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Phenylselenolate Mercury Alkyl Compounds, PhSeHgMe and PhSeHgEt: Molecular Structures, Protolytic Hg–C Bond Cleavage and Phenylselenolate Exchange†

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Abstract

The phenylselenolate mercury alkyl compounds, PhSeHgMe and PhSeHgEt, have been structurally characterized by X-ray diffraction, thereby demonstrating that both compounds are monomeric with approximately linear coordination geometries; the mercury centers do, nevertheless, exhibit secondary Hg...Se intermolecular interactions that serve to increase the coordination number in the solid state. The ethyl derivative, PhSeHgEt, undergoes facile protolytic cleavage of the Hg–C bond to release ethane at room temperature, whereas PhSeHgMe exhibits little reactivity under similar conditions. Interestingly, the cleavage of the Hg–C bond of PhSeHgEt is also more facile than that of the thiolate analogue, PhSHgEt, which demonstrates that coordination by selenium promotes protolytic cleavage of the mercury-carbon bond. The phenylselenolate compounds PhSeHgR (R = Me, Et) also undergo degenerate exchange reactions with, for example, PhSHgR and RHgCl. In each case, the alkyl groups preserve coupling to the ¹⁹⁹Hg nuclei, thereby indicating that the exchange process involves metathesis of the Hg–SePh/Hg–X groups rather than metathesis of the Hg–R/Hg–R groups.

Keywords

Mercury; selenolate; thiolate; methyl; ethyl

INTRODUCTION

The interaction between mercury and selenium is of considerable relevance to the toxicological properties of mercury.^{1,2} For example, selenium is an important component of antioxidants^{3,4} and coordination to mercury can reduce the bioavailability of selenium.^{5,6} Furthermore, selenium is present in a variety of biomolecules, such as selenocysteine, selenomethionine, selenoneine and Se-methylselenoneine,^{1,3,7–10} and the binding of

†Dedicated to Professor Catherine Housecroft on the occasion of her 60th birthday. Happy birthday, Catherine!

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mercury to the active sites of selenoenzymes can inhibit their functions.⁶ It has also been reported that selenoamino acids can cleave the Hg–C bond of methyl mercury species to yield mercury selenide *via* (MeHg)₂Se.¹¹ In addition to its selenophilicity, the thiophilicity of mercury is also recognized to be an important contributor to mercury toxicity.^{2,12,13} Since organomercury compounds are exceptionally toxic, it is especially pertinent to investigate the structures of mercury alkyl compounds that feature sulfur and selenium coordination. Therefore, we describe herein the molecular structures of PhSeHgR compounds and their reactivity towards protolytic cleavage of the Hg–R bonds and Hg–SePh exchange.

RESULTS AND DISCUSSION

1. Synthesis and Structural Characterization of PhSeHgR

Sodium ethylmercury thiosalicylate, [(Ar^{CO₂})SH_gEt]Na, more commonly known as Thimerosal or Merthiolate,^{14,15} has long found applications in a variety of products, including vaccine preservatives.^{14,16} Only recently, however, has the molecular structure of this compound been determined by X-ray diffraction and shown to be a two coordinate arylthiolate mercury ethyl derivative.¹⁷ While other arylthiolate mercury ethyl compounds have been structurally characterized by X-ray diffraction,^{17–19} there are no examples of selenolate counterparts listed in the Cambridge Structural Database.^{20,21} Therefore, it is noteworthy that we have synthesized the phenylselenolate mercury ethyl complex, PhSeHgEt, *via* the reaction of diphenyl diselenide with NaBH₄, followed by treatment with EtHgCl (Scheme 1), and determined its structure by X-ray diffraction (Figure 1). For comparison, we have also determined the molecular structure of the methyl derivative, PhSeHgMe^{21a} (Figure 2).

Both PhSeHgMe and PhSeHgEt possess approximately linear coordination geometries, and the Hg–C bond lengths are comparable to related two-coordinate mercury alkyl compounds with selenium donors (Table 1). Linear coordination is common for mercury^{22,23} and is often attributed to relativistic effects, although other factors have also been considered.²⁴

However, while two-coordination is well preceded for mercury, examples of two-coordinate organomercury compounds that feature a selenium co-ligand are not common. For example, there are only three other examples of two-coordinate species with a [Se–Hg–C] motif that are currently listed in the Cambridge Structural Database, each of which is a methyl derivative (Table 1).^{25,26,27}

The Hg–C bond length in PhSeHgCH₃ [2.087(6) Å] is within the range observed for the other derivatives (2.04 Å – 2.13 Å), while the Hg–SePh bond lengths of PhSeHgMe [2.4990(13) Å] and PhSeHgEt [2.4955(14) Å and 2.4940(14) Å] are comparable to, but slightly longer than that in the other arylselenolate organomercury complex, namely (2,4,6-Pr₃C₆H₂)SeHgMe [2.460(3) Å]. For additional comparison, these Hg–SeAr bond lengths are similar to those in the two-coordinate homoleptic derivative, Hg(SePh)₂ [2.4802(2) Å],²⁸ and the four-coordinate complex, [Tm^{Bu^t}]HgSePh [2.5244(4) Å].²⁹ It is, nevertheless, appropriate to point out that significantly longer Hg–Se bond lengths have been reported for compounds that feature Hg←Se dative covalent L-type interactions.³⁰ For example, the benzimidazole-2-selone derivative, [H(sebenzim^{Me})]₂HgCl₂ has bond lengths of 2.5732(5)

Å and 2.6090(5) Å,³¹ while those in [Hg₂(SePh₂)₄][ClO₄]₂ range from 2.65 Å to 2.92 Å.³² Such variability in bond lengths is by no means unique to Hg–Se interactions and is a common feature of dative covalent bonds.³³

