2.   MERCURY

E.C. CONSTABLE

CONTENTS

INTRODUCTION

    This review is a continuation of the 1981 Review of mercury published in
this journal in 1983 [1]. The format and content is generally similar to that
adopted in previous years, although a new section concerned with species
containing a mercury-to-heterometal bond has been introduced. The section
dealing with the use of mercury in organic synthesis has been retained. The
use of ^{199}Hg NMR spectroscopy is now becoming more routine, and the section
discussing this has been reduced to a bibliographic compilation of reported
spectra. As before, papers dealing with the physical and spectroscopic
properties of mercury halides have been omitted from the scope of this review,
as they were thought to be of little interest to the coordination chemist.

    I should like to thank Dr. Olga Kennard, Dr. Sharon Bellard and Dr Paul

Raithby for their aid in obtaining data from the Cambridge Crystallographic
Data Centre.

2.1 MERCURY(II)

2.1.1 *Halide and pseudohalide complexes*

The reaction of xenon difluoride with HgX_2 (X = Cl, Br or I) leads to the
formation of HgF_2, X_2 and Xe [2]. The reaction of HgF_2 with AsF_5 in anhydrous
HF has been investigated, and the product shown, by vibrational and X-ray
powder diffraction spectroscopy, to be $HgF_2 \cdot 2AsF_5$ (*i.e.* $Hg(AsF_6)_2$) [3]. The
mixed-halide compound HgClBr is prepared according to the equations:

$$Hg_2Cl_2(s) + Br_2(g) \longrightarrow 2HgClBr$$
$$HgCl_2(s) + HgBr_2(s) \longrightarrow 2HgClBr$$
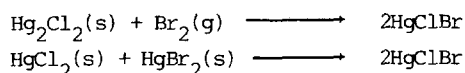
and exists in α and β forms, closely resembling those known for $HgCl_2$ [4].
HgI_2 is the product of the reaction of mercury(I) oxalate with molecular
iodine [5]. The enthalpy of formation of crystalline $HgBr_2$ at 298.15 K has been
determined as -175.5 ± 1.0 kJ mol^{-1} [6]. Structural studies of the compounds
$Hg(BrO_3)_2 \cdot 2H_2O$ and $K_2Hg(BrO_3)_2(NO_3)_2$ have been reported [7]. The use of
molten $HgBr_2$ as a stabilising solvent for mercury(I) species was described in
last years review [1], and a further example has appeared [8]. The reduction
of HgX_2 (X = Cl or Br) by zinc has been investigated, and the matrix-isolated
products characterised as ZnX and HgX [9]. The ^{15}N and ^{13}C NMR spectra of
$Hg(CN)_2$ and the ion $[Hg(CN)_4]^{2-}$ have been reported [10].

The γ-ray irradiation of $HgCl_2$ in either a sulphuric acid or alcohol glass
at 77 K results in the generation of HgCl, which has been characterised by
its EPR and vibrational spectra [11]. In hydrochloric acid glasses, the
product of such irradiation is the tetrachloromercurate(I) ion, $[HgCl_4]^{3-}$.
The equilibrium:

$$HgX_2 + Hg^{2+} \rightleftharpoons 2[HgX]^+$$

has been investigated [12]. In a related study, [199]Hg, ^{13}C and ^{15}N multinuclear
NMR techniques have been used in an investigation of the Hg^{2+}-$Hg(CN)_2$-D_2O
system in perchlorate rich medium. Evidence was presented for the formation of
the $[Hg_2(CN)_2]^{2+}$ ion [13]. The Raman spectra of solutions of $HgCl_2$ in
strong aqueous acid have been studied, and the changes in ν_S interpreted in terms
of the weakening of water(oxygen)-mercury interactions in strong acid [14].

Solutions of HgX_2 (X = Cl, Br or I) in dmso have been investigated by X-ray diffraction and Raman spectroscopic methods [15].

The ethyl acetate extraction of mercury(II) from chloride solution has been studied, and the extracted species shown to be of the stoichiometry $HgCl_2.2S$ [16].

The formation of halomercurate(II) anions continues to be of interest, and the interaction of $HgCl_2$ with aqueous chloride to form $[HgCl_3]^-$ and $[HgCl_4]^{2-}$ has been further studied [17]. At 25° C and i = 0, values for lgK $[HgCl_3]^-$ and lgK $[HgCl_4]^{2-}$ of 0.97 ± 0.14 and 1.61 ± 0.13 respectively have been determined. A spectroscopic investigation of $[Pr_4N][HgCl_3]$ has been reported, and it is concluded that, in the solid state, the anion forms halogen-bridged species with a symmetry lower than D_{2h} [18]. The anion-exchange extraction constants $K^{X-}_{HgX_3}$ for the extraction of $[HgX_3]^-$(X = Cl, Br or I) from HX medium by tri-octyloctadecylammonium salts in toluene have been reported [19]. The crystal structure of the complex $[C_6H_{13}N_4][HgCl_3]$ ($C_6H_{13}N_4$ = hexamethylenetetra-ammonium) has been described [20]. The anion consistes of planar trigonal $HgCl_3$ units, with longer axial Hg-Cl interactions completing a distorted trigonal bipyramidal configuration about the mercury, to give a chain structure (1).
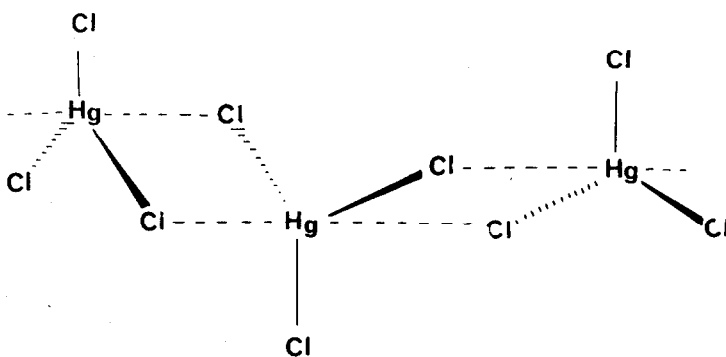

(1)

The related complexes $[n-Bu_4N][HgX_3]$ (X = Cl or I) are prepared by the reaction of HgX_2 with $[n-Bu_4N]X$ in acetone solution, and crystal structural analyses of the two compounds have been reported [21]. In the chloro species, the anion forms discrete bitetrahedral $[Hg_2Cl_6]^{2-}$ units, and the compound should thus be formulated $[n-Bu_4N]_2[Hg_2Cl_6]$. In contrast, $[n-Bu_4N][HgI_3]$ contains discrete $[HgI_3]^-$ anions, and, although there is no evidence for interactions between neighbouring HgI_3 units, the anions do not possess exact three-fold symmetry. The mixed trihalogenomercurate(II) species continue to be of interest,

and it is proposed that the anions in $[n-Pr_4N][HgCl_2X]$, formed in the reaction:

$$HgCl_2 + [n-Pr_4N]X \longrightarrow [n-Pr_4N][HgCl_2X]$$
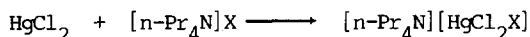
are actually dimeric $[Hg_2Cl_4X_2]^{2-}$ species [22,23]. On the basis of Raman spectroscopic studies, it is proposed that these anions possess structures (2) or (3).

(2)   (3)
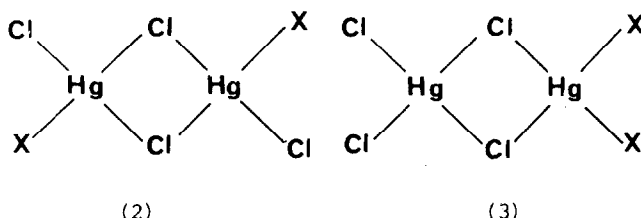
The reaction of $[n-Pr_4N][Hg_2Cl_4X_2]$ with bipy leads to the formation of complexes $[(bipy)HgClX]$(X = Br or I) [22]. In contrast, it is suggested that, in acetonitrile solution, the complex $[n-Pr_4N][HgI_2X]$ contains discrete trigonal planar HgI_3^- anions, although a dimeric structure is proposed for the solid state [24]. The compounds $KHgX_2CN \cdot H_2O$ (X = Cl or Br) are formed in the reaction of HgX_2 with KCN, and have been studied crystallographically [25]. The solid consists of linear HgX_2 and $Hg(CN)_2$ groups dispersed in a $K^+ X^-$ lattice. The complexes $HHgBr_2I \cdot 2py$ and $HHgBr_{3-x}I_x \cdot 3PhNH_2$ (x = 0,1 or 2) have been prepared by the reaction of the appropriate $HHgX_3$ etherate with pyridine or aniline [26]. These complexes are thought to possess a pyramidal geometry.

The thermal decomposition of $[Ph_2I]_2[Hg(CN)_4]$ has been studied by DTA and TG techniques; a phenyl group is transferred to the coordinated cyanide to produce an Hg – CNPh species [27]. The pseudohalide complexes $K_2[HgX_2Y_2]$ (X = Cl, Br, SCN or SeCN; Y = $N(CN)_2$ or $C(CN)_3$) have been prepared by the reaction of HgX_2 with KY in 1:1 methanol-acetone. The silver(I) salts have also been characterised [28]. The $CsI-HgI_2$ and also the mixed bromide-iodide systems have been investigated, and the $Cs_2HgBr_4-Cs_2HgI_4$ and $CsHg_2Br_5-CsHg_2I_5$ sections shown to be stable [29].

