr$.[5] [c] Irradiated in Pyrex in a RPR-100 Rayonet reactor at 350 nm. [d] Previously reported in ref 2. (ref 2: Hershberger, J.; Russell, G.A. Synthesis 1980, 475).

$$\mathrm{RCH{=}CHHgX + R'Y{-}YR' \xrightarrow{h\nu} RCH{=}CHYR' + XHgYR'}$$

X=Cl,Br,OAc

Y=S, R'=alkyl or aryl
Y=Se, Te, R'=phenyl

$$\mathrm{RCH{=}CHHgX + Z{-}Q \xrightarrow{h\nu} RCH{=}CHZ + XHgQ}$$

X=Cl,Br,OAc

$Z=PhSO_2$, Q=Cl
$Z=Me_2CH$, Q=I

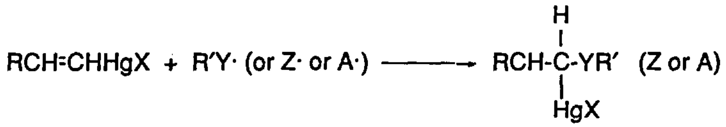
$$\mathrm{RCH{=}CHHgX + A^- \xrightarrow{h\nu} RCH{=}CHA + Hg^0 + X^-}$$

X=Cl,Br,OAc

$A^-=(RO)_2PO^-$, $PhP(OBu)O^-$, $AlkSO_2^{2-}$,
$ArSO_2^{2-}$, $AlkS^-$, ArS^-
(Alk=alkyl, Ar=aryl)

that are believed to proceed by the free-radical addition-elimination reaction presented in Scheme 16. Table 13 gives typical yields observed in these reactions.

<u>Scheme 16</u> (75)



$$\mathrm{RCH{=}CHHgX + R'Y\cdot\ (or\ Z\cdot\ or\ A\cdot) \longrightarrow RCH{-}\underset{HgX}{\overset{H}{C}}{-}YR'\ \ (Z\ or\ A)}$$

$$\mathrm{RCH{=}CH{-}YR'\ (Z\ or\ A) + HgX}$$

$$\mathrm{HgX + R'Y{-}YR' \longrightarrow XHgYR' + R'Y\cdot} \quad (1)$$

or

$$\mathrm{HgX + ZQ \longrightarrow XHgQ + Z\cdot} \quad (2)$$

or

$$\mathrm{HgX + A^- \longrightarrow Hg^0 + X^- + A\cdot} \quad (3)$$

or

$$\mathrm{HgSR \longrightarrow Hg^0 + RS\cdot} \quad (4)$$

Divinylmercurials also undergo a photostimulated reaction with aryldisulfides to give vinyl sulfides (reaction 5), however, primary alkyl disulfides do not react.

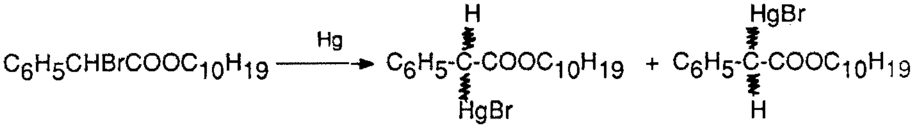
$$\mathrm{[(Ph)_2C{=}CH]_2Hg + PhSSPh \xrightarrow[PhH]{h\nu,\ 3hr} 2(Ph)_2C{=}CHSPh + Hg^0} \quad (5)$$

This reaction does not appear to involve intermediate vinyl radicals and chain propagation is suggested to occur by Scheme 16 followed by reactions 6 and 4.

$$(Ph)_2C{=}CHHg \text{ (from Scheme 16) } + PhSSPh \longrightarrow (Ph)_2C{=}CHHgSPh + PHS. \quad (6)$$

$$(Ph)_2C{=}CHHgSPh \xrightarrow{hv} (Ph)_2C{=}CHSPh + Hg^o \quad (4)$$

The L-menthyl esters of α-bromomercury-phenlyacetic acid, **82a** and **82b**, have been prepared by shaking L-menthyl α-bromophenyl acetates with metallic mercury [Rentor et al., Dokl. Akak. Nawk. SSSR, 88, 479 (1953) ; Izv. Akad. Nauk SSSR, Ser. Khim (1953) 649, 850], and their stereochemistry reinvestigated. (76)



$$C_6H_5CHBrCOOC_{10}H_{19} \xrightarrow{Hg} C_6H_5\text{-}\overset{H}{\underset{HgBr}{C}}\text{-}COOC_{10}H_{19} + C_6H_5\text{-}\overset{HgBr}{\underset{H}{C}}\text{-}COOC_{10}H_{19}$$

82a(R) 82b(S)

Reaction of **82a** and **82b** (**82a**,$[\alpha]_D^{20}$ =-132^o ; **82b**,$[\alpha]_D^{20}$=-18^o) with ammonia in chloroform gave the corresponding dialkyl mercurial, R_2Hg, ($[\alpha]_D^{20}$= -32^o and $[\alpha]_D^{20}$= -5^o, respectively) which upon treatment with one equivalent of $HgBr_2$ in THF gave the starting diastereomer.

Reaction of the hydridoorganotermetallic cluster, $HRu_3(CO)_9(C_6H_9)$, with C_6H_5X, (X=Br,I) gives **83** (77) which is dimeric in the solid state and exhibits asymmetrical bromine bridges. The ^{13}C NMR of a 15% ^{13}CO-enriched sample of **83** shows both axial-radial exchange at the unique ruthenium atom, Ru(l), ($\Delta G^{\neq}$ = 12.7 ± 0.5 kcal/mol) and CO-scrambling from licalized axial-radial exchange at Ru(2) and Ru(3) ($\Delta G^{\neq}$ = 14.8 ± 0.5 kcal/mole).

$$(C_6H_5)Ru_3(CO)_9H + C_6H_5HgX \xrightarrow[\text{reflux, 12hr}]{THF} (C_6H_9)Ru_3(CO)_3HgX + C_6H_6$$

83 , 30-40%

Compound **83** may also be prepared from the anion of **84** generated insitu with HgX_2 (X=Br,I).

$$\begin{tikzcd} HRr_3(CO)_9(C_6H_9) \arrow[r, "\text{KOH}", "\text{THF-EtOH}"'] & Ru_3(CO)_9(C_6H_9)^-K^+ + HgX_2 \arrow[d, "(25^o\text{,18 hr})"] \\ & \textbf{83} \end{tikzcd}$$

Reaction of **83** , (X=Br), with Ag(OAc) gave the corresponding acetate in good

$$(C_6H_9)Ru_3(CO)_9HgX + Ag(OAc) \xrightarrow[\text{(X=Br)}]{\text{THF}} (C_6H_9)Ru_3(CO)_9HgOAc + AgX$$

A recent check, by Okhlobystin et al. (78), of the effect of oxygen on the course of the protodemercuration of R_2Hg (R=electron withdrawing) in the presence of iodide anions, has cast doubts on the $S_E1(N)$ mechanism proposed by Reutov et al. [Izv. Akad. Nauk. SSSR, Ser. Khim, 1680 (1970)]. They observed 1) that in the complete absence of oxygen ($1x10^{-4}$ mm Hg) protodemercuration does not take place; and 2) exclusively RH is formed in $HCON(CH_3)_2$-D_2O (10%) and CH_3CN-D_2O (10%) mixtures and in CD_3CN-H_2O (10%) mixtures only RD is formed. It was asserted, therefore, that it was not protolysis that took place but the oxidation of R_2Hg by traces of oxygen present in the argon used in the initial experiments. The results obtained by Reutov et al. were thus suggested to be the product of experimental error. This assertion was later completely refted by Reutov et al. (79) when it was shown that bis(pentafluorophenyl)mercury is photolyzed under vacuum, forming pentafluorobenzene and that deuterophentafluorobenzene is produced when the D_2O-DMF-I^- system was used. The same results were also obtained in air; C_6F_5H is formed in H_2O-DMF-d and C_6F_5D in D_2O-DMF.

Razuvaev et al. (80) have examined the reactions of R_2Hg ($R=C_2H_5$, $(CH)_6CHCH_2$, C_4H_9, C_5H_{11}) with polychloromethanes, $CXCL_3$, (X=H,Cl) both in the absence and in the presence of O_2 (Table 14). Oxygen was found to lower the reaction temperature, increase the rate of reaction,and to influence the degree of

TABLE 14 (80)

Influence of Oxygen on the Reactions of Organo-mercury Compounds with CCl_4 and $CHCl_3$

Reactants		Reaction Conditions	Conversion, %	Reaction products, mole per mole of R_2Hg taken		
R_2Hg	$CXCl_3$			RHgCl	Hg	
$(iso\text{-}C_3H_7)_2Hg$	CCl_4	Without O_2, 100° C, 42 h	19	0.18	0.01	—
		O_2, 60° C, 20 h	98	0.92	0.06	Traces
		O_2, 20° C, 96 h	96	0.91	0.05	Traces
$(iso\text{-}C_3H_7)_2Hg$	$CHCl_3$	Without O_2, 100° C, 42h	40	0.37	0.03	—
		O_2, 50° C, 40 h	95	0.82	0.01	0.06
$(CH_3H_7)_2Hg$	CCl_4	Without O_2, 100° C, 60 h	27	0.03	0.24	—
		O_2, 100° C, 60 h	100	0.50	0.40	0.05
$(C_3H_7)_3Hg$	$CHCl_3$	Without O_2, 100° C, 42 h	20	0.03	0.17	—
		O_2, 100° C, 42 h	63	0.33	0.30	—
$(C_4H_9)_2Hg$	CCl_4	Without O_2, 100° C, 15 h	8	0.03	0.05	—
		O_2, 85° C, 15 h	65	0.41	0.10	0.07
$(C_6H_5)_2Hg$	$CHCl_3$	Without O_2, 150° C, 50 h	0			
		O_2, 150° C, 50 h	43	0.41	0.02	—

conversion as well as the proportions of the alkylchloromercury and mercury formed. In the thermal reaction of R_2Hg with $CXCl_3$ (X=H,Cl) the main product of the dealkylation of R_2Hg with a primary alkyl group (R= C_3H_7 and C_4H_9) is mercury, however, in the presence of oxygen RHgCl is preferentially formed. In the absence of O_2, thermal reaction of R_2Hg with CCl_4 gave homolysis of R_2Hg (equation 7) and induced decomposition as a result of the subsequent reaction of the radicals formed with CCl_4 (equation 8) or with R_2Hg (equation 9) to an extent of 50-95% depending on the nature of the compound.

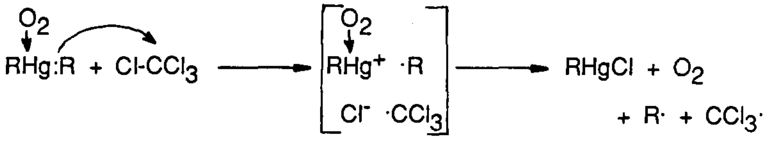
$$R_2Hg \longrightarrow R\cdot + RHg\cdot \qquad (7)$$

$$R\cdot\,(RHg\cdot) + CCl_4 \longrightarrow RCl(RHgCl) + CCl_3\cdot \qquad (8)$$

$$CCl_3\cdot + R_2Hg \longrightarrow CHCl_3 + R_{-H}\cdot\,HgR\cdot \qquad (9)$$

$$\begin{array}{l} \xrightarrow{a} R\cdot + Hg + R_{-H}(\text{olefin}) \\ \xrightarrow{b} RHg\cdot + R_{-H} \end{array}$$

The amount of induced decomposition decreases considerably when the reaction is conducted in the presence of O_2. Under these conditions, the primary process is the formation of a labile coordination complex $R_2Hg{\cdot}O_2$ between the organomercury compound and oxygen, which reacts directly with CCl_4 by a one-electron transfer mechanism to form radicals.



This process amounts to 30-50% and is accompanied by both induced decomposition and oxidation of the dialkylmercury (equations 10 - 12).

$$CCl_3\cdot + O_2 \longrightarrow CCl_3OO\cdot \qquad (10)$$

$$CCl_3OO\cdot + R_2Hg \longrightarrow R\cdot + RHgOOCl_3 \qquad (11)$$

$$RHgOOCCl_3 + R_2Hg \longrightarrow RHgOR + RHgOCCl_3 \longrightarrow RHgCl + COCl_3 \qquad (12)$$

Polarographic electroreduction of benzyl iodide and benzylmercuric iodide (81) has confirmed the previously reported mechanism for reduction[N. S. Hush, K. B. Oldham, J. Electroanal. Chem, 6 (1963) 34]: namely, that the iodide undergoes reaction with mercury to form benzylmercuric iodide, which is subsequently reduced, as is benzylmercuric iodide itself. The excellent Hammett correlation of the half wave potentials of the second wave (most negative potential) for a series of substituted benzyl iodides and benzyl mercuric iodides confirmed the previous suggestion [S. Wawzonek, R. C. Duty, J. H. Wagendnecht, J. Electrochem. Soc. 74 (1964) 111] that the second step in the electro-reduction is the reduction of the benzyl mercuryl radical and further suggests that the process is concerted with respect to carbon-mercury bond rupture.

8. MERCURY-FUNCTIONAL MERCURIALS:

A. Mercurials with Halogen and Oxygen Substituents

Methylmercury(II) nitrate reacts with 9-methylquanine (9-MeGua) in water to form complexes having stoichiometry [HgMe(9-MeGuaH$_{-1}$)], [HgMe(9-MeGua)](NO$_3$), [HgMe(9-MeGua)](NO$_3$)·H$_2$O and [(HgMe)$_2$(9-MeGuaH$_{-1}$)](NO$_3$). (82)

$$\text{HgMe(NO}_3\text{)} + \text{NaOH} + \text{9-MeGua} \rightarrow [\text{HgMe(9-MeGuaH}_{-1})] + \text{NaNO}_3 + \text{H}_2\text{O}$$

$$\text{HgMe(NO}_3\text{)} + \text{9-MeGua} \rightarrow [\text{HgMe(9-MeGua)}](\text{NO}_3)\cdot\text{H}_2\text{O}$$

$$2\,\text{HgMe(NO}_3\text{)} + \text{NaOH} + \text{9-MeGua} \rightarrow [(\text{HgMe})_2(\text{9-MeGuaH}_{-1})](\text{NO}_3) + \text{NaNO}_3 + \text{H}_2\text{O}$$

Both solid state infrared and solution ^{1}H NMR data indicate that the HgMe unit is bound to the same ring positions that were found for the corresponding guanidine complexes having similar stoichiometry. In [HgMe(9-MeGuaH$_{-1}$)] and [(HgMe)$_2$(9-MeGuaH$_{-1}$)](NO$_3$), the HgMe unit is bound to N(1) and both N(1) and N(7), respectively. In [(HgMe)$_2$(9-MeGua)](NO$_3$) and [HgMe(9-MeGua)](NO$_3$)·H$_2$O the HgMe unit is bound to N(7) with retention of a proton at N(1). The structure of the [HgMe(9-MeGua)](NO$_3$) complex is shown in (Figure 32).

Organomercuric peroxides (83), RHgOOHgR have been obtained in high yield by the reaction of the corresponding methoxides with H_2O_2 in methanolic solution at 20 - 25°C.

$$RHgOCH_3 + H_2O_2 \longrightarrow RHgOOH + CH_3OH$$

$$RHgOOH + RHgOCH_3 \longrightarrow RHgOOHgR + CH_3OH$$

$$2\ RHgOOH \longrightarrow RHgOOHgR + H_2O_2$$

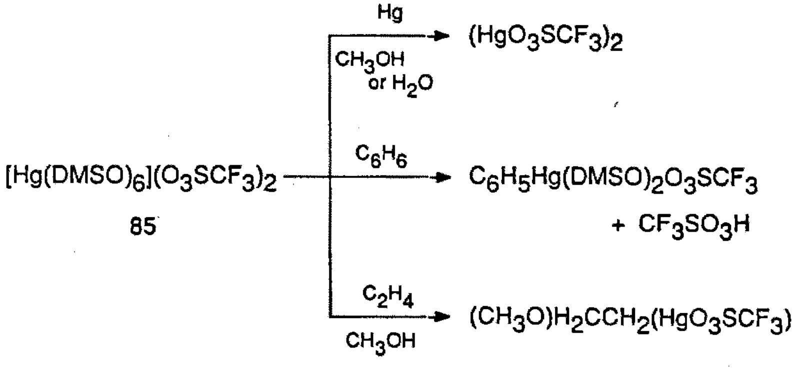
$R = C_6H_5$; $2,5\text{-}(CH_3)_2C_6H_3$;
$2,4,6\text{-}(CH_3)_3C_6H_2$

They are yellow , crystalline substances that react with acids to give the corresponding aryl mercury salt and H_2O_2. In benzene, ether or CH_2Cl_2 they react with excess H_2O_2 to afford products with the composition RHgOOH, (R= $2,5\text{-}(CH_3)_2C_6H_3^-$, $2,4,6\text{-}(CH_3)_3C_6H_2$).

$$RHg^+A^- + H_2O_2 \xleftarrow{HA} RHgOOHgR \xrightarrow[RHgOCH_3]{H_2O_2(\text{excess})} RHgOOH$$

B. <u>Mercurials with Sulfur and Selenium Substituents</u>

Bis(trifluoromethanesulfonato-O)hexakis(sulfinylbis[methane])mercury, **85**, $[Hg(DMSO)_6(O_3SCF_3)_2$, has been prepared by reaction trifluoromethane sulfonic acid with mercuric oxide in DMSO (84). Some reactions of, **85**, follow.

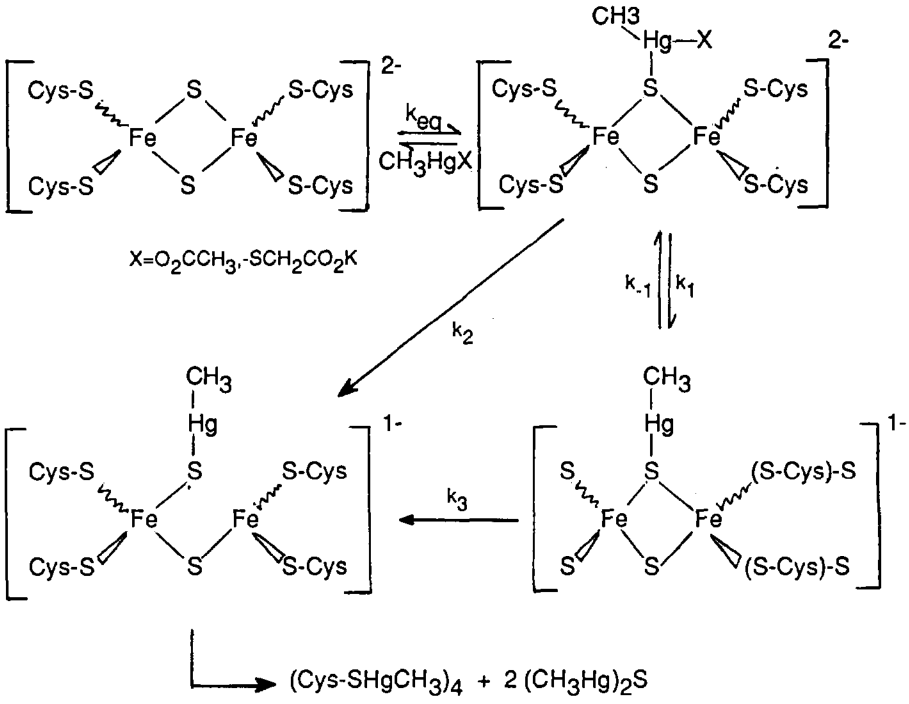


Arakawa, Bach and Kimura (85) have studied the kinetics of the rate of reaction of the $Fe_2S_2(SR)_4$ cluster of adrenodoxin (AD) with CH_3HgOAc and $CH_3HgSCH_2CO_2K$. Native AD reacts rapidly (~ 15s) and quantitatively with CH_3HgOAc at pH 7.4 (10 mM Na, K phosphate buffer) at 22°C. In contrast, $CH_3HgSCH_2CO_2K$ reacts very slowly, taking 5 hours for complete extrusion of iron and sulfur from AD at 22°C (pH 6.4). The latter was found to follow second order kinetics:

$$\text{rate} = k_1[CH_3HgSCH_2CO_2K][AD] = K_{obs}[AD]$$

{ $k_{obs} = 1.62 \times 10^{-3} s^{-1}$(av), {[AD] = 0.91 - 1.60 x 10^{-5}M} and is suggested to proceed as outlined in Scheme 17.

Scheme 17 (85)



Equilibrium constants for the exchange reactions between $(C_6H_5)_2Hg$, $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ derivatives of 2,6-dimethylthiophenyl, 1-thionaphthol ,8-mercapto-quinoline, 2-mercaptopyridine and 2-dimethylaminothiophenol , in chloroform, have been determined by PMR techniques (Table 15) (86).

$$(C_6H_5)_nMSC_6H_3(CH_3)_2\text{-2,6} + (C_6H_5)_nM^*SR \rightleftharpoons (C_6H_5)_nM^*SC_6H_3)_2\text{-2,6} + (C_6H_5)_nMSR$$

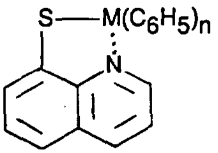
$(C_6H_5)_nM \neq (C_6H_5)_nM^* = C_6H_5Hg$,
$(C_6H_5)_2Sn$, $(C_6H_5)_3Pb$

R= 2-pyridyl, 8-quinolyl, 2-dimethylaminophenyl,
or 1-naphthyl

TABLE 15
Equilibrium constants in chloroform at 25°C for the reactions of $(C_6H_5)_nMSC_6H_3(CH_3)_2$-2,6 with $(C_6H_5)_nM^*SR$ (86)

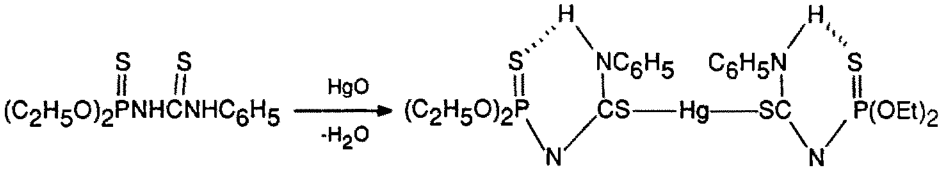
$(C_6H_5)_nM$	$(C_6H_5)_nM^*$	R	K
C_6H_5Hg	$(C_6H_5)_3Sn$	8-quinolyl	105
C_6H_5Hg	$(C_6H_5)_3Pb$	8-quinolyl	>200
$(C_6H_5)_3Sn$	$(C_6H_5)_3Pb$	8-quinolyl	25
C_6H_5Hg	$(C_6H_5)_3Sn$	1-naphthyl	1.1
C_6H_5Hg	$(C_6H_5)_3Pb$	1-naphthyl	0.9
$(C_6H_5)_3Sn$	$(C_6H_5)_3Pb$	1-naphthyl	1.4
C_6H_5Hg	$(C_6H_5)_3Sn$	2-pyridyl	0.9
C_6H_5Hg	$(C_6H_5)_3Pb$	2-pyridyl	3.6
C_6H_5Hg	$(C_6H_5)_3Sn$	2-dimethylaminophenyl	>100
C_6H_5Hg	$(C_6H_5)_3Pb$	2-dimethylaminophenyl	>100
$(C_6H_5)_3Sn$	$(C_6H_5)_3Pb$	2-dimethylaminophenyl	1.3

The deviation of the equilibrium constants from unity for the exchange reactions of the 2,6-dimethylthiophenol derivatives with those of 8-mercaptoquinoline is attributed to the existence of an intramolecular coordinative interaction in these derivatives; the strength of which increases in the order $Ph_3Pb < PH_3Sn < PhHg$.



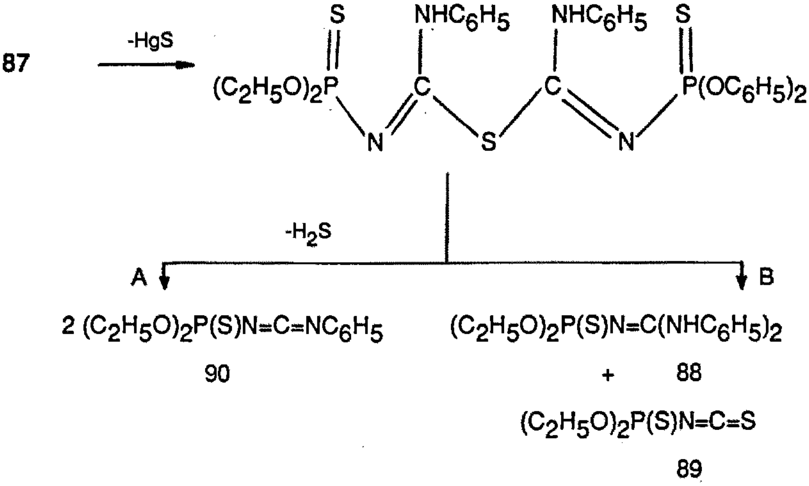
Results show that for the same donor atom the variation in the size of the chelate ring as well as the type of orbital hybridization exerts a marked influence on the relative stability of the chelate rings formed by the Ph_nMS groups.

N-diethoxythiophosphoryl-N′-phenylthiourea, **86**, reacts with mercuric oxide in hot acetone in the presence of magnesium sulfate and molecular sieves to give, **87**, (87).



86 87

When **87** is boiled in toluene, **88** and **89** are produced in 68% and 60% yields, respectively. In hot benzene **90** was also detected.



Several compounds of the type $R_nE\text{-}E'R_m$, ($R= CH_3, CF_3$,; E,E′= P, As, S, Se, Te, ; n,m=1,2), have been prepared as illustrated by equations 13,14, and 15 (88).

$$2\,(CF_3)_2PI + (CF_3Se)_2Hg \xrightarrow[3d]{20^oC} \underset{\text{quant.}}{(CF_3)_2PSeCF_3} + HgI_2 \qquad (13)$$

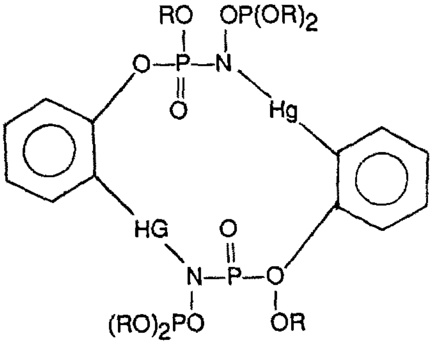
$$2\,(CF_3)_2AsI + (CF_3Se)_2Hg \xrightarrow[3d]{20^oC} \underset{\text{quant.}}{(CF_3)_2AsSeCF_3} + HgI_2 \qquad (14)$$

$$2\,CF_3SCl + (CF_3Se)_2Hg \xrightarrow[18hr]{20^oC} \underset{20\%}{(CF_3SSeCF_3} + HgI_2 \qquad (15)$$

The complexes $[L_2M(NCS)_2M'(SCN)_2]$ and $[ML_6][M'(SCN)_4]$, {M= Co(II), Ni(II) ; M'= Zn(II), Cd(II), Hg(II) ; L= aniline, p-toluidine, pyridine, nixotinamide, 2,2-bipyridine, 4-aminopyridine] have been prepared and their strtuctures proposed on the basis of a variety of physical and theoretical methods (89). The proposed structures were supported by quantitative values of softness, $E_n^{\neq}$, $E_m^{\neq}$. Total softness of M and M' and their difference $\Delta TE_n^{\neq}(M\text{-}M')$ were also derived and related to the structures of the complexes.

C. Mercurials with Nitrogen and Phosphorus Substituents

Reaction of imidodiphosphoric tetraphenyl ester with mercury(II) oxide gives the twelve membered ring system **91** (90). The structure of the product is shown in Figure 4.



91

Imidodiphosphoric tetraphenyl ester also reacts with C_6H_5HgOAc to give N-phenylmercury bis(phosphoric diphenylester)imido, **92**.

$$[(RO)_2P(O)]_2NH + RHgOAc \longrightarrow [(RO)_2P(O)]_2NHgR + HOAc$$

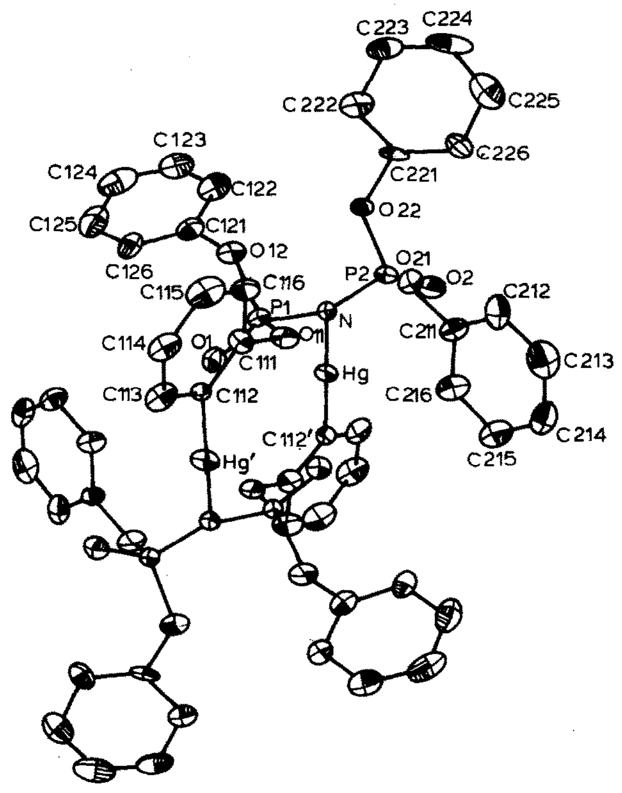


Figure 4. Molecular structure of $[HgP_2NO_6C_{24}H_{19}]$ showing 50% thermal ellipsoids. From H. Richter, E. Fluck & W. Schwarz, Z. Naturforsch. 35B, (1980) 578.

$Hg[CH_3N\text{-}B(CH_3)_2$ and $CH_3Hg\text{-}N(CH_3)\text{-}B(CH_3)_2$ have been prepared as described in equations 16 and 17 (91).

$$2\,(CH_3)_2B\text{-}N(CH_3)Li + HgCl_2 \longrightarrow 2\,LiCl + Hg[N(CH_3)\text{-}B(CH_3)_2]_2 \qquad (16)$$

$$(CH_3)_2B\text{-}N(CH_3)Li + CH_3HgCl \longrightarrow Li + CH_3Hg\text{-}N(CH_3)\text{-}B(CH_3)_2 \qquad (17)$$

The compounds are stable up to 80°C and show no association in solution or in the gaseous phase.

The synthesis of the N-organomercury nucliosides C_6H_5HgL (LH= quanosine, inosine, thimidine and uridine) has also been described (92). The tricyanomercurate(II) ion , $[Hg(CN)_3]^-$, has been isolated and characterized by infrared and Raman spectroscopy (93) and assignments proposed for the carbon-oxygen and mercury-carbon and HgC stretching and HgCN bending vibrations.

Nesmeyanov et. al. (94) have investigated the solution behavior of mixtures of diphenyltriazenes(DPT) and their ^{15}N-labelled arylmercury derivatives by ^{15}N and ^1H NMR methods. The ^{15}N NMR spectrum of a solution of the phenylmercury derivative of diphenyl triazine shows a single signal with mercury satellites (Table 16). Reduction of the temperature of a pyridine solution of the derivative to -80°C did not lead to marked signal broadening in the ^{15}N NMR spectrum. Thus, no definite conclusions could be drawn concerning the solution structure of these derivatives.