Although PhSeHgMe and PhSeHgEt have a primary coordination number of two, there are secondary Hg•••Se intermolecular interactions that serve to increase the coordination number in the solid state.²³ Specifically, each mercury center of PhSeHgR interacts with the selenium atoms of three adjacent PhSeHgR molecules. As such, the extended structure may be considered to be composed of dinuclear rectangular (PhSeHgR)₂ moieties that are linked together in a chain, as illustrated in Figure 3. For PhSeHgEt, the intermolecular Hg•••Se interactions range from 3.42 Å to 3.77 Å, while the values for PhSeHgMe range from 3.35 Å to 3.72 Å. The thiolate compounds, PhSHgMe and PhSHgEt, exhibit a similar extended structure, with intermolecular Hg•••S interactions that span the range of 3.24 Å to 3.78 Å for PhSHgMe and 3.23 Å to 4.45 Å for PhSHgEt.¹⁷ The phenolate compound PhOHgMe also possesses a similar type of packing arrangement, with intermolecular Hg•••O interactions in the range of 2.70 Å to 3.76 Å.³⁴ Two of the interactions [2.702(9) Å and 2.719(9) Å], however, are much smaller than the others, such that the compound has been described as comprising a stack of loosely associated dimers. In this regard, the principal difference between the selenolate and phenolate compounds is that each mercury center of PhSeHgR forms three comparable intermolecular Hg•••Se interactions, whereas PhOHgMe favors a single intermolecular Hg•••O interaction.

Spectroscopically, PhSeHgEt is characterized by a ¹⁹⁹Hg NMR signal at –815 ppm in C₆D₆, which is comparable to the values reported for related two-coordinate mercury alkyl compounds with sulfur or selenium co-ligands (Table 2).³⁵ The presence of the ¹⁹⁹Hg nucleus is also evident from the existence of satellites (16.9 % abundance) in both the ¹H and ¹³C{¹H} NMR spectra. Interestingly, while ¹J_{Hg–C} (1145 Hz) is considerably larger than ²J_{Hg–C} (63 Hz), ²J_{Hg–H} (159 Hz) is significantly smaller than ³J_{Hg–H} (232 Hz).³⁶ The latter trend has been observed for a variety of other EtHgX compounds, as illustrated in Table 3, and a plot of ²J_{Hg–H} versus ³J_{Hg–H} is characterized by the empirical expression ²J_{Hg–H} = 1.43 ³J_{Hg–H} (Figure 4). The magnitude of the coupling constants depends strongly on the nature of X and correlates approximately with its electronegativity.³⁷

Another interesting spectroscopic feature of PhSeHgEt pertains to the appearance of the ethyl group in the ¹H NMR spectrum. Specifically, rather than exhibiting the triplet and quartet associated with an A₂X₃ spin system, additional coupling is present in the 300, 400 and 500 MHz ¹H NMR spectra (Figure 5). The manifestation of the additional coupling is a consequence of second order effects and the spectra may be simulated with the following spectral parameters: δ(CH₂) = 0.86 ppm, δ(CH₃) = 1.00 ppm, and |³J_{H–H}| = 7.8 Hz.³⁸ However, whereas the principal NMR signals for the ethyl group of PhSeHgEt are not first-order, the outer ¹⁹⁹Hg satellite signals of the CH₂ and CH₃ groups exhibit a first order pattern. For example, at 500 MHz, the chemical shift difference for the outer quartet and outer triplet (which are associated with the same ¹⁹⁹Hg spin state)* is 0.52 ppm (*i.e.* 260 Hz), which is significantly greater than the ³J_{H–H} coupling constant (8 Hz) and is therefore consistent with a first-order appearance. The inner satellite signals are separated by 0.26

ppm (*i.e.* 129 Hz) and would also be expected to exhibit first-order behavior, but the quartet signal is obscured by the triplet of the primary resonance. The observation of a first-order pattern for the satellites of PhSeHgEt is in marked contrast to that observed for EtHgCl at 400 MHz, where the inner satellites appear as a *singlet* due to the chemical shifts of the corresponding CH₂ and CH₃ groups being coincidentally equivalent at this field.¹⁸

Examination of the data in Table 3 demonstrates that the difference in chemical shifts, $\delta = \delta(\text{CH}_2) - \delta(\text{CH}_3)$, is strongly influenced by the nature of X,³⁹ ranging from 0.98 ppm for EtHgClO₄, to -0.29 ppm for Et₂Hg. With respect to the molecular compounds, the value of δ correlates approximately with the electronegativity of X, with EtHgCl having a value of 0.63 ppm and Et₂Hg a value of -0.29 ppm.⁴⁰ Indeed, Et₂Hg is the only ethyl mercury compound of which we are aware for which the CH₃ group is downfield of the CH₂ group.^{41,||} Since the ¹J_{Hg-H} coupling constants are also influenced by the nature of X (Table 3), it is relevant to note that there are also approximate correlations between δ and ¹J_{Hg-H} (n = 2, 3), as illustrated in Figure 6.

2. Cleavage of the Hg–C bond of PhSeHgR

The toxicity of organomercury compounds is well known,² and Nature has developed a detoxification procedure that is achieved by the combined action of two enzymes, namely (i) organomercurial lyase (*MerB*) and (ii) mercuric ion reductase (*MerA*).^{2,42} *MerB* is essential because it catalyzes the protolytic cleavage of Hg–C bonds; as such, it is important to establish the factors that influence this reaction. In this regard, while two-coordinate mercury alkyl compounds of the type RHgX are notoriously inert towards cleavage of the Hg–C bond under physiological conditions,^{43,44,45} we have demonstrated that the *tris*(2-mercapto-1-*t*-butylimidazolyl)hydroborato complexes [Tm^{Bu}][†]HgR (R = Me, Et) undergo facile cleavage of the Hg–C bond by PhSH at room temperature due to the mercury center being able to access higher coordination modes.⁴⁶ To investigate further the factors that influence the cleavage of Hg–C bonds, we have examined the reactivity of PhSeHgR towards PhSH with the intention of probing the effect of selenolate *versus* thiolate coordination.