Clegg has investigated the crystal and molecular structures of the complexes $[M(NH_3)_6][HgCl_5]$ (M = Co or Cr) and has shown the anion to consist of a distorted trigonal bipyramidal $HgCl_5$ unit. The anion has three short equatorial Hg-Cl bonds (≈ 2.4 Å) and two longer axial Hg-Cl bonds (≈ 3.0 and 2.9 Å), and the metal is slightly out of the equatorial plane [30]. A crystal structure of the complex bis[bis(N,N'-di-n-butyldithiocarbamate)copper(III)][bis(N,N'-di-n-butyl-dithiocarbamato)copper(II) hexabromodimercurate(II) has been reported; the anion

consists of discrete edge-fused tetrahedral dinuclear units [31].

The crystal structure of the compound $Ag_2HgI_2(NO_3)_2 \cdot H_2O$ has been reported; the mercury is in HgI_2Ag_4 units (4) which form sheets between the anions [32].
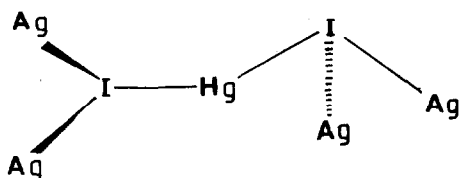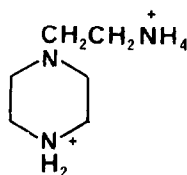
(4)   (5)

The reaction of N-(2-ammoniumethyl)piperazinium trichloride or tribromide $(LH_3X_3$; LH_3 = 5) with HgX_2 leads to the formation of complexes of stoichiometry LH_3HgX_5, but a crystal structural analysis of the compound has shown that it is more correctly described as $[LH_3][HgX_4]X$ [33]. The anion has a slightly distorted tetrahedral structure.

A number of tetrahalo and trihalomercurate(II) species have been examined by halogen nuclear quadrupole resonance spectroscopy, and the results appear to confirm the common occurrence of the $[Hg_2X_6]^{2-}$ ion in "HgX_3^-" compounds in the solid state [34].

The reaction of quinoline with HgI_2 gives the salt $[quinH][Hg_2I_5]$, whilst the related $[quinH]_2[Hg_3I_8]$ may be prepared by the reaction of $[quinH]_2[HgI_4]$ with HgI_2, or by melting $[quinH][HgI_3]$ in water [35]. The complex $[(3-Mepy)_2H]_2$ $[Hg_2I_6]$ has also been prepared [35]. It is suggested that the $[Hg_2I_6]^{2-}$ ion possesses D_{2h} symmetry, whereas $[Hg_2I_5]^-$ may have structures (6) or (7). The complex $[quinH]_2[Hg_3I_8]$ is probably better described as $[quinH]_2[HgI_3]_2 \cdot HgI_2$, as it shows an absorption at 210 nm, similar to that of the yellow form of HgI_2.
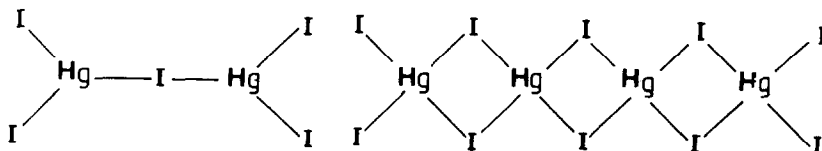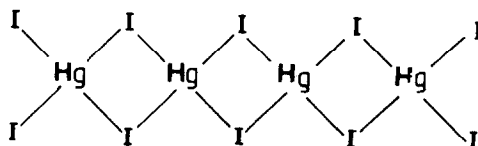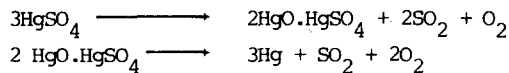

(6)   (7)

### 2.1.2 Complexes with oxygen donor ligands

Two groups have studied the thermal decomposition of mercury(II) sulphate [36,37]. On heating in either air or argon, sequential decomposition according

to the equations:

$$3HgSO_4 \longrightarrow 2HgO.HgSO_4 + 2SO_2 + O_2$$
$$2\,HgO.HgSO_4 \longrightarrow 3Hg + SO_2 + 2O_2$$

whereas simple vaporisation occurs in an SO_2 atmosphere [36]. A crystal structure of the complex [HgI(NO$_3$)] has shown the metal to be in an eight-coordinate O_6I_2 environment, with infinite zig-zag I-Hg-I-Hg-I- chains [38]. The HgClO$_4$-HClO$_4$-H$_2$O system has been investigated spectroscopically [39].

The crystal and molecular structure of the compound $C(HgOCOCF_3)_4$ has been determined; the Hg-C bond length is 2.042 Å, with Hg-C-Hg of 112.36° and 108.04° [40] The closest Hg-Hg interaction is at 3.393 Å. The complex [HgLX$_2$](L = ethyl 3-phenyl-2-cyanoacrylate, PhC=C(CN)CO$_2$Et) has been reported, and it is thought that the ligand acts as a bidentate *NO* donor [41]. Aromatic charge-transfer complexes of mercury(II) compounds have been known for many years, and have attracted considerable interest. A crystal structure of the compound $(C_6Me_6)Hg(O_2CCF_3)$ has revealed it to be a trifluoroacetate bridged dimer of structure (8), in which the the hexamethylbenzene acts as a η² ligand. The charge-transfer and magic angle spinning ^{1}H and ^{13}C NMR spectra of the solid closely resemble those of the solution, and it is suggested that this structure persists in solution [42].
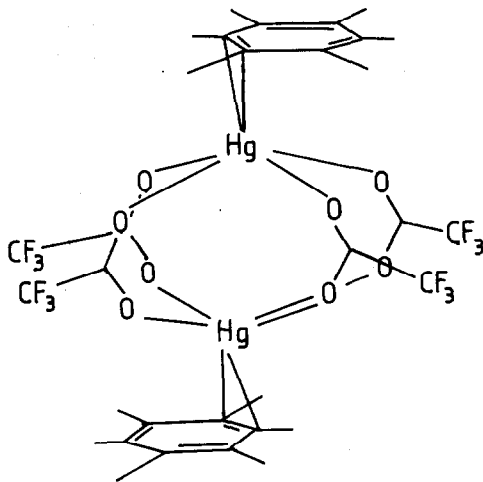

(8)

The complex $[HgL_2(SCN)_2]$ (L = 4-cyanopyridine N-oxide) has been characterised and is thought to possess a tetrahedral HgS_2O_2 coordination geometry, in which , the N-oxide acts as a monodentate oxygen donor [43]. The polymeric compounds $[ML]_n$ and $[ML(phen)]_n$ (H_2L = (9)) have also been reported, and it is thought that the ligand coordinates as a bridging bidentate, through the N-oxide oxygen atom and the carboxylate group [44]. The ESR spectrum of [Hg(salen)] (H_2salen = (10)) shows an isotropic resonance at g = 2.0023; the authors do not fully assign this resonance, but it might be due to a mercury(I) species [45].
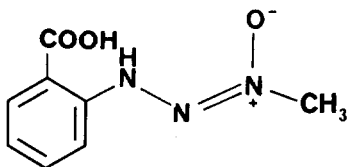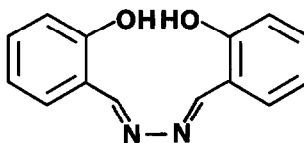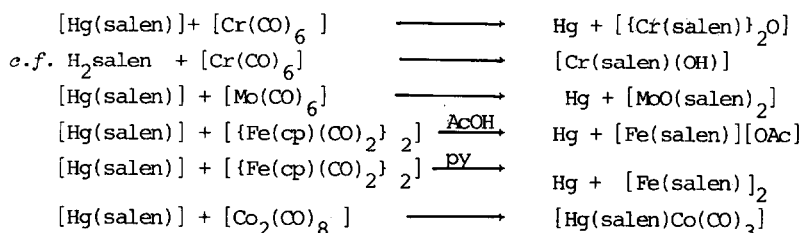

(9)   (10)

Treatment of [Hg(salen)] with a metal carbonyl results in a transmetallation reaction and the formation of metallic mercury:

$$[Hg(salen)] + [Cr(CO)_6] \longrightarrow Hg + [\{Cr(salen)\}_2O]$$

$c.f.$ $H_2salen + [Cr(CO)_6] \longrightarrow [Cr(salen)(OH)]$

$$[Hg(salen)] + [Mo(CO)_6] \longrightarrow Hg + [MoO(salen)_2]$$

$$[Hg(salen)] + [\{Fe(cp)(CO)_2\}_2] \xrightarrow{AcOH} Hg + [Fe(salen)][OAc]$$

$$[Hg(salen)] + [\{Fe(cp)(CO)_2\}_2] \xrightarrow{py} Hg + [Fe(salen)]_2$$

$$[Hg(salen)] + [Co_2(CO)_8] \longrightarrow [Hg(salen)Co(CO)_3]$$

2.1.3   Complexes with sulphur and selenium donor ligands

2.1.3.1   Thiols

The reaction of BaS with HgS at 600° leads to the formation of $BaHgS_2$, and both this compound, and the red complex Ba_2HgS_3 have been structurally characterised [46,47]. A mass-spectroscopic study of the dissociation of mercury(II) sulphide has been reported [48]. An infra-red and Raman spectroscopic study of the complex $Hg(SCF_3)_2$ in the solid state and in CS_2 solution and SF_6 matrix has been described [49].