Peringer (95) on the other hand, has used metal-ligand spin-spin coupling to examine the solution structures of compounds of the type $ArN_3(HgC_6H_5)Ar'$, **93**, and $(ArN_3AR')_2Hg$, **94**. The compounds studied are summarized in Table 17.

TABLE 16
Parameters of ^{15}N NMR spectra of solutiions of phenylmercury derivatives of diphenyltrizaenes at a temperature of 25°C. (94)

Substance	Solvent	c, M	δ, ppm	J, Hz
$C_6H_5{}^{15}N(HgC_6H_5)N={}^{15}NC_6H_5$	Pyridine	0.6	95	167 ± 0.5
"	"	0.1	95	165 ± 0.5
"	THF	0.2	94*	154 ± 0.5
$C_6H_5N(HgC_6H_5){}^{15}N=NC_6H_5$	Pyridine	0.2	-71	—

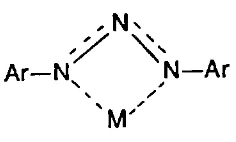
* It is interesting to note that the chemical shifts of the ^{15}N NMR signals of THF solutions of 4-dimethylaminophenylmercury and phenylmercury derivatives of diphenyltriazene labeled with the ^{15}N isotope in positions 1 and 3 were practically coincident. (Reproduced with permission from Plenum Publishing Corporation copyright 1979)

Table 17
Triazenato-Mercury Compounds Studied. (95)

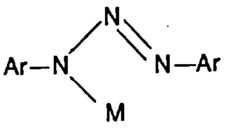
$ArN_3(HgC_6H_5)Ar'$	Ar	Ar′	No*
	phenyl	phenyl	1b
	2-chlorophenyl	phenyl	2b
	4-methylphenyl	4-methylphenyl	3b
	2-fluorophenyl	2-fluorophenyl	4b
	2-fluorophenyl	phenyl	5b
	2-fluorophenyl	2-chlorophenyl	6b
	2-fluorophenyl	2-nitrophenyl	7b
	2-fluorophenyl	2-pyridinyl	8b
	phenyl	2-pyridinyl	9b

*the corresponding triazenes are signed with a, the corresponding bistriazenato-mercury compound with c.

NMR data (^{15}N and ^{199}Hg) indicates rapid intermolecular C_6H_5Hg exchange in **93** where Ar = 2-pyridinyl. π-Triazaallyl bonded or σ-triazaallyl structures (a and b, respectively) associated with rapid intramolecular exchange between N(1) and N(3) are indicated in the other diaryl triazenes of compounds **93** and **94**.



(a)



(b)

p-Aminobenzoic acid, nicotinic acid, sulfanilic acid and pyridine(3)-sulfonic acid react with mercury(I) nitrate and perchlorate to give products having compositions $(Hg_2L)NO_3$, [L= $NH_2C_6H_4CO_2^-$, $C_5H_4NCO_2^-$], and $(Hg_2L)ClO_4$, [L= $C_5H_4NCO_2^-$] (96). The infrared spectra of the compounds indicate that they have a chain structure containing the units $[\text{-Hg-}H_2N^+C_6H_4\text{-COO-Hg-}]NO_3^-$ and $[\text{-Hg-}^+NC_5H_4\text{-COO-Hg-}]X^-$, ($X^-$ = NO_3, ClO_4). Reaction with the two sylfonic acids gave $Hg_2[H_2NC_6H_4SO_3]_2$ and $Hg_2[NC_5H_4SO_3]_2{\cdot}H_2O$. The x-ray crystal structure of the latter compound revealed a zwitterionic structure in which the Hg_2 group is linked to the pyridine nitrogen (Figure 5).

Tobias et. al., (97) have used a competitive reaction technique based on Raman perturbation difference spectrophotometry to study the reactions of several electrophiles, including CH_3Hg^+, with a mixture of four nucleotides (5′-GMP, 5′-CMP, 5′-AMP and 5′-UMP) at pH 7. Methylmercury(II) was shown to exhibit a high selec-

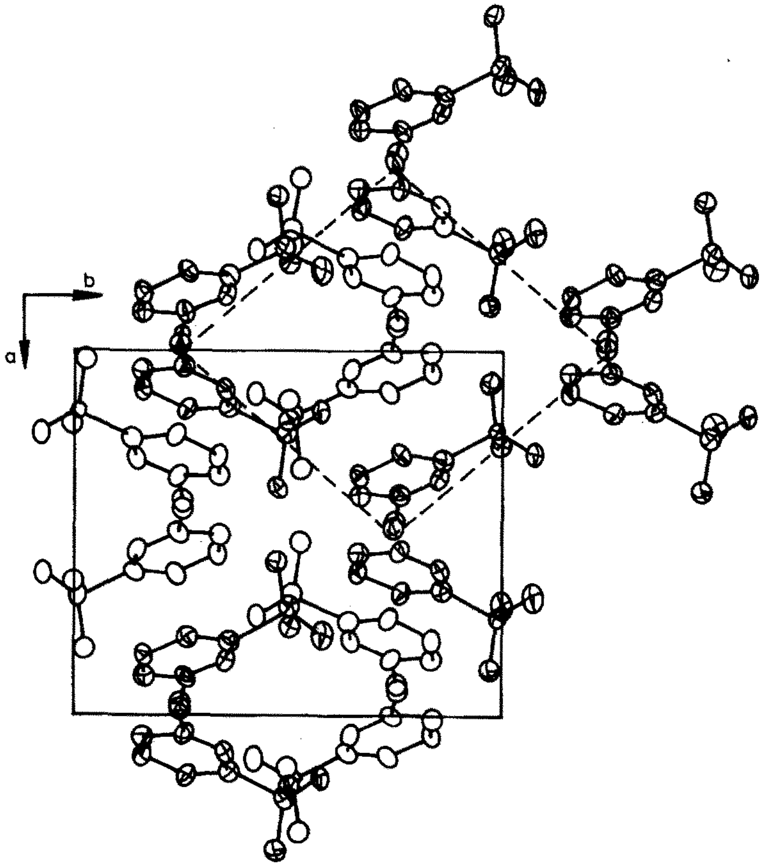


Figure 5. Packing diagram of bis[pyridine(3)-sulfonate]dimercury(i)-dihtdrate. The crystal consists of discrete units in which the sulfonate groups adopt a cis rather than tran- arrangement. Relevant distances and angles include: [Hg-Hg, 2.494(1)Å ; Hg-N, 2.203(13)Å ; Hg-O_4, 2.620(11)Å ; Hg-O_1, 2.680(12)Å ; Hg-O_2, 2.967(11)Å ; Hg-Hg-N, 165.6(2)° ; Hg-Hg-O_2, 103.3(2)° ; Hg-Hg-O_4, 108.4(2)° ; O_1-Hg-O_4, 161.3(3)° ; N-Hg-O 85.2(3)° ; N-Hg-O_1, 82.2(3)°]. From Von K . Brodersen, R. Dolling & G Liehr, Z. anorg. allg. Chem., 464 (1980) 17.

tivity for attack at N-H bonds and binds to UMP N(3) when $0<r_t$ (total metal : total phosphate) ≤ 0.3. When $r_t \geq 0.4$, and all the UMP has been used up, it binds to N(1) of GMP and when $r_t > 0.7$ reaction also occurs with CMP, N(3). Significant binding to AMP does not occur. The selectivity observed is the same as the protein basicity; H_1-UMP$^-$ > H_1-GMP$^-$ > CMP > AMP.

Phosphonito-mercury compounds, $C_6H_5(n\text{-}C_4H_9O)P(O)HgX$, ($X{=}C_6H_5$(N-$C_4H_9O$)P(O), Cl, Br, I, CN, C_6H_5, OAc, O_3ScF_3, SCN, SC_6H_5, SC_2H_5 and 2,5-pyrrolidindionato-N) have been prepared by reaction of the corresponding phosphinic acid ester with HgO or HgO + HgX_2 (98). Bis(O-n-butyl-P-phenyl-phosphanito-P)mercury was obtained according to reactions 18 and 19.

TABLE 18 (98)

NMR Parameters of Phosphonito-mercury Compounds $C_6H_5(n\text{-}C_4H_9O)P(O)HgX^a$.

X	$\delta(^{199}Hg)^b$	$\delta(^{31}P)^b$	$^1J(^{31}P\text{-}^{199}Hg)^c$
Cl	1231	85.6	10525
Br	1132	86.1	10288
I	921	89.9	9684
CN	1254	88.1	9136
C_6H_5	1356	116.7	4608
$C_4H_4NO_2{}^d$		81.6	10277
$C_6H_5(n\text{-}C_4H_9O)P(O)$	1217	111.3	5506
OAc	964	77.5	11080
SCN		89.5	9975
SC_6H_5	1309	94.2	7904
SC_2H_5	1391	98.7	7271

[a] ca. 0.75 M solutions in pyridine, 300K.

[b] In ppm to high frequency of aqueous $Hg(ClO_4)_2$ (2 mmol HgO/ml 60% $HClO_4$) or 85% h_3PO_4

[c] in Hz

[d] 2,5-Pyrrolidindionato-N.

$$2\,C_6H_5(n\text{-}C_4H_9O)P(O)H + HgO \rightarrow [C_6H_5(n\text{-}C_4H_9O)P(O)]_2Hg + H_2O \qquad (18)$$

$$2\,C_6H_5(n\text{-}C_4H_9O)P(O)H + Hg(OAc)_2 \rightarrow [C_6H_5(n\text{-}C_4H_9O)P(O)]_2 + 2\,HOAc \qquad (19)$$

The compound decomposes at room temperature although it is stable below 263K. Mixed mercury complexes were obtained according to the equation (20).

$$C_6H_5(n\text{-}C_4H_9O)P(O)H + HgO + HgX_2 \rightarrow 2\,C_6H_5(n\text{-}C_4H_9O)P(O)HgX + H_2O \qquad (20)$$

X= Cl, Br, I, CN, C_6H_5, OAc, O_3SCF_3, SCN,
SC_6H_5,SC_2H_5, 2,5-pyrrolidindionato-N

TABLE 19 (98)

NMR Parameters of Phosphonito-mercury Compounds $C_6H_5(n\text{-}C_4H_9O)P(O)HgX^a$.

X	$\delta(^{199}Hg)^b$	$\delta(^{31}P)^b$	$^1J(^{31}P\text{-}^{199}Hg)^c$
Cl	1283	69.2^e	13630^e
Br	1184	72.8^e	13313^e
I	983	79.2^e	12563^e
CN	1298	78.5	11635
C_6H_5	1371	112.6	5993
$C_4H_4NO_2^d$		71.6	12820
$(EtO)_2P(O)$	1294	103.4^e	7601^e
OAc	1012	63.8^e	14034^e
O_3SCF_3	1004	61.4	14127
SCN	1383	71.7	13127
SC_6H_5	1353	85.4	10165
SC_2H_5	1420	91.7	9266

[a] ca. 0.75 M solutions in pyridine, 300K.

[b] In ppm to high frequency of aqueous $Hg(ClO_4)_2$ (2 mmol HgO/ml 60% $HClO_4$) or 85% h_3PO_4

[c] in Hz

[d] 2,5-Pyrrolidindionato-N.

[e] Similar values have been reported in ref. 9

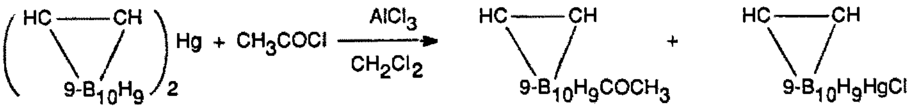
^{31}P and ^{199}Hg NMR parameters for the compounds are presented in Tables 18 and 19, respectively, and are discussed in Section 10B.

D. B-Mercurated Carboranes

Treatment of bis(9-m-carboranyl)mercury(II), **95**, with CH_3COCl in the presence of aluminum chloride gave 9-acetyl-m-carborane, **96**. together with 9-chloromercuri-m- carborane, **97**, and m-carborane (99).

$$\underset{95}{(9\text{-m-}C_2B_{10}H_{11})_2Hg} + CH_3COCl \xrightarrow[CH_2Cl_2]{AlCl_3} \underset{96\ (40\%)}{m\text{-}HCB_{10}H_9(9\text{-}COCH_3)CH} + \underset{97}{HCB_{10}H_9(9HgCl)CH}$$

Bis(9-o-carboranyl)mercury, **98**, reacts similarly to give 9-acetyl-o-carborane, **99**, and 9-chloro-mercuri-o-carborane, **100**:



97 98 100

The bis(carboranyl)mercury compounds are prepared by symmetrization of the 9-chloromercuriocarboranes, **101**, using $LiAlH_4$ in ether.

$$\underset{101}{2C_2B_{10}(9\text{-}HgCl)H_{11}} + LiAlH_4 \xrightarrow[20^{\circ}]{\text{ether}} (9\text{-}C_2B_{10}H_{11})_2Hg + LiCl + Hg + H_2 + AlH_4$$

E. Mercurials with Transition Metal Substituents

The compounds $[(\text{Diene})(RN_3R')_2MHgCl]_2$, (M=Ir ; Diene=COD ; R=$CH_3$, C_2H_5 ; R'=p-$CH_3C_6H_4$: M=Rh ; Diene= COD, NOR ; R=CH_3, C_2H_5, p-$CH_3C_6H_4$;

R′=p-$CH_3C_6H_4$), [COD= 1,5-cyclooxtadiene ; NOR= norbornadiene], have been prepared by reaction of $[(Diene)MCl]_2$ with $Hg(RN_3R')_2$ and by reaction of $[\{(Diene)\text{-}MCl\}_2(HgCl_2)]_2$ with $[Ag(RN_3R')]_n$, (100).

$$[(Diene)MCl]_2 + 2\,Hg(RN_3R')_2 \longrightarrow [(Diene)(RN_3R')MHgCl]_2$$

$$[\{(Diene)MCl\}_2(HgCl_2)_2 + 4/n\,[Ag(RN_3R')]_n \rightarrow [(Diene)(RN_3R')_2MHgCl]_2 + 4AgCl$$

The complexes are monomeric in solution with configurations around the Ir(Rh) atom similar to that in the solid state. Fluxional processes, which occur for M-Rh but not for M=Ir, involve a dynamic process consisting of interchange of the bridging and chelating triazenido group via monodentate intermediates. The x-ray crystal structure of the Iridium complex , $[(COD)(E_pTT)_2IrHgCl]_2$, (E_pTT= c_2H_5-N_3-p-$CH_3C_6H_4$), has been determined .The complex is a chloride-bridged dimer with one triazenido group chelating to the Iridium atom and one triazanido group bridging an Ir-Hg bond (2.62Å). The mercury lies out of the Ir-C(18)-N(4)-N(5)-N(6)-C(20) plane by 1.27Å. This deformation is attributed to steric hindrance between the mercury atom and the ethyl group of the chelating triazenido ligand.

Complexes having the composition $\{(Diene)[RNC(Y)NR']_2RhHgCl\}$, (Diene= 1,5-cyclooctadiene, norbornadiene : Y= H ; R=R′= $CH(CH_3)_2$; R= CH_3, $CH(CH_3)_2$, p-$CH_3C_6H_4$, R′= p-$CH_3C_6H_4$ and Y= CH_3 ; R=R′= p-$CH_3C_6H_4$),may be prepared in almost quantitative yields as described below (101). ^1H and ^{13}C NMR data indicate

$$[(Diene)RhCl]_2 + 2\,[Hg\{RNC(Y)NR'\}_2] \rightarrow 2\,[(Diene)\{RNC(Y)NR'\}_2RhHgCl]_2$$

$$[\{(Diene)RhCl\}(HgCl_2)]_2 + 4/n\,[Ag\{RNC(Y)NR'\}]_n \rightarrow [(Diene)\{RNC(Y)NR'\}_2RhHgCl]_2 + 4\,AgCl$$

that the complexes are monomeric in solution and are suggested to have a structure containing one chelating and one bridging amidino ligand that undergoes rapid interchange . They react with strong acids to give starting material and in the

$$[(\mathrm{Diene})\{\mathrm{RNC(Y)NR'}\}_2\mathrm{RhHgCl}]_2 + {}^{*}\,\mathrm{HCl} \rightarrow [\{(\mathrm{Diene})\mathrm{RhCl}\}(\mathrm{HgCl_2})]_2 + 4\,[\mathrm{RN(H)C(Y)N(H)R'}]\mathrm{Cl}$$

presence of a more acidic triazanido or amidino group undergo rapid substitution of the formamidino groups. The order of substitution is

di-p-tolyltriazene > methyl-p-tolyltriazene > di-p-tolylformamidine ~ di-p-tolylacetamidine > i-propyl-p-tolylformamidine > di-i-propylformamidine.

Use of unsymmetrically substituted alkylarylformamidino groups affords two isomers, one with both N-alkyl groups bonded to rhodium cis- to mercury and one with a N-alkyl and an N-aryl group cis- to mercury . Increasing the size of the alkyl group to i-propyl gave the isomer having both N-aryl groups cis to mercury.

Lemoine et. al. (102) have detected the presence of an intermediate M· radical, [$\mathrm{M^-} \rightarrow \mathrm{M\cdot} + e$ followed by $\mathrm{M\cdot} \rightarrow 1/2\ \mathrm{M_2}$], during the electro-oxidation of the linear trimetallic complexes M-Hg-M , [M= $\mathrm{Co(CO)_4}$, $\mathrm{Fe(CO)_3NO}$, $\mathrm{Mn(CO)_3}$, $\mathrm{Cr(CO)_3}$-(η-$\mathrm{C_5H_5}$), $\mathrm{Mo(CO)_3}$(η-$\mathrm{C_5H_5}$) and $\mathrm{W(CO)_3}$(η-$\mathrm{C_5H_5}$).

Oxidative addition reactions of $\mathrm{Hg(O_2CR)_2}$ with cis-[$(o\text{-}\mathrm{Me_2NCH_2C_6H_4})_2\mathrm{Pt^{II}}$] ,**102**, and [$\{oo'\text{-}(\mathrm{Me_2NCH_2})_2\mathrm{C_6H_3}\}\mathrm{Pt^{II}Br}$], **103**, produces novel stable aryl platinum-mercury compounds (103). Reactions of, **102**, with $\mathrm{Hg(O_2CR)_2}$, (R=Me, $\mathrm{Pr^i}$) in $\mathrm{CHCl_3}$ or toluene afforded a quantitative yield of the monomercuric complexes **104a,b**.

$$\mathbf{102} + \mathrm{Hg(O_2CR)_2} \longrightarrow [(o\text{-}\mathrm{Me_2NCH_2C_6H_4})_2(\mu\text{-}\mathrm{RCO_2})\mathrm{PtHg(O_2CR)}]$$

104a : R=Me 104b: R= $\mathrm{Pr^i}$

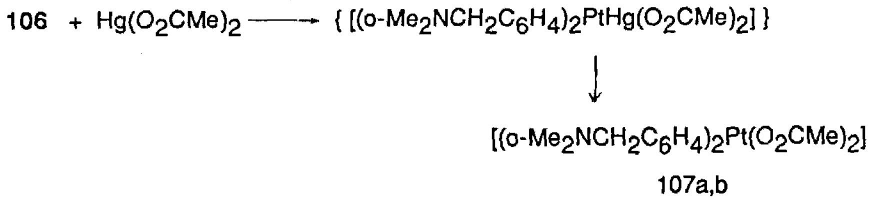
Reaction of **103** with $\mathrm{Hg(O_2CR)_2}$ in methylene chloride afforded the yellow monomeric complexes **105a,b**.

$$\mathbf{103} + \mathrm{Hg(O_2CR)_2} \longrightarrow [\{oo'\text{-}(\mathrm{Me_2NCH_2})_2\mathrm{C_6H_3}\}(\mathrm{RCO_2})(\mu\text{-}\mathrm{RCO_2})\mathrm{PtHgBr}]$$

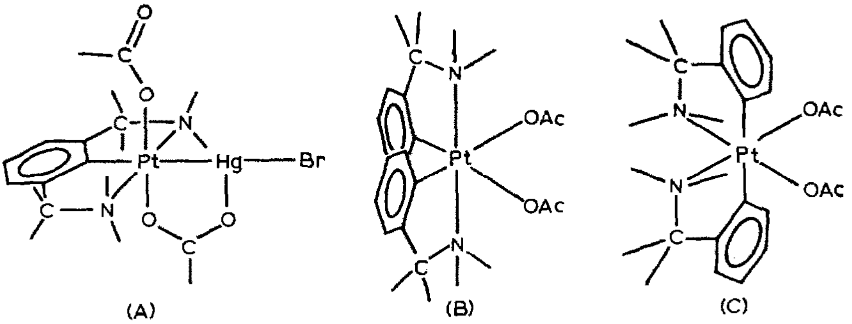
105a : R=Me 105b : R= $\mathrm{Pr^i}$

Insoluble compounds are obtained from similar reactions of **102** and **103** with $\mathrm{HgCl_2}$ instead of $\mathrm{Hg(O_2CR)_2}$. The structure of **104a** has been determined (see Section 8c).

The products **105a** and **105b** have the structures proposed in Figure 6A. Reaction of trans-[(o-$Me_2NCH_2C_6H_4)_2Pt$], **106**, with $Hg(O_2CMe)_2$ in chloroform or toluene affords the two isomers **107a** and **107b** , in a 1 : 8 ratio, which were assigned structures 6B and 6C, respectively.



$$\begin{array}{l} \mathbf{106} + Hg(O_2CMe)_2 \longrightarrow \{[(o\text{-}Me_2NCH_2C_6H_4)_2PtHg(O_2CMe)_2]\} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad [(o\text{-}Me_2NCH_2C_6H_4)_2Pt(O_2CMe)_2] \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \mathbf{107a,b} \end{array}$$

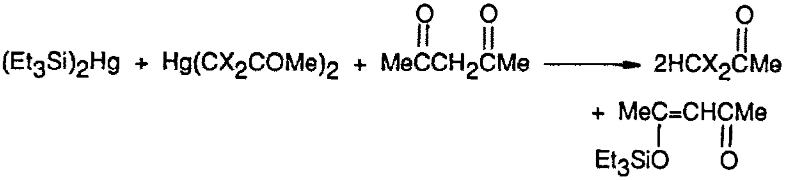


(A) (B) (C)

Figure 6. Proposed structures (A) for compound 105 and (B) and (C) for isomers 107a and 107b, respectively. From F. M. Antonius, Van Der Ploeg , G. Van Koten and K. Vrieze, J. Chem. Soc., Chem. Comm., (1980) 469.

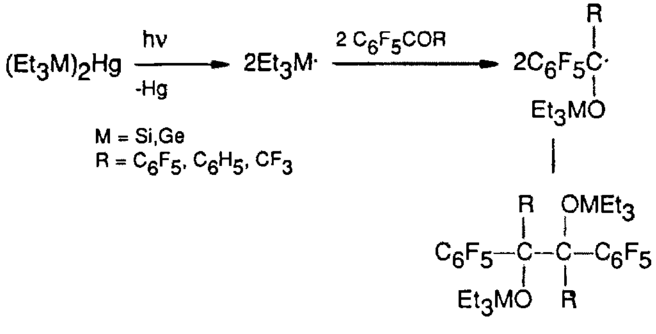
F. <u>Mercurials with Group IV Substituents</u>

The reaction of Bis(triethylsilyl)mercury with mercuribisdiazoacetone, $Hg[C(N_2)C\text{-}OMe]_2$ in inert solvents (hexane, THF, DME) is known to proceed by simple radical exchange to give $Et_3SiHgC(N_2)COMe$, which then undergoes subsequent demercuration to give α-triethylsilyldiazoacetone and mercury [Izv., 1886 (1976)]. A recent report (104) has shown, however, that in ketones (acetone, diethyl ketone, pinacolin, acetylacetone) the reaction can proceed with involvement of the solvent.Under these condition, the direction of the process is determined by the nature of the solvent and the heteroatom attached to mercury. In pinacolin the reaction proceeds smoothly to give the usual demercuration products of the intermediate $Et_3SiHgC(N_2)COMe$. In moist acetone on the other hand, besides mercury (95% yield), the reaction gives $HC(N_2)COMe$, diacetone alcohol and Et_3SiOH in a 1:1:1 ratio. Reaction in moist diethyl ketone gives $Et_3SiOCHEt_2$, Et_3SiOH and $HC(N_2)COMe$ in a 4:5:1 mole ratio. In acetylacetone, Hg (98%), 2-(triethyl)siloxy-2-penten-4-one and diazoacetone were isolated. A similar set of products was obtained by the reaction of $(Et_3Si)_2Hg$ with $Hg(CH_2COMe)_2$ in acetylacetone.



$$(Et_3Si)_2Hg + Hg(CX_2COMe)_2 + MeC(=O)CH_2C(=O)Me \longrightarrow 2HCX_2C(=O)Me + MeC(OSiEt_3)=CHC(=O)Me$$

Combined photolysis of $Hg(SiEt_3)_2$ or $Hg(GeEt_3)_2$ with decafluorobenzophenone, pentafluorobenzophenone, or oxtafluoroacetophenone in n-hexane at 30 - 40°C, in the absence of oxygen, leads to the formation of polyfluorinated ketyls that, under normal conditions, undergo reversible dimerization (105).

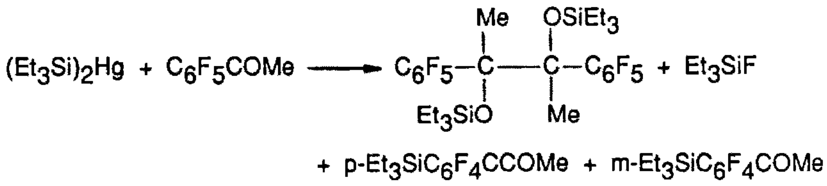


$$(Et_3M)_2Hg \xrightarrow[-Hg]{h\nu} 2Et_3M\cdot \xrightarrow{2\,C_6F_5COR} 2C_6F_5C^{\cdot}(R)(OMEt_3)$$

$$C_6F_5C(R)(OMEt_3)\text{–}C(R)(OMEt_3)C_6F_5$$

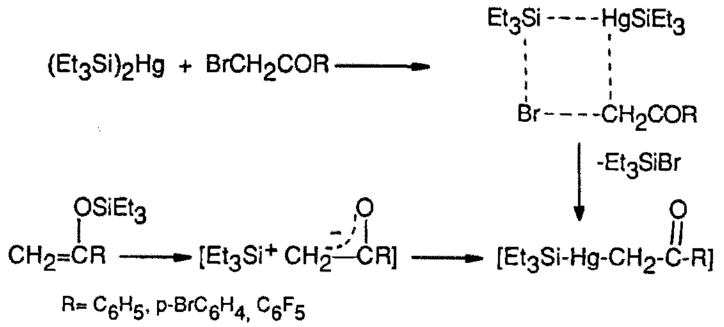
M = Si,Ge
R = C_6F_5, C_6H_5, CF_3

In all cases where the initial ketone contains a C_6F_5 group, Et_3MF (M=Si,Ge) is formed as a by product due to the competing reaction of $Et_3M\cdot$ radicals with the perfluoroaromatic ring to give the m- and p-substituted polyfluorinated ketones.

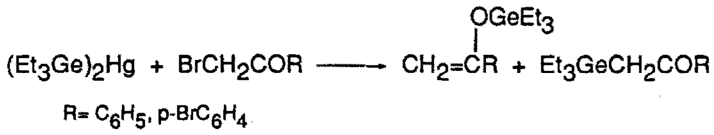


$$(Et_3Si)_2Hg + C_6F_5COMe \longrightarrow C_6F_5-\underset{Et_3SiO}{\overset{Me}{C}}-\underset{Me}{\overset{OSiEt_3}{C}}-C_6F_5 + Et_3SiF + p\text{-}Et_3SiC_6F_4CCOMe + m\text{-}Et_3SiC_6F_4COMe$$

Bis(triethylsilyl)mercury reacts with α-bromoacetophenones in benzene to give, together with mercury and Et_3SiBr, the corresponding O-silylated enols in high yields. (106)



Bis(triethylgermyl)mercury reacts similarly but gives a mixture of the isomeric triethylgermyl O- and C-derivatives. With 1-bromo-1-phenyl-2-propanone only the O-derivative is formed.



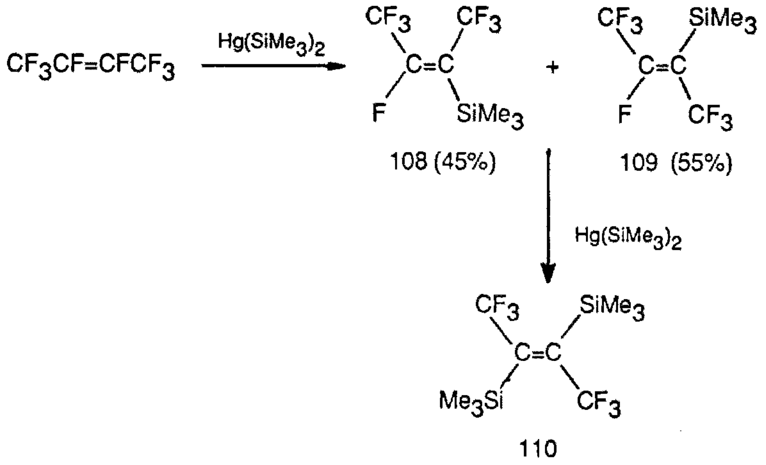
$$(Et_3Ge)_2Hg + BrCH_2COR \longrightarrow CH_2{=}\overset{OGeEt_3}{C}R + Et_3GeCH_2COR$$

R= C_6H_5, p-BrC_6H_4

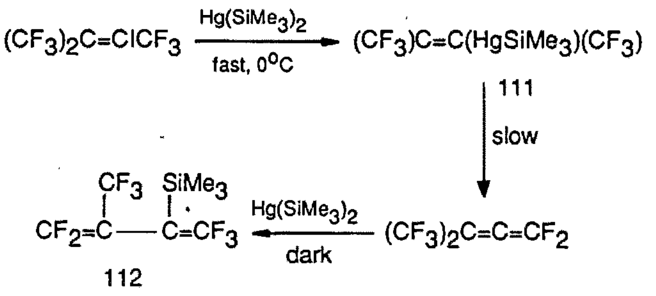
$$PhCHBrC(O)Me + (Et_3M)_2Hg \xrightarrow[-Et_3Br]{-Hg} PhCH{=}C(Me)OMEt_3$$

M=Si,Ge

A further study of the reaction of bis(trimethylsilyl)mercury with fluorinated alkenes has been reported. (107). Reaction with perfluorocyclohexane and pentane give the 1-trimethylsilylperfluorocycloalkanes in ca. 75% yield. With octafluoro-but-2-ene a mixture of cis- and trans-2,3,3,3-tetrafluoromethyl- propenyltrimethyl- silane, **108**, and, **109**, is obtained which upon further reaction with $(Me_3Si)_2Hg$ gave 1,1,1,4,4,4-hexa- fluorotrans-2,3-bis(trimethylsilyl)but-2-ene, **110**,in high yield. Irradiation of cis-1,2-di- fluoroethylene and bis(trimethylsilyl)mercury also gave a mixture of cis- and trans-2- fluorovinyltrimethylsilane.