Interestingly, whereas the thiolate compound PhSHgEt reacts only slowly with PhSH at room temperature, and requires elevated temperatures to liberate ethane efficiently,^{19e} the selenolate compound PhSeHgEt reacts rapidly, with evolution of ethane proceeding over the course of one day at room temperature.[†] As such, it is evident that coordination by selenium promotes protolytic Hg–C bond cleavage, a result that is of relevance to the observation that various selenium-containing biomolecules can promote demethylation of methyl-mercury species.^{7e,11}

*The observation that the outer satellite signals (and likewise the inner satellite signals) are associated with the same ¹⁹⁹Hg spin state is a consequence of the fact that ²J_{Hg-H} and ³J_{Hg-H} have opposite signs.

||For an image of the ¹H NMR spectrum of Et₂Hg in CDCl₃, which shows that the chemical shift of the CH₃ group is downfield of the CH₂ group, see the Structural Database for organic compounds: http://sdb.sdb.aist.go.jp/sdb/cgi-bin/direct_frame_top.cgi (SDBS #10645).

†The mercury product is tentatively identified as heteroleptic (PhS)Hg(SePh), which undergoes redistribution to form a mixture with (PhS)₂Hg and (PhSe)₂Hg.

Also of note, protolytic cleavage of the Hg–Et bond of PhSeHgEt is significantly more facile than cleavage of the Hg–Me bond. For example, whereas elimination of ethane from the reaction of PhSeHgEt and PhSH is complete after a period of 1 day at room temperature, negligible quantities of methane are liberated from a mixture of PhSeHgMe and PhSH under comparable conditions. The observation of more facile Hg–Et rather than Hg–Me bond cleavage is in accord with the behavior of the corresponding thiolate system, PhSHgR,^{19e} but contrasts with the report that protonolysis of RHgI by HClO₄ and H₂SO₄ exhibits the opposite trend.^{43b,45} The differences observed in these systems indicate that there is much to be learned regarding the factors that influence Hg–C bond cleavage and, consequently, mercury detoxification.

3. Degenerate exchange reactions involving PhSeHgR

PhSeHgR undergo facile degenerate exchange reactions. For example, ¹H NMR spectroscopic studies demonstrate that a mixture of PhSeHgMe and MeHgCl exhibit a single resonance attributable to the methyl groups (Figure 7), as does a mixture of PhSeHgMe and PhSHgMe (Figure 8).[‡] A mixture of PhSeHgEt and EtHgCl likewise exhibit a single set of signals for the ethyl groups (Figure 9). The observation of a single set of resonances for the alkyl groups indicates that the exchange processes are in the fast exchange regime.⁴⁷ In addition, a single ¹⁹⁹Hg{¹H} NMR spectroscopic signal is observed for a mixture of PhSeHgMe and MeHgCl, and also for a mixture of PhSeHgEt and EtHgCl.

Two possible mechanisms for the degenerate exchange processes involve (i) Hg–R/Hg–R metathesis and (ii) Hg–SePh/Hg–X metathesis,[§] as illustrated in Scheme 2. Of these, the latter is more consistent with the ¹H NMR spectroscopic data. For example, the fact that the exchange averaged alkyl signals in the mixture of PhSeHgR and RHgCl retain ¹⁹⁹Hg coupling (albeit a weighted average of the exchanging species) indicates that Hg–C bond cleavage does not occur on the timescale associated with the observed exchange process.^{48,49}

Further evidence that Hg–R bond metathesis in this system is not facile on the NMR timescale is also provided by the fact that the ¹⁹⁹Hg{¹H} NMR spectrum of a mixture of PhSeHgMe and PhSeHgEt exhibits two distinct ¹⁹⁹Hg NMR spectroscopic signals (Figure 10), rather than the single signal that would be expected if the alkyl groups were to undergo exchange.

The above observations are in accord with other studies involving RHgX compounds which indicate that metathesis involving Hg–X bonds is more facile than those involving Hg–R bonds,^{50,51} presumably due to the availability of lone pairs on X that favor 4-centered transition states of the type illustrated in Scheme 2.⁵⁰ In this regard, it should be noted that although a previous investigation proposed Hg–R/Hg–R metathesis involving RHgX compounds (*e.g.* MeHgI³⁷) in order to explain the greater linewidth of the mercury satellites in the ¹H NMR spectra, it is now recognized that this observation is more appropriately

[‡]Exchange between PhSeHgMe and MeHgCN on the NMR timescale has also been reported. See reference 21a.

[§]While the Hg–SePh/Hg–X metathesis illustrated in Scheme 2 is depicted as bimolecular, we note that other exchange mechanisms are possible, including those that are dissociative in nature.

rationalized in terms of scalar relaxation of the second kind.⁵² Specifically, quadrupolar relaxation of the adjacent iodine nucleus induces relaxation of the ¹⁹⁹Hg nucleus, thereby increasing the linewidth of the satellite signals relative to the central signal.^{51,53}

SUMMARY

In summary, X-ray diffraction studies demonstrate that the phenylselenolate mercury alkyl compounds, PhSeHgMe and PhSeHgEt, are best described as monomeric with approximately linear coordination geometries; the mercury centers do, nevertheless, exhibit secondary Hg•••Se intermolecular interactions that serve to increase the effective coordination number. The mercury-carbon bond of PhSeHgEt is readily cleaved by PhSH to release ethane; significantly, the reaction is more facile than that of the thiolate analogue, PhSHgEt, which thereby demonstrates that coordination by selenium promotes protolytic cleavage of the mercury-carbon bond. Protolytic cleavage of the Hg–Et bond of PhSeHgEt is also significantly more facile than cleavage of the Hg–Me bond, which is of note because a different trend was reported for the cleavage of RHgI by HX. In addition to reactivity associated with the Hg–Et bond, the phenylselenolate compounds PhSeHgR (R = Me, Et) also undergo degenerate exchange reactions with RHgX (X = Cl, SPh) *via* metathesis of the Hg–SePh/Hg–X groups, evidence for which is provided by the observation that the weighted average signal for the alkyl groups in the ¹H NMR spectra preserves coupling to the ¹⁹⁹Hg nuclei.