The complexes $[Hg(SR)_2]$ (R = n-Bu, t-Bu or Ph) have been prepared in very good

yield from the electrochemical oxidation of mercury into an acetonitrile solution
of RSH or RSSR [50]. A wide range of thiolate and selenate complexes of mercury
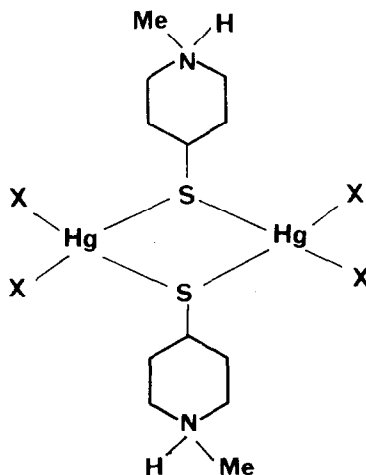have been studied by multinuclear (^{1}H, ^{13}C and ^{199}Hg) NMR techniques [51]. A
number of complexes of the Zwitterionic ligand 1-methyl-4-mercaptopiperidine (11),
including [Hg$_2$L$_2$X$_4$] (X = Br or I) have been described [52] . These complexes are
thought to have the thiolate bridged structure (12). Binuclear complexes [MHgL$_2$]
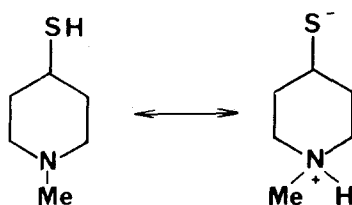
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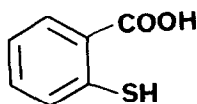
(13)

(12)

(M = Pb or Cd; H$_2$L = (13)) are formed in the reaction of M(NO$_3$)$_2$ with [Hg(LH)$_2$]
[53]. ^{199}Hg and ^{1}H NMR studies of these complexes suggest that the mercury is
bonded to the two sulphur atoms, whilst the heteroatom is bonded to oxygen. A
number of selenato complexes, including [Hg(SeMe)$_2$],[{ HgCl(py)(SeEt)}$_4$] and
[{HgCl(py)$_{\frac{1}{2}}$(t-BuSe)}$_4$] have been prepared and structurally characterised [54].
[Hg(SeMe)$_2$] is polymeric, with selenium acting as a bridging bidentate atom ,
and each mercury being four-coordinate (14); this is in contrast to the two
coordinate structures commonly found for [Hg(SR)$_2$] species. [{ HgCl(py)(SeEt)}$_4$]
possesses an eight-membered Hg$_4$Se$_4$ ring system, with each mercury being in an
Se$_2$ClN environment (15), whilst [{HgCl(py)$_{\frac{1}{2}}$(t-BuSe)}$_4$] also possesses an Hg$_4$Se$_4$
ring system, and is isomorphous with the corresponding 4-methylpyridine complex,
with two trans -annular chloride bridges(16). Complexes of mercury with
1-phenyl-3-methyl-4-phenylazopyrazole-5(4H)-thione (17) [55] and 'thiolhistidine'
(18) [56] have been reported. The interaction of a range of N and N , N'
substituted imidazoline-2(1H)-thiones have been prepared and structurally charac-
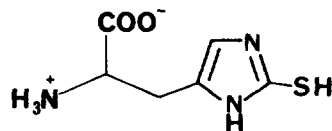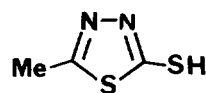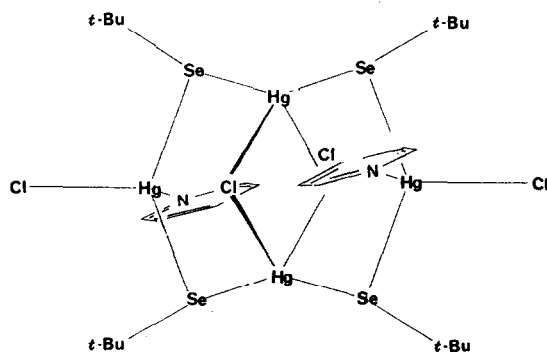terised [57]. With 3-ethylimidazoline-2(1H)-thione (LH) the complexes
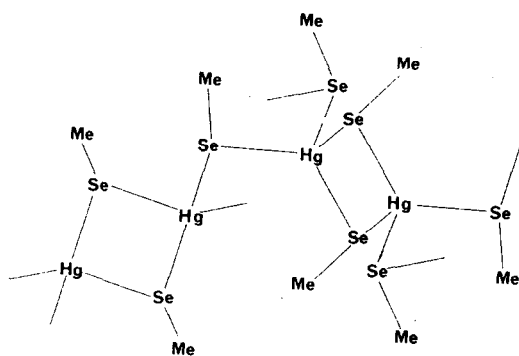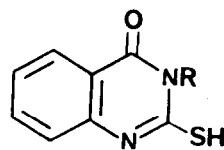
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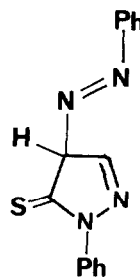
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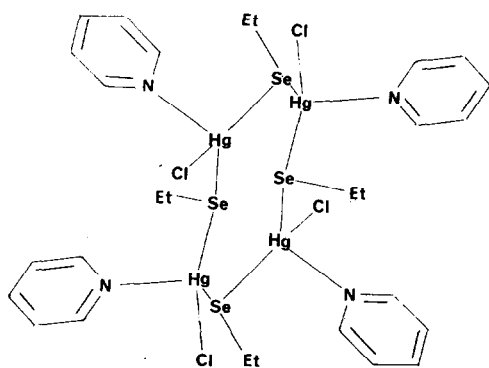
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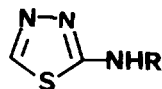
(21)

$[HgL_2X_2]$ (X = Cl, Br or I) are formed, and $[HgL_2Cl_2]$ has been shown to possess a pseudo-tetrahedral environment about the mercury, which is coordinated to the two chloride ions and the sulphur of the thione, with a weak hydrogen bonding interaction between the chloride and the NH of the imidazoline. In contrast, 1,3-diethylimidazoline-2(1*H*)-thione forms the polymeric complex $[\{HgLCl_2\}_n]$, which has also been structurally characterised [57] . The complexes $[HgL(NO_3)]$, $Hg(LH)L_2$, $HgL_2.NH_3$ and $HgX_2.2HL$ (LH = 19; X = Cl or Br) have been reported; all are non-electrolytes in dmf solution [58]. The complexes $[Hg_2L_2Cl_2]$ (LH = 20) have also been described [59]. Complexes with the 1,3,4-thiadiazole (21) have also been reported [60].

2.1.3.2 Thioethers

Ginsburg has reported the 1:1 complexes of the thioethers (22) – (25) with $HgCl_2$ [61].
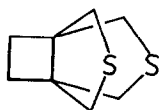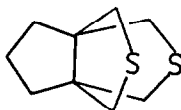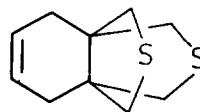
| (22) | (23) | (24) | (25) |

2.1.3.3 Thioamides and related ligands

The complexes $[HgL_2X_2]$ (L = 26; X = Cl or Br) have been described, and on the basis of ^1H and ^{13}C NMR studies, it is suggested that the metal is in a tetrahedral S_2X_2 environment, with the terminal thioamide sulphur of the ligand coordinated to the metal [62]. Complexes with 2-thiopyrrole-1,2-dicarboximide and *N*-carbamoylpyrrole-2-thiocarboxamide have also been reported [63]. The thiosemicarbazone complexes $[HgLX_2]$)L = PhC(Me)=NNHCSNH_2; X = Cl, NO_3 or \frac{1}{2}SO_4) [64], and $[HgL_2]$ (IIL = (2-furyl)CH=NNHCSNH_2) [65] have been characterised; the latter ligand is thought to act as a bidentate *NS* donor. Complexes with the thiourea (27) [66] and the thiohydrazide of salicylic acid (28) [67] have also been reported.
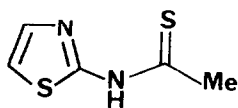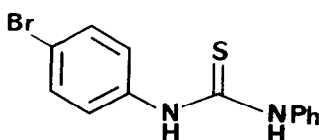
| (26) | (27) | (28) |

Thiocarbamates continue to be of interest as ligands, and a crystal structural analysis of the complex $[HgLCl_2]$ (L = $Me_2NCSOEt$) has been reported [67]. The metal is in a five-coordinate trigonal bipyramidal geometry, with the two chlorine ions, and one sulphur atom forming the trigonal plane, and interactions with two more distant chlorine atoms completing the axial coordination. A structural analysis of mercury(II) dithiocarbamate, which forms a two-dimensional polymeric network, has also been reported [69]. The ligand exchange reactions between mercury(II) dithiocarbamate and Hg^{2+} in dmso solution has been studied [70]. The novel complex $[HgL_2]$ (HL = $(EtO)_2P(O)NHCS_2H$) has been described [71].

2.1.3.4 Phosphine sulphides

A number of triethyl thiophosphate complexes, including $[HgL_4][ClO_4]_2$ (L = $(EtO)_3PS$) have been characterised [72]. The complex shows both P=O and P=S stretching frequencies in the vibrational spectrum, and evidence is presented for the equilibrium;

$$(EtO)_3P=S \quad\rightleftharpoons\quad (EtO)_2(EtS)P=O$$

The treatment of $(Ph_2P=S)_3CH$ with HgX_2 leads to a monomeric product, $[HgLX]$, in which the ligand is either behaving as a tridentate S_3 tripod, or as a C-bonded monodentate [73]. A multinuclear (^{31}P and ^{199}Hg) NMR study of some phosphine sulphide complexes has been reported [74].