2-Iodoperfluoro-(3-methylbut-2-ene) gave iodotrimethylsilane and **111**. β-elimination of mercury and fluorotrimethylsilane from **111** gave perfluoro-(3-methybuta-1,2-diene), which reacts with $Hg(SiMe_3)_2$ in the dark to give **112** almost quantitatively.



Sodium and potassium tetrakis(trimethylsilyl)aluminate have been synthesized (108) by reaction of sodium or potassium with bis(trimethylsilyl)mercury and tris(trimethylsilyl)aluminum.

$$2M + Hg(SiMe_3)_2 + Al(SiMe_3)_3{\cdot}Et_2O \xrightarrow{Et_2O\,/\,pentane} MAl(SiMe_3)_4{\cdot}xEt_2O$$

$$M = Na, K$$

Sodium and potassium tetrakis(trimethylsilyl)aluminate complexes coordinated with diethylether, tetrahydrofuran or 1,2-dimethoxyethane are available by dissolving the unsolvated compounds in the appropriate ether.

Photolytic cleavage of bis(pentachlorodisilyl)mercury gives n-decachlorotetrasilane, (n-Si_4Cl_{10}) (109) and bis(t-butyl)mercury has been shown to react with

$$(Cl_5Si_2)_2Hg \xrightarrow{\Delta H,\ h\nu} n\text{-}Si_4Cl_{10} + Hg$$

pentachlorodisilane to give the corresponding silylmercury compound.

$$2HSi_2Cl_5 + (t\text{-butyl})_2Hg \longrightarrow (C_5Si_2)_2Hg + 2\ i\text{-butane}$$

Two silylzirconium compounds, $(\eta\text{-}C_5H_5)_2ZrCl[Si(CH_3)_3]$ and $(\eta\text{-}C_5H_5)_2Zr[Si(CH_3)_3]_2$, have been prepared by the reaction of $Hg[Si(CH_3)_3]_2$ with $(\eta\text{-}C_5H_5)_2ZrCl_2$ in refluxing benzene (110).

$$(\eta\text{-}C_5H_5)_2ZrCl_2 \xrightarrow[C_6H_6/5d/reflux]{Hg(SiMe_3)_2} \underset{58\%}{(\eta\text{-}C_5H_5)ZrCl[Si(CH_3)_3]} + \underset{11\%}{(\eta\text{-}C_5H_5)_2Zr[Si(CH_3)_3]_2}$$

While $(\eta\text{-}C_5H_5)ZrCl[Si(CH_3)_3]$ was shown to be unreactive toward 1-hexyne (55 - 60°) and CO (350 psi), the Zr-Si bond is cleaved by electrophiles such as Cl_2, HCl and $AlCl_3$.

Gummie, Safarik and Strausz (111) have reported evidence for the cross disproportionation of trimethylsilyl radicals generated by the room temperature photolysis of $Hg(SiMe_3)_2$ vapor. The ratio $k_c/k_d = 0.05 \pm 0.01$ and is independent of N_2 pressure up to 200 torr. Photolysis in the presence of a hydrogen donor, such as $HSiR_3$, leads to hydrogen abstraction by $Me_3Si\cdot$

$$[Me_3Si]_2Hg \xrightarrow[\lambda \geq 300nm]{h\nu} 2\,Me_3Si\cdot + Hg^o$$

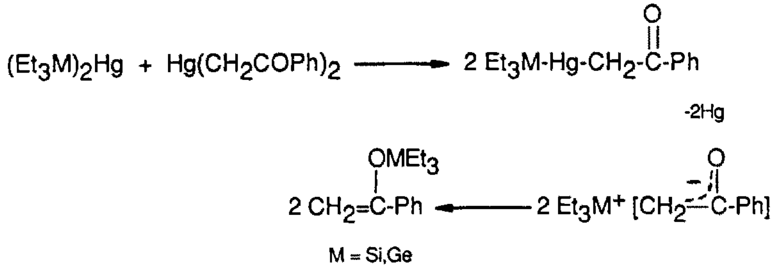
$$2\,Me_3Si\cdot \xrightarrow{k_c} Me_3Si\text{-}SiMe_3$$

$$2\,Me_3Si\cdot \xrightarrow{k_d} Me_3SiH + Me_2SiCH_2$$

$$[Me_3Si]_2Hg \xrightarrow{\text{wall}} Me_3SiOSiMe_3 + Hg^o$$

The reactions of $Hg(SiEt_3)_2$ and $Hg(GeEt_3)_2$ with α-mercurated ketone and α-bromoketone have been investigated (112). The exchange reaction of α-mercury bisacetophenone with $Hg(SiEt_3)_2$ and $Hg(GeEt_3)_2$ in THF at 65°C results in a high yield of the corresponding O-substituted enol ethers (Scheme 19).

Scheme 19 (45)



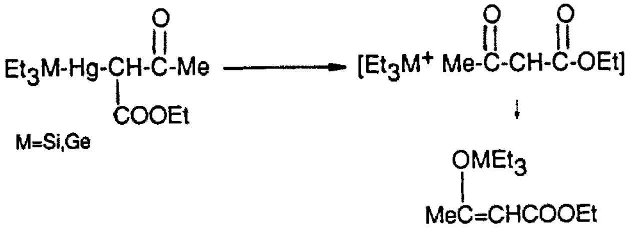
$$(Et_3M)_2Hg + Hg(CH_2COPh)_2 \longrightarrow 2\,Et_3M\text{-}Hg\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}Ph$$

$$\xrightarrow{-2Hg}$$

$$2\,CH_2{=}\overset{OMEt_3}{\overset{|}{C}}\text{-}Ph \longleftarrow 2\,Et_3M^+\,[CH_2 \overset{-}{=} \overset{O}{\overset{\|}{C}}\text{-}Ph]$$

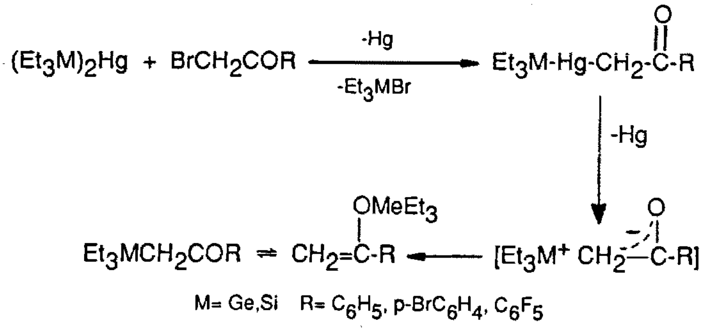
M = Si,Ge

With $Hg(GeEt_3)_2$ a mixture of both O- and C- derivatives is obtained in a ratio of 86 : 14. Reaction of equimolar amounts of α-mercury biscyclohexanone and $Hg(SiEt_3)_2$ or $Hg(GeEt_3)_2$ gives 1-triethylsiloxy-and1-triethylgermoxy-1-cyclohexene, respectively. In THF, reaction with mercury bisacetoacetic ester yields the ethyl ester of B-triethylsiloxycrotonic acid and its germanium analog, respectively.



α-Bromocarbonyl compounds derived from enolizable ketones and aldehydes also react with the mercurials $Hg(MEt_3)_2$ (M = Si,Ge) to give the corresponding silyl or germyl enol ethers in high yield (Scheme 20). However, reactions involving $Hg(GeEt_3)_2$ again yield mixtures of O- and C-germylated products.

Scheme 20 (45)

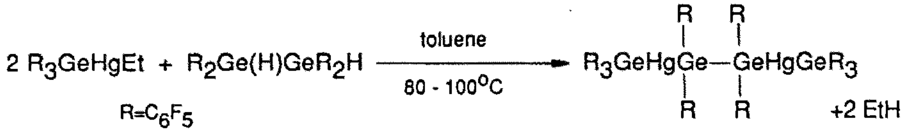


The reactivity of the α-bromoacetophenones is ehanced by a decrease in the electron-donating ability of the aromatic ring in the order:

$$BrCH_2COC_6H_5 < BrCH_2COC_6H_4Br\text{-}p < BrCH_2COC_6F_5$$

With α,α′-dibromoketones, enol ethers having bromine bound to the sp^3carbon atom are formed.

1,1,2,2-Tetrakis(pentafluorophenyl)digermane (113) reacts with ethyl[tris(pentafluorophenyl)germyl]mercury to give the stable oligomeric germylmercury compound **113**.



$$2\,R_3GeHgEt + R_2Ge(H)GeR_2H \xrightarrow[80-100^{o}C]{toluene} R_3GeHg\overset{R}{\underset{R}{Ge}}-\overset{R}{\underset{R}{Ge}}HgGeR_3 \quad +2\,EtH$$

$R=C_6F_5$

113

Reaction of **113** with $Pt(PPH_3)_3$ results in the addition of two equivalents of platinum to give **114** for which the actual atomic arrangement is not known.

$$[R_3GeHgGeR_2\text{-}]_2 + PtL_3 \xrightarrow[20^{o}C]{benzene} R_3GePtL_2HgGeR_2GeR_2\text{-}HgPtL_2GeR_3 + L$$

$L=PPh_3$ 114

Reaction of **113** with $Pd(PPh_3)_3$ also appears to give a palladium containing oligomer. A ploymetallic compound (114) with a Pt-Ge-Ge-Hg chain was obtained in the reaction of Et_2Hg with the mixed dihydride **115**.

$$HPtL_2Ge(C_6F_5)GeC_6F_5H + Et_2Hg \xrightarrow[50-60^{o}C]{benzene} HPtL_2Ge(C_6F_5)Ge(C_6F_5)HgEt$$

115 $(L=PPh_3)$ $+ EtH\cdot$

Ionic germylmercury complexes of praseodymium (115) have similarly been prepared by the hydride method from the reaction of $(t\text{-}BuO)PrCl_2\cdot THF$, $(t\text{-}BuO)_3Pr$ and $[(Me_3Si)_2N]_3Pr$ with $(C_6F_5)GeH$ in the presence of $[(C_6F_5)_3Ge]_2Hg$ at 50-55^{o} in dimethoxyethane.

$$(t\text{-}BuO)PrCl_2 + (C_6F_5)_3GeH + [(C_6F_5)_3Ge]_2Hg \xrightarrow{DME} t\text{-}BuOH +$$

$$\{[(C_6F_5)_3Ge]_3Hg\}PrCl_2\cdot 3DME$$

78%

$$\text{(t-BuO)}_3\text{Pr} + 3\,(\text{C}_6\text{F}_5)_3\text{GeH} + 2\,[(\text{C}_6\text{F}_5)_3\text{Ge}]_2\text{Hg} \xrightarrow{\text{DME}} 3\,\text{t-BuOH} + \underset{68\%}{\{[(\text{C}_6\text{F}_5)_3\text{Ge}]_7\text{Hg}_2\}\text{Pr}\cdot 3\text{DME}}$$

$$[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Pr} + (\text{C}_6\text{F}_5)\text{GeH} + [(\text{C}_6\text{F}_5)_3\text{Ge}]_2\text{Hg} \xrightarrow{\text{DME}} \underset{82\%}{\{[(\text{C}_6\text{F}_5)_3\text{Ge}]_6\text{Hg}_2\}\text{PrN}(\text{SiMe}_3)_2\cdot 3\text{DME}}$$

Reaction of $\text{Hg}[\text{Ge}(\text{C}_6\text{F}_5)_3]_2$ with thallium metal in dimethoxyethane gives mercury (33%) and the thallium derivative ,**116**, for which IR spectral data suggests the ionic structure $\{[(\text{C}_6\text{F}_5)_3\text{Ge}]_3\text{Hg}\}^-\text{Tl}^+\cdot 1.5\text{DME}$ (116).

$$3\,[(\text{C}_6\text{F}_5)_3\text{Ge}]_2\text{Hg} + \text{Tl} \xrightarrow[95^\circ\text{C, 5h}]{\text{DME}} 2\,\underset{116}{[(\text{C}_6\text{F}_5)_3\text{Ge}]_2\text{Hg}^-\cdot\text{Tl}^+\text{Ge}(\text{C}_6\text{F}_5)_3\cdot 1.5\text{DME}} + \text{Hg}^0$$

Reaction of bis(dimethylphenylsilyl)mercury with lithium or potassium in hexane or benzene gave mercury and complexes **117** and **118**, respectively (117). Complex

$$\underset{\text{M=Li(117), K(118)}}{[\text{C}_6\text{H}_5(\text{CH}_3)_2\text{Si}]_2\text{Hg} + \text{M}} \rightleftharpoons 1/2\,\underset{117\text{ , }118}{[\text{C}_6\text{H}_5(\text{CH}_3)_2\text{Si}]_4\text{HgM}_2} + 1/2\ \text{Hg}$$

118 was was also prepared by transmetallation of **117** with K in benzene. If M= Li

$$[\text{PhMe}_2\text{Si}]_2\text{HgLi}_2 + \text{K} \xrightarrow{\text{benzene}} [\text{PhMe}_2\text{Si}]_2\text{HgK}_2$$

and cyclopentane is used as the solvent **117** as well as $[\text{C}_6\text{H}_5(\text{CH}_3)_2\text{Si}]_3\text{HgLi}$ are formed. Some reactions of the complexes follow:

$$[PhMe_2Si]_4HgLi + 2\,(C_2H_5)_4NI \xrightarrow[20^oC,1h]{toluene} [PhMe_2Si]_4Hg[N(C_2H_5)_4]_2 + 2\,LiI$$

$$117,118 + 2\,(Me)_2Si(H)Cl \longrightarrow [(C_6H_5)Me_2Si]_2Hg + 2MCl + PhMe_2SiSiMe_2H$$

$$117 + 2\,CH_3CO_2H \longrightarrow 2\,CH_3CO_2Li + 2\,PhMe_2SiH + [(PhMe_2Si)_2Hg]$$

$$\Big\downarrow \text{1 day}$$

$$Hg + PhMe_2SiOAc + PhMe_2SiH$$

8. COMPLEXES OF MERCURIALS AND ORGANOMERCURIALS:

A. Complexes of Organomercurials

Bis(trichlorovinyl)mercury form isolable 1:1 complexes with 2,2′-bipyridyl, 1,2-bis(diphenylphosphino)ethane, 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline, and 3,4,7,8-tetramethyl-1,10-phenanthroline (118). They are the first reported examples of bis(alkenyl)mercury complexes. Although no complexes could be isolated with pyridine, 2,4,6-trimethylpyridine, thiophene, N,N,N′,N′-tetramethylethane-1,2-diamine, triphenylphosphine or 2,5-dithiahexane, ^1H NMR data did indicate the presence of a weak ligand-mercury interaction in solution. On the basis of infrared, ^1H NMR, ^{35}Cl NQR and mass spectral data it was concluded that the acceptor properties of $(Cl_3C_2)_2Hg$ are intermediate between that of $(C_6H_5)_2Hg$ and $(C_6F_5)_2Hg$.

Bis[methylmercury(II)] complexes with dithiol ligands, having stoichiometry $[Hg_2Me_2L]$, where L= trans-1,2-dimercaptocyclohexane, 3,4-dimercaptotolune and endo-cis-2,3-dimercapto-bicyclo[2.2.1]heptane, have been prepared (119). Both solution NMR studies and a crystal structure determination of trans-1,2-dimercaptocyclohexanebis[methylmercury(II)] , $[\,Hg_2Me_2(S_2C_6H_{10})]$,(see Figure 11), indicate chelation of the dithiol with mercury.

Dutta and Sutapathi (120) have reported the preparation of a series of phenylmercury(II) compounds from pyridine- and quinoline-carboxylic acids , [PhHg(Pic), $C_6H_5Hg(Nic)$ and $C_6H_5Hg(Quin)$, (PicH = picolinic acid, NicH = nicolinic acid and

QuinH = quinolinic acid)]. The compounds, prepared by reacting PhHgOAc with an equivalent amount of the acid in hot ethanol, exhibit linear two coordination about mercury. PhHg(Pic)(PicH), prepared by reacting picolinic acid with PhHgOAc or basic $PhHgNO_3$ in ethanol, is suggested to be 5-coordinate with the carboxylic hydrogen hydrogen-bonded to the oxygen of the CO_2 group of the picolinate ligand. The complex [PhHg(Dipic)HgPh] has also been prepared from the reaction of PhHgOAc with one equivalent of dipicolinic acid in a 1:1 ethanol-water mixture however its structure is not known. The complex $[C_6H_5Hg(Nic)HgC_6H_5]NO_3$ was prepared by reaction of equivalent amounts of basic phenylmercuric nitrate and nicotinic acid in hot ethanol and exhibits a binuclear structure with one PhHg(II) coordinated to the heterocyclic nitrogen and the second PhHg(II) unit bound to the carboxylic group. N-Phenylmercury-adenine has been prepared by the reaction of PhHgOH or PhHgOAc with adenine in water at room temperature.(121)

Both dialkylmercury (R_2Hg) and tetraalkyl metal compounds (R_4M) of the group 4A elements (M=Pb,Sn,Ge and Si) have been shown to form weak charge-transfer complexes with iodine in carbon tetrachloride (122). Selected data for the complexes are presented in Table 20. The complexes are weak with formation constants, K, that are generally less than 5 M^{-1} for the dialkylmercury compounds.

$$R_2Hg + I_2 \rightleftharpoons R_2HI_1$$

The frequency of the charge-transfer bands ($h\nu_{CT}$) varies linearly with the vertical ionization potential with a slope of 0.43 for dialkylmercury.

$$h\nu_{CT} = mI_D + \text{constant}$$

The deviation of the slope from unity indicates variability in the separation, $r_{DA,}$ in the charge-transfer complexes of R_2Hg and the magnitude of r_{DA} is determined by the steric properties of the alkyl metal. The steric effects have been evaluated by two methods. In the direct method, the role of steric effects in determining the charge transfer transition energy is associated with the coulombic term (e^2/r_{DA}) in the first-order treatment of weak complexes according to the Mulliken theory. The mean separation r_{DA} calculated from measured values of ν_{CT}, I_D and the vertical electron affinity of iodine are found to increase with decreasing values of the ionization potentials in a manner analogous to that observed for the charge transfer complexes of tetracyanoethylene (TCNE) with the same series of alkyl metals. By an indirect method, the steric effects are evaluated relative to Me_3Hg with the difference ΔE, taken as the relative change in steric effects, being virtually the same in both the TCNE and iodine complexes. Formation constants for the charge-transfer complexes of iodine with these same alkylmetal compounds have been measured in methylene chloride (123), however, for the dialkyl mercury compounds, the side reaction leading to iodinolysis is very rapid in methylene chloride . As a result, the change in iodine absorbance due to complex formation could not be clearly distinguished from that due to further reaction thereby frustrating efforts to measure the formation constants in this medium. On the other hand, the rate constants for iodinolysis of dialkyl mercury compounds at 25°C (124) were , on the other hand, measured in carbon tetrachloride and are presented below. The rates were too fast to measure in methylene chloride.

Compound	rate constant k, M-1s^{-1}
Me_2Hg	7.8×10^{-4}
EtHgMe	6.5×10^{-2}
n-Pr_2Hg	0.63
n-Bu_2Hg	0.62
i-Pr_2Hg	0.26

TABLE 20

Selected Data on the Charge Transfer complexes of AlkylMercury compounds and Iodine. (122)

Compound	$h\nu_{CT}$,eV	$^aK,M^{-1}$	εK, x $10^2M^{-2}cm^{-1}$	$\varepsilon,M^{-1}cm^{-1}$	ε^2/r_{DA},eV	r_{DA},Å
Me_2Hg	4.17	0.07	7.5	1.1×10^4	3.56	4.04
EtHgMe	3.93	0.63	13.3	2.1×10^3	2.96	4.35
n-Pr_2Hg	3.73	1.5	18.7	1.3×10^3	2.96	4.86
n-Bu_2Hg	3.72	4.7	27.9	5.9×10^2	3.03	4.75
i-Bu_2Hg	3.77	4.5	25.3	5.6×10^2	2.93	4.91

^{a}Calculated for the εK values presented

Fukusumi, Wong and Kochi (125) have compared the electron transfer rate constants for the alkylmetals, R_4M (M= Sn, Pb) and R_2Hg with tris(1,10-phenanthroline)iron(III), hexachloroiridate(IV) and tetrachanoethylene (TCNE). Electron transfer from the alkylmetals to FeL_3^{3+} (L= 1,10-phenanthroline) follows the Marcus correlation with the predicted slope, α=0.5, for an outer-sphere mechanism. However, both $IrCl_6^{2-}$ and TCNE show deviations which vary with the steric bulk of the alkylmetal, indicative of an inner sphere mechanism. An inner sphere mechanism for these latter cases are further indicated by election-transfer rates which can be $10^7 - 10^9$ times faster than those predicted by the Marcus equation.

The anoidic peak potentials in the irreversible cyclic voltammograms of various homoleptic alkyl metals (R_4Si, R_4Ge, R_4Sn and R_2Hg) in acetonitrile exhibit a linear correlation with their ionization potentials I_D as determined in the gas phase (126). The most significant feature of the correlation is the insensitivity to ligand steric effects. Increased branching at either the α or β carbon leads to minimum deviations from the correlation line. The mechanism of the heterogeneous electron transfer is thus described as an outer-sphere process which depends only on the driving force for the one electron oxidation.

Stone, Camiciole and Baird (127) have examined the reactions of dimethylmercury in a high-pressure chemical ionization source using methane as the reagent gas. Ionization of $(CH_3)_2Hg$ at low methane pressures (0.1 - 3 torr) gives CH_5^+ and $C_2H_5^+$ as the major ions. In the presence of $\sim 2 \times 10^{-5}$ torr of $(CH_3)_2Hg$ at 0.1 torr produced CH_3Hg^+ and $(CH_3)_2HgH^+$ in roughly equal amounts. Increasing the total pressure and/or increasing the concentration of $(CH_3)_2Hg$ led to the appearance of the $(CH_3)_3Hg_2^+$ ion. Both $(CH_3)_2Hg^+$ and $(CH_3)_2HgH^+$ react with $(CH_3)_2Hg$ to give $(CH_3)_3Hg_2^+$. The $(CH_3)_3Hg_2^+$ ion is a methylmercury cation donor and leads to formation of complexes containing the $(CH_3)Hg^+$ moiety. For example, $(CH_3)_3Hg_2^+$ reacts with benzene to afford $CH_3HgC_6H_6^+$

$$(CH_3)_3Hg_2^+ + C_6H_6 \longrightarrow CH_3HgC_6H_6^+ + (CH_3)_2Hg$$

The dissociation energy of the complex is ~100kJ mole^{-1}, which implies the

TABLE 21 (128)

The Adducts 119a - 119e $(CF_3CO_2)_2Hg \cdot L$

Com- pound	L	Yield %	Decomp. temp., °C	Found, %		Formula	Calculated, %	
				Hg	element		Hg	element
119a	$P(C_6H_5)_3$	84	184-185	28.59 29.14	P 4.28 4.36	$C_{22}H_{15}F_6HgO_4$	29.21	P 4.51
119b	$N(C_2H_5)_3$	67.5	94-95	38.44 38.25	N 2.32 2.54	$C_{10}H_{15}F_6HgO_4$	38.18	N 2.65
119c	$(CH_3)_2S$	65	174-175	40.63 41.01	S 6.28 6.41	$C_6H_6F_6HgO_4S$	41.15	S 6.56
119d		15	139-140	39.57 39.17	—	$C_8H_8F_6HgO_4$	39.11	—
119e	$(CH_3)_2S{=}O$	32	229-230	39.36 39.62	S 6.17 6.27	$C_6H_6F_6HgO_5S$	39.93	S 6.36

(Beproduced with permission from Plenum Publishing Corporation copyright 1979) existence of a bond that is much stronger than that expected due to simple electrostatic attraction. A series of complexing agents was studied and the order of stability for the complexes found was;

$$(C_2H_5)_3N > (C_2H_5)_2NH \gg i\text{-}C_3H_7C_6H_5 > C_2H_5C_6H_5 >$$
$$CH_3C_6H_5 > C_6H_5I > C_6H_6 > C_6H_5Br > C_6H_5Cl > C_6H_5F$$

and studies with olefins gave the order

cycloheptatriene > cis-1,3-pentadiene > cyclohexene > benzene

B. HgX_2 Complexes:

Mercury trifluoroacetate, unlike mercuric acetate, has been shown to be analogous to $HgCl_2$ in its ability to form adducts , **119a-e**, with electron-donor ligands (Table 21) (128).

$$Hg(O_2CCF_3)_2 + L \longrightarrow \underset{\text{119e-a}}{(CF_3CO_2)_2Hg \cdot L}$$

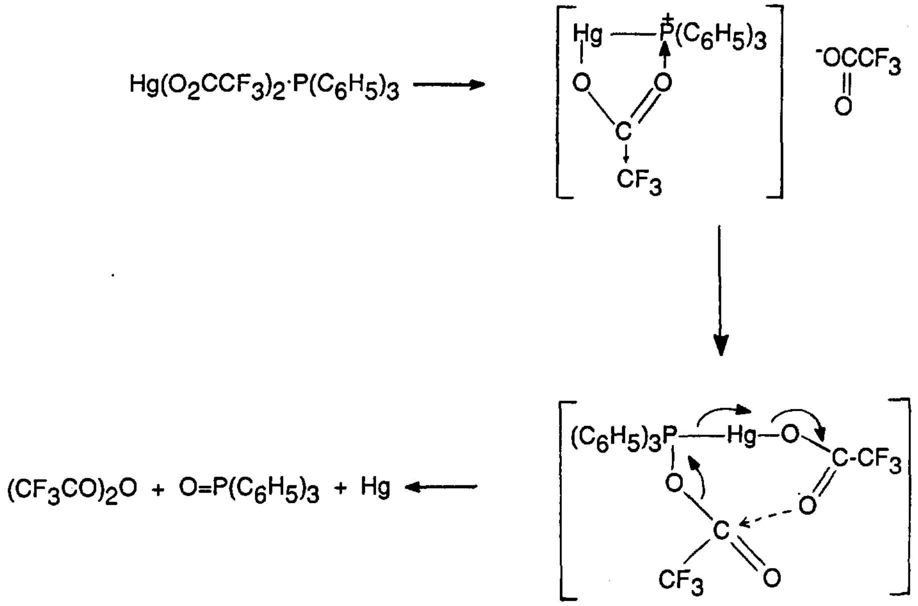
L= $(C_6H_5)_3P$ (a) ; $N((C_2H_5)_3$ (b) ; $(CH_3)_2S$ (c) ;
O O (d) ; $(CH_3)_2S{=}O$ (e)

With the exception of compounds **119b** the compounds are all quite stable at room temperature. When heated, compounds **119c-e** decompose into their original components and **119a** decomposes in accordance with Scheme 21. The adduct **119b** on the other hand decomposes by the above scheme both at room temperature and when heated. $Hg(O_2CCF_3)_2$ also reacts with $P(OEt)_3$ to give **120** via a typical Arbuzov rearangement:

$$Hg(O_2CCF_3)_2 + P(OC_2H_5)_3 \longrightarrow [\,(C_2H_5O)_3\text{-}P\text{—}HgO_2CCF_3\,]\,{}^{-}O_2CCF_3$$

$$(C_2H_5O)_2P(O)O_2CCF_3 + Hg \longleftarrow C_2H_5O_2CCF_3 + (C_2H_5O)_2P(O)HgO_2CCF_3$$

Scheme 21



Fukuzumi and Kochi (129) have studied the influence of the ligand X on the reactivity of mercury(II) derivatives, HgX_2, as electrophiles in the cleavage of two tetraalkyl tin compounds in methylene chloride.

$$HgX_2 + R_4Sn \longrightarrow R_3SnX + RHgX$$

$R = CH_3, n\text{-}C_4H_9$
$X = Cl, Br, CN, O_2CR'_3$

In each case the rate of electrophilic cleavage, as measured by the disappearance of Hg(II), followed second order kinetics. The second order rate constants for Me_4Sn and $n\text{-}Bu_4Sn$ span a range of more than 10^5 and depend on the mercury(II) electrophile. Mercuric bromide is the least reactive and mercury trifluoroacetate the most reactive in qualitative agreement with their Lewis acidity.

Mercury(II)cyanide and thiocyanate form 1:1 complexes with benzo(f)quinoline. (130). The complexes Hg(benz)$(CN)_2$ and Hg(benz)$(SCN)_2$, (benz=benzo(f)-quinoline) are monomeric neutral species exhibiting a three coordinate trigonal planar environment about mercury in the solid state. The benzo(f)quinoline is coordinated through the pyridine ring nitrogen and in the thiocyanate complex S-bonded SCN groups are indicated.

The 2-, 3- and 4-benzoylpyridine complexes of $HgCl_2$, $HgBr_2$, $Hg(CN)_2$ and $Hg(SCN)_2$ have also been prepared (Table 22) (131). The 1:2 complexes, $HgCl_2{\cdot}L_2$, (L= 3-BP, 4-BP ; BP= benoylpyridine), are monomeric in the solid state with four-coordinate tetrahedral structures. The 1:1 complexes, $HgCl_2$(2-BP) and $HgBr_2{\cdot}L$, (L= 2-BP, 3-BP, 4-BP) , are believed to be monomeric three-coordinate structures with terminal cyanide groups and nitrogen of the organic ligand around the mercury atoms in the solid state. $Hg(SCN)_2$ also gave monomeric 3-coordinate complexes with 3- and 4-benzoyl pyridine and exhibiting S-bonded thiocyanate groups.

The 1,1-dipyrazolylcycloalkane complexes of the type MLX_2, ML_2X_2, $MLX_2{\cdot}H_2O$ and $MLX_2{\cdot}2H_2O$, [M= Co(II) , Ni(II), Zn(II), Hg(II) ; L= 1,1-dipyrazolylcyclobutane (but) , 1,1-dipyrazolylcyclopentane (pent) , 1,1-dipyrazolylcyclohexane (hex) , 1,1-dipyrazolylmethylcyclohexane (mhex)], have been isolated (100). The mercury complexes, $HgCl_2$(but), $HgCl_2$(pent), and $HgCl_2$(hex) have been obtained in 33%, 65%, and 34% yields, respectively, and ^1H NMR data show the pyrazolyl rings to be equivalently coordinated to mercury.

The complexes $C_5H_5M(CO)(NO)(PPh_3){\cdot}HgCl_2$, (M=Mo, W), are produced upon addition of an equimolar quantity of $HgCl_2$ to red solutions of the complexe C_5H_5M-$(CO)(NO)(PPh_3)$ in methylene chloride. (133)

Grim,Samuel and Walton (134) have prepared and characterized several compounds of the monoselenide derivative of bis(diphenylphosphino)methane including $[(C_6H_5)_2P(Se)CH_2P(C_6H_5)_2]HgX_2$ where X=Cl,Br, and I.The phosphorus-selenium coupling constants were found to decrease by about 100± 10 Hz upon chelation in $(dppmSe)HgBr_2$ compared to the decrease of 130 ± 10 Hz in the monodentate ligand complexes $(n\text{-}Bu_3PSe)_2MX_2$ where M=Cd or Hg and X=Cl, Br, or I.

C. Structures of Mercurial Complexes

Structure of $Hg(NO_3)_2(PPh_3)_2$:

(Figure 7) (135). The mercury exhibits a highly distorted tetrahedral environment. Relavant structural data reported are : Hg-P = 2.451(1)Å ; Hg-O = 2.507(4)Å ; P-Hg-P = 131.8(1)° ; O-Hg-O = 70.0(2)°.