EXPERIMENTAL SECTION

General Considerations

NMR spectra were measured on Bruker 300 DPX, Bruker 400 Avance III, and Bruker Avance 500 DMX spectrometers. ¹H NMR spectra are reported in ppm relative to SiMe₄ (δ = 0) and were referenced internally with respect to the protio solvent impurity (δ 7.16 for C₆D₅H, 7.26 for CDCl₃ and 2.50 for Me₂SO-*d*₅).⁵⁴ ¹³C{¹H} NMR spectra are reported in ppm relative to SiMe₄ (δ = 0) and were referenced internally with respect to the solvent (δ 128.06 for C₆D₆ and 77.16 for CDCl₃).⁵⁴ ¹⁹⁹Hg{¹H} NMR spectra are reported in ppm relative to Me₂Hg (δ = 0) and were obtained by using the $\Xi/100\%$ value of 17.910822.⁵⁵ Coupling constants are given in hertz. IR spectra were recorded as KBr pellets on a Nicolet iS10 FT–IR spectrometer (ThermoScientific), and the data are reported in reciprocal centimeters. Mass spectra were obtained on a JEOL JMS-HX110HF tandem mass spectrometer using fast atom bombardment (FAB). Ph₂Se₂ was purchased from Strem Chemicals, EtHgCl was purchased from Alfa Aesar and all other chemicals were purchased from Sigma-Aldrich. *CAUTION: All mercury compounds are toxic and appropriate safety precautions must be taken in handling these compounds.*

X-ray structure determinations

Single crystal X-ray diffraction data were collected on a Bruker Apex II diffractometer and crystal data, data collection and refinement parameters are summarized in Table 4. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on *F*² with SHELXTL (Version 2008/4).⁵⁶

Synthesis of PhSeHgMe

PhSeHgMe was synthesized by a method related to that in the literature.^{21a} An ethanol solution (50 mL) of diphenyl diselenide (264 mg, 0.85 mmol) was treated with an ethanol solution (20 mL) of sodium borohydride (65 mg, 1.7 mmol). The yellow solution slowly turned colorless over a period of several minutes, and the resulting solution was treated with an ethanol solution (30 mL) of MeHgCl (423 mg, 1.7 mmol). The suspension was stirred for 2.5 hours, allowed to settle, and filtered. The volatile components of the filtrate were removed *in vacuo* leaving PhSeHgMe as a yellow powder (395 mg, 63%). Anal. calcd. for PhSeHgMe: C, 22.6; H, 2.2. Found: C, 22.7; H, 2.0. ¹H NMR (C₆D₆): 0.21 [s, ²J_{Hg-H} = 155, 3 H of C₆H₅SeHgCH₃], 6.93 [m, 3 H of C₆H₅SeHgMe], 7.59 [m, 2 H of C₆H₅SeHgMe]; ¹H NMR (CDCl₃): 0.95 [s, ²J_{Hg-H} = 155, 3 H of C₆H₅SeHgCH₃], 7.17 [m, 3 H of C₆H₅SeHgMe], 7.56 [m, 2 H of C₆H₅SeHgMe]. ¹³C NMR (CDCl₃): 16.4 [¹J_{Hg-C} 1080 Hz, 1 C of PhSeHgCH₃], 126.2 [1 C of C₆H₅Hg], 126.3 [1 C of C₆H₅Hg], 129.1 [2 C of C₆H₅Hg], 135.9 [2 C of C₆H₅Hg]. ¹⁹⁹Hg NMR (C₆D₆): -658. IR Data (KBr pellet, cm⁻¹): 3059 (w), 2990 (w), 2905 (m), 1658 (w), 1572 (s), 1471 (vs), 1431 (s), 1322 (w), 1292 (w), 1263 (w), 1179 (w), 1159 (w), 1067 (s), 1018 (s), 996 (m), 889 (w), 767 (m), 726 (vs), 687 (vs), 663 (s). FAB-MS m/z = 372.0 [M]⁺, M = PhSeHgMe.