2.1.4 Complexes with amine, amide and related ligands

The assignment of the Hg-N stretching mode in $[Hg(NH_3)_2Cl_2]$ has proven to be controversial in the past, but new results derived from an intensive study of the deuterium and ^{15}N labelled complexes have resulted in the assignment of the Raman active stretch at 407 ±1.0 cm^{-1} to the a_{1g} mode, and the infra-red band at 518.5 cm^{-1} to the a_{2u} ν_{as} Hg-N stretch [75]. The reaction of $K_2[Hg(SCN)_4]$ with hexamethylenetetramine leads to the formation of $[Hg_4(NCS)_8L]$ (L = hexamethylene-tetramine) [76]. This is the first example of a tetradentate complex of this ligand, and it is proposed that the compound has structure (29) in both the solid state and in solution.

Mercury complexes of D,L-2,3-diaminopropanoic-N, N'-dimalonic acid, $(HO_2C)_2CHNHCH_2CH(CO_2H)NHCH(CO_2H)_2$ have been reported [77]. A number of amide complexes, including $[HgLCl_2]$ (L = Me_2NCOCH_3) [78], $[HgL_2]$ (L = $EtCONH_2$) [79] and $[HgL_2Cl_2]$ (L = 30) [80] have been reported, and in each case the ligand is thought to act as an NO donor, although in the case of (30) it is proposed that it is the nitrogen atom of the heterocyclic ring rather than that of the amide
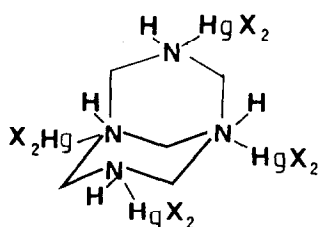
(29)
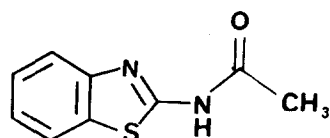
(30)

which is coordinated to the metal. Complexes with ethylenebiguanide [81] and a number of dipeptides [82] have also been characterised.

1,4-Diazabutadienes (α,α'-diimines,) may act as σ,σ'- N,N'-bidentate, rigid $\sigma - N$, fluxional $\sigma - N \leftrightarrow \sigma - N'$, bridging bidentate or $\sigma - N, \eta^2 - C=N'$ bidentate ligands. A range of ArN=CRCR=NAr ligands have been investigated, and the complexes [HgLX$_2$] (L = ArN=CRCR'=NAr; X = Cl or Br) are thought to be monomers with a chelating $\sigma,\sigma'- N,N'$ ligand [83]. The N-aminorhodanine complexes [HgL$_2$X$_2$] and [HgL$_{1.5}$(ClO$_4$)$_2$] (L = 31; X = Cl or Br) have been reported [84].

Interest in triazenato complexes continues, and an interesting reaction with phosphines has been reported. Treatment of [(Ar$_2$N$_3$)$_2$Hg] (Ar = 2-fluorophenyl)
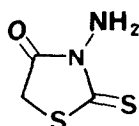
(31)

with ^{t}Bu$_2$PH leads to the formation of an Hg$_3$P$_3$ ring system (32) [85]. In the reaction with Cych$_2$PH, the initially formed Hg$_3$P$_3$ heterocycle rearranges to the Hg$_4$P$_4$ system (33) [85].
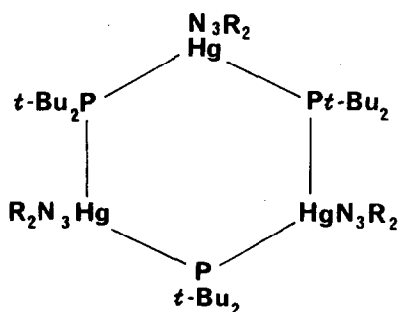
(32)
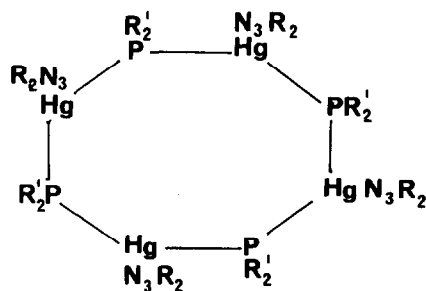
(33)

A number of mixed ligand triazenato species $[(EtO)_2P(O) Hg(N_3Ar_2)]$ have been prepared by redistribution equilibration, and the reaction with PPh_3 to give $[(Ar_2N_3)Hg\{(O)P(OEt)_2\}(PPh_3)]$ has been described [86].

2.1.5 Complexes with nitrogen heterocycles

The complexes $[HgL_2Cl_2]$ (L = 34; Ar = Ph) and $[HgLCl_2]$ (L = 34; Ar = 4-HOC_6H_4) have been reported [199], as have complexes with a range of substituted imidazoles [200]. In general, 1-substituted imidazoles gave mononuclear $[HgL_2X_2]$ complexes, whereas unsubstituted (on nitrogen) ligands gave rise to polymeric products. The mercury salt of 5-nitrotetrazole is proposed as an alternative detonator to lead azide [201].
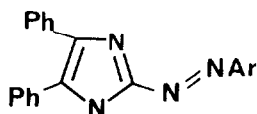
(34)

The ^{13}C NMR spectra of $[HgCl_2(py)_2]$ has been recorded, and the results interpreted in terms of the π-cloud delocalisation in the molecule [202]. Halogen NQR spectra of $[HgX_2L_2]$ (X = Cl or Br; L = py or PPh_3) have also been reported [34]. The crystal structures of $[HgX_2(py)_2]$ (X = Cl or Br) have been redetermined [203]. $[HgCl_2(py)_2]$ forms a polymeric one-dimensional array of trans-$HgCl_4N_2$ octahedra, sharing two opposite edges, whereas $[Hg(py)_2X_2]$ (X = Br or I) form discrete psudotetrahedral molecules. Structures have also been reported for the complexes $[Hg(py)(MeCHOHCHMe)][O_2CCF_3]$ [204], $[Hg(bipy)(O_2CCF_3)_2]$ [205], $[Hg(CF_3)_2(terpy)]$ [206] and $[\{Hg(O_2CCF_3)_2\}_2(tpt)]$ [207]. The extraction of mercury from acidic thiocyanate medium by solutions of diphenyl-2-pyridyl-methane has been studied [208].

Mercury(II) complexes of cinchonine (35) [87] and a number of nucleosides have been reported [88].
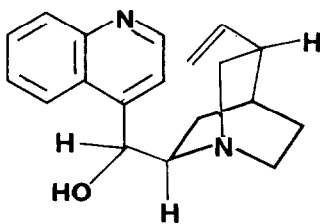
(35)

2.1.6   Complexes with phosphorus, arsenic and antimony donor ligands

The crystal and molecular structure of the β -form of $[HgCl_2(PBu_3)_2]$ has been reported [89] ; the complex is a dichloro-bridged dimer in the solid state, in contrast to the tetrameric structure of the α-form discussed in last years review In solution there is some association between adjacent dimers. The crystal structures of $[Hg(CN)_2(PPh_3)_2]$ and $[Hg(NO_3)_3(PPh_3)_2]$ have been reported, and a correlation with ^{31}P chemical shifts made [90]. The cyanide complex possesses a distorted tetrahedral structure, which may be regarded as being on the reaction path between a truly tetrahedral molecule and a trigonal$\{[Hg(CN)_2(PPh_3)] + PPh_3\}$ system; $[Hg(NO_3)_2(PPh_3)_2]$ is a six-coordinate species with crystallographic C_2 symmetry, and unequal Hg-O bond lengths of 2.507 and 2.79 Å. The electrochemical reduction of $[HgX_2(PR_3)_2]$ (X = Cl, Br or I) has been studied, and the unusual two-electron process:

$$2e^- \; + \; [HgX_2(PR_3)_2] \; \longrightarrow \; Hg(1) \; + \; 2PR_3 \; + \; 2X^-$$

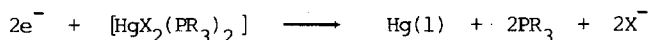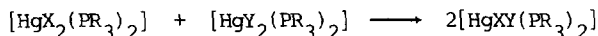demonstrated [91]. A correlation between the redox potential for this reduction and NMR parameters ($\delta \, ^{31}P$, $\delta \, ^{199}Hg$ and J_{P-Hg}) was demonstrated, and NMR techniques were also used to investigate the halide exchange reaction:

$$[HgX_2(PR_3)_2] \; + \; [HgY_2(PR_3)_2] \; \longrightarrow \; 2[HgXY(PR_3)_2]$$

The reaction of R_2PH with triazenato complexes to produce Hg_nP_n heterocycles has been mentioned earlier (2.1.4) [85].

A number of novel diphosphine complexes have been reported this year, including a species thought to be the phosphoniumfluorenylide complex (36) [92]. A complex with the phosphorus analog of H_4edta, $(HO_2CCH_2)_2PCH_2CH_2P(CH_2CO_2H)_2$ has been reported [93]. The reaction of *trans*-$[Pt(C{\equiv}CR)_2(\eta'-dppm)_2]$ (R = Ph or $4-MeC_6H_4$) with $HgCl_2$ leads to the formation of (37) [94]; analogous compounds of the type $[Y_2Pt(dppm)HgCl_2]$ are formed from the reaction of $[Pt(\eta^2-dppm)_2]Cl_2$ with HgY_2 (Y = CN, OAc/HC${\equiv}$CR) [95]. A crystal structural analysis of the pseudotetrahedral complex $[HgBr_2(Ph_2PCH{=}CHPPh_2)]$ has been reported [90].