TABLE 22 (131)

Analytical and i.r. spectral data (cm^{-1})

Compound	m.p. (C)	Molecular weight (calculated)	Metal (%) (calculated)	Anion (%) (calculated)
2-BP				
$Hg(2\text{-}BP)Cl_2$	138	452 (454)	44.1 (44.0)	15.6 (15.6)
$Hg(2\text{-}BP)Br_2$	127	433 (433)	37.0 (37.0)	29.4 (29.5)
$Hg(2\text{-}BP)(CN)_2$	239	376 (435)	46.2 (46.0)	
3-BP				
$Hg(3\text{-}BP)_2Cl_2$	132	504 (637)	31.0 (30.9)	11.1 (11.0)
$Hg(3\text{-}BP)Br_2$	170	585 (543)	37.0 (37.0)	29.8 (29.5)
$Hg(3\text{-}BP)_2(CN)_2$	88	569 (618)	32.5 (32.4)	
$Hg(3\text{-}BP)(SCN)_2$	90	insol.	40.2 (40.1)	23.5 (23.3)
4-BP				
$Hg(4\text{-}BP)_2Cl_2$	131	597 (637)	31.0 (30.9)	11.1 (11.0)
$Hg(4\text{-}BP)Br_2$	172	519 (543)	36.9 (36.8)	29.0 (29.5)
$Hg(4\text{-}BP)(CN)_2$	80	457 (435)	46.2 (46.0)	
$Hg(4\text{-}BP)(SCN)_2$	110	insol. (40.1)	40.2 (23.3)	23.5

TABLE 22 (Cont.) (131)

Analytical and i.r. spectral data (cm^{-1})

Compound	νC=O	$\nu C\overset{\cdots}{-}N$ $\nu C\overset{\cdots}{-}N$	Ring vibrations	νM-X	
2-BP	1654	1590	990,603,401		
		1562			
Hg(2-BP)Cl_2	1656	1615	1016,630,416		298
		1585			
Hg(2-BP)Br_2	1647	1615	1015,626,416		230
		1585			
Hg(2-BP)$(CN)_2$	1650	1605	1019,640,410	νCN	2180
		1590		νHg-C	423
				δHgCN	328
3-BP	1657	1590	999,601,402		
		1563			
Hg$(3\text{-}BP)_2Cl_2$	1658	1616	1024,615,418		299
		1595			
Hg(3-BP)Br_2	1645	1615	1021,630,415		240
		1600			
Hg$(3\text{-}BP)_2(CN)_2$	1660	1616	1027,630,415	νCN	2180
		1598		νHg=C	420
				δHgCN	330
Hg(3-BP)$(SCN)_2$	1658	1620	1027,630,425	νCN	2136
		1590		νCS	695
				δSCN	443
					429
				νHg-SCN	297
4-BP	1655	1570	998,601,405		
		1557			
Hg$(4\text{-}BP)_2Cl_2$	1655	1595	1020,619,432		298
		1579			
Hg(4-BP)Br_2	1661	1600	1028,640,430		225
		1585			
Hg(4-BP)$(CN)_2$	1655	1610	1018,632,418	νCN	2181
		1595		νHg-C	422
				δHgCN	329
Hg(4-BP)$(SCN)_2$	1652	1618	1020,618,425	νCN	2138
		1598		νCS	700
				δSCN	450
					432
				νHg-SCN	300

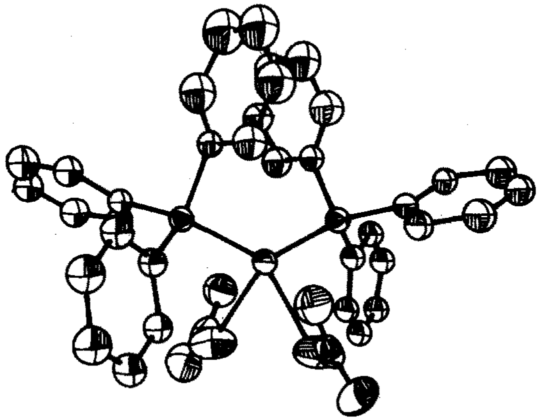


Figure 7. Molecular structure of $Hg(NO_3)_2(PPh_3)_2$. From H. B. Buergi, R. W. Kunz, and P. S. Pregosin, Inorg. Chem., 19 (1980) 3707.

α-Mercuric chloride-tributylphosphine complex:

(Figure 8) (136) . The crystal is composed of pairs of dimers weakly linked together into a tetrameric arrangement. There are a total of six unique Hg-Cl bridge distances ranging from 2.29 to 3.38Å in length and both four- and five-coordinate mercury atoms are found.

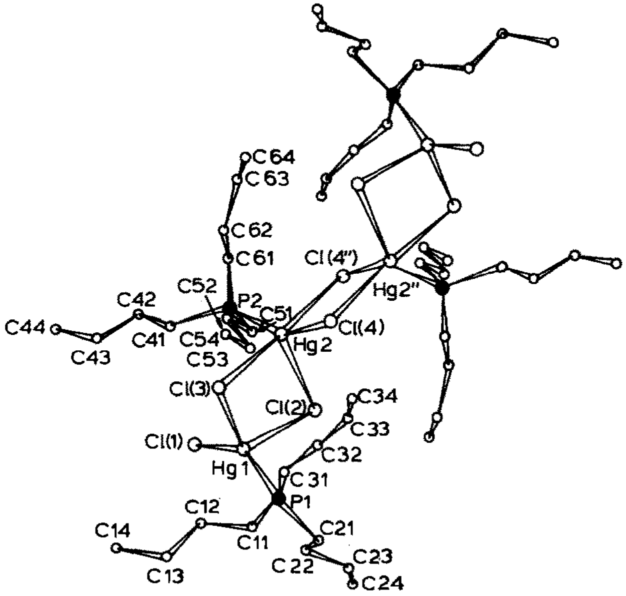


Figure 8. The molecular structure of $HgCl_2(PBu_3)$. From N. A. Bell, M. Goldstein, T. Jones, and I. W. Nowell, Inorg. Chim. Acta, 43 (1980) 87.

Mercury(II)chloride-1,2,5-triphenylphosphole complex:

(Figure 9) (136). The crystal consists of centrosymmetric dimers with mutually trans ligands and an asymmetric $HgCl_2Hg$ bridging unit [Hg-Cl_{brids},- 2.542(13)Å, 2.747(14)Å ; Hg-Cl(2)-Hg, 93.5(4)°]. The mercury is four coordinate, whth bond angles ranging from 86.5 to 127.8°, with the P-Hg-$Cl_{terminal}$ being the largest, and Hg-$Cl_{terminal}$= 2.404(1)Å, Hg-P = 2.438(10)Å and Hg-Hg = 3.855(4)Å.

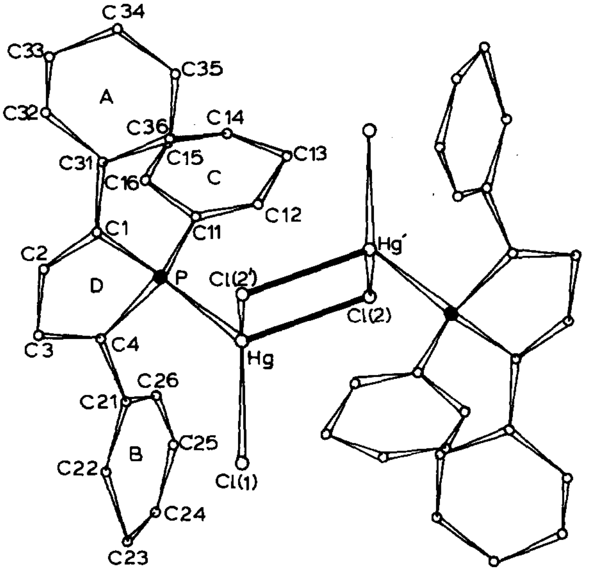


Figure 9. The molecular structure of $HgCl_2$(1,2,5-triphenylphosphole). From N. A. Bell, M. Goldstein, T. Jones, and I. W. Nowell, Inorg. Chim. Acta, 43 (1980) 87.

Mercury(II)chloride-triphenylphosphine complex:

(Figure 10) (136). The crystals consist of centrosymmetric dimers with mutually trans ligands and a nearly symmetric Hg-Cl(2)-Hg bridging unit [Hg-Cl_{brid}= 2.623(8)Å ; Hg-Cl(2)-Hg = 94.6(3)°]. The mercury is four coordinate with bond angles ranging from 85.4 to 128.7°, with the P-Hg-$Cl_{terminal}$angle being the largest, and Hg-$Cl_{terminal}$= 2.370(10)Å , Hg-P = 2.406(7)Å and Hg-Hg = 3.88(3)Å.

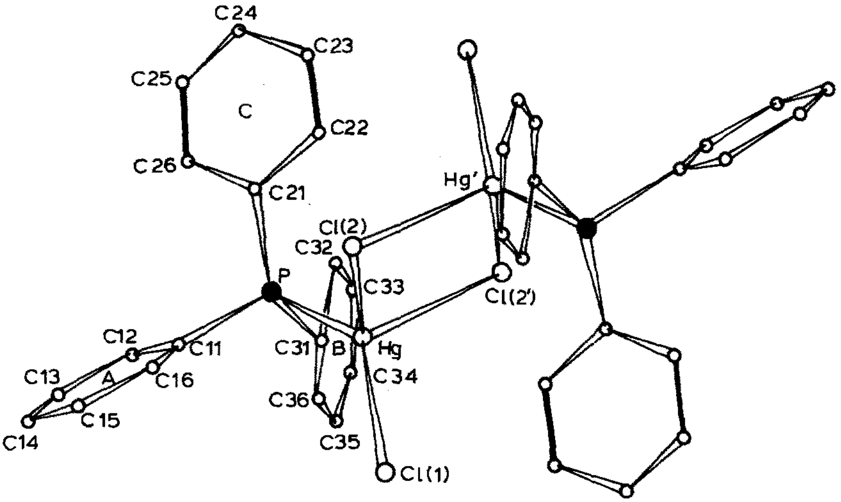


Figure 10. The molecular structure of $HgCl_2(PPh_3)$. From N. A. Bell, M. Goldstein, T. Jones, and I. W. Nowell, Inorg. Chim. Acta, 43 (1980) 87.

Trans-1,2-dimercaptoxyxlohexanebis[Methyl]mercury(II):

(Figure 11) (119). One of the mercury atoms Hg(2), is essentially linearly bonded to

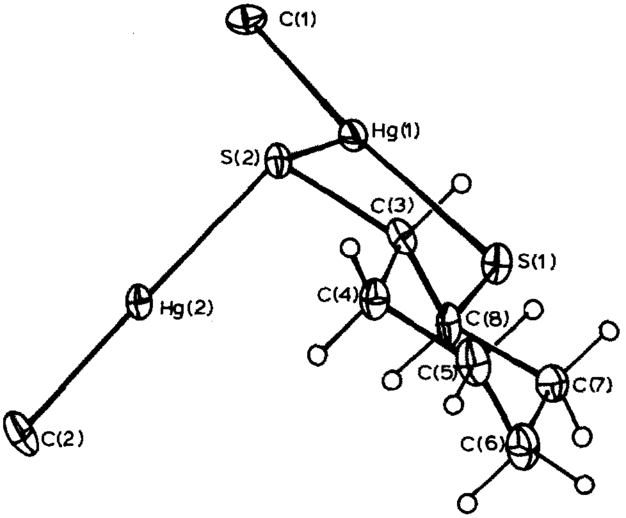


Figure 11. Molecular structure of trans-1,2-dimercaptocyclohexanebis[methylmercury(II)] . From N. W. Alcock, P. A. Lampe and P. Moore, J. Chem. Soc., Dalton, (1980) 1472.

S(2), [S(2)-Hg(2)-C(2) = 177.1(5)^{o} ; Hg-S(2) = 2.363(4)Å ; Hg(2)-C(2) = 2.08(2)Å], whereas the other, Hg(1), is coordinated principally to S(1), [Hg(1)-S(1) =2.367(4)Å ; Hg(1)-C(1) = 2.12(2)Å] but also makes a much easier bond with S(2),[Hg(1)-S(2) = 2.857(3)Å]. as a result, the S(1)-Hg(1)-C(1) angle is significantly distorted from linearity , (i.e 167.8(5)^{o}).

Mercuric Chloride: (3)

In this redetermination by x-ray diffraction, the mercury is linearly co-ordinated [Cl(1)-Hg-Cl(2), 178.9(5)^{o} ; Hg-Cl(1), 2.284(12)Å ; Hg-Cl(2), 2.301 (14)Å] to the two chlorine atoms. Each mercury also participates in four non-bonded interactions; two to Cl(1), (3.37Å and 3.44Å) and two to Cl(2), (3.39Å and 3.48Å).

1,15-Bis(2-bromophenyl)-2,5,8,11,14-pentaoxapentadecane Mercury Dibromide:

(Figure12) (138). The ligand wraps around the cation in a nearly circular manner such that all of the oxygen atoms are coordinated to Hg, [Hg····O, 2.72 - 3.06Å ; O····Hg····O, ~60^{o}], in an almost perfect hexagonal arrangement.

Mercury(II) Sulfate Monohydrate:

(Figure 13) (139). In this reinvestigation of the structure by both x-ray and Neutron diffraction methods, the Hg atom is coordinated to one sulfate oxygen atom and one water molecule forming discrete $HgSO_4 \cdot H_2O$ groups connected by hydrogen bonds [Hg-O(3), 2.179(2)Å (x-ray), 2.191(2)Å (Neutron) : Hg-O(w), 2.228(2)Å, (x-ray), 2.179(2)Å (Neutron)]. Four more distant oxygen atoms of different sulfate tetrahedra complete an irregular oxtahedron around Hg, [Hg-O($2^{I,II}$), 2.50(1)Å (x-ray), 2.503(5)Å (Neutron) ; Hg-O($2^{III,IV}$), 2.514(1)Å (x-ray), 2.507(5)Å (Neutron)]. The water was found to be involved in two normal hydrogen-bonding interactions

(O_W-H····O, 1.902(5)Å, O_W····H-O, 2.264(9)Å) and exhibiting a normal tetrahedral environment.

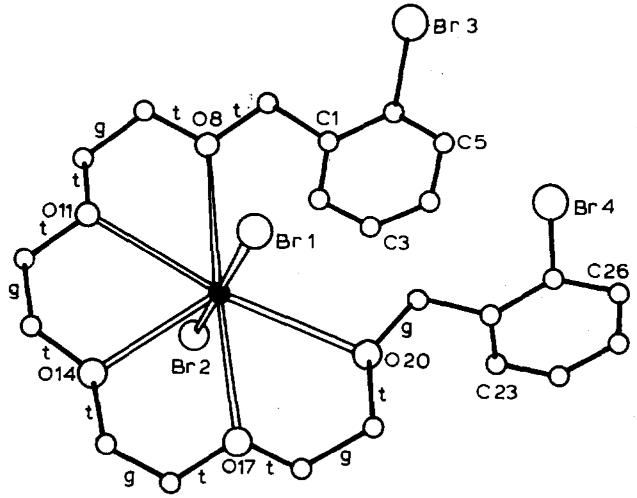


Figure 12 Molecular structure of 1,15-bis(2-bromophenyl)-2,5,8,11,14-pentaoxa-pentadecamercury(II) dibromide. Radii are arbitrary, t and g indicate tortion angles trans or (-)gauche. From G. Weber, Acta Cryst., B36, (1980) 2779.

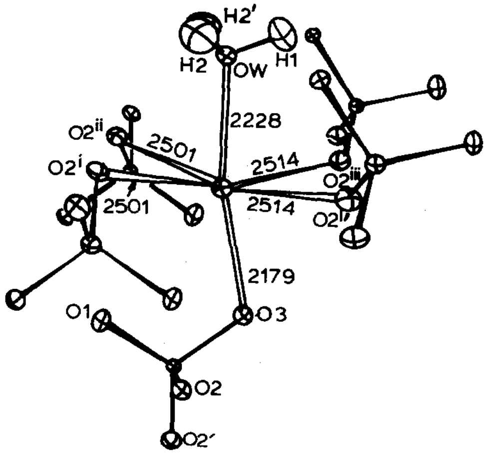


Figure 13. The coordination around the mercury atom in mercury(II) sulfate monohydrate. From C. Stalhandske, Acta Cryst., B36, (1980) 23

Structure of $[Ru_3(CO)_9C_6H_9)HgBr]_2$:

(Figure 14) (77). The tetranuclear metal clusters of three ruthenium and one mercury atom in a butterfly arrangement, are joined by asymmetrical Hg-Br-Hg bridged, (Hg-Br = 2.505(3)Å, 3.084(3)Å ; Br-Hg-Br = 85.9(1)°). The mercury atom bridges Ru(2) and Ru(3) with bond distances of 2.733(2)Å and 2.739(2)Å, respectively, and Ru(2)-Ru(3) distance of 2.900(3)Å.

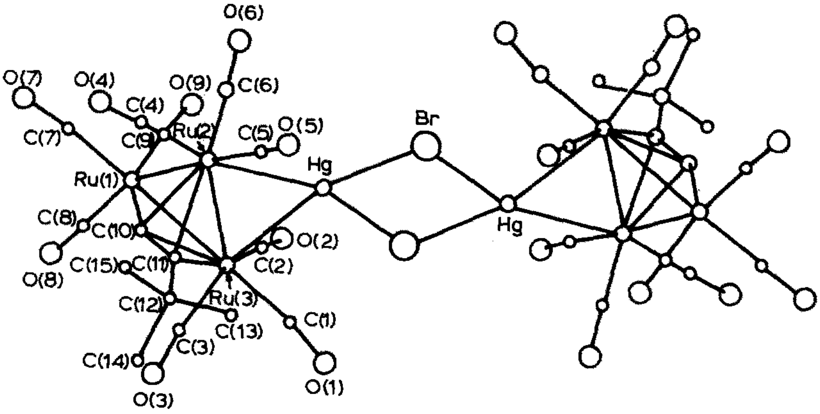


Figure 14. Molecular structure of $[Ru_3(CO)_9(C_6H_9)HgBr]_2$. From R. Fahmy, K. King, E. Rosengerg, A. Tiripicchio, M. T. Camellini, J. Am. Chem. Soc., 102(1980)3626.

Structure of rac-α-(μ-acetato-O,O')-b-(O-acetatomercurio)-cf,de-bis[2-(dimethyl-aminomethyl)-phenyl-N,c]platinum :

(Figure 15) (103). The structure is composed of discrete mononeric units in which platinum is bound to two chelating o-$Me_2NCH_2C_6H_4$ ligands, a mercury atom and an acetato group that bridges the platinum and mercury atoms. Relavant distances and angles include: Pt-Hg= 2,513(1)Å ; Hg-O(1)= 2.62(1)Å ; Hg-O(3)= 2.10(1)Å ; Hg-Pt-N(1)= 90.1(2)° ; Hg-Pt-O(2)= 93.3(2)Å ; Hg-Pt-C(10)= 88.5(3)° ; Pt-Hg-O(1)= 80.5(2)° ; Pt-Hg-O(3)= 172.3(2)° ; O(1)-Hg-O(3)= 103.9(3)°. The Pt-Hg distance, 2.513(1)Å, is as expected for a single Pt-Hg bond. The bridging acetato group is asymmetrically bonded and the Pt,Hg,O(1),O(2),C(19) and C(20) atoms are coplanar [max dev. from planarity= 0.02Å]

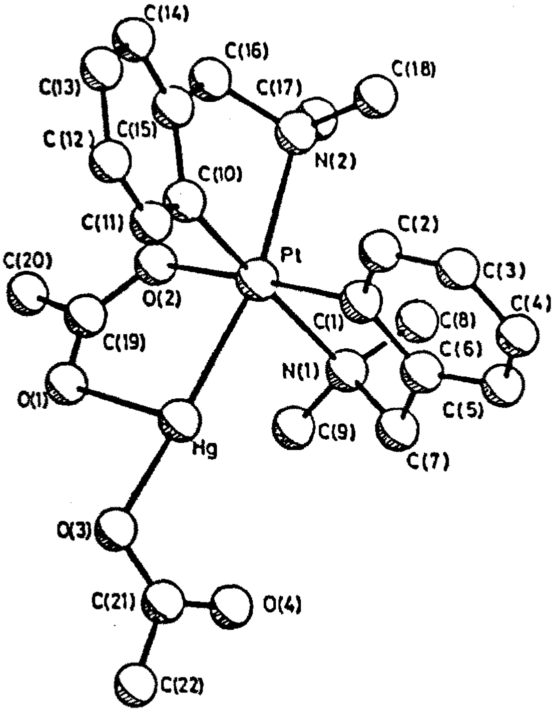


Figure 15. PLUTO drawing of the molecular structure of [(o-Me$_2$NCH$_2$C$_6$H$_4$)$_2$-(μ-MeCO$_2$)PtHg(O$_2$CMe)]. From F. M. Antonius, J. Van Der Ploeg, G. Van Koten and K. Vrieze, J. Chem. Soc., Chem. Comm., (1980) 469.

9. STRUCTURAL STUDIES OF ORGANOMERCURIALS AND RELATED COMPOUNDS:

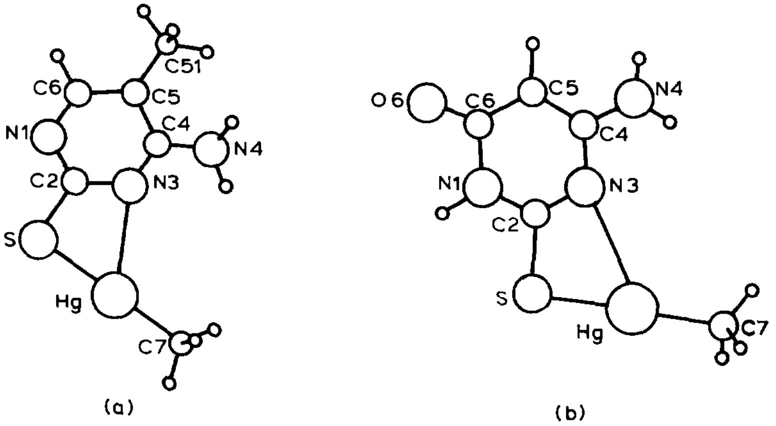
When deciding the effective, as opposed to the characteristic, coordination number for mercury, the value of the van der Walls radius of mercury is of crucial importance. Based on the mercury-mercury distances in metallic mercury, Grdneci [Quart. Rev. Chem. Soc., 19, 303 (1965)] has proposed 1.50Å as the van der Waals radius, but also suggested that distances less than 1.73Å plus the van der Waals radius of a potential donor atom also are indicative of some form of bonding. Based on a consideration of recent crystallographic data, Cany and Deacon (140) have compiled evidence to suggest that the van der Waals radius should lie at the conservative end of the range and hence propose 1.73Å conveniently corresponding to Grdenic's upper limit.

(4-Amino-5-methyl-2-pyrimidine thiolato)methyl mercury(II):

(Figure 16 a) (141). CH_3Hg^+ is bonded to S with a C(7)-Hg-S angle that is essentially linear, 178.6(4)^{o}, and Hg-S and Hg-C(7) distances of 2.393(4)Å, respectively. There is also a secondary intramolecular interaction to N(3), Hg···N(3) = 2.80(2)Å, as well as an additional intermolecular Hg···S interaction of 3.67(2)Å.

(4-Amino-2-mercapto-6-pyrimidinoato)methyl Mercury(II):

(Figure 16b) (141). The CH_3Hg^+ unit is bonded to S with a C(7)-Hg-S angle of 178.6(9)^{o} and Hg-S and Hg-C(7) diatances of 2.380(6)Å and 2.09(2)Å, respectively. There is also a secondary intramolecular interaction to N(3), Hg···N(3) = 2.95(2)Å, as well as intermolecular O····H-N hydrogen bonding of the carbonyl oxygen to an adjacent amino-hydrogen (O····N = 2.76(3)Å).



(a) (b)

Figure 16. The molecular structure of (a) (4-amino-5-methyl-2-pyrimidinethiolato)-methylmercury(II) and (b) (4-amino-2-mercapto-6-pyrimidinonato)methyl-mercury(II). From D. A. stuart, L. R. Nassimbeni, A. T. Hutton, K. R. Koch; Acta Cryst. B 36, (1980) 2227-2230.

Methyl-(I) and Phenylmercury(II) dithizonate(II):

(Figure 17) (142). Both crystals consist of discrete molecules in which the Hg atom exhibits planar, T-shaped geometry, with the dithizone residue acting as a bidentate ligand coordinating through both S and N, The imino proton participates in a weak intramolecular hydrogen bonding interaction, [N(5)H····S = 2.40(9)Å,(I) ; 2.43(8)Å,(II)], which stabilizes the N_2CN_2 chain in an anti, S-trans configuration relative to the formal C=N and C-N bonds. There is a weak secondary intermolecular interaction between the mercury atom and a symmetry related sulfur atom (Hg···S = 3,69(2)Å,(I) ; 3,58(2)Å,(II)]. The approximate overall planarity of the dithizane residue as well as bond distance data suggest marked delocalization of the π-electrons within the N_2CN_2 chain and one of the phenyl rings.

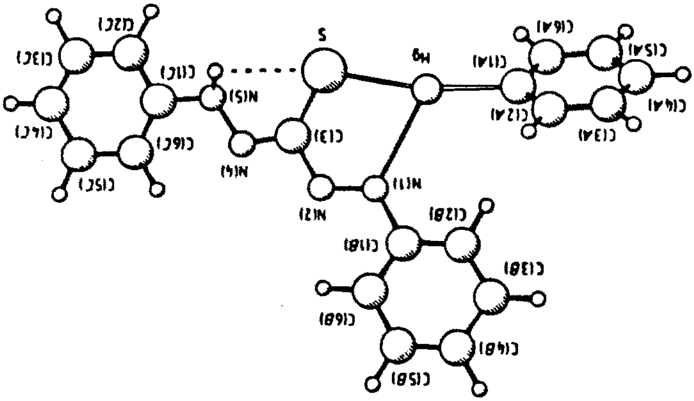


Figure 17. Molecular structure of phenylmercury(II) dithizonate; in methylmercury(II) dithizonate a methyl group replaces phenyl ring A. The dashed line indicates a hydrogen bond. From A. T. Hutton, H.M.N. Irving and L. R. Nassimbeni, Acta Cryst., B 36 (1980) 2064.

Benzamido(phenyl)mercury(II):

(Figure 18) (143). The mercury is two coordinate with Hg-C and Hg-N distances of 2.02(2)Å and 2.04(2)Å, respectively, and a C-Hg-N angle of 179°. A weak intermolecular hydrogen bond (O····N = 3.15(3)Å) is suggested and the relatively small angle of twist, 8(1)°, suggest that the amide group may exist in the enol form.

µ3-(Adeninato-N^3,N^7,N^9)-tris[methylmercury(II)]:

(Figure 19) (144). Ring sites N(3), N(7), and N(9) are linearly coordinated to

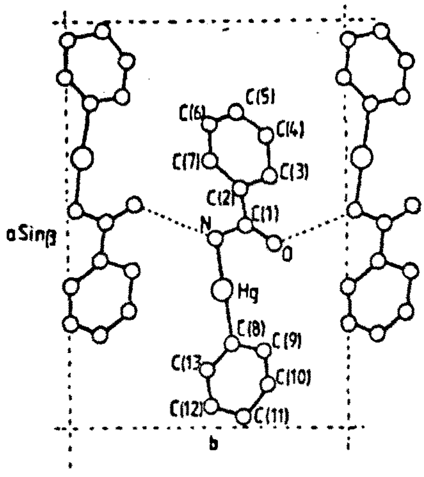


Figure 18. Projection of part of the unit cell of Benzamido(phenyl)mercury(II) along c. From J. Halfpenny, R. W. H. Small, Acta Cryst., B 36 (1980) 2786

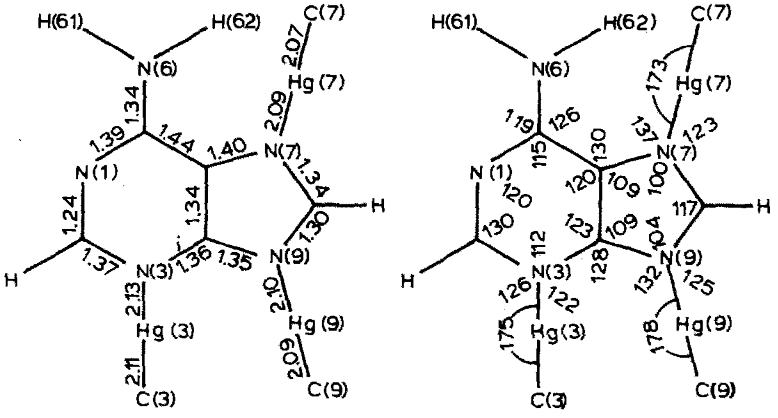
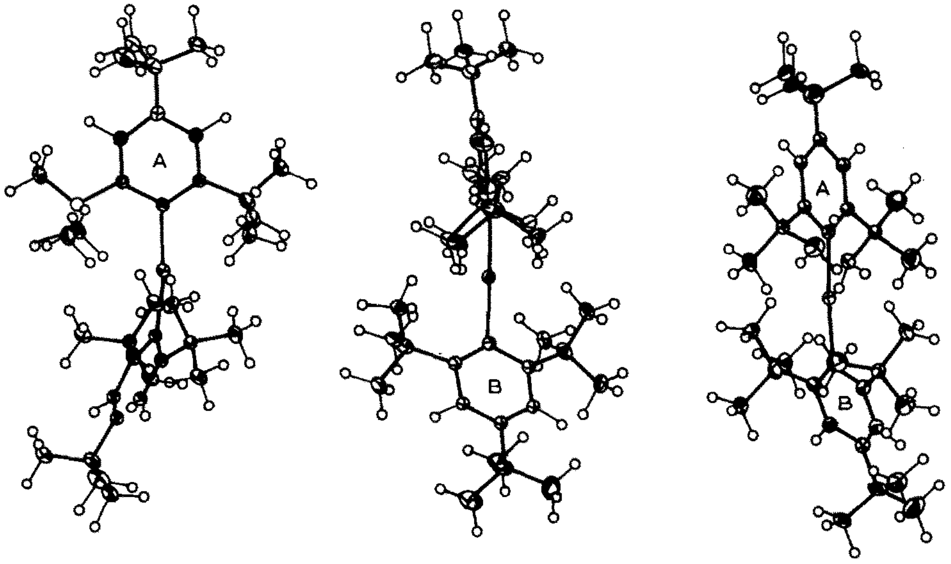


Figure 19. Interatomic distances (Å) and bond angles (°) for μ_3-(adeninato-N^3,N^7, N^9)-tris[methylmercury(II)]. Standard deviations are 0.02 - 0.04 Å on distances and 2° on angles (except N-Hg-C, 1°). From J. Hubert and A. L. Beauchamp, Acta Cryst., B 36 (1980) 2613.

methylmercury groups, ($Hg\text{-}N_{av}$ = 2.11Å ; $Hg\text{-}C_{av}$ = 2.09Å). The [adeninato-$(CH_3Hg)_3$]$^{2+}$ cations are held together by an intricate network of Hg····O contacts with adjacent nitrate oxygens, (Hg····O = 2.62 - 3.02Å).