Synthesis of PhSeHgEt

An ethanol solution (60 mL) of diphenyl diselenide (274 mg, 0.88 mmol) was treated with an ethanol solution (15 mL) of sodium borohydride (66 mg, 1.7 mmol). The yellow solution slowly turned colorless over a period of several minutes and the resulting solution was treated with an ethanol solution (25 mL) of EtHgCl (466 mg, 1.76 mmol). The suspension was stirred for 10 hours, allowed to settle, and filtered. The volatile components of the filtrate were removed *in vacuo* leaving PhSeHgEt as a yellow powder (488 mg, 72%). Anal. calcd. for PhSeHgEt: C, 24.9; H, 2.6. Found: C, 25.0; H, 1.6. ¹H NMR (C₆D₆, 500 MHz): 0.85 [t, ³J_{H-H} = 8, 3 H of PhSeHgCH₂CH₃], 0.99 [q, ³J_{H-H} = 8, 2 H of PhSeHgCH₂CH₃], 6.92 [m, 3 H of C₆H₅SeHgEt], 7.59 [m, 2 H of C₆H₅SeHgEt]; ¹H NMR (CDCl₃, 500 MHz): 1.37 [t, ³J_{H-H} = 8, 3 H of PhSeHgCH₂CH₃], 1.80 [q, ³J_{H-H} = 8, 2 H of PhSeHgCH₂CH₃], 7.17 [m, 3 H of C₆H₅SeHgEt], 7.55 [m, 2 H of C₆H₅SeHgEt]. ¹³C NMR (C₆D₆): 13.6 [²J_{Hg-C} = 63 Hz, 1 C of PhSeHgCH₂CH₃], 31.8 [¹J_{Hg-C} 1145 Hz, 1 C of PhSeHgCH₂CH₃], 126.1 [1 C of C₆H₅HgEt], 129.2 [2 C of C₆H₅HgEt], 136.1 [2 C of C₆H₅HgEt] (note: the *ipso* carbon is obscured by the solvent); ¹³C NMR (CDCl₃): 14.0 [²J_{Hg-C} = 63 Hz, 1 C of PhSeHgCH₂CH₃], 32.4 [¹J_{Hg-C} 1145 Hz, 1 C of PhSeHgCH₂CH₃], 126.3 [1 C of C₆H₅HgEt], 126.4 [1 C of C₆H₅HgEt], 129.1 [2 C of C₆H₅HgEt], 135.9 [2 C of C₆H₅HgEt]. ¹⁹⁹Hg NMR (C₆D₆): -815. IR Data (KBr pellet, cm⁻¹): 3066 (w), 3053 (w), 2965 (m), 2942 (m), 2919 (w), 2855 (m), 1573 (s), 1471 (s), 1433 (s), 1372 (w), 1295 (w), 1172 (m), 1066 (m), 1017 (s), 997 (m), 960 (w), 896 (w), 730 (vs), 690 (vs), 663 (s), 672 (m), 615 (w). FAB-MS m/z = 386.0 [M]⁺, M = PhSeHgEt.

Reactivity of PhSeHgEt towards PhSH

A solution of PhSeHgEt (10 mg, 0.026 mmol) in C₆D₆ (0.7 mL) was treated with PhSH (2.7 μL, 0.026 mmol) and transferred to an NMR tube equipped with a J. Young valve. The reaction was monitored by ¹H NMR spectroscopy, thereby demonstrating the release of

C₂H₆ over a period of 1 day at room temperature, accompanied by the formation of a precipitate which is assigned as a rapidly interconverting mixture of (PhS)Hg(SePh), (PhS)₂Hg and (PhSe)₂Hg in solution.

Reactivity of PhSeHgMe towards PhSH

A solution of PhSeHgMe (10 mg, 0.027 mmol) in C₆D₆ (0.7 mL) was treated with PhSH (2.8 µL, 0.027 mmol) and transferred to an NMR tube equipped with a J. Young valve. The sample was monitored by ¹H NMR spectroscopy, thereby demonstrating that there is negligible formation of CH₄ over a period of 1 day at room temperature.

NMR spectroscopic investigation of degenerate exchange involving PhSeHgMe and MeHgCl

A solution of PhSeHgMe (6 mg, 0.016 mmol) and MeHgCl (4 mg, 0.016 mmol) in C₆D₆ (0.7 mL) was transferred to an NMR tube equipped with a J. Young valve. The sample was examined by ¹H NMR spectroscopy, thereby demonstrating a single resonance attributable the mercury methyl groups. Similarly, a solution consisting of PhSeHgMe (7 mg, 0.019 mmol) and MeHgCl (5 mg, 0.020 mmol) in C₆D₆ (0.7 mL) was examined by ¹⁹⁹Hg{¹H} NMR, thereby demonstrating a single resonance.

NMR spectroscopic investigation of degenerate exchange involving PhSeHgMe and PhSHgMe

A solution of PhSeHgMe (6 mg, 0.016 mmol) and PhSHgMe (5 mg, 0.015 mmol) in C₆D₆ (0.7 mL) was transferred to an NMR tube equipped with a J. Young valve. The sample was examined by ¹H NMR spectroscopy, thereby demonstrating a single resonance attributable to the mercury methyl groups.

NMR spectroscopic investigation of degenerate exchange involving PhSeHgEt and EtHgCl

A solution of PhSeHgEt (5 mg, 0.013 mmol) and EtHgCl (3 mg, 0.011 mmol) in C₆D₆ (0.7 mL) was transferred to an NMR tube equipped with a J. Young valve. The sample was examined by ¹H NMR spectroscopy, thereby demonstrating a single resonance attributable the mercury ethyl groups. Similarly, a solution consisting of PhSeHgEt (15 mg, 0.039 mmol) and EtHgCl (10 mg, 0.038 mmol) in C₆D₆ (1.5 mL) was examined by ¹⁹⁹Hg{¹H} NMR, thereby demonstrating a single resonance.

NMR spectroscopic investigation of exchange involving PhSeHgMe and PhSeHgEt

A solution of PhSeHgMe (6 mg, 0.016 mmol) and PhSeHgEt (6 mg, 0.016 mmol) in C₆D₆ (0.7 mL) was examined by ¹⁹⁹Hg{¹H} NMR spectroscopy, which showed independent signals for PhSeHgMe and PhSeHgEt, thereby indicating that exchange of methyl and ethyl groups is not facile on the NMR timescale.