The reaction of $^tBu_2P(O)H$ with HgO or $Hg(OAc)_2$ leads to the formation of the complex $[^tBu_2P(O)_2Hg]$, which has been characterised by ^{31}P and ^{199}Hg NMR spectroscopy. The ligand is thought to be *P*-bonded to the metal [96]. A combination of ^{31}P and ^{199}Hg NMR techniques has also been used in a study of the complexes $[HgY(PR_3)_n((EtO)_2P{=}O)]$ (Y = OAc, O_3SCF_3, Cl, Br, I, S_2CNEt_2, $S_2P(OEt)_2$ or $(EtO)_2P{=}O$), and it is suggested that the diethylphosphito ligand is *P*-bonded in these compounds also [97]. The mixed ligand complexes $[(EtO)_2P(O)Hg(N_3Ar_2)]$

Ph$_2$P

Ph$_2$P

Cl

Cl

Hg

Hg

Cl

Cl

(36)

Ph$_2$P

RC≡C

Ph$_2$P

Pt

C≡CR

PPh$_2$

Hg

Cl

Cl

PPh$_2$
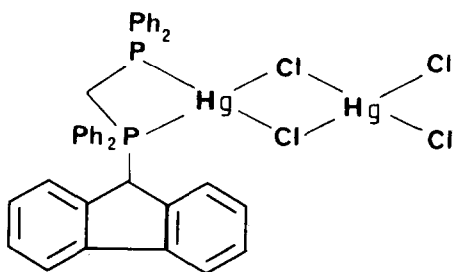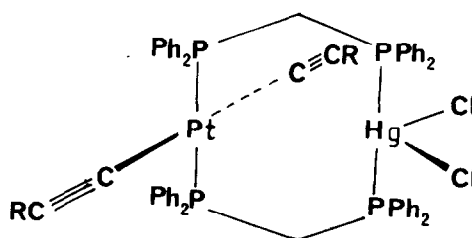
(37)

have been discussed earlier (2.1.4) [86]. The reaction of Hg(NO$_3$)$_2$ with
(RO)$_2$P(O)CH$_2$CONEt$_2$ results in the formation of [{Hg((RO)$_2$P(O)CHCONEt$_2$)(NO$_3$)}$_2$]
[98]. The dimeric structure has been confirmed by an X-ray crystallographic

Co

(EtO)$_2$P

O

P(OEt)$_2$

O

P(OEt)$_2$

O
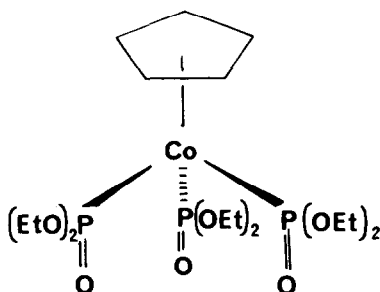
(38)

study. The novel tripod ligand (38) has been shown to form mercury(II)
complexes [99]. Complexes with amino(cyclophospazenes) [100] and 1-arylarsolanes
[101] have also been reported.

2.1.7 Complexes with macrocyclic ligands

Few macrocyclic complexes of mercury(II) have been reported this year, and the
potential of such species in metal-exchange reactions has not yet been fully
explored. A crystal structure of the complex [HgLCl$_2$].HgCl$_2$ (L = [18]-ane-
1,4,7,10-O$_4$-13,16-S$_2$) has been reported (39) [102]. The ligand is a bidentate
S,*S*'-exodentate donor, and the metal is in a distorted *HgS$_2$Cl$_2$* tetrahedron,
with the chloride ions bridging to the second mercury atom. The addition of a
range of axial ligands to [Hg(TPP)] has been studied [103].
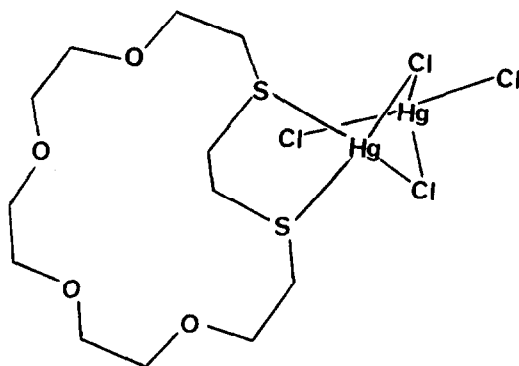
(39)

2.1.8   Aqueous solution chemistry of mercury(II)

Studies on the mercury(II) catalysed aquation of octahedral transition metal complexes continue to be reported, and the involvement of binuclear chloro-bridged $[M-Cl-Hg]^{x+}$ species is now well established. Complexes which have been studied include trans - $[Rh(en)_2Cl_2]^+$ [104], $[Rh(NH_3)_5X]^{2+}$ (X = Cl or Br) [105], $[Rh(NH_3)_5I]^{2+}$ [106], $[Rh(en)_2Cl_2]^+$ [107], mer - $[Rh(OH_2)_3Cl_3]$ [108], cis- $[Co(pn)_2ClL]^{2+}$ (L = py, Himid or Hbenzimid) [109], $[Cr(NH_3)_5Cl]^{2+}$ [105], cis- $[Cr(NH_3)_4(OH_2)Cl]^{2+}$ [105], trans -$[CrLXCl]^{2+}$ (L = tetramine) [110], $[Co(en)_2Cl(imidH)]^{2+}$ [111] and $[(NO)(H_2O)_4Cr(\mu-NC)Hg]^{3+}$ [112]. The heterobinuclear intermediate is best established for the rhodium(III) systems, and detailed kinetic studies of the reactions:

$$[Rh(NH_3)_5I]^{2+} + Hg^{2+} \xrightarrow{K} [Rh(NH_3)_5(\mu-I)Hg]^{4+}$$

$$[Rh(NH_3)_5(\mu-I)Hg]^{4+} \xrightarrow{k} [Rh(NH_3)_5(OH_2)]^{3+} + [HgI]^+$$
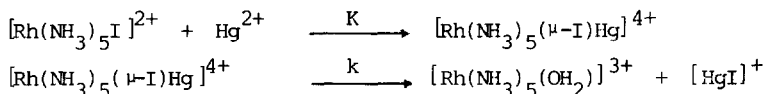
have been reported [106]. The precise mercury(II) species implicated in the catalysis is not yet fully established, and may vary from system to system. In the mer-$[Rh(OH_2)_3Cl_3]$ hydration, the catalytically active species are Hg^{2+} and $[HgCl]^+$, with $HgCl_2$ showing very little effect [108]. Probably the most important study this year has been the structural characterisation of the binuclear complex cis - $[Rh(en)_2Cl_2]$ Cl.$HgCl_2$, which is formed from the reaction of cis-$[Rh(en)_2Cl_2][NO_3]$ with $Hg(NO_3)_2$ in chloride medium. The crystal structure of this complex clearly shows the role of the mercury in forming the μ -chloro bridge [107]. The displacement of cyanide ion from $[Fe(CN)_6]^{4-}$ by 4-nitroso-diphenylamine has been shown to be mercury catalysed, and it is proposed that a

seven coordinate transition state is implicated [113].

2.2   MERCURY(I)

2.2.1   Halide and pseudohalide complexes

The use of mercury(II) halides as a solvent for mercury(I) compounds continues to be of interest, and the mixed ligand complexes $[Hg_2XY]$ (X = halide; Y ≠ halide) have been studied in molten $HgBr_2$ [8]. The reaction of Hg_2Cl_2 with bromine has been discussed in Section 2.1.1 [4]. A number of mononuclear mercury(I) compounds have been described, and HgX (X = Cl or Br) have been characterised as the products of the reduction of HgX_2 by metallic zinc (using matrix-isolation Raman spectroscopic methods) [9]. The thermodynamic properties of the HgH molecule have been calculated [114]. The formation of mercury(I) compounds in the γ-irradiation of $HgCl_2$ has been discussed in Section 2.1.1 [11].

2.2.2   Complexes with oxygen donor ligands

The thermal decomposition of mercury(I) sulphate to mercury(0) and mercury(II) sulphate has been studied [36,37]. Studies of mercury(I) carboxylates in solution [115] and in the polycrystalline solid state [116] have been reported. The reaction of Hg_2F_2 with AlF_3 in 5M hydrofluoric acid results in the formation of $Hg_2AlF_5 \cdot 2H_2O$, which has been characterised crystallographically. The structure consists of AlF_6 octahedra sharing two *trans* fluorides, with the quasi-linear $[(H_2O)HgHg(H_2O)]^{2+}$ cation situated between these chains (Hg-Hg, 2.511 Å; Hg-O; 2.144 Å) and interacting with four fluorine atoms (Hg-F, 2.827, 2.894 Å) to give a pseudo-octahedral F_4HgO environment [117]

2.2.3   Complexes with oxygen donor ligands

A review of mercury(I) complexes with nitrogen donor ligands has appeared [118] A wide range of complexes with heterocyclic ligands have been characterised, including $[Hg_2L_nX_2]$ (L = py, 1,4-diazine, 1,3,5-triazine, 1,4-dioxane or 1,3-dithiane; X = NO_3, SiF_6, OAc, O_2CCCl_3, ClO_4 or BF_4) [119].