Bis(2,4,6-tri-tert-butylphenyl)mercury (-155^{o}C):

(Figure 20) (5). The molecule shows considerable distortion from idealized D_{2d} symmetry. The observed distortions are attributed to nonbonded H····H and Hg····H interactions and descriptions of the distortions were developed from idealized molecular parameters. The aryl rings are roughly perpendicular (dihedral angle = 70.8^{o}) with Hg-C distances of 2.077(6)Å and 2.083(6)Å and C-Hg-C angle of 173.4(2)^{o}.



(a) = 0°   (b) = 90°   (c) = 120°

Figure 20. Three perspective views of bis(2,4,6-tri-tert-butylphenyl)mercury with (a) ring A. flat, followed by (b) 90^{o} rotation and (c) 120^{o} rotation of the molecule. Note the severe distortion with ring B. From J. C. Huffman, W. A. Nugent and J. K. Kochi, Inorg. Chem. 19 (1980) 2749.

L-Menthyl ester of α-bromobis(triphenylphosphine)platinum-mercuriphenyl acetic acid:

(Figure 21) (145). The most significant aspect of this structure is the square planar cis-arrangement of the phosphine ligands around platinum. The mercury is linearly coordinated ,(Pt-Hg-C(7) = 176^{o}), with Hg-Pt and Hg-C(2) distances of 2.499(2)Å

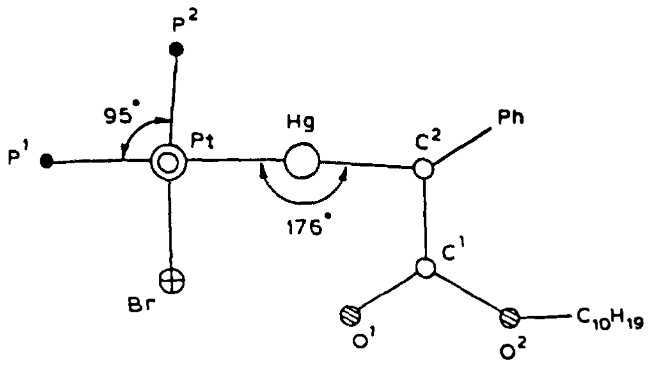


Figure 21. The essential part of the molecular structure of L-menthyl ester of α-bromobis(triphenylphosphine)platinum-mercuriphenyl acetic acid. From G. Z. Suleimanov, V. V. Bashilov, A. A. Musaev, V. I. Sokolov and O. A. Reutov, J. Organomet. Chem., 202 (1980) C61.

and 1.96Å , respectively. The Hg-Pt distance is significantly shorter than previously observed and is atributed to the presence of the alkyl rather than the strongly electron-withdrawing perfluorinated groups found in previous structures.

L-Menthyl ester of S-α-bromomercuriphenyl acetic acid: (145)

The molecules are packed pairwise as dimers inwhich each mercury is essentially linearly coordinated to carbon and bromine,(Hg-C = 2.05Å ; Hg-Br = 2.46Å), with a secondary intermolecular Hg····Br interaction (Hg····Br = 3.23Å). A relatively short Hg-O distance, 3.22Å, as well as a small, 25.8°, dihedral angle between planes favor intramolecular coordination between mercury and oxygen.

trans-Bis(3-dimethylsulfoniocyclopentadienylide)-di-μ-iodo-diiododimercury(II): (Figure 22) (146). The compound is an iodine bridged dimer [$\text{Hg-I}_{\text{bridge}}$= 2.896(1), 3.031(1)Å ; $\text{Hg-I}_{\text{extermal}}$= 2.706(1)Å] with a Hg-C σ-bond licalized at C(13), even though NMR evidence has suggested that in solution some molecules with the σ-bond localized at C(12) also exist. The ylide S-C distance, 1.712(8)Å, is slightly longer than that in the unsubstituted ylide, 1.712(8)Å.

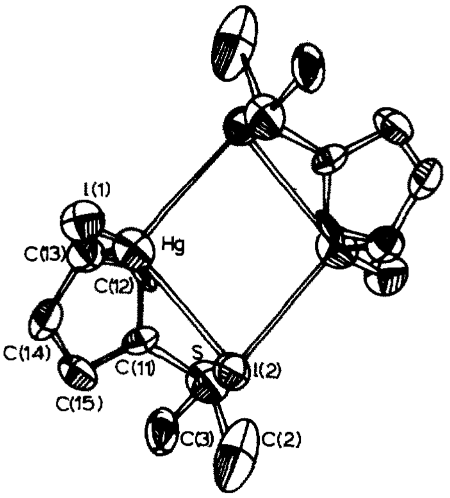


Figure 22 Molecular structure of trans-bis(3-dimethylsulfoniocyclopentadienylide)-di-μ-iodo-diiododimercury(II) [H atoms omitted]. From. N. C. Baenziger and R. M. Flynn, Acta Cryst., B 36 (1980) 1642.

Mercury(II) ethylxanthate:

(Figure 23) (147). The crystals consist of mica-like two dimensional sheets formed by mutual bridging of the Hg(II) and ethyl xanthate ions. The mercury(II) ion is bonded to four sulfur atoms, (Hg-S = 2.417(4) - 2.854(4)Å), which adopts a distorted tetrahedral arrangement with large and small S-Hg-S angles of $147.7(1)^{o}$ and $84.3(1)^{o}$, respectively.

Bis(2,3,4,5-tetrafluorophenyl)mercury:

(Figure 24) (148). The mercury is linearly coordinated with Hg-C distances of 2.096(16)Å . The rings are coplanar thereby maximizing the separation of the two ortho-fluorine atoms and minimizing their electrostatic repulsion.

Bis(benzamido)mercury(II):

(Figure 25) (149). The mercury is approximately linearly coordinated to two nitrogen atoms, [Hg-N = 2.06(3)Å, 2.04(2)Å ; N-Hg-N = $172(1)^{o}$],and equatorially coordinated

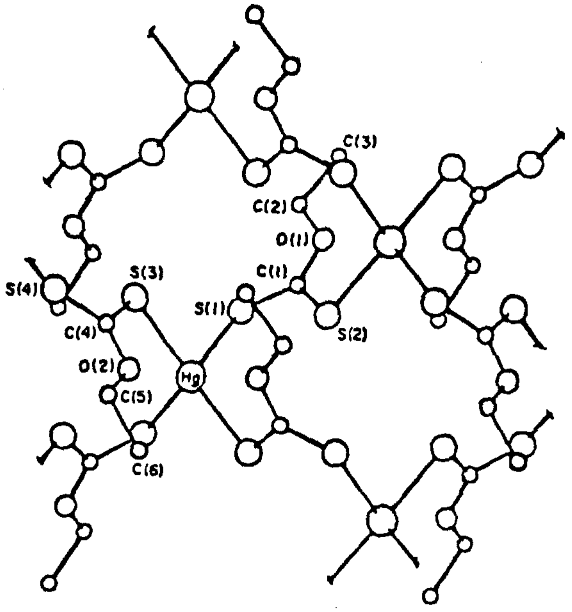


Figure 23. The two-dimensional sheet structure of mercury(II) xanthate. From C.Chieh, and K. J. Moynihan, Acta Cryst., B 36 (1980) 1367.

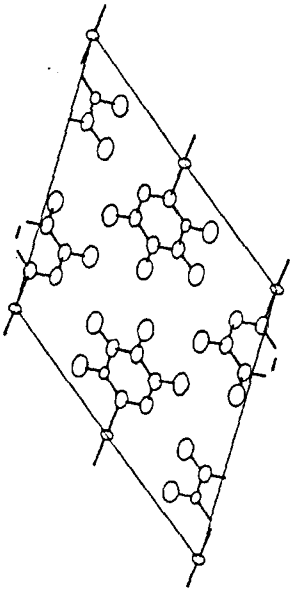


Figure 24. Projection showing the unit cell contents of bis(2,3,4,5-tetrafluorophenyl)mercury down the a axis. From D. S. Brown, A. G. Massey and D. A. Wickens, J. Organometal. Chem. 194 (1980) 131

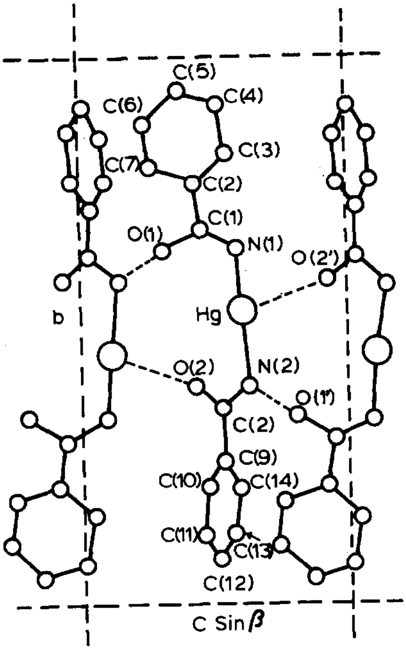


Figure 25. Projection along a of part of the unit cell of bis(benzamido)mercury(II). From J. Halfpenny and R. W. Small, Acta Cryst., B 36 (1980) 1194.

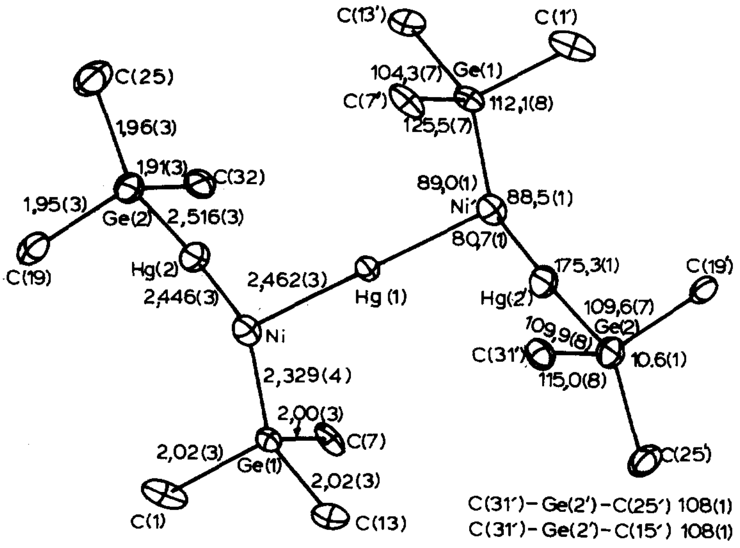


Figure 26. Molecular structure of $C_{28}H_{70}Ge_4Hg_3Ni_2$. From L. N. Zakharov, Yu. T. Struchkov, Cryst. Struct. Comm. 9 (1980) 549.

to two oxygen atoms of adjacent molecules, [Hg-O = 2.67(2)Å, 2.83(3)Å ; O-Hg-O = 76°]. There is also a weak intramolecular hydrogen bond suggested, [N····O = 3.03(5)Å]. One of the benzamido ligands is suggested to be in the enolic form.

Interaction product of Nickelocene with Bis(triphenylgermyl)mercury, $C_{82}H_{70}Ge_4Hg_3Ni_2$:

(Figure 26) (150). The crystal is composed of discrete molecules and solvating toluene molecules. Both molecules are situated on centers of symmetry with Hg-Ni distances of 2.462(3)Å and 2.446(3)Å and a Hg-Ge distance of 2.516(3)Å.

Dichloro-1-diphenylphosphino-2-disthylaminoethane mercury(II),(138K):

(Figure 27) (151). The mercury atom is covalently bound to two chlorine atoms and the nitrogen and phosphorus atoms of the chelated bidentate ligand , [Hg-Cl = 2.446(3)Å, 2.443(3)Å ; Hg-P = 2.417(3)Å ; Hg-N = 2.641(11)Å ; H-Hg-P = 77.7°]. The

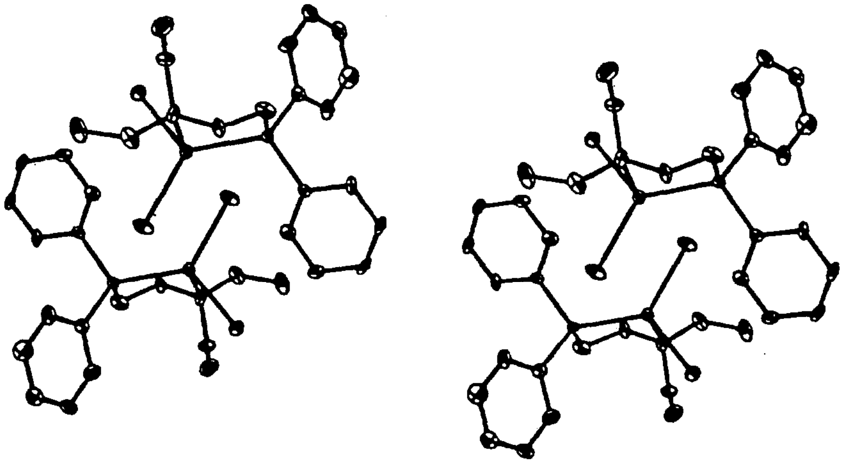


Figure 27 A stereo view of two monomeric units of $HgCl_2[(C_6H_5)_2PC_2H_4N(C_2H_5)_2]$ related by a center of symmetry. From P. K. Sen Gupta, L. W. Houk, D. van der Helm and M. B. Hossain, Inorganica Chimica Acta 4 (1980) L235

atoms adopt a highly distorted tetrahedral arrangement about mercury as evidenced by the wide variation in the X-Hg-Y angles which range from 77.7(3)^{o} to 127.3(1)^{o}. Some Hg-P dπ-dπ bonding is also suggested.

Dichloronicotine mercury(II):

(Figure 28) (152). In this structure each nicotine molecule is bound to two adjacent mercury atoms, one through the pyrrolidine nitrogen, (Hg-N = 2.397Å), and the other through the pryidine nitrogen, (Hg-N = 2.454Å), forming endless polymeric chains. Mercury is further coordinated to two chlorine ligands, (Hg-Cl = 2.364Å, 2.384Å), resulting in a highly distorted tetrahedral environment about mercury.

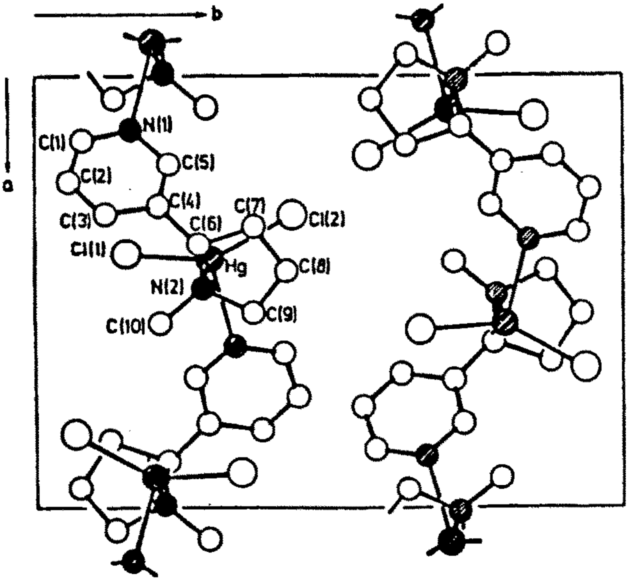


Figure 28. Projection of the unit cell of dichloronicotinemercury(II) parallel to c. From M. R. Udupa and B. Krebs, Inorg. Chim. Acta, 40 (1980) 161.

Tribenzo[b.e.h][1.4.7]trimercuronin,[HgC_6H_4]$_3$:

(Figure 29) (153). This is a redetermination of the monoclinic form (space group $P2_{1/c}$). Each mercury atom is approximately linearly coordinated, (Hg-C = ~2.06Å ;

C-Hg-C = ~176°), with mercury-mercury contact distances of 3.56(0)Å, 3.52(0)Å, and 3.51(0)Å for the bridged and 3.67(0)Å and 3.82(0)Å for the nonbridge atoms. The molecule was also found to be trimeric rather than hexameric as previously assumed [D. Grdenic, Chem. Ber., 92, 231 (1959)].

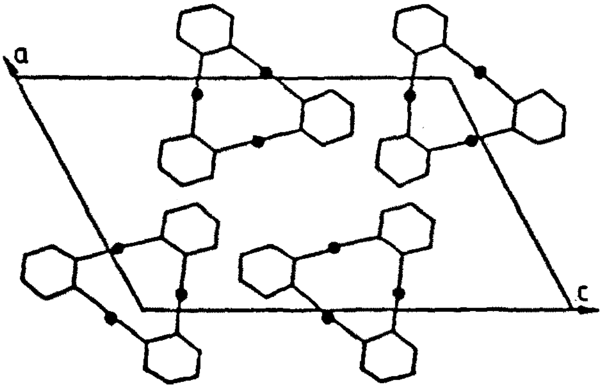


Figure 29. Projection of the unit cell of monoclinic tribenzo[b,e,h][1,4,7]trimercuronin down the b axis. From D. S. Brown, A. G. Massey, and D. A. Wickens, Inorg. Chim. Acta, 44 (1980) L193.

Diortho-tolylmercury:

(Figure 30) (154). The crystals consist of individual molecular units with the mercury atom located on the crystallographic 2-fold axis. The C-Hg-C fragment is nearly linear with an angle of 178.0(4)° and Hg-C distances of 2.09(1)Å. The methyl groups lie on the same side of the molecule and are twisted with respect to one another by 58.9°.

α-Chloromercurycamphene:

(Figure 31) (155). The mercury is linearly bound C(1), [Hg-C(1) = 2.09(2)Å ; Hg- Cl = 2.352(2)Å ; Cl-Hg-C(1) = 177.7(3)Å]. The intracyclic angles are less and the exocyclic angles considerably greater than tetrahedral. A short C(1)-C(2) bond, 1.44(3)Å, does not appear to be attributable to σ,π-conjugation, but rather to a delocalization of the electron in the C(8)-C(2)-C(1) chain, as is characteristic of the camphene molecule.

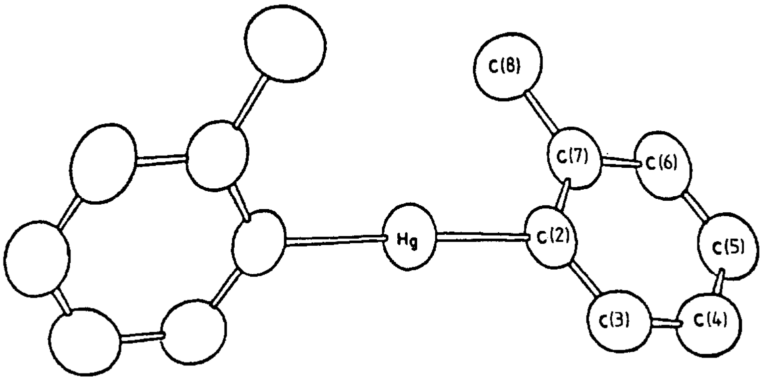


Figure 30. Molecular structure of di(o-tolyl)mercury. From D. Liptak, W. H. Ilsley, M. D. Glick and J. P. Oliver, J. Organometal. Chem., 191 (1980) 339.

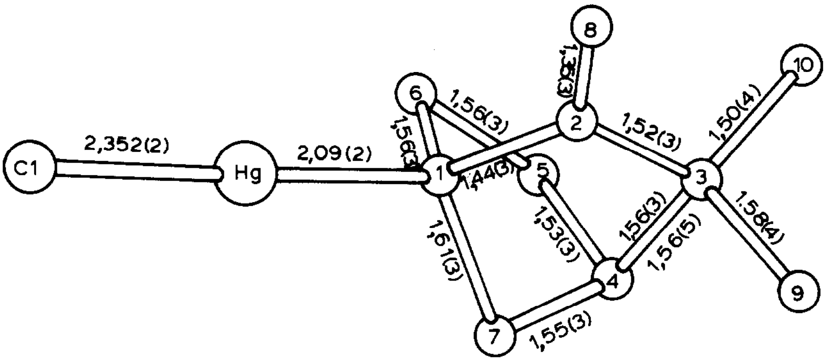


Figure 31. Molecular structure of α-chloromercurycamphene. From V. G. Andrianov, Yu. T. Struchkov, V. A. Blinova and I. I. Kritskaya, Izv. Akad. Nauk SSSr, Ser. Khim., 9 (1979) 2021. (Reproduced with permission from Plenum Publishing Corporation copyright 1979)

9-Methyladenine-methylmercuric nitrate complex (1:1):

(Figure 32) (156). The structure consists of a un-coordinated nitrate ion and a $CH_3Hg(m^9Ade)^+$, (m^9Ade = 9=methyladenine), complex in which the mercury is bound to N(1). The mercury exhibits linear coordination, (C-Hg-N = 175.6°), and forms normal bonds with N(1) of the pyrimidine ring , (Hg-N 2.13(1)Å), and a methyl group, (Hg-C = 2.07(1)Å). The structure provides further evidence that CH_3Hg^+ ions, unlike many other metallic species, show a preference for N(1) as the first bonding site in adenine rings.

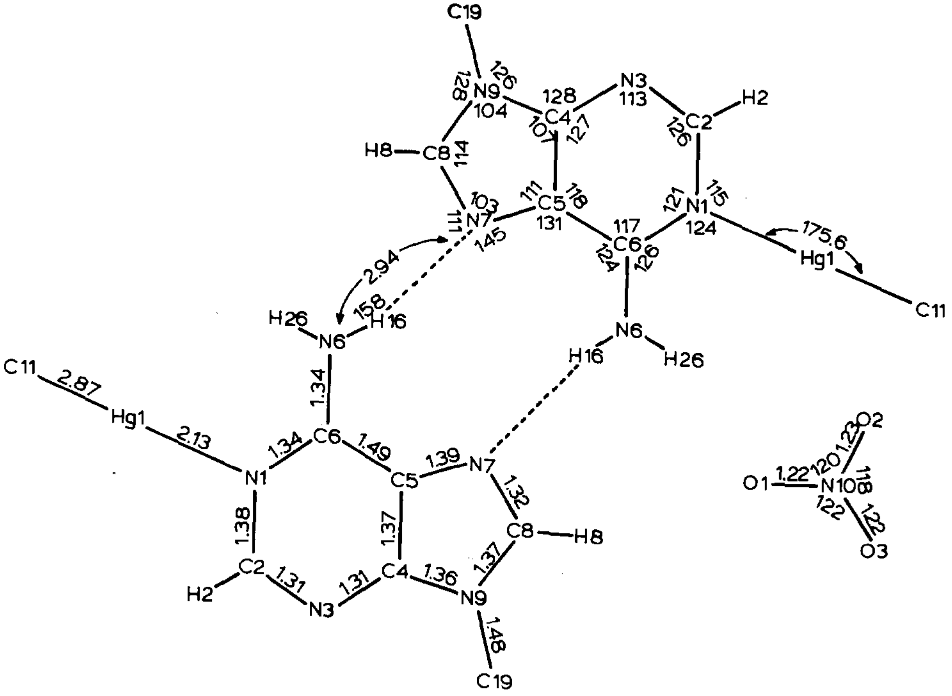


Figure 32. Molecular structure of 9-methyladenine-methylmercuric nitrate complex. From M. J. Olivier and A. L. Beauchamp, Inorg. Chem., 19 (1980) 1064.

7α-(thioacetyl)-(17R)-spiro-androst-4-ene-17.2(3H)-furan mercury(II)bromide:

(Figure 33) (157). The geometry around mercury is described as a distorted triangle of two sulfur and one bromine atom, (Hg-S = 2.455(2)Å, 2.502(1)Å ; Hg-Br = 2.707(1)Å). An intermolecular Hg···Br interaction, 2.840(1)Å, is also observed. Thus both bromine and sulfur atoms act as bridges between the mercury atoms.

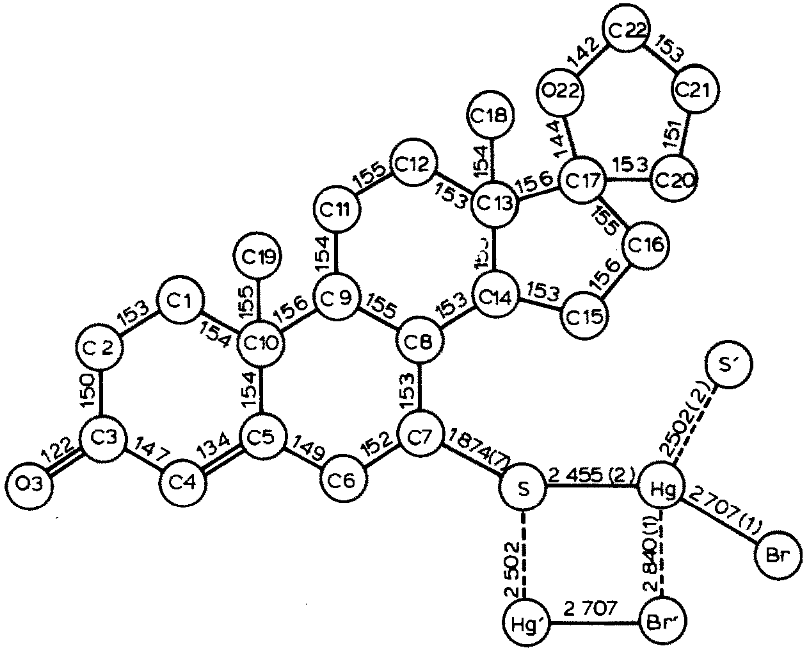


Figure 33. Molecular structure of the 7α-(thioacetyl)-(17R)-spiro[androst-4-ene-17,2(3H)-furan]-mercury(II)bromide complex. From A. Terzis, J. B. Faught, and G. Pouskoulelis, Inorg. Chem., 19 (1980) 1060.

catena-{Di-μ-chloro-tetrakis-μ-(N,N-diethyl-dithiocarbamato-S,S′-trimercury(II)}:

(Figure 34) (158). The structure consists of polymeric chains in which the repeating unit has three mercuric ions linded by two Cl$^-$ and four unsymmetrically bridged dithiocarbanate ligands. The eight Hg-S distances in the asymmetric unit range from 2.406(8)Å to 2.587(6)Å and the Hg-S-C angles range from 94.1 to 107.1(6)^o. The Hg-Cl bridging distances range from 2.661(8) - 2.771(7)Å.

Bis(trichlorovinyl)mercury-3,4,7,8-tetramethyl-1,10-phenanthroline:

(Figure 35) (159). The structure exhibits a weak but significant donor-acceptor interaction between the phenanthroline ligand and bis(trichlorovinyl)mercury. The ligand is weakly coordinated to mercury with long Hg-N distances, (2.687(6)Å,

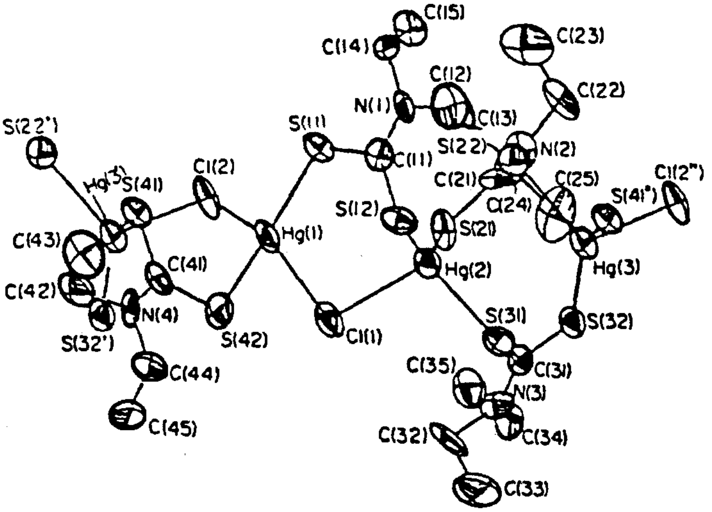


Figure 34. Molecular structrue of catena-{di-μ-chloro-tetrakis-μ-(N,N-diethyl-dithiocarbamao-S,S')]-trimercury(II). From L. Book and C. Chieh, Acta cryst., B 36 (1980) 300.

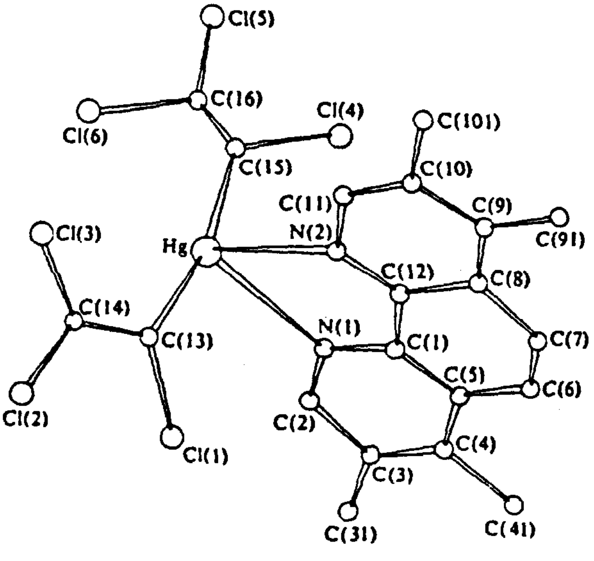


Figure 35. Molecular structure of bis(trichlorovinyl)mercury-3,4,7,8-tetramethyl-1,10-phenanthroline.From N.A. Bell and I. W. Nowell, Acta cryst., B 36 (1980) 447.

2.629(9)Å), and a small N-Hg-N angle, 61.4(2)°. The C-Hg-C skeleton is significantly distorted from linearity, [C-Hg-C = 164.8(3)° ; Hg-C = 2.082(10)Å, 2.091(10)Å].

Chlorobis(ethyldimethylphosphine)mercury(II)trichloro-(ethyldimethylphosphine)mercurate(II):

(Figure 36) (160). The complex is best described as being composed of $Hg\{(CH_3)_2(C_2H_5)P\}_2Cl^+$ cations and $Hg\{(CH_3)_2(C_2H_5)P\}_2Cl_3^-$ anions linked by chlorine bridges. The cation contains an almost linear P-Hg-P , 172.3°, arrangement and the anion shows considerable tetrahedral distortion about mercury with angles at the metal ranging from 98.2° to 132.9°. The cation exhibits overall trigonal bipyramidal geometry about mercury with Hg-P distances of 2.40Å and Hg-Cl distances of 2.69Å, 3.07Å, and 3.25Å.

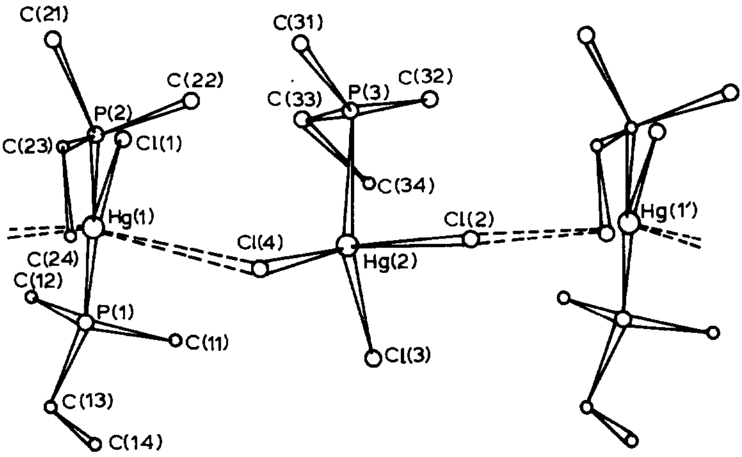


Figure 36. (a) Projection of the unit cell of $(Me_2EtP)_3(HgCl_2)_2$ alont a and (b) part of the chain running parallel to c showing the atomic numbering scheme. From N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, Acta Cryst., B 36, (1980) 708.