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APPENDIX A. Supplementary Data

CCDC 1057236–1057237 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/contents/retrieving.html> or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk

References

1. (a) Prince RC, Gailer J, Gunson DE, Turner RJ, George GN, Pickering IJ. *J Inorg Biochem.* 2007; 101:1891–1893. [PubMed: 17644180] (b) Gailer J. *Coord Chem Rev.* 2007; 251:234–254. (c) Gailer J. *Appl Organometal Chem.* 2002; 16:701–707. (d) Cuvín-Aralar MLA, Furness RW. *Ecotoxicol Env Safety.* 1991; 21:348–364. [PubMed: 1868791] (e) Ikemoto T, Kunito T, Tanaka H, Baba N, Miyazaki N, Tanabe S. *Arch Environ Contam Toxicol.* 2004; 47:402–413. [PubMed: 15386135] (f) Magos L, Webb M, Clarkson TW. *Crit Rev Toxicol.* 1980; 8:1–42. [PubMed: 7002474] (g) Khan MAK, Wang F. *Environ Toxicol Chem.* 2009; 28:1567–1577. [PubMed: 19374471] (h) Yang D-Y, Chen Y-W, Gunn JM, Belzile N. *Environ Rev.* 2008; 16:71–92.
2. (a) Syversen T, Kaur P. *J Trace Elem Med Biol.* 2012; 26:215–226. [PubMed: 22658719] (b) Clarkson TW, Magos L. *Crit Rev Toxicol.* 2006; 36:609–662. [PubMed: 16973445] (c) Mutter J, Naumann J, Guethlin C. *Crit Rev Toxicol.* 2007; 37:537–549. [PubMed: 17661216] (d) Berlin, M.; Zalups, RK.; Fowler, BA. “Mercury” in *Handbook on the Toxicology of Metals*. 3rd. Elsevier Academic Press Inc; San Diego: 2007. p. 675–729.(Chapter 33)
3. (a) Roman M, Jitaru P, Barbante C. *Metallomics.* 2014; 6:25–54. [PubMed: 24185753] (b) Lu J, Holmgren A. *J Biol Chem.* 2009; 284:723–727. [PubMed: 18757362] (c) Papp LV, Lu J, Holmgren A, Khanna KK. *Antioxid Redox Signal.* 2007; 9:775–806. [PubMed: 17508906] (d) Papp LV, Holmgren A, Khanna KK. *Antioxid Redox Signal.* 2010; 12:793–795. [PubMed: 19905883] (e) Wessjohann LA, Schneider A, Abbas M, Brandt W. *Biol Chem.* 2007; 388:997–1006. [PubMed: 17937613] (f) Tinggi U. *Environ Health Prev Med.* 2008; 13:102–108. [PubMed: 19568888] (g) Ninomiya M, Garud DR, Koketsu M. *Coord Chem Rev.* 2011; 255:2968–2990. (h) Ferguson LR, Karunasinghe N, Zhu ST, Wang AH. *Mutat Res-Fundam Mol Mech Mutagen.* 2012; 733:100–110. (i) Naithani R. *Mini-Rev Med Chem.* 2008; 8:657–668. [PubMed: 18537721] (j) Valko M, Rhodes CJ, Moncol J, Izakovic M, Mazur M. *Chem Biol Interact.* 2006; 160:1–40. [PubMed: 16430879] (k) Tapiero H, Townsend DM, Tew KD. *Biomed Pharmacotherapy.* 2003; 57:134–144. (l) Bjelakovic G, Nikolova D, Gluud L, Simonetti RG, Gluud C. *JAMA.* 2007; 297:842–857. [PubMed: 17327526] (m) Michiels C, Raes M, Toussaint O, Remacle J. *Free Rad Biol Med.* 1994; 17:235–248. [PubMed: 7982629] (n) Chen J, Berry MJJ. *Neurochem.* 2003; 86:1–12.
4. (a) Köhrle J. *Biochimie.* 1999; 81:527–533. [PubMed: 10403185] (b) Reddy CC, Massaro EJ. *Fundam Appl Toxicol.* 1983; 3:431–436. [PubMed: 6357927] (c) Frost DV, Lish PM. *Ann Rev Pharmacol Toxicol.* 1975; 15:259–284. (d) Carland, M.; Fenner, T. *Metallotherapeutic Drugs and Metal-Based Diagnostic Agents: The Use of Metals in Medicine*. John Wiley and Sons; Hoboken, NJ: 2005. Chapter 17 (e) Sanmartín C, Plano D, Font M, Palop JA. *Curr Med Chem.* 2011; 18:4635–4650. [PubMed: 21864284] (f) Duntas LH. *J Clin Endocrinol Metab.* 2010; 95:5180–5188. [PubMed: 20810577] (g) Schomburg L. *Nat Rev Endocrinol.* 2012; 8:160–171. [PubMed: 22009156] (h) Tiekink ERT. *Dalton Trans.* 2012; 41:6390–6395. [PubMed: 22252404]
5. (a) Fálnoga I, Tušek-Žnidarić M. *Biol Trace Elem Res.* 2007; 119:212–220. [PubMed: 17916944] (b) Fálnoga I, Tušek-Žnidarić M, Stegnar P. *BioMetals.* 2006; 19:283–294. [PubMed: 16799866] (c) Sasakura C, Suzuki KT. *J Inorg Biochem.* 1998; 71:159–162. [PubMed: 9833321]
6. (a) Wang, F.; Lemes, M.; Khan, MA. *Kin Environmental Chemistry and Toxicology of Mercury*. Cai, Y.; Liu, G.; O'Driscoll, N., editors. John Wiley & Sons; New Jersey: 2012. Chapter 16 (b) Ralston NVC, Ralston CR, Blackwell JL III, Raymond LJ. *Neurotoxicology.* 2008; 29:802–811. [PubMed: 18761370] (c) Carvalho CML, Chew E-H, Hashemy SI, Lu J, Holmgren A. *J Biol Chem.* 2008; 283:11913–11923. [PubMed: 18321861]
7. (a) Yamashita Y, Yamashita M. *J Biol Chem.* 2010; 285:18134–18138. [PubMed: 20388714] (b) Yamashita Y, Yabu T, Yamashita M. *World J Biol Chem.* 2010; 1:144–150. [PubMed: 21540999] (c) Yamashita Y, Amlund H, Suzuki T, Hara T, Hossain MA, Yabu T, Touhata K, Yamashita M.