2.3   ORGANOMERCURY(II)

2.3.1   Halide and pseudohalide complexes

Alkylmercury(II) fluorides are formed in the reaction of xenon difluoride

with HgR_2 (along with xenon, RF and R_2) [2]. A number of hydrido species $RHgH$
(R = Me or Et) have been electrochemically characterised in methanol solution
[120]. The resonance stabilised carbanion $[(Me_2P=S)_3C]^-$ gives a stable complex
$[ClHgC(Me_2P=S)_3]$, which is formed in the reaction of the lithium salt with $HgCl_2$
in good yield [121]. A range of perfluoroalkyl compound $[RHgR']$ or $[R_2Hg]$ have
been prepared by the reaction of the appropriate perfluoroalkyl Grignard reagent
with HgX_2 or $[R'HgX]$ [122]. A ^{199}Hg NMR investigation of the equilibrium

$$HgX_2 \;+\; [(Cl_2C=CCl)_2Hg] \;\rightleftharpoons\; 2\,[HgX(Cl_2C=CCl)]$$
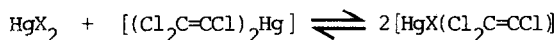
has been reported [123]. Multinuclear NMR studies of a number of $[ArHgCl]$ [124]
and $ArCH_2C(OMe)(R)CH_2HgCl$ complexes [125] have also been reported, and the
observations on the latter species are consistent with an intramolecular
π-interaction in non-donor solvents (40) [125] . The vibrational spectra of
the acetylide species $[MeHgC{\equiv}CX]$(X = Cl or Br) have been reported [126], as have
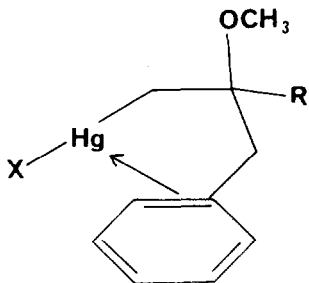
(40)

PES spectra for a number of $[RHgCl]$(R = alkyl or aryl) compounds [127,128].

The reaction of $[PhHgX]$(X = Cl, Br, I or CN) with PR_3 is reported to lead to
the formation of $[(R_3P)_2HgX_2]$ [129]. A number of reactions of organomercury(II)
halides have been reported, including the interaction of RHgCl with Ph_2Hg [130],
the thermal decomposition of $[PhCH(O_2{}^tBu)CH_2HgCl]$ [131] and the thermal
decomposition of thienylmercury(II) halides [132]. The reaction of
8-(1-bromoethyl)quinoline with mercury results in the formation of the alkyl
species (41) (ML_n = HgBr) in a racemic form. This racemate may be resolved with
(+)-D-camphor-10-sulphonic acid, and undergoes a transmetallation reaction with
$(Ph_3P)_4Pd$ to give (41) (ML_n = Pd(Ph$_3$P)Br) [133].
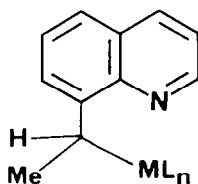
(41)

2.3.2 *Complexes with oxygen donor ligands*

The reaction of [PhHg(OAc)] with Cu(SeCN)$_2$ or copper(II) sulphate in the presence of KSeCN gives low yields of PhSeCN, together with Ph$_2$Se and Ph$_2$Se$_2$ [134] The two latter products have been shown to arise from the reaction of PhSeCN with PhHgX (X = OAc or Cl) in the presence of copper(II). A crystal structure of the complex [C(HgO$_2$CCF$_3$)$_4$] has been reported [40], and is discussed in Section 2.1.2

2.3.3 *Complexes with sulphur donor ligands*

Further studies of the blue-yellow photochromism of [RHgL] (HL = dithizone, 42) species have been reported [135]. A spectroscopic study of the mercapto-amide complexes [MeHg(S(CH$_2$)$_n$CONHMe)] (n = 1,2 or 3) have established a weak interaction between the metal and the nitrogen or oxygen of the amide group [136]. A crystal structural analysis of the complex [MeHgSCH$_2$CONHMe] has confirmed this, and demonstrates a weak Hg-O interaction to give a five-membered chelate ring in this case [136]. The structure of the complex [PhHgL] (LH = 2-(*N,N* - dimethylamino)thiophenol) has also been determined (at -120°C), and shows the formation of a similar five-membered chelate ring, this time with an Hg-N inter-action (43) [137].
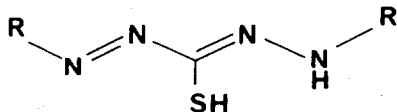
(42)
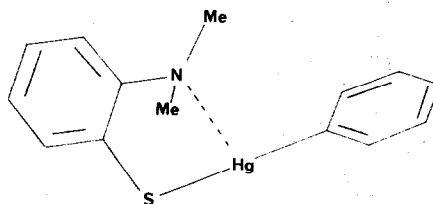
(43)

2.3.4   Complexes with nitrogen donor ligands

As in previous years, the interest in the ecological and biochemical properties of organomercury species has provided the impetus for the study of such complexes, and particular attention has been paid to the structural properties of methylmercury(II) nucleoside complexes.

Crystal structures of $[(MeHg)_2L][ClO_4].H_2O$ (LH = adenine) [138], $[MeHgL].\frac{1}{2}H_2O$ (LH = thymine) [139], $[MeHgL].\frac{1}{2}NaNO_3$ (LH = thymine) [139], $[(MeHg)_2L][NO_3].2H_2O$ (LH = adenine) [141] and $[(MeHg)_2L][NO_3]$ (LH = 1-methylcytosine) [142] have been reported. Associated spectroscopic studies of the methylmercury(II) complexes of adenine [143], 9-methyladenine [144] and cytidine [145] have also been reported.

A number of complexes of $[RHgCl](R = 4-HO_2CC_6H_4)$ with amines have been described [146]. The complexes (44) $(ML_n = HgCl)$ and (45) (M = Hg) are prepared by the reaction of (44) or (45) $(M = ML_n = Li)$ with $HgCl_2$, and undergo facile transmetallation reactions with $Pd(OAc)_2$, $[Pt(dba)_2]$ or $[Pt(cod)_2]$ to produce (44) $(ML_n = Pd(OAc))$ or (45) (M = Pd or Pt) [147]. The sulphonamide complexes
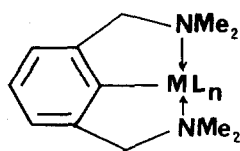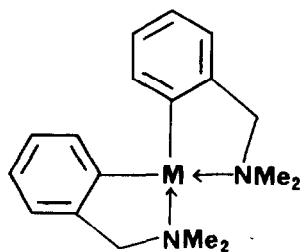
(44)   (45)

$[ArN(SO_2Ph)HgPh]$ $(Ar = 4-O_2NC_6H_4)$ [148] and $[MeSO_2N(Cl)HgPh][149]$, the latter prepared by the reaction of $MeSO_2NClBr$ with $[Ph_2Hg]$, have been reported, as has the related $[ArNHHgPh]$ $(Ar = 4-O_2NC_6H_4)$ [148].

Complexes of methylmercury(II) with a wide range of pyridines, imidazoles and pyrazoles have been investigated by NMR techniques, and correlations drawn between lgK_H of the ligand and $^2J_{H-Hg}$ [150]. A crystal structure of the complex [PhHgL] LH = 2-phenylsulphonylimino-1,2-dihydrothiazole) has been reported [151]. There are weak intermolecular Hg-N and Hg-O interactions as shown in (46). The complexes $[MeHgL][NO_3]$ (L = 1-(2-pyridyl)pyrazole or bis(1-pyrazolyl)methane) have been reported [152]and structurally characterised [153]. In each case the metal shows interactions with the nitrate ions. The reaction of basic $PhHg(NO_3)$ with a series of 2-substituted benzimidazoles leads to the formation of
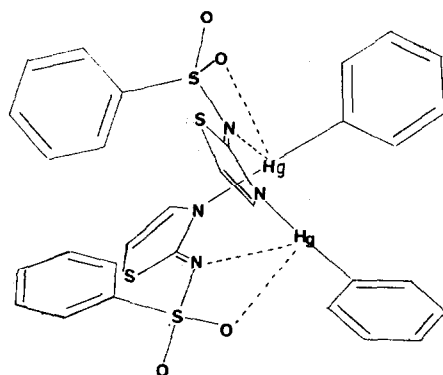
(46)

binuclear complexes [PhHg(L)HgPh][NO$_3$], in which it is proposed that the deprotonated benzimidazole acts as a bridging bidentate ligand [154].

2.4   COMPOUNDS WITH MERCURY-HETEROMETAL BONDS

The reaction of [Nb(cp)$_2$H$_3$] with [Hg(S$_2$CNEt$_2$)$_2$] in benzene gives the reddish-brown compound [Nb(cp)$_2${Hg(S$_2$CNEt$_2$)}$_3$] which has been characterised crystallo-graphically, and shown to possess a near-planar Hg$_3$Nb cluster framework [155]. A number of reactions of mercury-manganese and mercury-rhenium complexes have been reported, and the species [CuHgMn(CO)$_5$], [(PPh$_3$)$_2$BrPtHgRe(CO)$_5$], [BrHgM(CO)$_5$] (M = Mn or Rh), [Br$_2$(PPh$_3$)$_2$Pd(Mn(CO)$_5$HgMn(CO)$_5$] and [HgMn(CO)$_5$] have all been described [156]. The complexes [M(cp)$_2${Hg(S$_2$CNEt$_2$)}$_2$] (M = Mo or W) have been prepared in a number of ways, and a crystal structure of the complex with molybdenum has been reported [157]. A *trianglo-* Hg$_2$Mo cluster is formed (47).
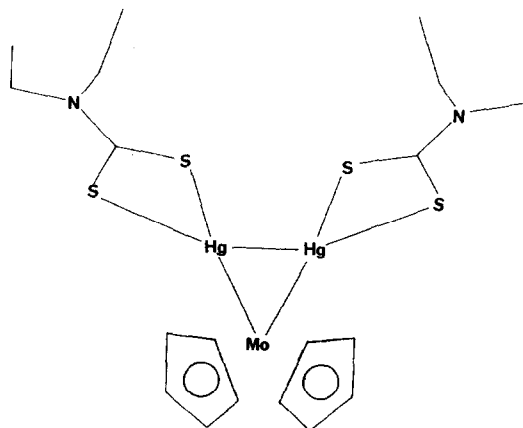
(47)