Dibromo(2,4-dimethylpyridine)mercury(II):

(Figure 37) (161). The structure is polymeric with mercury exhibiting penta-coordination. The (2.4-dimethylpyridine)$HgBr_2$ units are linked by bromine bridges to give single chains running parallel to the c axis. The coordination sphere about mercury is best described as an elongated trigonal bipyramid, [Hg-N =2.21(2)Å ; Hg-Cl = 2.621(3)Å - 3.548(4)Å]. The 2,4-dimethylpyridine ring is effectively planar and is twisted relative to the N-Hg-Br_2 mean plane by 22.6^{o}.

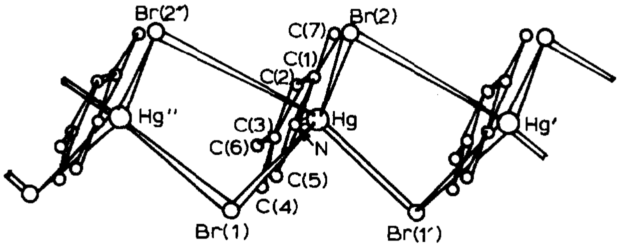


Figure 37. A single chain of dibromo(2,4-dimethylpyridine)mercury running parallel to the c direction. From N. A. Bell, M. Goldstein, T. jones, and I. W. Nowell, Acta Cryst., B 36 (1980) 710.

(2-Benzylpyridine)methyl mercury(II) nitrate:

(Figure 38) (162). The mercury exhibits linear geometry, [C(1)-Hg-N(1) = 180(1)^{o}], with Hg-C(1) and Hg-N(1) distances of 2.07(3)Å and 2.10(2)Å, respectively. A weak intramolecular π-interaction between Hg and a C—C bond of the phenyl ring is suggested by Hg-C distances of 3.23(2)Å and 3.33(3)Å.

Phenyl(pyridine)mercury(II) trifluoroacetate:

(Figure 39), (163). The asymmetric unit consists of two independent $HgPhpy^+$ ions, (Ph = phenyl ; py = pyridine), and two $CF_3CO_2^-$ ions. Mercury is bound to two six-membered rings in each cation , however, the two bonds to Hg(1) are appreciably

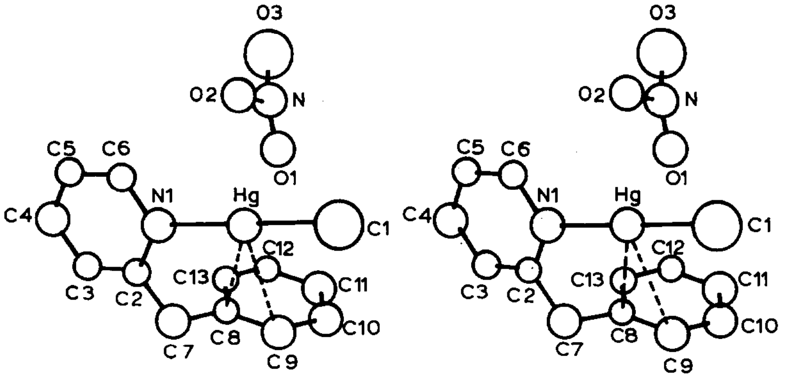
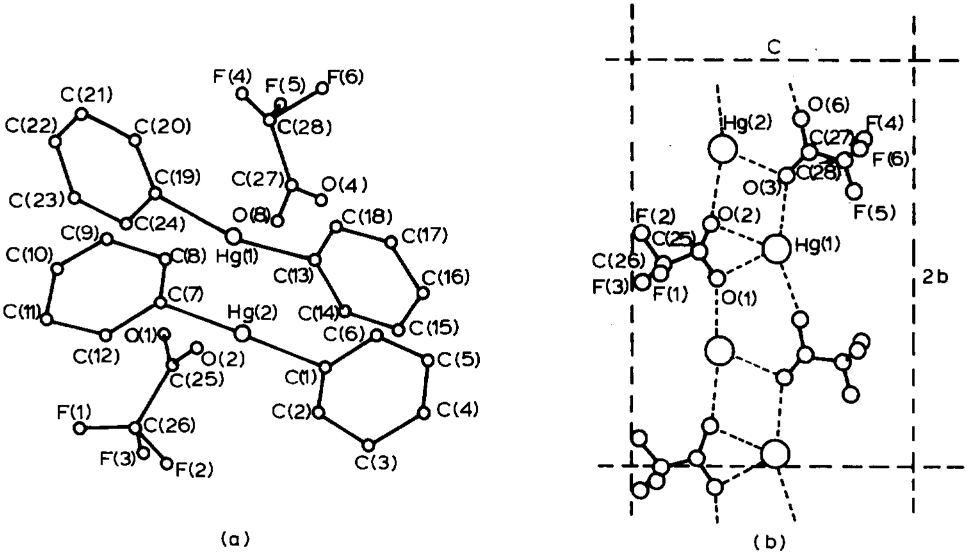


Figure 38. A stereoscopic view of the sturcture of (2-benzylpyridine)methylmercury(II) nitrate. From A. J. Canty, N. Chaichit and B. M. Gatehouse, Acta Cryst., B 36 (1980) 786.



(a)

(b)

Figure 39. (a) A view of one unit of Phenyl(pyridine)mercury(II) trifluoroacetate and (b) a projection of part of the structure along a showing Hg····O coordination (phenyl and pyridine rings have been omitted for clarity. From J. Halfpenny and R. W. H. Small, Acta Cryst., B 36 (1980) 938.

non-linear, [C(13)-Hg(1)-C(19) = 167(2)°], whereas Hg(2) exhibits distinctly linear geometry, [C(1)-Hg(2)-C(7) = 178(2)°]. The Hg-C(N) distances are 2.01(4)Å and 2.11Å for Hg(1) and 2.09(4)Å and 2.12(4)Å for Hg(2) but it must be emphasized that the nitrogen and carbon attached to mercury could not be reliably differentiated. The cations are bound into continuous bonds by a system of Hg····O bonds involving the trifluoroacetate counter ions.

Tris(1,10-phenanthroline)mercury(II) trifluoromethanesulfonate, [295(1)K]:

(Figure 40) (164). The unit cell is comprised of discrete $Hg(phen)_3{}^{2+}$ cations, trifluoromethane sulfonate anions and disordered poorly defined ethanol molecules. The cation is centered about a crystallographic two-fold axis and provides one of the very few examples of a regular six-coordination for mercury(II). A twist angle of 14.9° about the pseudo-threefold axis suggests that the geometry about mercury is closer to trigonal prismatic than octrahedral. The mean trans N-Hg-N angle is 154.52° and $Hg\text{-}N_{mean}$ is 2.40Å.

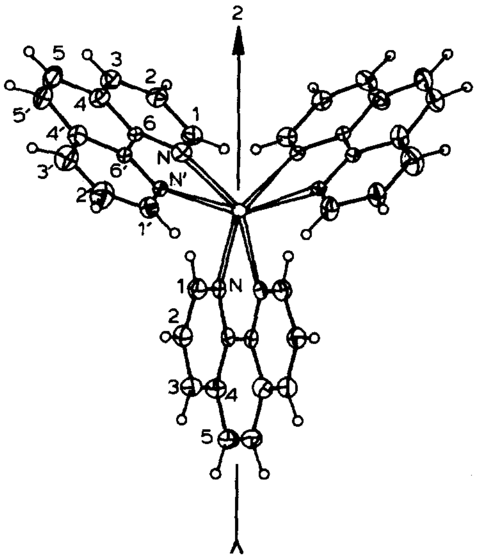


Figure 40. A projection of the $[Hg(Phen)_3]^{2+}$ cation down its pseudo-threefold axis. From G. B. Deacon, C. L. Raston, D. Tunaley, and A. H. White, Aust. J. Chem., 32 (1979) 2195.

Trifluoromethyl(methyl)mercury: (165)

The molecular structure has been determined in the gas phase by a joint analysis of electron diffraction and microwave data. The following geometric parameters (r_{av} values) were found: [r(Hg-CH_3) = 2.052(5)Å ; r(Hg-CF_3) = 2.116(4)Å ; r(C-F) = 1.354(2)Å ; r(C-H) = 1.079(14)Å ; <FCF = 105.7^{o} and <HCH = 107.0(1.5)^{o}]

2,2,4,4,6,6,8,8,-Octamethyl-2,4,6,8-tetrasilya-1,5-mercuracyclooctane:

(Figure 41) (166). The compound contains linear Si-Hg-Si fragments, (Hg-Si_{av} = 2.503(4)Å), linked by methylene bridges forming an eight membered ring that adopts the chair confomation. The across ring Hg-Hg distance is 3.286(2)Å.

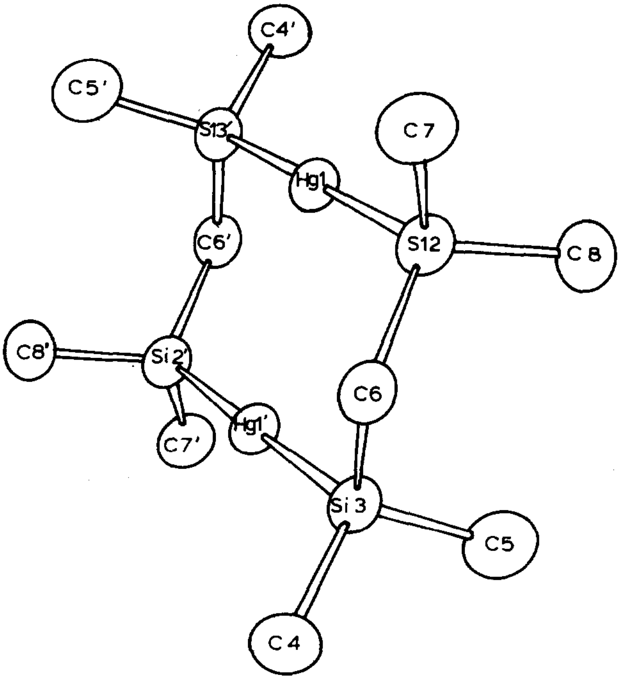


Figure 41. The molecular structure of 2,2,4,4,6,6,8,8,-octamethyl-2,4,6,8-tetrasilya-1,5-mercuracyclooctane. From W. H. Ilsley, E. A. Sadurski, T. shaaf, M. J. Albright, T. J. Anderson, M. D. Glick and J. P. Oliver, J. Organometal. Chem., 190 (1980) 257.

Bis(triphenylsilyl)mercury:

(Figure 42) (166). The molecules are centrosymmetric with a linear Si-Hg-Si skeleton and Hg-Si = 2.490(4)Å. The triphenylsilyl groups adopt the staggered confonation with the phenyl groups tilted in a propellor-like fashion.

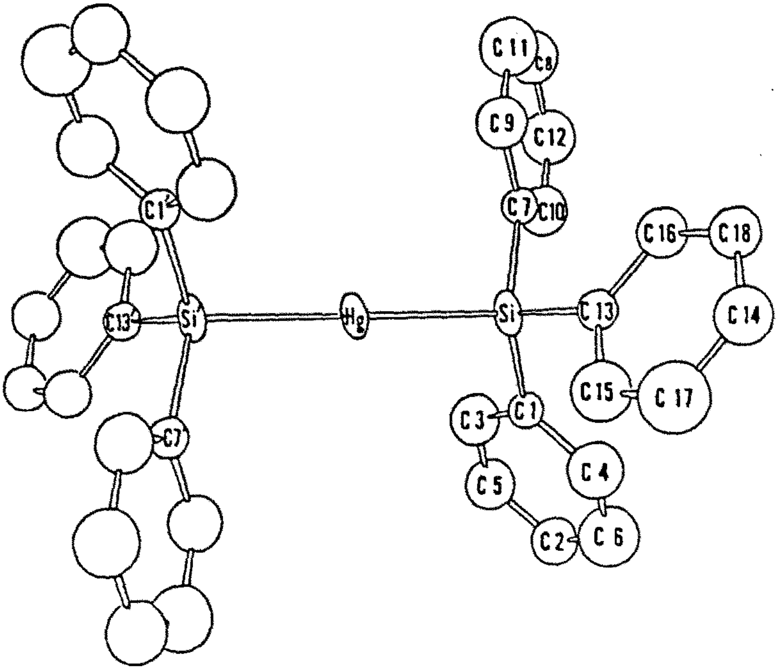


Figure 42. The molecular structure of bis(triphenylsilyl)mercury(II). From W. H. Ilsley, E. A. Sadurski, T. Schaaf, M. J. Albright, T. J. Anderson, M. D. Glick and J. P. Oliver, J. Organometal. Chem., 190 (1980) 257.

(Di-2-pyridylmethane)methyl mercury(II) nitrate:

(Figure 43) (167). The methylmercury unit is bound to two nitrogen atoms, one at 2.16(1)Å , (C-Hg-N = 172(1)$^{\mathrm{o}}$), and the other at 2.75(2)Å. The coordination geometry about mercury may best be reqarded as a distorted "T-shape", however, there is an additional interaction to a nitrate oxygen, (Hg····O = 2.76(2)Å).

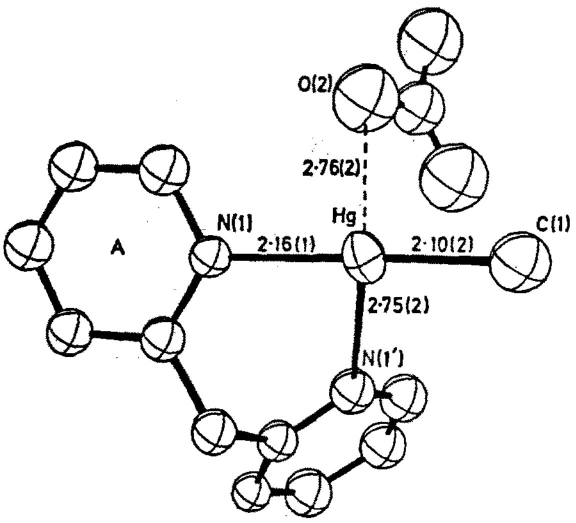


Figure 43. The molecular structure of (di-2pyridylmethane)methylmercury(II) nitrate. From. A. J. Canty and G. Hayhurst, J. Chem. Soc. Chem. Comm., (1980) 316.

(4,4′,4″-Triethyl-2,2′:6′,2″-teepuridyl)methylmercury(II) nitrate:

(Figure 44) (167) The methylmercury unit is bonded to three nitrogen atoms one at 2.25(2)Å, [C-Hg-N = 170(1)^{o}], and two at 2.52(2)Å and 2.60(2)Å. The mercury exhibits highly distorted square planar geometry, however, there is an additional Hg····O contact at 2.79(2)Å.

Structure of $Li_2H(SiMe_2Ph)_4$:

(Figure 45) (168). The crystal consists of discrete molecular units in which the lithium cations are enclosed in a cage of silicon and carbon atoms. The mercury sits on a two-fold axis of symmetry and is surrounded by a slightly distorted tetrahedral arrangement of the silicon atoms, (Hg-Si = 2.493(2)Å and 2.549(2)Å). The Li-Si distances range from 2.90(1)Å - 3.04(1)Å and the Li-Hg distance is 2.58(1)Å. The close approach of the lithium atoms to a C—C bond on two adjacent phenyl groups, (Li-C = 2.42(2) - 2.54(2)Å), suggests that the structure is best described as a tight ion pair in which the lithium atoms exhibit normal π-type interactions to two adjacent phenyl rings.

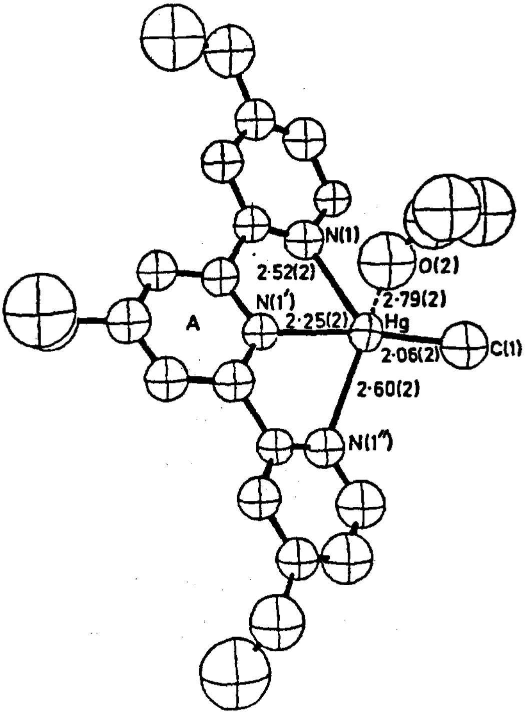


Figure 44. The molecular structure of (4,4′,4″-triethyl-2,2′ ; 6′,2″-terpuridyl)methylmercury(II) nitrate. From A. J. Canty and G. Hayhurst, J. Chem. Soc. Chem. Comm., (1980) 316.

Structure of $Li_2Hg(SiMe_3)_4$:

(Figure 46) (168). The crystal consists of zig-zag chains of $Li_2Hg(SiMe_3)_4$ units linked together by the lithium atoms, which serve as bridges between the $Hg(SiMe_3)_4^{2-}$ units. The mercury atom sits on a crystallographic two-fold axis and symmetry and is surrounded by a distorted tetrahedral arrangement of silicon atoms, [Hg-S = 2.549(2)Å and 2.539(2)Å]. The most interesting aspect of this structure is the location of the lithium atoms. They lie close to one of the Si-C bonds, (Li-Si = 2.69(1)Å ; Li-C = 2.32(2)Å), and a carbon atom on an adjacent $Hg(SiMe_3)_4^{2-}$ units, (Li·····C = 2.45(1)Å). These distances are strongly suggestive of significant multicentered bonding as is typically found in "electron deficient" systems.

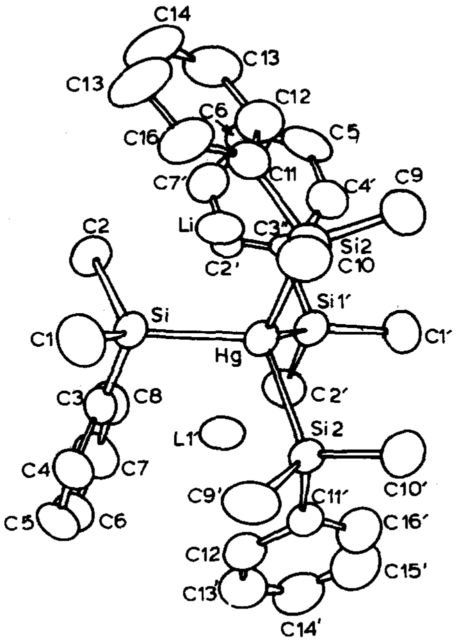


Figure 45. The molecular structure of $Li_2Hg(SiMe_2Ph)_4$. From W. H. Ilsley, M. J. Albright, T. J. Anderson, M. D. Glick and J. P. Oliver, Inorg. Chem., 19 (1980) 3577.

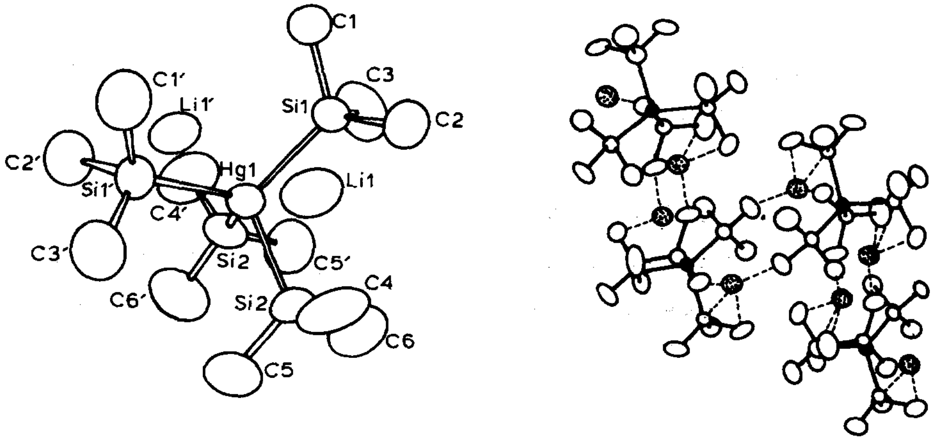


Figure 46. (a) The molecular structure of $Li_2Hg(SiMe_3)_4$ and (b) a packing diagram showing a segment of the zig-zag-chain arrangement within the crystal where the lithium atoms act as bridges between the various $Hg(SiMe_3)_4^{2-}$ ions. The dotted lines indicate possible multicentered interactions. From W. H. Ilsley, M. J. Albright, T. J. Anderson, M. D. Glick and J. P. Oliver, Inorg. Chem., 19 (1980) 3577.

μ-(Adeninato-N3,N7,N9)tris[methylmercury(II)] perchlorate:

(Figure 47) (169). The crystals are composed of two crystallographically independent [Ademimato$(CH_3Hg)_3]^{2+}$ ions in which the methylmercury groups are linearly bonded to N3, N7, and N9, {C-Hg-N = 177(1)°, Hg-N = 2.08(3)Å, Hg-C = 2.05(4)Å] of a deprotonated adenine ring. One half of the cations are associated in a dimeric pair with strong N(6)—H(6)······N(1) hydrogen bonds while the remaining cations are packed as individual species. The most interesting characteristic of the structure is the apparent absence of affinity of N(1) for mercury.

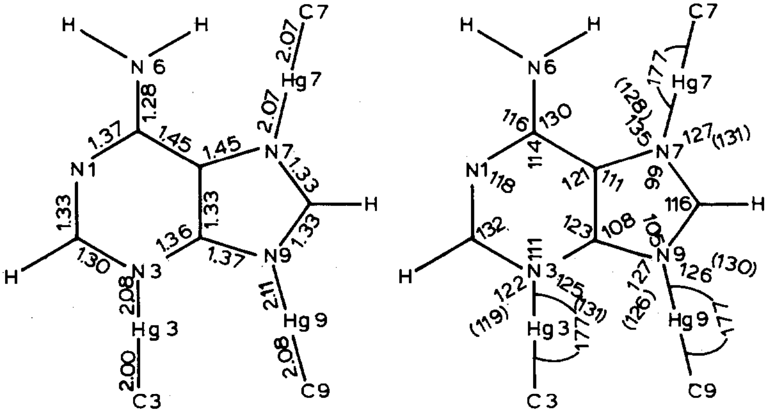


Figure 47. Average interatomic distances and bond angles in [Adeninato$(CH_3Hg)_3]$ (ClO_4).The two values for C-N-Hg angles refer to cation No. 1 (unparenthesized) and cation No. 2 (parenthesized), respectively. The standard deviations on bond lengths are 0.04 - 0.05Å, except for Hg-N(C), 0.02 - 0.04Å, and on bond angles, 3°, except for C-Hg-N, 1°. From J. Hubert and A. L. Beauchamp, Can. J. Chem., 58(1909)1439.

Phenylmercury derivative of 2-chlorodiazoaminobenzene:

(Figure 48) (170). The mercury atom is covalently bound to N(1) at a distance of 2.14Å with a secondary intramolecular coordination to N(3) at a distance of 2.46Å. The N(1),N(2),N(3),Hg fragment is planar and the intramolecular HgCl distance is 3.6Å.

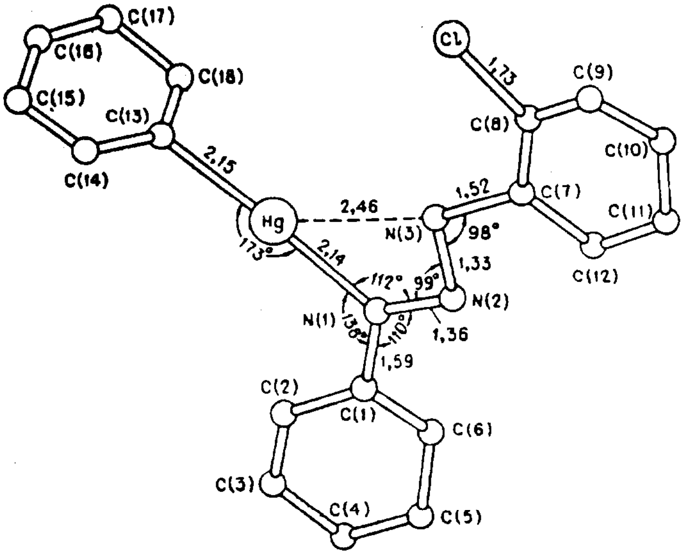


Figure 48. Molecular structure and geometric parameters of the phenylmercury derivative of 2-chlorodiazoaminobenzene in the crystal. (Reproduced with permission from Plenum Publishing Corporation copyright 1979)

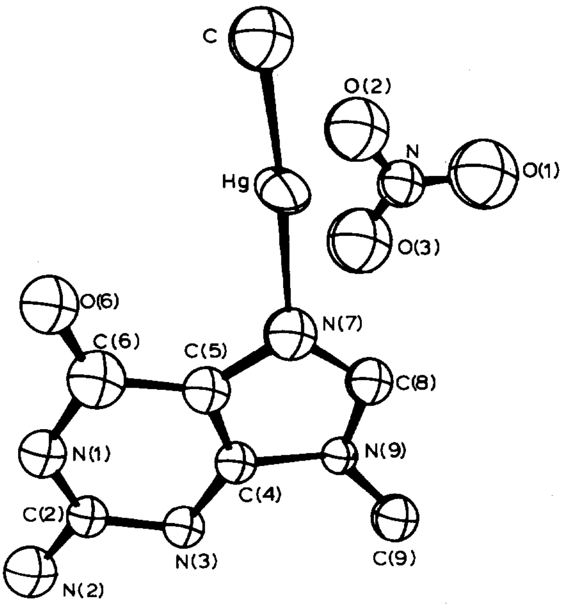


Figure 49. Molecular structure of [HgMe(9-MeGua)][NO_3]. From [A. J. Canty, (the late) R. S. Tobias, N. Chaichit, B.M. Gatehouse, J. Chem. Soc., Dalton, (1980) 1693].

(9-Methylguanine)-methylmercury(II) Nitrate:

(Figure 49) (82). The crystals are composed of individual $[HgMe(9\text{-}MeGua)]^+$ cations and nitrate anions. The $Hg^{II}Me$ group is bound to N(7) of the purine ring (Hg-C, 2.06(2)Å ; Hg-N(7), 2.09(2)Å ; C-Hg-N(7), 175(1)°). The mercury atom also interacts weakly with nearby nitrate ions, with Hg····O distances of 2.75(2)Å and 2.99(2)Å.

10. SPECTROSCOPY STUDIES OF ORGANOMERCURY COMPOUNDS:

A. VIBRATIONAL SPECTROSCOPY

Vibrational assignments have been proposed for $Hg(C_2H_5)X$, (X = Cl, Br, I), and $HgBr(C_2D_2)$ (171). In addition, force field calculations afforded carbon-mercury force constants of 2.643, 2.417, and 2.465 for X = Cl, Br, and I, respectively.

The Infrared and Raman spectra of a series of alkylthiomercury(II) halides, Hg(SR)X, (R= Me, Et, Pr^n, Pr^i, Bu^i, Bu^s and X= Cl, Br, I) exhibit three structural types in the solid state (172). Monomeric compounds, (R= Pr^i, X= Br, I), exhibit one ν(Hg-S), (240-220 cm^{-1}), and one $\nu(Hg\text{-}X)_t$, (205-195 cm^{-1}, X= Br ; ca. 180 cm^{-1}, X- I), in the region characteristic of terminal bonds. Dimeric compounds, (R= Pr^i, X= Cl, ; R= Bu^s, X= Cl,Br), with bridging halogens or interactions between mercury and halogen atoms exhibit one ν(Hg-S), (290-230 cm^{-1}), and one $\nu(Hg\text{-}X)_b$, (220-215 cm^{-1}, X= Cl ; ca. 180 cm^{-1}, X= Br). The polymeric compounds, (R= Et, Pr^n, Bu^i, Bu^n ; X= Cl, Br, I), which have $Hg\text{-}S_2\text{-}Hg$ rings and strong intermolecular mercury-halogen interactions , are characterized by four ν(Hg-S), (350-190 cm^{-1}), and one $\nu(Hg\text{-}X)_b$, (185-155 cm^{-1}, X= Cl ; 170-130 cm^{-1}, X= Br ; 135-125 cm^{-1}, X= I), In pyridine solution all of the compounds are monomeric with ν(Hg-S) and ν(Hg-X) typical of terminal bonds.

Canty and Devereux (173) have studied the vibrational spectra of MeHgOPh and PhHgOR, (R= Ph, Me, Et). Both the solution and solid state spectra of RHgOPh, (R= Me, Ph), indicate monomeric structures with ν(Hg-O) near 600 cm^{-1}. The complexes PhHgOR, (R= Me, Et), on the other hand, are dimeric in the solid state with ν(OHgO) modes in the region 500-430 cm^{-1}.

Raman and Infrared spectra of the complexes $MeHg(pyx)ClO_4$, $Hg(pyx)_n(ClO)_2$, and $Hg_2(pyx)_n(ClO_4)$, (pyx= pyridine or a pyridine derivative ; n=2, sometimes 4), have allowed assignment of the Hg-N , (160-260 cm^{-1}), and Hg-Hg, (110-160 cm^{-1}), stretchidng frequencies (174). For the $MeHg(pyx)_nClO_4$ complexes v(Hg-C) appears in the region from 558 to 572 cm^{-1} in the Raman spectra (Table 23).

TABLE 23

Raman Frequencies of the Symmetric Methyl Hg-C and Hg-N Vibrations in $CH_3Hg(pyx)ClO_4$ Complexes. (174)

Complex	v(CH_3-Hg) cm^{-1}	v_s(Hg-N)
2-$MeC_5H_4NHgMe^+ClO_4^-$	567s	204m
3-$MeC_5H_4NHgMe^+ClO_4^-$	570s	212m
4-$MeC_5H_4NHgMe^+ClO_4^-$	572s	194s
2-$EtC_5H_4NHgMe^+ClO_4^-$	558s	204s
3-$CNC_5H_4NHgMe^+ClO_4^-$	563s	202w
4-$CNC_5H_4NHgMe^+ClO_4^-$	562s	214m
2-$ClC_5H_4NHgM\ ^+ClO_4^-$	561s	187m
3-$ClC_5H_4NHgMe^+ClO_4^-$	567s	208m
2-$BrC_5H_4NHgMe^+ClO_4^-$	561s	177m
3-$BrC_5H_4NHgMe^+ClO_4^-$	565s	201m
$C_5H_5NHgMe^+ClO_4^-$	565 vs	206w
$C_5D_5NHgMe^+ClO_4^-$	565vs	193w

The infrared spectra of the carbon-hydrogen stretching region of CHD_2 substituted dimethylzinc, -cadmiun and -mercury have been used to predict r_0CH values upon which are based new geometries for the molecules (133). The geometries predicted , however, differ little from those previously reported. For $(CH_3)_2Hg$ the structural parameters obtained are: $r_0CH_{pred.}$= 1.096Å ; <HCH = 109.2°, and r_0HgC = 2.093Å.

The vapor phase infrared spectra of the diethyl derivatives Et_2M, (M= Zn, Cd, Hg), have been obtained in the range 400 - 4000 cm^{-1}(176) and correspond to linear molecular geometry. A dependence of the wave numbers of the antisymmetrical vibrational stretching modes on the reduced carbon-metal mass and the first dissociation energy D_1 is also reported.