- Fish Sci. 2011; 77:679–686. (d) Yamashita M, Yamashita Y, Ando T, Wakamiya J, Akiba S. Biol Trace Elem Res. 2013; 156:36–44. [PubMed: 24197605] (e) Yamashita M, Yamashita Y, Suzuki T, Kani Y, Mizusawa N, Imamura S, Takemoto K, Hara T, Hossain MA, Yabu T, Touhata K. Mar Biotechnol. 2013; 15:559–570. [PubMed: 23709046]
8. Ogra Y, Anan Y. Biol Pharm Bull. 2012; 35:1863–1869. [PubMed: 23123457]
9. Klein M, Ouerdane L, Bueno M, Pannier F. Metallomics. 2011; 3:513–520. [PubMed: 21331438]
10. (a) Jacob C, Giles GI, Giles NM, Sies H. Angew Chem Int Ed Engl. 2003; 42:4742–4758. [PubMed: 14562341] (b) Roy G, Sarma BK, Phadnis PP, Mugesh G. J Chem Sci. 2005; 117:287–303. (c) Silks LA. Phosphorus Sulfur Silicon Relat Elem. 1998; 136:611–616.
11. Khan MAK, Wang FY. Chem Res Toxicol. 2010; 23:1202–1206. [PubMed: 20499893]
12. Tai HC, Lim C. J Phys Chem A. 2006; 110:452–462. [PubMed: 16405317]
13. (a) Rooney JPK. Toxicology. 2007; 234:145–156. [PubMed: 17408840] (b) Guzzi G, La Porta CAM. Toxicology. 2008; 244:1–12. [PubMed: 18077077]
14. Geier DA, Sykes LK, Geier MR. J Toxicol Environ Health – Part B. 2007; 10:575–596.
15. Powell HM, Jamieson WA. Am J Hygiene. 1931; 13:296–310.
16. (a) Ohno H, Doi R, Kashima Y, Murae S, Kizaki T, Hitomi Y, Nakano N, Harada M. Bull Environ Contam Toxicol. 2004; 73:777–780. [PubMed: 15669718] (b) Gil S, Lavilla I, Bendicho C. J Anal At Spectrom. 2007; 22:569–572. (c) Fagundes A, Marzochi MCA, Perez M, Schubach A, Ferreira A, Silva JP, Schubach T, Marzochi KBF. Acta Tropica. 2007; 101:25–30. [PubMed: 17227669] (d) Meyer BK, Ni A, Hu B, Shi L. J Pharm Sci. 2007; 96:3155–3167. [PubMed: 17722087]
17. Melnick JG, Yurkerwich K, Buccella D, Sattler W, Parkin G. Inorg Chem. 2008; 47:6421–6426. [PubMed: 18533648]
18. Sattler W, Yurkerwich K, Parkin G. Dalton Trans. 2009:4327–4333. [PubMed: 19662310]
19. For some structurally characterized arylthiolate mercury methyl and related compounds, see reference 17 and (a) Chieh C. Can J Chem. 1978; 56:560–563. (b) Castiñeiras A, Hiller W, Strähle J, Bravo J, Casas JS, Gayoso M, Sordo J. J Chem Soc Dalton Trans. 1986:1945–1948. (c) Almagro X, Clegg W, Cucurull-Sánchez L, González-Duarte P, Traveria M. J Organomet Chem. 2001; 623:137–148. (d) Aupers JH, Howie RA, Wardell JL. Polyhedron. 1997; 16:2283–2289. (e) Melnick JG, Yurkerwich K, Parkin G. Inorg Chem. 2009; 48:6763–6772. [PubMed: 20507113]
20. Cambridge Structural Database (Version 5.33). *3D Search and Research Using the Cambridge Structural Database*, Allen FH, Kennard O. Chemical Design Automation News. 1993; 8(1):1 & 31–37.
21. For examples of organomercury selenolate compounds that are not listed in the Cambridge Structural Database, see: (a) Canty AJ, Carty AJ, Malone SFJ. Inorg Biochem. 1983; 19:133–142. (b) Pelletier E, Sauriol F, Wharf I. Inorg Chim Acta. 1987; 138:99–101.
22. (a) Casa JS, García-Tasende MS, Sordo J. Coord Chem Rev. 1999:193–195. 283–359. (b) Holloway CE, Melnik M. J Organomet Chem. 1995; 495:1–31. (c) Rabenstein DL. Acc Chem Res. 1978; 11:100–107.
23. (a) Wright JG, Natan MJ, MacDonnell FM, Ralston DM, O'Halloran TV. Prog Inorg Chem. 1990; 38:323–412. (b) Kuz'mina LG, Struchkov YT. Croat Chem Acta. 1984; 57:701–724.
24. (a) Pyykkö P, Desclaux J-P. Acc Chem Res. 1979; 12:276–281. (b) Pyykkö P. Chem Rev. 1988; 88:563–594. (c) Kaupp M, von Schnering HG. Inorg Chem. 1994; 33:2555–2564. (d) Tossell JA, Vaughan DJ. Inorg Chem. 1981; 20:3333–3340.
25. Bochmann M, Coleman AP, Powell AK. Polyhedron. 1992; 11:507–512.
26. Carty AJ, Malone SF, Taylor NJ. J Organomet Chem. 1979; 172:201–211.
27. Carty AJ, Malone SF, Taylor NJ, Canty AJ. J Inorg Biochem. 1983; 18:291–300.
28. Emge TJ, Romanelli MD, Moore BF, Brennan JG. Inorg Chem. 2010; 49:7304–7312. [PubMed: 20690740]
29. Melnick JG, Yurkerwich K, Parkin G. J Am Chem Soc. 2010; 132:647–655. [PubMed: 20020759]
30. (a) Green MLH. J Organomet Chem. 1995; 500:127–148. (b) Parkin, G. Comprehensive Organometallic Chemistry III Volume 1, Chapter 1.01. Crabtree, RH.; Mingos, DMP., editors. Elsevier; Oxford: 2007. (c) Green JC, Green MLH, Parkin G. Chem Commun. 2012; 48:11481–11503. (d) Green MLH, Parkin G. J Chem Educ. 2014; 91:807–816.