The phosphide complexes $[Hg\{PPh_2M(CO)_5\}_2]$ and $[(Me_3Si)_2NHg(PPh_2)M(CO)_5]$
M = Cr, Mo or W) are prepared according to:

$$[Hg\{N(SiMe_3)_2\}_2] \quad + \quad [M(CO)_5(PPh_2H)] \longrightarrow [(Me_3Si)_2NHg(PPh_2)M(CO)_5]$$

$$[(Me_3Si)_2NHg(PPh_2)M(CO)_5] \quad + \quad [M(CO)_5(PPh_2H)]$$

$$\downarrow$$

$$[Hg\{PPh_2M(CO)_5\}_2]$$
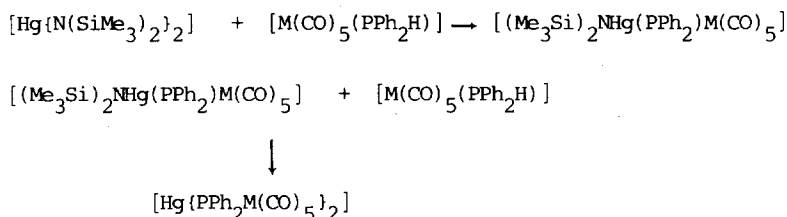
but probably only show Hg-P rather than Hg-M interactions [158]. The crystal and
molecular structure of the complex $[Mo(cp)_2(HgSEt)_2]$ has been reported [159].

The complexes $[(\mu-RS)(\mu-RHgS)Fe_2(CO)_6]$ (R = Me or Et) have been described,
but as indicated in the formulation above do not contain any direct Hg-M bonds
[160]. The structure is as shown in (48).
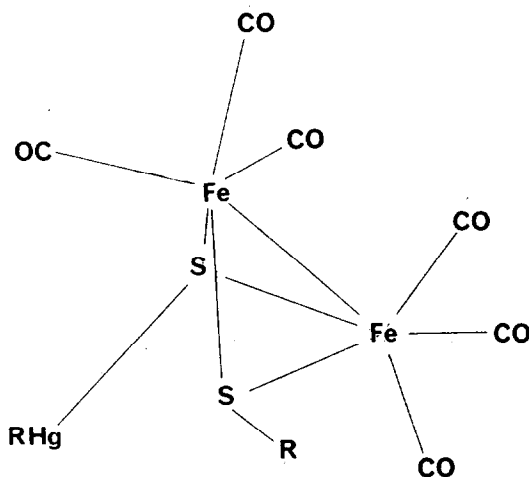
(48)

The reactions of HgX_2 with a range of $HCoL_4$ species results in the formation
of trigonal bipyramidal complexes $[(XHg)CoL_4]$ (X = Cl, Br or I; L = phosphite
or CO) [161]. The crystal structure of the dimercury bridged compound
$[\{N(CH_2CH_2PPh_2)_3CoHg\}_2]$, formed in the reaction of $[N(CH_2CH_2PPh_2)_3CoCl][BPh_4]$

with sodium amalgam has been reported [162]. The reaction of $HgCl_2$ with a thf solution of $Na[Rh(PPh_3)_2(CO)_2]$ results in the formation of $[Hg\{(Ph_3P)_2Rh(CO)_2\}_2]$ [163]. $[PtL(CO)(C{\equiv}CR)Cl]$ reacts with $[Hg(C{\equiv}CR)_2]$ to give $[LPt(CO)(C{\equiv}CR)_2]$ (L = PPh_2Me), and it is proposed that an octahedral Hg-Pt bonded species is formed as an intermediate in this and related reactions [164]. A square-pyramidal complex containing an Hg-Pt bond has been structurally characterised [165]. The electrochemical behaviour of the complexes (49), (50) and (51) have been investigated [166]. The reaction of $[PtCl_2L_2]$ (L = 2,6-dimethylphenylisonitrile) with sodium amalgam in the presence of excess L results in the formation of the clusters $[HgPt_6L_{12}]$ and $[Pt_7L_{12}][167]$.
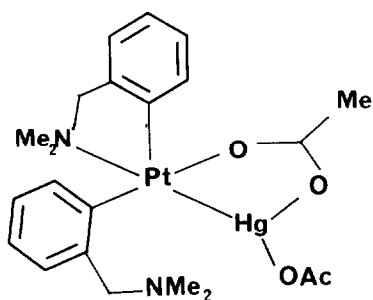
(49)
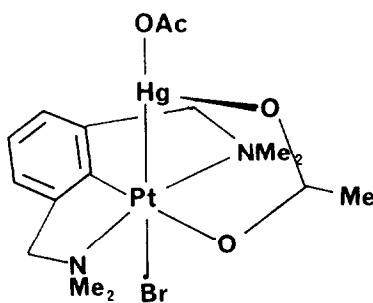
(50)
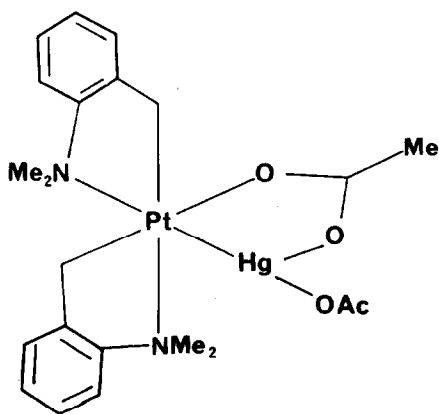
(51)

The electrochemical oxidation of mercury in contact with liquid sulphur dioxide solutions of $[Me_4N][AsF_6]$ leads to the formation of tri- and tetranuclear complexes. Similar reactions occur with $[NMe_4][SbF_6]$, and the compounds $[Hg_3AsF_6]$ and $[Hg_3SbF_6]$ have been isolated [168]. Traces of $[(Me_3E)_2Hg]$ (E = Si or Ge) are formed in the reaction of Me_3ECl with Al, Mg, Ca or Li in the presence of mercury, and this observation has been developed into a high-yield synthesis of $[(Me_3E)_2Hg]$ from the reaction of Me_3ECl with lithium amalgam [169]. The reaction of $[(Ar_3Ge)_2Hg]$ (Ar = C_6F_5) with lanthanide metals results in the formation of $(Ar_3Ge)_7Hg_2Ln$ in high yield [170]. Raman studies of the complexes $Ph_3Te.HgX_3$ and $(Ph_3Te)_2HgX_4$ (X = Cl, Br or I) have revealed Te-Hg but not Te-X stretching frequencies (ν Te-Hg 105 cm^{-1}), and the compounds are thus formulated $[Ph_3Te-HgX_3]$ and $[Ph_3Te-HgX_4-TePh_3]$ in the solid state [171]. The compounds are 1:1 electrolytes, and it is proposed that they ionise:

$$[Ph_3Te-HgX_3] \rightleftharpoons [Ph_3Te]^+ + [HgX_3]^-$$

$$[Ph_3Te-HgX_4-TePh_3] \rightleftharpoons [Ph_3TeHgX_4]^- + [Ph_3Te]^+$$
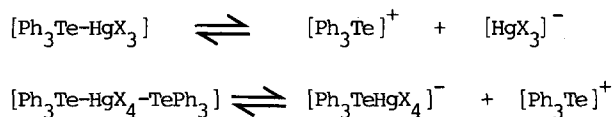
2.6   MERCURY IN ORGANIC SYNTHESIS

Many of the best-known applications of mercury to organic synthesis involve the addition of an HgYX species across a multiple bond, to produce either an organomercury compound with a C-Hg bond, or a demercuration product derived from this. A number of variations on this basic theme have been developed over the years to allow the formation of a range of C-x bonds, and to permit novel intramolecular reactions in suitable cases.

The mechanism of addition of water or hydrogen chloride to acetylene or ethylene in the presence of mercury(II) compounds has been further investigated [172], and the mercuration of $ArCH=CHCO_2Me$ by $Hg(OAc)_2$ studied [173].

A synthesis of mitosenes has been reported in which a key step is the intra-molecular displacement of halide from a vinyl bromide by an amine in the presence of $Hg(OAc)_2$, to produce the indole (52) [174]. γ-Acetylenic alcohols are cyclised by $HgCl_2$ to the tetrahydrofuran derivatives (53), and this offers a route to prostaglandins [175]. The reaction of $[PhHgO_2CCF_3]$ with acrylic acid in the presence of $H_2[PtCl_6]$ results in the formation of low yields (15%) of $PhCH=CHCO_2H$ [176]. $RCOCH=CHCO_2H$ is converted to $RCOCH=CHCOCH=CH_2$ by $Hg(OAc)_2$/ vinyl acetate in the presence of BF_3 and hydroquinone; the product is readily decomposed by aqueous $Hg(OAc)_2$ [177].