A study has been made of the infrared and ultraviolet spectra of various organomercury derivatives of o-nitrophenol and o-thiophenol (177). The o-nitrophenolates of phenyl mercury show two bands in the $v_s(NO_2)$ region , one at 1338 cm^{-1} and the other at 1350 cm^{-1}, as well as free NO_2 groups. Intramolecular coordination of the nitro group to mecury was noted in the phenylmercury derivatives of o-nitrothiophenols. Complexation constants, K_c, for these compounds with pyridine, DMSO and hexamethylphosphorotriamide have been determined in benzene and revealed that the intramolecular co-ordination within the ortho derivatives leads to a marked reduction in K_c when compared to K_c for the para derivatives.

Force constants for the internal and lattice vibrations of CH_3HgX, (X=Cl, Br, I) were determined on the basis of a $D^7{}_{4h}$ layer structure (178). The internal HgX stretching force constants were found to be lower by 18, 16 and 14% for Cl, Br, and I, respectively, than for the same compounds in benzene solution. On the other hand, the mercury-carbon stretching force constants are slightly higher.

B. Nuclear Magnetic Resonance Spectroscopy

^1H and ^{13} C NMR data have been obtained for the chloromercurimethanes, $CH_{4-n}(HgCl)_n$, ($1 \leq n \leq 4$) (179) . Data obtained include: (^1H) ppm = 0.77, 1.30, 1.59 (n = 1,2,3) ; (^{13}C) ppm = 5.85, 20.23, 35.80, 50.91 (n = 1,2,3,4) ; $^1J(^{199}Hg-^{13}C)$ (Hz) = 1678, 1782, 1827, 1797 (n = 1,2,3,4) ; $1J(^{13}C-^1H)$(Hz) = 137.3, 147.2, 153.8 (n = 1,2,3) and $^2J(^{199}Hg-^1H)$(Hz) = 218, 171, 124, (n = 1,2,3). The variations in ^1J(C-H) and ^2J(Hg-H) are suggested to result from varying 2s contributions from carbon to the C-H and C-Hg bonds.

The ^2J and $^3J(^{199}Hg-^1H)$ and ^1J(C-Hg) coupling constants of compounds [RC(O)CH(R')]HgBr and $[RC(O)CH(R')]_2Hg$, derived from the three ketones, 2,2-dimethyl-3-pentanone, 1-mesityl-1-propanone and 1-mesityl-1-ethanone, have been determined by ^{13}C and ^{199}Hg NMR methods (180) and are consistent with C-metalation (Table 24).

The ^{31}P and ^{199}Hg NMR of the compounds HgX_2P_2, $Hg_2X_4P_2$, mixtures thereof,

TABLE 24

Values of the coupling constants (Hz) ^2J. and $^3J(^{199}Hg-^1H)$ and $^1J(^{13}C-Hg)$ in the ^{199}Hg and ^{13}C for the mercury compounds $R-^1CO-^2CH(R')-Y$ (179)

Compound	R	R′	Y	Solvent	$^2J(HgH)$	$^3J(HgH)$
I	t-Bu	Me	HgBr	C_6D_6	330	252
II	t-Bu	Me	$(Hg)^{1/2}$	C_6D_6	189	126
III	Mesityl	Me	HgBr	C_6D_6	390^b	232
IV	Mesityl	Me	$(Hg)^{1/2}$	C_6D_6	205	128
					205	134
V	Mesityl	H	HgBr	$CDCl_3$	290^b	
VI	Mesityl	H	$(Hg)^{1/2}$	$CDCl_3$	277	

Compound	multiplicity^a	$^1J(CHg)$	Observations	
I	dq	1341	$^2J(C(1)-Hg) \sim 118$	$^2J(Me-Hg) \sim 134$
II	t sept.	605	$\Delta\nu(^{199}Hg) \sim 202$	$^2J(C(1)-Hg) \sim 65$
	t sept.	614		
III	t q			
IV	t sept.	584		
	t sept.		$\Delta\nu(^{199}Hg) \sim 18$	
V	t			
VI	quint.	647		

^{a} d : doublet t : triplet q : quadruplet quint : quintuplet sept : septuplet.

^{b} Solvent + ε DMSO

and the oligomers $Hg_2X_4P_3$, $Hg_3X_6P_2$ and $Hg_4X_8P_2$, (x = Cl, Br, I ; P=PBu_3) have also been reported (127). Data obtained on the components $HgX_2(PBu_3)_2$ and $Hg_2X_4(PBu_3)_2$ are presented in Table 25 and are in general agreement with those previously reported [S.O. Grim, P. J. Lui, and R. L. Keiter, Inorg. Chem. 13 (1974) 342]. The results confirm that the 1:1 and 1:2 complexes have one and two phosphorus atoms co-ordinated to mercury, respectively. The presence of two isomers of $Hg_2I_4(PBu_3)_2$ was also comfirmed. For $HgI_4(PBu_3)_2$,on the other hand, the results indicate that the ^{31}P resonance at 6.3 ppm is associated with the doublet in the ^{199}Hg spectrum ($J_{p,Hg}$5150 Hz) and the resonance at 18.3 ppm is associated with the ^{199}Hg triplet ($J_{p,Hg}$ 4310 Hz) rather than the reverse as previously reported

TABLE 25

^{31}P and ^{199}Hg n.m.r. data for the complexes $HgX_2(PBu_3)_2$ and $Hg_2X_4(PBu_3)_2$
^{31}P chemical shifts measured relative to external 85% H_3PO_4; ^{199}Hg chemical shifts measured relative to external 1 M phenylmercury acetate in dimethyl sulfoxide (181)

At 30°C

Compound	$\delta(^{31}P)$	$J_{P,Hg}$	$\delta(^{199}Hg)$	$J_{Hg,P}$
$HgCl_2(PBu_3)_2$	30.0	5100	1015 t	5100
$HgBr_2(PBu_3)_2$	23.0	4750	980 t	4750
$HgI_2(PBu_3)_2$^{A}	12.1	4100	725 t	4090
$Hg_2Cl_4(PBu_3)_2$	34.2	7510	670 d	7500
$Hg_2Br_4(PBu_3)_2$	27.6	6650	425 d	6650
$Hg_2I_4(PBu_3)_2$^{B}	6.3	5150	-300 d	5130
asymmetric	18.3	4310	865 t	4350
isomer		-2050 s	—	

At -120°C

Compound	$\delta(^{31}P)$	$J_{P,Hg}$	$\delta(^{199}Hg)$	$J_{Hg,P}$
$HgCl_2(PBu_3)_2$	27.3	5150	1040 t	5150
$HgBr_2(PBu_3)_2$	22.2	4860	995 t	4880
$HgI_2(PBu_3)_2$^{A}	10.7	4320	850 t	4250
$Hg_2Cl_4(PBu_3)_2$	32.2	7510	690 d	7500
$Hg_2Br_4(PBu_3)_2$	25.6	6800	460 d	6830
$Hg_2I_4(PBu_3)_2$^{B}	4.7	5400	-210 d	5360
asymmetric	16.5	4600		
isomer				

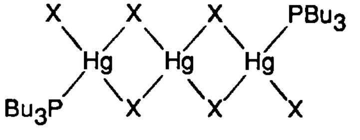
[A] The ^{199}Hg resonances for this compound were broad at low temperature

[B] This compound also gave broad signals in the mercury spectrum at low temperature. In addition, the proportion of asymmetric isomers decrease with decreasing temperature so the ^{199}Hg spectrum for the unsymmetrical isomer at low temperature was not found.

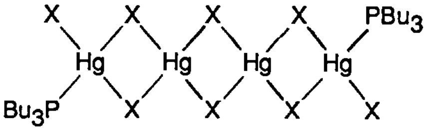
by Grim and coworkers. Mixtures of the halide complexes $HgX_2(PBu_3)_2$ exhibit rapid halogen exchange and

$$HgX_2(PBu_3)_2 + HgX'_2(PBu_3)_2 \rightleftharpoons 2\,HgXX'(PBu_3)_2$$

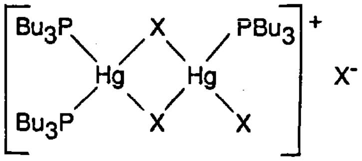
mixtures of the dimers, $Hg_2X_4(PBu_3)_2$, (X=Cl, Br), show rapid halogen exchange even to -120°C. Mixtures of $Hg_2I_4(PBu_3)_2$ with $Hg_2Cl_4(PBu_3)_2$ or $Hg_2Br_4(PBu_3)_2$ produce symmetrical and asymmetrical isomers. Data obtained for compounds $Hg_3X_6(PBu_3)_2$; $Hg_4X_8(PBu_3)_2$, (X= Cl, Br, I), and $Hg_2X_4(PBu_3)_3$ were interpreted in terms of the structures a, b, and c, respectively.



a



b



c

Cotton and Dakternieks (182) have investigated methylene chloride solutions of the mercury(II) halide complexes of tris(4-methoxyphenyl)phosphine by ^{31}P and ^{199}Hg NMR spectroscopy. At room temperature the phosphines exchange at an appreciable rate and halogen exchange is fast. At -50°C both phosphine and halogen exchange are slow on the NMR time scale and halogen redistribution reactions are observed. Complexes with tributylphosphine selenide were also investigated. This ligand is labile and exchanges rapidly on the NMR time scale at room temperature.

The ^{31}P and ^{199}Hg NMR data for the $HgX_2(pmp)_2$ and $HgX_2(pmp)$, [X=Cl,Br, I ; pmp = tris(4-methoxyphenyl)phosphine] complexes are presented in Table 26. The ^{31}P spectra of the $HgX_2(pmp)_2$, (X=Cl, Br), complexes exhibit broad ^{199}Hg satellites, however, $HgI_2(pmp)_2$ gave a broad signal with no visible satellites. At -50°C all three gave sharp ^{31}P NMR spectra with sharp satellites. The ^{199}Hg spectra when X=Cl or Br were broad at room temperature and when X= I no spectrum was observed. At -50°C, however, they all gave sharp triplets. For both types of complexes the ^{199}Hg resonance frequency decreases from Cl → Br → I as does the

TABLE 26

^{31}P and ^{199}Hg n.m.r. data for tris(4-methoxyphenyl)phosphine complexes (182)

^{31}P chemical shifts measured relative to external 85% H_3PO_4. ^{199}Hg chemical shifts measured relative to external 1M phenylmercury acetate in dimethyl sulfoxide. Coupling constants are given to the nearest 5 Hz, Phosphorus chemical shifts to 0.1 ppm and mercury and selenium chemical shifts to 5 ppm

		At 30°C		
Compound	$\delta(^{31}P)$	$J_{P, Hg}$	$\delta(^{199}Hg)$	$J_{Hg,P}$
$HgCl_2 (pmp)_2$	24.6	4790	980 t	4790
$HgBr_2 (pmp)_2$	18.9	4300	780 t	4280
$HgI2 (pmp)_2$	3.9	—		
$Hg_2Cl_4 (pmp)_2$	34.6	7810	645 d	7720
$Hg_2Br_4 (pmp)_2$	25.4	6750	340 d	6695
$Hg_2I_4 (pmp)_2$	7.3	4985	-475 d	4920
		At -50°C		
Compound	$\delta(^{31}P)$	$J_{P, Hg}$	$\delta(^{199}Hg)$	$J_{Hg,P}$
$HgCl_2 (pmp)_2$	24.6	4900	1005 t	4930
$HgBr_2(pmp)_2$	19.0	4410	830 t	4430
$HgI_2(pmp)_2$	4.2	3395	365 t	3430

coupling constant. Mixtures of $HgX_2(pmp)_2$ show rapid halogen exchange at room temperature, but at -50°C the exchange is reduced sufficiently so that the individual components are observed.

$$HgX_2(pmp)_2 + HgX_2'(pmp)_2 \longrightarrow 2\, HgXX'(pmp)_2$$

The complexes $HgX_2(PPh_3)_2$, (X= NO_3,Cl,Br,SCN,I and CN) have been studied by ^{31}P NMR techniques (183) and x-ray structural data are provided for the NO_3 and CN compounds (Figure 7). Table 27 presents ^{31}P chemical shifts, δ, and ^{31}P-^{199}Hg coupling constants, $^1J(Hg,P)$, for the complexes, as well as data for the complexes HgI_2P_2, [P= $P(m\text{-}CF_3C_6H_4)_3$, PPh_3, $(Ph_2PCH_2CH_2)_2S$, $PPh_2(CH_2Ph)$, $P(n\text{-}Bu)_2Ph$, $P(n\text{-}Bu)_3$, and $P(C\text{-}Hx)_3$]. The NMR data can be related to several physicochemical parameters and larger values of $^1J(^{199}Hg,^{31}P)$ are observed for

TABLE 27

^{31}P NMR Data for the Mercury-Phosphine Complexes HgX_2P_2 (183)

P	X	δ	^1J(Hg,P)Hz	T,K
PPh_3	NO_3	40.4	5925	210
PPh_3	CH_3COO	34.5	5510	220
PPh_3	Cl	28.3	4675	250
PPh_3	Br	21.8	4156	240
PPh_3	SCN	31.3	3725	220
PPh_3	I	1.2	3074	220
PPh_3	CN	17.9	2617	210
$P(m\text{-}CF_3\text{-}C_6H_4)_3$[a]	I	3.7	2922	170
$P(m\text{-}CF_3\text{-}C_6H_4)_3$	I	7.7	3201	220
$PPh_2(CH_2Ph)$	I	11.9	3624	210
$P\text{-}n\text{-}Bu_2Ph$	I		3726	
$P\text{-}n\text{-}Bu_3$	I	9.6	4221	220
$P\text{-}n\text{-}Et_3$	I	20.1	4239	215
$P(c\text{-}Hx)_3$	I	37.7	3491	220
PSP[c]	I	-4.5	3420	220
$P(c\text{-}Hx)_2Ph$	I	17.7	3689	220

[a] In acetone-d_6.

[b] (a) S. O. Grim, P. J. Lui, and R. L. Keiter, Inorg. Chem., 13, 342 (1974) ; (b) P. L. Goggin, R. J. Goodfellow, D. M. McEwan, and K. Kessler, Inorg. Chim. Acta, 44, L111 (1980).

[c] PSP = $(PH_2PCH_2CH_2)_2S$

TABLE 28 (182)

^{31}P, ^{77}Se and ^{199}Hg n.m.r. data for tributylphosphine selenide complexes

Complex	$\delta(^{31}P)$	$J_{P,Se}$	$\delta(^{77}Se)$	$J_{Se,P}$	$\delta(^{199}Hg)$
$HgCl_2(Bu_3PSe)_2$	46.4	512	1535 d	518	325 s
$HgBr_2(Bu_3PSe)_2$	44.7	542	1540 d	542	-105 s
$HgI_2(Bu_3PSe)_2$	43.4	562	1525 d	557	-1115 s
$HgCl_4(Bu_3PSe)_2$	45.1	527	1555 d	532	330 s
$HgBr_4(Bu_3PSe)_2$	47.4	500	1485d	505	-335 s
$HgI_4(Bu_3PSe)_2$	46.0	535	1480 d	545	-1395 s

TABLE 29 (184)

Chemical shifts of HgX_2 in different media.[a]

	$HgCl_2$	$HgBr_2$	HgI_2
Ethylenediamine		1112.0	566.2
Pyridine	1104.8	762.1	29.2
Aniline			-346.8
Hexamethylphosphoramide	951.2		-694.0
Methylsulfoxide	997.5	322.2	-734.7
Methylsulfoxide[d]	885.5	316.9	-746.8
N,N-Dimethylacetamide	888.5	280.3	-873.0
N,N-Dimethylformamide	859.9	265.7	-853.3
1-Methyl-2-pyrrolidinone	876.5	258.6	-905.9
1,1,3,3-Titramethylurea	877.5	245.2	-930.5
N-Ethylacetamide	873.7	240.0	-976.3[b]
Ethylalcohol	894.2	229.6	
Methylalcohol	870.6	222.5	
2-Ethoxyethanol	861.1	208.9	-992.8
Triethylphosphate	860.7	201.9	-1034.0
Tributylphosphate	865.7	191.0	-1062.1
Tributylphosphate[d]	864.9	184.7	-1076.1
Tetrahydrofuran	839.5	171.2	-1062.6
2-Methoxyethylether	808.6	160.1	-1026.9
Acetonitrile	826.9	115.7[b]	
2-Butanone	804.9	84.5	
n-Butylacetate	812.3	84.0[b]	
Ethylacetate	804.5	81.5[b]	
p-Dioxane			-1109.2[c]
Tetramethylenesulfone	772.6[b]		-1205.2[c]
Nitrobenzene			-1298.1[c,c]

[a] 0.5 m, 308 K, in ppm to high frequency of aq. $Hg(ClO_4)_2$. [b] Supersaturated (0.5m), [c] Saturated. [d] 1 m. [e] 408 K.

harder ligands than for the softer ones. Values for the $^1J(^{199}Hg,^{31}P)$ coupling constants values have been calculated using extended-Huckel methods. The trends obtained are in accord with the experimental findings and suggest that the ligand X as well as the P-Hg-P angle makes important contributions to changes in

$^1J(^{199}Hg,^{31}P)$. Both solution andd solid state data reveal a marked distortion of these molecules from idealized tetrahedral geometry. The solid state data also suggest a correlation between the P-Hg-P angle and the Hg-P distances: a decrease in the P-Hg-P angle being accompanied by an increase in the Hg-P bond length. Tributylpholphine selenide complexes of the mercury halides were also studied (182). At room temperature the ^{31}P NMR spectrum consisted of a single peak showing only selenium-77 satellites and the mercury-199 NMR spectrum was a singlet (Table28). The ^{31}P and ^{77}Se NMR spectra were almost the same in each case in marked contrast to the PBu_3 and pmp complexes whose spectra vary considerably with respect to the attached halogen.

The ^{199}Hg chemical shifts of HgX_2, (X = Cl,Br,I) have been determined in a number of nonaqueous solvents (184) and found to vary over a range of 2400 ppm (Table29).A rather complicated temperature dependence was also noted (Table 30).

TABLE 30

Temperature depencence of chemical shifts.[a] (184)

		$HgCl_2$	$HgBr_2$	HgI_2
Pyridine	0.5 m[b]	68	-92	-283
Methylsulfoxide	0.5 m[b]	19	-74	-241
Methylsulfoxide	0.5 m[c]	15	-75	-235
Methylsulfoxide	1 m[b]	17	-71	-243
Methylsulfoxide	1 m[c]	15	-73	-234
Tributyl phosphate	1 m[b]	-3	-68	-176

[a] In Hz. [b] v318K - v308K. [c] v328K - v318K.

The chemical shifts, δ_F(ppm), of the compounds $ArHgC_6H_4F$-4 have been determined by ^{19}F-^1H NMR in C_6H_5Cl (185). The data, as presented in Table 31, indicate that the ability of the mercury to transfer electronic effects from the aromatic substituents is lower than that of a methylene bridging group.

TABLE 31

δ_F(ppm) For the Compounds $ArHgC_6H_4F$ relatived to $C_6H_5F^a$ (185)

Ar=	δ_F(ppm)
$4\text{-}(CH_3)_2NC_6H_4\text{-}$	0.30
$4\text{-}CH_3OC_6H_4\text{-}$	-0.04
$4\text{-}CH_3C_6H_4\text{-}$	0.04
$C_6H_5\text{-}$	-0.16
$4\text{-}FC_6H_4\text{-}$	-0.37
$3\text{-}FC_6H_4\text{-}$	-0.52
$4\text{-}ClC_6H_4\text{-}$	-0.44
$3\text{-}ClC_6H_4\text{-}$	-0.55
$3\text{-}CF_3C_6H_4\text{-}$	-0.69
$3,4\text{-}Cl_2C_6H_3\text{-}$	-0.78
$3,5\text{-}Cl_2C_6H_3\text{-}$	-0.91
$3,4,5\text{-}Cl_3C_6H_2\text{-}$	-1.15

Strelenko et al. (186) have examined the temperature and concentration dependence of the ^{199}Hg chemical shifts of $Hg(CH_2COC_2H_5)_2$, **121**, and $Hg(CH_2CO\text{-}CH_2CO_2CH_3)_2$, **122**, in benzene solution. Both the NMR and IR data indicate self association of **121** and **122** in solution with the formation of weak intermolecular coordination bonds, $Hg \leftarrow :O{=}C$. The self association constants, K, have been determined for both **121** and **122** and are presented in Tables 32 and 33, respectively.

TABLE 32

Self association constant, K, and free molecule (δ_A) and selfassociate (δ_{A2})-mercury -199 chemical shifts for compound 121 at various temperatures. (186)

T(°C)	K(l/mole)	$-\delta_A$(ppm)	$-\delta_{A2}$(ppm)
25	8.7 ± 0.3[a]	735.9 ± 0.5[a]	858.6 ± 0.9
35	7.1 ± 0.4	735.1 ± 0.9	857.2 ± 1.5
45	6.1 ± 0.4	733.0 ± 0.9	855.3 ± 1.8
55	5.3 ± 0.4	730.6 ± 0.9	853.8 ± 2.3
65	4.5 ± 0.4	728.0 ± 1.0	852.7 ± 3.0
75	3.9 ± 0.4	725.3 ± 1.0	852.3 ± 3.7

[a] Standard deviation.

TABLE 33

Self association constant, K, and free molecule (δ_A) and selfassociate (δ_{A2}) mercury -199 chemical shifts for compound 122 at various temperatures. (186)

T(°C)	K (l/mole)	$-\delta_A$(ppm)	$-\delta_{A2}$(ppm)
25	4.1 ± 0.3[a]	843.3 ± 0.6[a]	932.8 ± 1.4[a]
35	3.7 ± 0.2	842.3 ± 0.4	931.3 ± 1.1
45	3.3 ± 0.1	841.1 ± 0.3	930.1 ± 1.0
55	3.0 ± 0.2	839.9 ± 0.4	928.9 ± 1.5
65	2.7 ± 0.2	838.5 ± 0.6	927.9 ± 2.3
75	2.4 ± 0.3	837.2 ± 0.7	927.2 ± 3.4

[a] Standard deviation.

Thermodynamic parameters, for the self association are as follows:

Compound	ΔH(kcal/mole)	ΔS(e.u.)
121	-3.2 ± 0.1	-6.5 ± 0.5
122	-2.1 ± 0.1	-4.4 ± 0.5

Phenyl group exchange between $[Hg(DMSO)_6](O_3SCF_3)_2$ and $[C_6H_5Hg(DMSO)_2](O_3SCF_3)$ has been investigated by ^1H, ^{13}C and ^{199}Hg NMR spectroscopy (187).

$$RHg^+ + (Hg\text{-}Hg)^{2+} \rightleftharpoons (RHg\text{-}Hg)^+ + Hg^{2+} \qquad (21)$$

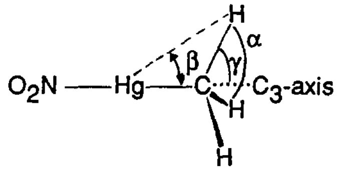
Addition of Hg_2^{2+} to a solution of $C_6H_5Hg^+$ did not result in direct exchange, but rather, phenyl group exchange occurs between $C_6H_5Hg^+$ and Hg^{2+} formed as a result of the disproportionation of Hg_2^{2+} (equation 21).

$$Hg_2^{2+} \rightleftharpoons Hg^{2+} + Hg^o$$
$$C_6H_5Hg^+ + Hg^{2+} \rightleftharpoons Hg^{2+} + C_6H_5^+$$

The reaction follows second order kinetics with bimolecular rate constants $k_2 = 1.3\times10^4$ l/mol s in methanol and $k_2 = 3.1\times10^2$ l/mol s in DMSO.

The ^1H and ^{13}C NMR spectrum of CH_3HgNO_3 have been recorded in both nematic and lyotropic liquid crystals (188) and used to determine the complete r_α-structure. Structural parameters are presented in Table 34.

TABLE 34
Structural parameters of methylmercury nitrate in the nematic ZLI phase and lyotropic phase. Only the corrected values are reported.[a] (188)

	Parameter	ZLI 1167	Lyotropic Phase
	β/deg.	23.67 ± 0.08	23.9 ± 0.2H
	γ/deg.	71.66 ± 0.06	72.29 ± 0.04
	α/deg.	110.58 ± 0.04	111.17 ± 0.06
	r(H-H)†/pm	180.36 ± 0.02	181.00 ± 0.05
	r(Hg-H)†/pm	259.4 ± 0.8	257.5 ± 2.0
	r(Hg-C)†/pm	2.03 ± 0.09	202.0 ± 2.0
	S_{C_3}	-0.07140 ± 0.00001	-0.03466 ± 0.00001

---

[a] The values reported here are those corresponding th the corrected coupling constants.
† r(C-H) fixed to 109.7 pm.

The r_α-structure of dimethylmercury has also been determined in the nematic ZLI 1167 liquid crystal (189). The study confirms earlier results, indicating that the structure is essenticlly independent of the liquid crystal solvent. The Hg-C distance was found to be 207.97 ± 0.05 pm (vibrational corrections included) and is similar to that obtained with other spectroscopic methods. Shielding anisotropies of 370 ± 0.3 ppm and 7325 ± 55 ppm for ^1H and ^{199}Hg, respectively, were obtained.

The C-H, C-F, Hg-C, Hg-H and Hg-F spin-spin coupling constants of CF_3HgCH_3, in hexadeuterobenzene, have been determined (190). The J(Hg-H) and J(Hg-F) coupling constants were also measured in nematic Merck ZLI 1167, ZLI 1132 and Phase IV liquid crystals heated to isotropic states. The indirect coupling constants determined in benzene-d6 using ^1H, ^{13}C and ^{199}Hg resonances are shown in Table

35. The J(Hg-H) and J(Hg-F) values measured in the isotropic states of the liquid crystal solvents at different temperatures are presented in Table 36. A comparison between coupling constants in CF_3HgCH_3, $(CH_3)_2Hg$ and NO_3HgCH_3 are give in Table 37. The Rα-structure of CF_3HgCH_3 was also determined in the nematic ZLI 1132, ZLI 1167 and Phase IV liquid crystals. Internuclear distances ratios, bond angles and orientational parameters are given in Table 38.

Table 35
The indirect coupling constants of CF_3HgCH_3, as determined in hexadeuterobenzene . (190)

Coupling	Value(Hz)
^1J(C-H)	133.6 ± 0.2
^1J(C-F)	-360.7 ± 0.3
$^1J(Hg\text{-}CH_3)$	976.8 ± 0.3
$^1J(Hg\text{-}CF_3)$	1740.7 ± 0.7
^2J(Hg-H)	-139.47 ± 0.05
^3J(Hg-F)	926.4 ± 0.1
^3J(C-H)	-3.7 ± 0.2
^3J(C-F)	11.8 ± 0.2
^4J(H-F)	0.44 ± 0.05

TABLE 36
The Hg-H and Hg-F spin-spin coupling constants (in Hz) of CF_3HgCH_3 in the liquid crystals Phase IV, ZLI 1132 and ZLI 1167. Estimated error limits are 0.2 Hz for both coupling constants. (190)

T(K)	Phase IV		ZLI 1132		ZLI 1167	
	J(Hg-H)	J(Hg-F)	J(Hg-H)	J(Hg-F)	J(Hg-H)	J(Hg-F)
313			-137.5	9.49.1		
323	-137.2	945.1	-137.8	950.2	-137.8	956.0
343	-136.9	947.3	-137.6	952.5	-137.5	958.2
363	-136.6	948.9	-137.2	954.5	-137.4	959.3
300[a]	-137.5	942.7	-137.8	947.7	-138.0	955.1

[a] The J values were obtained by extrapolation.

TABLE 37

Comparison of some indirect coupling constants in CF_3HgCH_3, $(CH_3)_2Hg$ and NO_3HgCH_3 in various solvents (190)

Coupling constants	CF_3HgCH_3	$CH_3HgCH_3{}^{1a}$	NO_3HgCH_3
^1J(C-H)	133.6^a	129.5^b 129.3^c	140.6^d
^1J(Hg-CH_3)	976.8^a	693.3^b 699.5^c 693.8^f 699.2^i	1697^g 1794^d
^1J(Hg-CF_3)	1740.7^a		
^2J(Hg-F)	942.7^e 947.7^h 955.1^j		
^2J(Hg-H)	-139.47^a -137.5^e -137.8^h -138.0^j	-102.1^b -103.0^c -102.2^f -102.6^i -102.2^k	-259.3^d -242.5^g
^3J(C-H)	-3.7^a	-1.8^b -1.8^c	

^{a} In C_6D_6 ; 24.6 wt. %. ^{b} In C_6D_6 ; 55 mol%. ^{c} In C_6D_6 ; 10 mol%. ^{d} In D_2O ; 2.6 mol% ^{e} In Phase IV ; 8.8 wt%. ^{f} In Phase IV ; 15 mol%. ^{g} In ZLI 1167 ; 8.8 wt%. ^{h} In ZLI 1132 ; 17.3 wt%. ^{i} In Phase V ; 15 mol%. ^{j} in ZLI 1167 ; 25.5 wt%. ^{k} In MMBA ; 3 mol%.

The ^{199}Hg NMR chemical shifts, equilibrium constants, solvent effects and kinetic properties of XHgCN, (X=Cl, Br, OAc, CF_3SO_3, SCN, SEt ans Ph), have been investigated (191). Table 39 summarizes the ^{199}Hg chemical shifts obtained for the mixed species, XHgCN. The chemical shifts were found, without exception, to be between those of the respective symmetric compounds $Hg(CN)_2$ and HgX_2.

^{199}Hg NMR spectra of solutions of $(2XC_6H_4)_2N_3HgY$, (X= Me,F,Cl,Br,I ; Y= Cl,Br,I,CN) and $(2XC_6H_4)_2N_3HgN_3(2ZC_6H_4)_2$, (X=Me,F ; Z= H,Me,F,Cl,Br,I) have been investigated (Tables 40 and 41, respectively) (192). The spectra exhibit three lines consistent with the presence of both the asymmetric and the symmetric componds in solution.

TABLE 38

Internulcear distance ratios, bond angles and orientation parameters in CF_3HgCH_3 as determined in three different liquid crystals. The values correspond to the vibrationally corrected coupling constants . (190)

Parameter	Phase IV	ZLI 1132	ZLI 1167	El. Diffr.^{a} + microwave
r_{HH}/r_{CH}	1.638 ± 0.001	1.620 ± 0.008	1.652 ± 0.007	1.611
r_{CC}/r_{CH}	3.89 ±0.07	3.84 ± 0.40	3.71 ± 0.17	3.862
r_{HgCH_3}/r_{CH}	1.888 ± 0.003	1.72 ± 0.02	1.85 ± 0.02	1.902
r_{HgCF_3}/r_{CH}	2.00 ± 0.07	2.12 ± 0.40	1.86 ± 0.17	1.960
r_{CF}/r_{CH}	1.43 ± 0.29			1.255
-HHgC$_2$(deg)	23.12 ± 0.03	24.3 ± 0.2	23.9 ± 0.2	
-HCH(deg)	109.90 ± 0.01	108.19 ± 0.08	111.40 ± 0.07	107.3 ± 1.5
-FHgC$_4$(deg)	30 ± 10			
-FCF(deg)	114 ± 9			105.7 ± 0.2
S_{C_3}^{b}	0.0939 ± 0.0003	0.0150 ± 0.0005	-0.0143 ± 0.0003	

^{a}Calculated from the results of ref 5. ^{b} Assuming r_{CH}= 1.079Å

On the other hand, only one ^{199}Hg NMR signal is displayed by the organomercuriotriazenes $(2XC_6H_4)_2N_3HgC_6H_5$, (X= Me,F,Cl,Br,I). A three line spectra was also observed in a 2:1:1 solution of HgT (TH= 1,3-diaryl-1-triazene), $HgCl_2$ and HgBr indicative of the following fast ligand exchange process.

$$\mathrm{HgCl + HgBr \rightleftharpoons 2\,Hg(Cl)Br}$$

$$\mathrm{THgCl + HgBr_2 \rightleftharpoons THgBr + Hg(Cl)Br}$$

$$\mathrm{THgBr + HgCl_2 \rightleftharpoons THgCl + Hg(Cl)Br}$$

$$\mathrm{THgCl + THgBr \rightleftharpoons THgBr + THgC}$$

An interesting feature of the spectra of the $(2X_6H_4)N_3HgY$ and $(2XC_6H_4)_2N_3HgN_3$-$(2ZC_6H_4)_2$ complexes is the resonance position of the asymmetric species relative to the symmetric compounds described by the factor ;

TABLE 39

^{199}Hg Chemical shifts and equilibrium constants for the mixed species XHgCN (191)

Species	Solvent	$\delta(^{199}Hg)^a$	K^b	f^c
ClHgCN	Methylsulfoxide	997	3.7	0.257
	2-Ethoxyethanol	969		0.249
	Tributyl phosphate	974		0.243
	Pyridine	1266	2.6	0.226
BrHgCN	Methylsulfoxide	828	0.69	0.289
	2-Ethoxyethanol	789		0.270
	Tributyl phosphate	788		0.270
	Pyridine	1137	0.27	0.318
IHgCN	Methylsulfoxide	519	0.066	0.291
	2-Ethoxyethanol	441		0.271
	Tributyl phosphate	446		0.271
	Pyridine	893	0.097	0.327
AcOHgCN	Methylsulfoxide	711	300	0.343
	2-Ethoxyethanol	651		0.359
	Pyridine	967	5.2	0.404
CF_3SO_3HgCN	Methylsulfoxide	709	0.69	0.334
NCSHgCN	Pyridine	1370	0.24	-0.699
EtSHgCN	Pyridine	1452	0.98	-0.665
PhSHgCN	Pyridine	1385	0.65	-0.879
PhHgCn	Pyridine	1377	>10000	0.227

[a] 0.2m, 308K, in ppm to high frequence of aq. $Hg(ClO)_2$

[b] $K=(XHgCN^2/(Hg(CN)_2(HgX_2)$

[c] $f= (\delta(Hg(CN)_2) - \delta(XHgCN)/| \delta(Hg(CN) - \delta(HgX_2)|$

$$f=[\partial(HgY_2)-\partial(XHgY)]/[(\partial(HgY_2)-\partial(HgX_2)].$$

The $\partial(^{199}Hg)$, for the mixed compounds, $(2XC_6H_4)_2N_3HgN_3(2ZC_6H_4)_2$, moves toward $\partial(^{199}Hg)$ for $[(2ZC_6H_4)N_3]_2Hg$ and then beyond it in the order Z = Me < F < Cl < Br < I . These complexes are the first asymmetric mercury compounds whose resonance is found outside the range of the respective symmetric species.

TABLE 40
NMR Parameters of $(2XC_6H_4)_2N_3HgY^a$ (192)

Y	Cl		Br		I		CN		C_6H_5	
X	$\delta(^{199}Hg)^b$	f^c	$\delta(^{199}Hg)^b$	f^c	$\delta(^{199}Hg)^b$	f^c	$\delta(^{199}Hg)^b$	f^c	$\delta(^{199}Hg)^b$	f^c
Me	858	0.54	685	0.65	350	0.52	1023	0.44	1216	0.40
F	877	0.43	721	0.24	384	0.64	996	0.43	1149[d]	0.44
Cl	848	0.52	662	0.63	308	0.48	1023	0.41	1202	0.40
Br	851	0.51	660	0.64	199	0.47	1042	0.38	1212	0.39
I	866	0.52	660	0.84	271	0.40	1063	0.37	1227	0.39

[a] solutions of 0.5 mmol $[(2XC_6H_4)_2N_3]_2Hg$ and HgY_2/ml pyridine, 300K
[b] in ppm to high frequency of aqueous $Hg(ClO_4)_2$ (2mmol HgO/ml 60% $HClO_4$)
[c] $f = (\delta(HgY_2) - \delta((2XC_6H_4)_2N_3HgY))/(\delta(HgY_2) - \delta([(2XC_6H_4)_2N_3]_2Hg))$
[d] P. Peringer, Inorg. Chim. Acta, in press

Roberts, Vidusek and Bodenhausen (193) have used ^{199}Hg NMR to examine the adducts between ethylmercury phosphate and a variety of amino acids (Table 42). The study indicates that ^{199}Hg NMR can be a useful probe in studying the interactions of mercury compounds with proteins. An observed chemical shift difference of 300 ppm between HgN and HgS adducts was more than enough to allow differentiation between ethylmercury(II) bound to cystenic or EMP bound to histidene or tryptophan residues in a given protein.

Mercury derivatives of aldehydes, ketones and allylic compounds have been studied by ^{13}C NMR, vibrational (Raman), UV photoelectron spectroscopy, polarography and negative ion mass spectroscopy (194). The data obtained support results of earlier studies in that they show σ-π conjugation of the carbon-mercury bond with C=O and C=C bonds. The degree of conjugation is largely determined by geometric factors.

Olah et. al. (18) have studied the long lived ethylene, cyclohexene and norbonene mercurinium ions, prepared in super acid $[FSO_3H/SbF_5/SO_2]$ by ^{13}C and ^{199}Hg NMR spectroscopy. The cyclohexene mercurinium ion gave a ^1H NMR spectrum identical with that previously reported [G. A. Olah & P. R. Clifford, J. Am.

TABLE 41
NMR Parameters of $(2XC_6H_4)_2N_3HgN_3(2ZC_6H_4)_2$[a] (192)

X	Z	$\delta(^{199}Hg)$[b]	f[c]	$J(^{19}F - ^{199}Hg)$[d]
Me	H	678	0.40	
	Me	647		
		635[e]		
	F	608	0.56	
	Cl	630	0.42	
	Br	631	0.37	
	I	628	-2.41	
F	H	638[f]	0.46	
	Me	604	0.40	84
	F	574[g]		80
	Cl	607	0.78	71
	Br	628	1.31	74
	I	661	1.41	72
Cl	Cl	604		
Br	Br	600		
I	I	639		

[a] solutions of 0.5mmol $[(2XC_6H_4)_2N_3]_2Hg$ and $[(2ZC_6H_4)_2N_3]_2Hg$/ml pyridine, 300K; for X = F and Z = Me, F, Cl, Br, I : 263K

[b] in ppm to high frequency of aqueous $Hg(ClO_4)_2$ (2mmol HgO/ml 60% $HClO_4$)

[c] $f = (\delta([(2XC_6H_4)_2N_3]_2Hg - \delta((2XC_6H_4)_2N_3HgN_3(2ZC_6H_4)_2) / (\delta([(2XC_6H_4)_2N_3]_2Hg) - \delta([(2ZC_6H_4)_2N_3]_2Hg))$

[d] in Hz [e] in benzene [f] supersaturated [g] P. Peringer, Inorg. Chim. Acta, in press

Chem. Soc. 95 6067] consisting of three slightly broadened singlets at δ^1H 7.85, 2.58, and 1.60. The mercury coupling constants to the alpha and beta protons are $J_\alpha(^{199}Hg\text{-}^1H) = 174$ Hz and $J_b(^{199}Hg\text{-}^1H) = 248$ Hz, respectively. The proton decoupled ^{13}C NMR at -60°C shows three sharp singlets [$\delta^{13}C$ 151.71(α), 28.35β) and 20.95(γ) ; $J(^{199}Hg\text{-}^{13}C) = 160$ Hz] corresponding to a symmetric cyclohexene mercurinium ion. The $^{199}Hg(^1H)$ spectrum exhibits a slightly broadened resonance centered at $\delta^{199}Hg = -1764.7$ (referred to external dimethylmercury). The ^{13}C NMR spectrum of trhe norbornene mercurinium ion (-70°C) exhibited four signals indicative of a symmetrical bridged ion. The vinylic carbon appear at $\delta^{13}C$, 151.47

TABLE 42 (193)

^{199}Hg Chemical shifts and linewidths of ethyl mercury adducts

Adduct[a]	pH	^{199}Hg Chemical Shift (ppm)	^{199}Hg Linewidth[c] (Hz)
EMP[d]	3.2	0	10 ± 1
EMP	7.1	31.4 ± 0.4	44 ± 7
EM-Inidazole	8.2	191.1 ± 0.4	53 ± 6
EM-Histidine	5.6	189.2 ± 0.8	277 ± 14
EM-Tryptophan	3.1	256 ± 10	-
EM-Glycine	3.8	7 ± 10	-
EM-Glycine	7.5	231 ± 10	-
EM-Aspartate	2.6	-3 ± 10	-
EM-Aspartate	8.6	38 ± 10	-
EM-3′,5′-c-AMP	7.2	49 ± 10	-
EN-3′,5′-c-AMP	7.4	162 ± 10	-
EM-Cysteine	2.6	566 ± 10	-
EM-2-mercaptoethanol	7.3	608 ± 10	-
EM-thiosalicylate	8.5	500.1 ± 0.1	32 ± 3

[a] Concentrations vary from 10 - 160 mM

[b] Reference is 155 mM EMP in $^{2}H_2O$ (pH 3.2); 295 K. Actual ^{199}Hg resonance at 48, 297, 652 ± 11 Hz in 270 MHz spectrometer

[c] No Linewidth indicated if shift determined by spin-echo method only

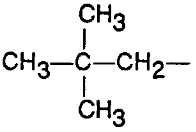
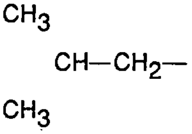
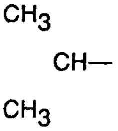
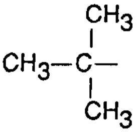
[d] EMP = ethylmercury phosphate

[J(^{199}Hg-^{13}C) = 240 Hz], carbons 1 and 4 resonate at δ^{13}C, 47.39 [J(^{199}Hg-$^{13}C_\beta$) = 120 Hz], and carbons 5 and 6 at δ^{13}C 21.31 with J(^{199}Hg-$^{13}C_{5,6}$) = 260 Hz. Carbon 7 appears at δ^{13}C 48.55 with J(^{199}Hg-$^{13}C_7$) = 75 Hz. The ^{13}C and ^{199}Hg NMR spectra exhibit a temperature dependence consistent with equilibrium via rapid hydride and Wagner-Merwin shifts. The ^{1}H NMR spectrum of the ethylene mercurinium ion (-10°C) shows a single resonance at δ 7.31 [J(^{199}Hg-^{1}H) = 160 Hz] and the ^{13}C NMR spectrum shows a broad peak centered at δ^{13}C 147.7. No ^{199}Hg absorption could be obtained for the ion.

The chemical shifts of a series of alkylmercuric bromides were also reported (Table 43). The effect of a methyl group on the ^{199}Hg chemical shifts were calculated and

TABLE 43

^{199}Hg chemical shifts of alkylmercury bromides (18)

R HgBr	No. of β	δ(^{199}Hg), ppm	Calc., δ ppm	Deviation (%)
CH_3-	—	959.1* 956.1 ± 3 953.1	—	—
 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-$	0	-1055.5	1039	-16 (0.47)
 $\begin{matrix}CH_3 & \\ & CH-CH_2- \\ CH_3 & \end{matrix}$	1	-1061.3	1049	-12 (0.35)
$CH_3-CH_2-CH_2-$	2	-1078.0	1079	+1 (0.03)
$CH_3-CH_2-CH_2-CH_2-$	2	-1079.0	—	—
$CH_3-(CH_2)_3-CH_2-$	2	-1073.0	—	—
CH_3-CH_2-	3	-1108.15	1099	-9 (0.45)
 $\begin{matrix}CH_3 & \\ & CH- \\ CH_3 & \end{matrix}$	6	-1250.4	1239	-11 (0.55)
 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-$	9	-1361	1379	+18 (0.9)

All chemical shifts are referred to pure dimethylmercury. All determinations were performed on 1 M solutions in dimethyl sulfoxide at room temperature.
* From M. A. Sens, N. K. Wilson, P. D. Ellis & J. D. Odon, J. Mag. Res. 19, 323 (1975).

found to be -140 ppm, +20 ppm, -1 ppm and +5 ppm for the α, β, γ, and δ effects, respectively.

C. Electronic Spectroscopy

Electronic spectroscopy and electrical conductivity methods have been used to study the raction of DMSO with a series of o- and p-nitrothiophenol derivatives of the type $ArSMR_n$, (MR_n= C_6H_5Hg, $(C_6H_5)_3Sn$, $(C_6H_5)_2Sb$ and $(C_6H_5)_4Sb$; Ar= o- and p-nitrothiophenol). (195). The absorption bands of the p-nitrothiophenol derivatives show a bathochromic shift relative to uncomplexed p-nitrothiophenol in benzene solution, however, the shift is less pronounced than in the case of the p-nitrophenol derivatives [L.M. Epshtein, et al. Izv. Akad. Nauk SSSR, Ser. Khim, 2515 (1978)] In DMSO an equilibrium is established between the molecular complexes and ions. The values of the complexation constants, K_{comp}, range from 0.7 to 4 liters/mole and fall off in the order

$$ArSHgPh > ArSH\ ,\ ArSSbPh_2 > ArSPbPh_3 > ArSSbPh_4 > ArSSnPh_3$$

Anderson and Maki (196) have studied the triplet state kinetics of $CH_3Hg(II)$ complexes with benzimidazole, (HBIm), and triptophan, (Trp). they found that the heavy-atom effect in these complexes leads to a reduction in the individual sublevel lifetimes due primarily to an increase in the radiative rate constant. The effect also causes radiative enhancement of triplet-state decay with the in-plane spin sublevels being most affected in both complexes. For example, the triplet state lifetimes are reduced by a factor of 40 for $CH_3HgHBIm^+$ and a factor of 800 for the CH_3HgTrp complex. Polarized phosphorescence excitation measurements gave P = -0.18 over the $^1L_a$and ^1L_b absorption bands indicating out-of-plane polarization; whereas for $CH_3HgHBIm^+$, P = 0.06 over ^1L_a and P = -0.06 over ^1L_b indicative of in-plane polarization. The electronic absorption spectra of Group II and IVB pentafluorophenyl-organo di- and polymetallic compounds have also been (Table 44) (197).Compounds of the type $Ph_3^FGe\text{-}X\text{-}GePh_3^F$ show an appreciable hypsochromic shift with the introduction of X= Cd,Hg into the molecule. The magnitude of the shift, $\Delta\lambda$, increases from 8nm for Cd to 18nm for Hg and decreasing with increasing atomic number of the Group IVB element, ($\Delta\lambda$ = 23nm, 18nm, 8nm for Si, Ge, and Sn, respectively). The shift is suggested to be a result of intramolecular coordination of the orthofluorine atoms of the Ph^F ring with the Cd or Hg atom.

Imai and coworkers (198) have reported the vibrational spectra and normal coordinate calculations for methylethynylmercury(II)-d_0,-d_1,-d_3 and -d_4. The Hg-CH_3 and Hg-CCH stretching frequencies have been assigned to the bands at

501 cm^{-1} and 425 cm^{-1}, respectively. The Hg-CCH force constant was determined to be 2.83 mdyn $Å^{-1}$.

TABLE 44 (197)

Selected Values for λ_{max} of the Longwave Absorption Bands (Ph^F=C_6F_5, L = PPh_3)

Compound	λ_{max}, nm, in pentane	λ_{max}, nm, CH_2CL_2
$Ph_3{}^FSiSiPh_3{}^F$	239 sh, 273	272
$Ph_3{}^FGeGePh_3{}^F$	239 sh, 268	268
$Ph_3{}^FSnSnPh_3{}^F$	243 sh, 268 sh	268 sh
$Ph_3{}^FSiHgSiPh_3{}^F$	250	252
$Ph_3{}^FGeHgGePh_3{}^F$	250, 257 sh	250sh,257
$Ph_3{}^FSnHgSnPh_3{}^F$	260, 276 sh	260 sh, 278
$Ph_3{}^FGeHg(Ph_2{}^F)Ge]_2$	256, 287, 317	255, 285, 315
$Ph_3{}^FGeHgPtL_2GePh_3{}^F$	267, 323, 350 sh	267, 323, 350 sh
$Ph_3{}^FSnHgPtL_2SnPh_3{}^F$	273, 285 sh, 335, 360 sh	273, 282 sh, 332, 335 sh

The ultraviolet and visible spectra of the compounds $Hg(SiCl_{3-x}R_x)_2$ (R=Me,Ph), $Hg(GeMe)_2$ and $Hg[Si(SiMe_3)_3]_2$ have been studied and tentative assignments proposed based on Extended Huckel calculations (Table 45) (199). In cyclohexane all compounds exhibit three characteristic bands: two at ~4eV and one at ~6eV (Table 46). The 4eV transitions have been assigned to transitions from the ground state, ${}^1A_1$, to ${}^1B_1$ and ${}^1A_2$ states, respectively. The 6eV transition has been assigned to a transition to an excited ${}^1A_1$ state. All transitions are between orbitals centered principally on mercury.

The complexation of molecular oxygen with aryl mercury compounds and phenyl derivatives of Group IV and V elements has been studied by electronic spectroscopy (200,201). Quenching constants Kq have been determined, under conditions of static quenching, for reaction with both O_2 and t-butyl peroxide. The results obtained for the organomercury derivatives (R_2Hg, R= p-$CH_3OC_6H_4$, p-$(CH_3)_2NC_6H_4$, p-CH_3-

TABLE 45 (199)

A comparison of Observed and Calculated Transition Energies for Selected Silyl - and Germyl - Mercury Derivatives having C_{2v} Symmetry

Compound	Band C		Band B		Band A	
	calcd.	obs.	calcd.	obs.	calcd.	obs.
$Hg(SiMe_3)_2$	3.54	3.18	3.63	3.78	5.76	5.79
$Hg(SiMe_2Cl)_2$	3.33	3.48	3.51	4.00	5.39	5.85
$Hg(SiMeCl_2)_2$	3.31	3.75	3.38	4.32	5.49	5.70
$Hg(SiCl_3)_2$	3.39	4.00	3.49	4.66	6.00	5.69
$Hg(GeMe_3)_2$	3.61	3.41	8.72	3.86	5.82	5.39
$Hg[Si(SiH_3)_3]_2$[a]	3.40	3.18	3.50	3.63	6.35	6.05

[a] The observed energies are those for $Hg[Si(SiMe_3)_3]_2$.

TABLE 46 (199)

A list of the major absorption maxima and extinction coefficients for silyl- and germyl-mercury compounds obtained in cyclohexane, THF and Et_3N.

Compound	Solvent	C		B		A	
		A	e	A	e	A	e
$Hg(SiMe_3)_2$	C_6H_{10}	3900	$1.1x10^2$	3280	$3.7x10^2$	2142	$2.6x10^4$
	THF	3700	$7.6x10^1$	3125	$2.9x10^2$	2125	$2.2x10^4$
	Et_3N	3860	$8.7x10^1$	3310	$2.8x10^2$	(obscured)	
$Hg(SiMeCl_2)_2$	C_6H_{10}	3308	$8.4x10^1$	2870	$3.7x10^2$	2175	$2.2x10^4$
	THF	2950	$5.0x10^1$	2550	$7.0x10^2$	2155	$1.8x10^4$
$Hg(SiMe_2Cl)_2$	C_6H_{10}	3560	$1.6x10^2$	3100	$6.2x10^2$	2120	$5.5x10^4$
	THF	3200	$1.6x10^2$	2740	$4.4x10^2$	2135	$2.2x10^4$
$Hg(SiCl_3)_2$	C_6H_{10}	3100	$1.4x10^2$	2660	$1.1x10^3$	2180	$1.8x10^4$
	THF	2700	$1.3x10^2$	2400	$1.7x10^3$	2150	$8.7x10^3$
$Hg[Si(SiMe_3)_3]_2$	C_6H_{10}	3900	$2.3x10^2$	3415	$7.6x10^2$	2050	$1.0x10^5$
				(2750	$1.4x10^4$)		
				(2580	$2.5x10^4$)		
				(2400	$3.0x10^4$)		
	THF	3900	$1.8x10^2$	3410	$7.2x10^2$	(out of range)	
				(2775-	$7.6x10^3$)		
				(2510	$2.6x10^4$)		
$Hg(GeMe_3)_2$	C_6H_{10}	3640	$1.8x10^2$	3215	$6.0x10^2$	2300	$4.6x10^4$
	THF	2550	$1.2x10^2$	2955	$5.2x10^2$	2275	$4.0x10^4$
	Et_3N	3640	$1.9x10^2$	3180	$5.5x10^2$	(obscured)	
$Hg(SiMe_2Ph)_2$	C_6H_{10}	3870	$1.8x10^2$	3300	$9.8x10^2$	2650	$9.0x10^3$
$Hg(SiMePh_2)_2$	C_6H_{10}	3795	$1.2x10^2$	3250	$1.7x10^3$	2740	$1.4x10^4$
$Hg(SiPh_3)_2$	C_6H_{10}	3850		3300		2850	
$Hg_2Si_4C_{10}H_{28}$	C_6H_{10}		(4350	$1.3x10^2$)			
			(3840	$6.3x10^2$)			

C_6H_4, C_6H_5, p-FC_6H_4, p-$C_2H_5COOC_6H_4$, C_6H_5; C_6H_5HgCl) are summarized in Table 47. In this series, Kq decreases with an increase in the π-donor properties of the organomercury derivative. Since neither the donor ability of the compound nor steric effects significantyly alter Dq the series show themselves to the typical V-acceptors forming π,v-complexes.

Shabanov et. al. (202) have determined the quenching constants, K_q, of the complexes R_2Hg, [R = C_6F_5, p-$C_2H_5CO_2C_6H_5$,p-FC_6H_4, C_6H_5, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$,p-$(CH_3)_2NC_6H_4$ and C^6H_5HgL (L= Cl, CCl_3)], with t-butylphosphine (TBP) and molecular oxygen as well as the frequencies of the charge transfer bands for these complexes with benzene .

The quenching constants, K_q, as determined by the Stern-Volmer equation

$$I_p^{TBP}/I_p = 1 + K_q[TBP]$$

TABLE 47

K_q Values of Complexes of Organomercury Compounds with TBP (K_qTBP) and O_2 (K_qO_2) and Frequencies of Charge-Transfer bands v^1_{CT} in Absorption Spectra of = Charge-Transfer Complexes (CTC) of These Compounds with Benzene. (202)

Sample NO.	Compound	$K_{qTBP}\cdot 10^{-2}$ liter ·mol^{-1}	$K_qO_2\cdot 10^{-2}$ liter·mol^{-1} (according) Shabanov and Kuznetsov	$v^1_{CT}\cdot cm^{-1}$
1	$(C_6F_5)_2Hg$	1.15	4.8	36400
2	C_6H_5HgCl	1.05	4.4	36550
3	(p-$C_2H_5CO_2C_6H_4)_2Hg$	0.80	4.0	36680
4	(p-$FC_6H_4)_2Hg$	0.70	3.9	36850
5	$(C_6H_5)_2Hg$	0.55	3.8	37000
6	(p-$CH_3C_6H_4)_2Hg$	0.45	3.8	37050
7	$C_6H_5HgCCl_3$	0.35	3.4	
8	(p-$CH_3OC_6H_4)_2Hg$	0.15	2.5	37600
9	[(p-$CH_3)_2NC_6H_4]_2Hg$	0.05	2.9	

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where I_p and I_p^{TBP} represents the intensity of phosphorescence in the absence and the presence of the quencher (TBP) ,respectively, are presented in table 47. It was found that the organomercury compound , upon complexation with TBP and oxygen, exhibits primarily σ-accepter properties, although they also display some π-donor properties but to a much lesser degree. Complex formation between the arylmercury derivatives and aromatic hydrocarbons, (C_6H_6, C_6H_5-CH_3, $C_6H_5C_2H_5$, p-$(CH_3)_2C_6H_4$, 1,3,5-$(CH_3)_3C_6H_3$, C_6H_5-OCH_3, $C_6H_5OC_2H_5$), was also examined (202) Benzene and its derivatives were found to compete with molecular oxygen during complex formation with the arylmercury derivative. Complexation of the benzene derivative with diphenylmercury results in the appearance of a new absorption band, v_{CT} ,with a frequency close to 3700 cm^{-1} (Table 48). This is taken as evidence for the formation of a donor-acceptor complex with the organomercury compound directly amalogous to the π-π type charge transfer complexes formed between π-donors and tetracyanoethylene.

TABLE 48 (202)

Charge-Transfer Frequency Values in Electronic Absorption Spectra of CTC of π-Donors with DiphenylMercury ($v^3{}_{CT}$) and Tetracyanoethylene ($v^3{}_{CT}$)

Sample	π-Donor	$v^3{}_{CT}.cm^{-1}$	$v^3{}_{CT}.cm^{-1}$ (according to Egorochkin et. al.
1	C_6H_6	37000	26050
2	$C_6H_5CH_3$	36500	24650
3	$C_6H_5C_2H_5$	36570	24250
4	p-$(CH_3)_2C_6H_4$	36000	24100
5	1,3,5-$(CH_3)_3C_6H_3$	35700	21700
6	$C_6H_5OCH_3$	34960	19650
7	$C_6H_5OC_2H_5$	34720	19300

[a] From a. N. Egorochkin, V. A. Kuznetsov, et. al., Dokl. Akad. Nauk SSSR, 227, 373 (1976) (Reproduced with permission from Plenum Publishing Corporation copy-right 1979)

Donckt and Antheunis (203) have investigated the effect of external pressure on the interaction between 9-cyanoanthracene and benz-(a)-anthracene in the S_1 state with dimethyl mercury in n-hexane and acetoniturle. In acetonitrile, 9-cyanoanthracene and dimethylmercury do not form an exciplex, but rather the fluorescence quenching involves a Eyring type activated complex. The quenching in n-hexane appears to take place by means of a contact complex as illustrated by the following equation.

$$A(S_1) + Hg(CH_3)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A(S_1)\cdot Hg(CH_3)_2 \xrightarrow{k_2} A(T_2)\cdot Hg(CH_3)_2$$

The rate constant for quenching in n-hexane is $(6.6 \pm 0.5) \times 10^7$ dm^3 mol^{-1} s^{-1} and the Arrhenius activation energy (E_a) is 8 ± 1 kJ mol^{-1}. In acetonitrile $k_Q = (4.0 \pm 1.0) \times 10^7$ $dm^3 mol^{-1} s^{-1}$ and E_a/kJ $mol^{-1} = 16 \pm 2$. Exciplex formation has, however, been confirmed in the quenching of benz-(a)-anthracene by dimethylmercury in polar solvents and a volume contraction for the system of -9 ± 2 $cm^3 mol^{-1}$ is consistent with the exciplex formation. The rate constants for quenching are k_Q(n-hexane) = $(3.3 \pm 0.3) \times 10^9$ dm^3 mol^{-1} s^{-1} and k_Q(acetonitrile) = $(3.30 \pm 0.3) \times 10^9$ dm^3 mol^{-1} s^{-1} and the enthalpy of formation of the complex between +30 and +60°C is : ΔH_f (n-hexane) = 4 ± 1 kJ mol^{-1} ; ΔH_f (acetonitrile) = 8 ± 1 kJ mol^{-1}.

High resolution He I_α (21.2 eV) and He II_α (40.8 eV) gas-phase photoelectron spectra have been obtained for the group 2B alkyls, R_2M, (M= Zn, Cd, Hg ; R= Me,Et ; and for Cd, R= n-Pr and Me_3SiCH_3) (204). The spectra of the compounds R_2M, (M=Cd, Hg ; R=Me, Et) exhibit two metal-carbon bonding orbitals at low binding energies (8-12 eV). Slightly higher in energy is a characteristically broad and intense (He I) band assigned to the carbon-hydrogen bonding orbitals (12-14 eV) and for the longer chain alkyls there is a band at ~15 eV associated with the alkyl group. The "core-like" d-levels appears as a series of peaks at high bonding energy (15-19 eV). The most prominant feature of the spectra is the dramatic increase in the intensity of the d-levels (Zn 3d, Cd 4d, and Hg 5d) relative to the valence-level intensities between He I and He II photon spectra. Plots of relative photoionization cross sections (normalized to the M $nd_{5/2}$ peak for Me_2M (M=Zn,Cd and Hg) show a rapid decrease in the C-H σ, C-M σ_u, and C-M σ_g levels. The only exception to this general behavior is the photoionization cross section of the Hg-C σ_g -bonding level in Me_2Hg which decreases only slightly between He I_α and He II_α radiations. This behavior is attributed to the mixing of Hg 5d character with the σ_g-bonding level.

11. ANALYTICAL ASPECTS OF ORGANOMERCURY CHEMISTRY

Pal and Saxena (205) have reported a new procedure for the identification of mono- and di- olefins in the presence of each other. The olefinic mixture is treated with excess mercuric acetate in a 1 : 1.2 molar ratio (olefin to mercuric acetate) in 25ml methanol in the presence of a catalytic amount of water and acetic acid. This mixture is then stirred for one hour at room temperature, applied to paper strips and eluted with a solution prepared from 50ml acetone, 10ml ammonia, and 0.5g ammonium carbonate. The strips are then dried and sprayed with a diphenyl carbazon solution. The R_f for the mono olefin is 0.5 and for the diolefin the R_f is 0.05.

A reasonably accurate and precise method for the analysis of blood for methylmercury has been described by Goolvard and Smith (206). The technique involves a three-stage solvent extraction and gas chromatography using an electron-capture detector and uses an internal standard (EtHgCl) to correct for losses during the separation procedure.

Polyurethane foam has been found to be a good trapping material for the quantitative recovery of mercury produced during the combustion of organomercury compounds (207). Various combustion methods have been investigated and the foam was found to function efficiently with all combustion procedures examined. The simultanious determination of mercury together with carbon and hydrogen was also achieved by trapping the mercury in polyurethane foam packed in a standard Pregl absorption tube, connected externally between the combustion and water absorption tubes, and determined gravimetrically.

The extraction of mercury(II) from aqueous solutions of $Hg(NO_3)_2$ and $HgCl_2$ with zolon red dissolved in n-butanol has also been reported (208).

Minagawa and Takizawa (209) describe the use of chelate resin preconcentration for the simultanious determination of traces of inorganic and organic mercury in fresh water The resin [Sumichelate Q-10 (Sumitomo Chemicals)] is a vinyl polymer containing dithiocarbamate groups which bind strongly with mercury but not with alkali and alkaline earth metals. Both forms of mercury can be collected from pH 1 to 11. Collected mercury is readily eluted with a slightly acidic aqueous 5% thiourea solution. The detection limit ot the method is 0.2 ng l^{-1} for both forms.

Hydrochloric acid-potassium permanganate and bromine monochloride have been used to break down organic mercury compounds for the determination of mercury by cold vapor atomic absorption spectrometry (210). Both procedures give quantitative recovery of mercury and the deterction limit (3σ) is 0.06 µg Hg l^{-1}.

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