(52)

(53)
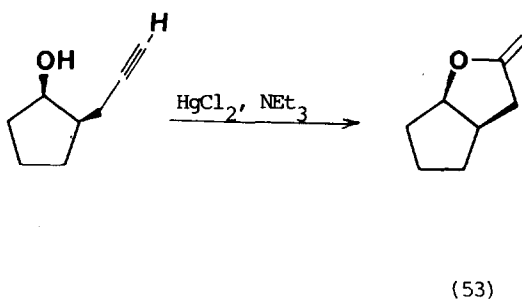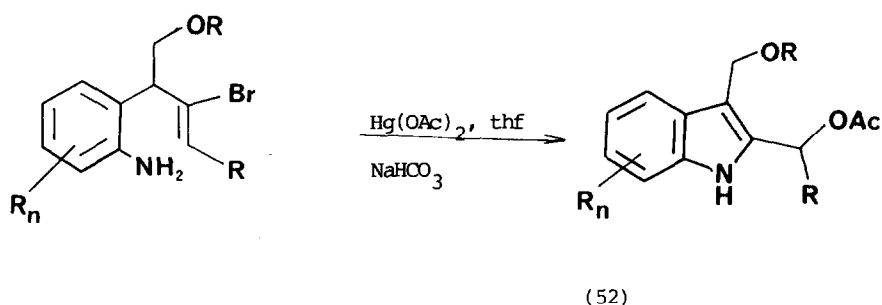
The aminomercuration-demercuration sequence continues to be of synthetic utility, and Barluenga has prepared 4-aryltetrahydro-1,4-thiazine 1,1-dioxides (54) from divinylsulphone and ArNH$_2$ by this method [178].

(54)
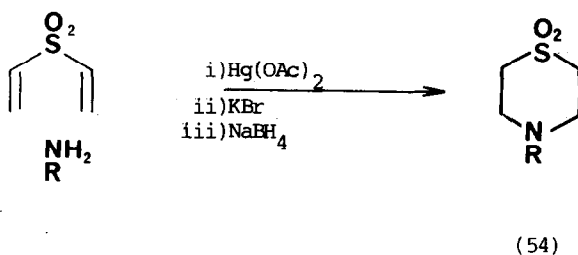
The transmetallation of RCH=CHHgCl with Li$_2$[PdCl$_4$] occurs smoothly in cyclo-olefins to give η^3-allylpalladium(II) species (55) [179].

Mercury compounds have been found to be very effective in the hydrolysis of 1,3-oxathiolanes [180,181,182], and it is proposed that a 1:1 complex is formed, prior to transfer of a coordinated water molecule from mercury to carbon. Mercury salts are also useful in the preparation of hemiacetals from acetals

(55)
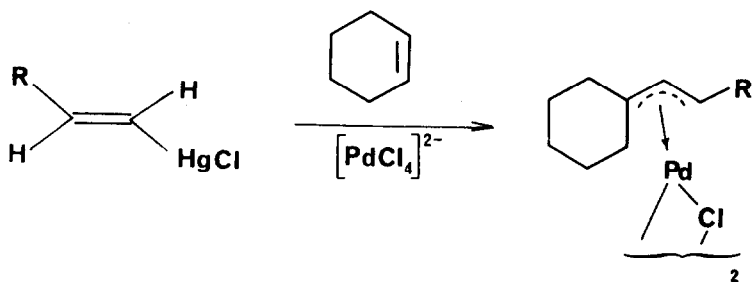
since $RHC(OR)(OH)$ is only *slowly* hydrolysed in the presence of Hg^{2+}, in contrast to the rapid hydrolysis of $RHC(OR)_2$ [183]. Solutions of HgO in $H[BF_4]$ have been recommended for the hydrolysis of dithioketals and orthoesters, and are claimed to be superior to $HgO/BF_3.Et_2O$ [184]. Mercury trifluoroacetate supported on polystyrene is claimed to be a superior reagent for the hydrolysis of thioacetals and thioketals, and has the advantages of easy work up, and not catalysing acetal or ketal formation [185]. At 190-210°, orthoformates are converted to dialkyl carbonates by mercury(II) acetate [186].

The mercuration of aromatic compounds is of considerable theoretical and practical importance, and cross polarisation magic angle spinning ^{13}C NMR spectra of the solid compounds $Hg(SbF_6)_2.2ArH$ (ArH = C_6Me_5H, $1,2,4,5-C_6H_2Me_4$, $1,2,3,4-C_6H_2Me_4$ and benzene) have been reported [187]. In the case of the first two compounds the spectra are consistent with static η^1-Hg-C bonding at the unsubstituted carbon, whereas the other two compounds gave time-averaged spectra indicating C_s (or C_2) and C_6 symmetry respectively. ^{13}C NMR studies of SO_2 solutions of the $1,3,5-R_3C_6H_3$ complexes also indicated an η^1 bonding mode. These results are not inconsistent with the η^2 mode observed in C_6Me_6 compounds [42]. The mercuration of $(EtO)_2PAr$ has been investigated [188].

Coupling and cross-coupling reactions are of importance in organic chemistry, and some recently reported examples of mercury mediated couplings include:

$$ArHgCl \; + \; CO \quad \xrightarrow[Rh(CO)_2Cl_2]{HMPA, \; ^nBu_4NI} \quad ArCOAr \qquad [189]$$

$$Ar_2Hg \; + \; Ar'X \quad \xrightarrow[{[PhPd(PPh_3)_2I]}]{HMPA, \; ^nBu_4NI} \quad ArAr' \qquad [190]$$
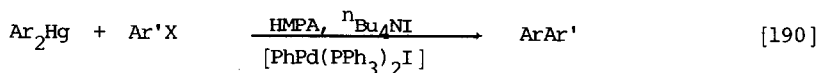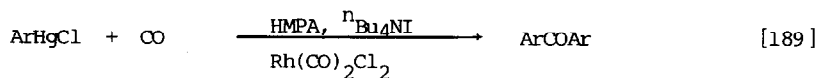
LiCuMe$_2$ and Li$_2$CuMe$_3$ are powerful reagents for cross-coupling reactions with organomercury(II) compounds, and an intensive study of such reactions has been reported [191]. A coupling reaction to produce the palladium complex (56) has also been described [192].

(56)
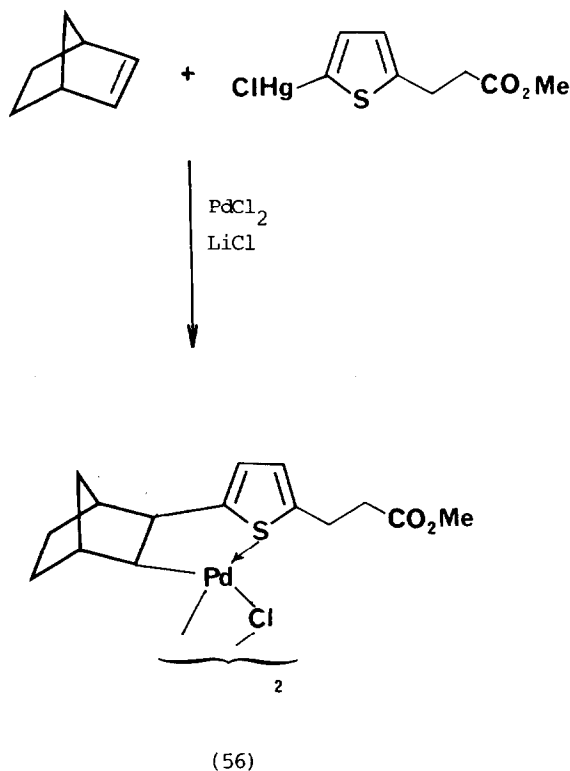
2-Methyl or 4-Methylpyrrilium salts are mercurated to $-CH_2HgX$ derivatives on treatment with HgX$_2$ [193,194]. 1-Arylpiperidines are converted to 2-piperidones (57) by Hg(OAc)$_2$/edtaH$_4$ [195] . The reaction of 1,3-bishydrazones with Hg(OAc)$_2$ results in the formation of pyrazoles [196]. Other applications reported this year include:

$$(Et_3E)_2Hg \ + \ BrCH_2COR \ \longrightarrow \ (Et_3E)OCR=CH_2 \quad (E = Si \ or \ Ge) \ [197]$$

$$RCH(HgX)COR' \ + \ R_2CHO \ \xrightarrow{BF_3} \ R_2CH(OH)CHRCOR' \qquad [198]$$

$$> \ 80\% \ \text{erythro}$$

98%   **2%**
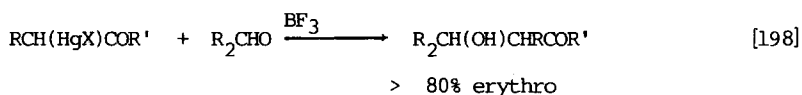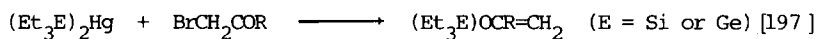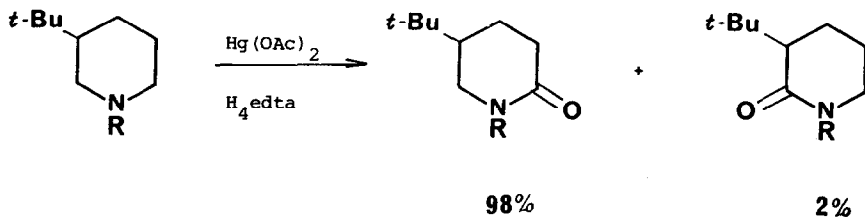
2.6 ^{199}Hg NMR SPECTROSCOPY

This section consists of a bibliographic listing of papers reporting ^{199}Hg NMR data, arranged according to the Section in which they are discussed.

2.1.1	[13]
2.1.3.1	[51], [53]
2.1.3.4	[74]
2.1.4	[86]
2.1.6	[91], [96], [97]
2.3.1	[123], [124], [125], [127]
2.4	[158], [159]

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