31. (a) Palmer JH, Parkin G. *Polyhedron*. 2013; 52:658–668. [PubMed: 23543946] (b) Palmer JH, Parkin G. *J Am Chem Soc*. 2015; 137:4503–4516. [PubMed: 25822075]
32. (a) Brodersen K, Liehr G, Rosenthal M, Thiele GZ. *Naturforsch (B)*. 1978; 33:1227–1230. (b) Brodersen K, Liehr G, Rosenthal M. *Chem Ber-Recl*. 1977; 110:3291–3296.
33. Haaland A. *Angew Chem Int Ed Engl*. 1989; 28:992–1007.
34. Canty AJ, Devereux JW, Skelton BW, White AH. *Can J Chem*. 2006; 84:77–80.
35. For other compilations of ^{199}Hg NMR data of mercury thiolate compounds, see reference 23a and Carlton L, White D. *Polyhedron*. 1990; 9:2717–2720.
36. In cases where the signs of the coupling constants for mercury ethyl compounds have been measured, $^2J_{\text{Hg-H}}$ are negative, whereas $^3J_{\text{Hg-H}}$ are positive. See: Anet FAL, Sudmeier JL. *J Magn Reson*. 1969; 1:124–138.
37. Hatton JV, Schneider WG, Siebrand W. *J Chem Phys*. 1963; 39:1330–1336.
38. We note, however, that the ^1H NMR chemical shifts of PhSeHgEt are concentration dependent. Similar variations are also observed for MeHgCl and EtHgCl and could possibly indicate the existence of an equilibrium with a dimeric form. In this regard, it is worth noting that PhHgOMe is dimeric in benzene, while other PhHgOR derivatives exist as an equilibrium mixture of monomer and dimers. See: Bloodworth AJ. *J Chem Soc (C)*. 1970:2051–2056.
39. (a) Evans DF, Maher JP. *J Chem Soc*. 1962:5125–5128. (b) Narasimhan PT, Rogers MT. *J Am Chem Soc*. 1960; 82:34–40.
40. It is important to note that data illustrating the opposite trend in $\delta(\text{CH}_3)$ and $\delta(\text{CH}_2)$ chemical shifts of EtHgX compounds have been compiled, as illustrated by Tables 6 and 7 in: Petrosya VS, Reutov OA. *J Organomet Chem*. 1974; 76:123–169. However, there are discrepancies in these data. For example, $\delta(\text{CH}_3)$ and $\delta(\text{CH}_2)$ for Et_2Hg in CCl_4 are listed as -1.27 and -1.01 , respectively, in Table 6, but are listed as 1.27 and 1.01 in the text on page 130. Furthermore, values of 0.06 and 0.37 ppm are reported for Et_2Hg in Table 7. It is possible that these discrepancies are a result of different chemical shift conventions in the early literature.
41. Dessy RE, Flaatt TJ, Jaffé HH, Reynolds GF. *J Chem Phys*. 1959; 30:1422–1425.
42. (a) Moore MJ, Distefano MD, Zydowsky LD, Cummings RT, Walsh CT. *Acc Chem Res*. 1990; 23:301–308. (b) Walsh CT, Distefano MD, Moore MJ, Shewchuk LM, Verdine GL. *FASEB J*. 1988; 2:124–130. [PubMed: 3277886]
43. (a) Kreevoy MM. *J Am Chem Soc*. 1957; 79:5927–5930. (b) Kreevoy MM, Hansen RL. *J Am Chem Soc*. 1961; 83:626–630.
44. (a) Strasdeit H, von Döllen A, Saak W, Wilhelm M. *Angew Chem Int Ed*. 2000; 39:784–786. (b) Wilhelm M, Deeken S, Berksen E, Saak W, Lützen A, Koch R, Strasdeit H. *Eur J Inorg Chem*. 2004:2301–2312.
45. Nugent WA, Kochi JK. *J Am Chem Soc*. 1976; 98:5979–5988.
46. Melnick JG, Parkin G. *Science*. 2007; 317:225–227. [PubMed: 17626880]
47. Bryant RG. *J Chem Educ*. 1983; 60:933–935.
48. Faller, JW. *Dynamic NMR Spectroscopy in Organometallic Chemistry*. In: Crabtree, RH.; Mingos, DMP., editors. *Comprehensive Organometallic Chemistry III*. Vol. 1. Elsevier; Oxford: 2007. Chapter 1.15
49. Furthermore, the observation of ^{199}Hg satellites in the ^1H NMR spectra of individual samples of PhSeHgR and RHgX indicates that degenerate Hg-R/Hg-R metathesis does not occur. We also note that neither ^{199}Hg – ^{77}Se coupling nor long range ^{199}Hg – ^1H coupling involving the phenyl group are observed in the ^1H NMR spectra of PhSeHgR . Since long range ^{199}Hg – ^1H coupling has been observed in mercury alkyl and aryl compounds,^{a–d} the absence of these couplings may possibly be associated with facile exchange of the phenylselenolate ligand. (a) Singh G, Reddy GS. *J Organomet Chem*. 1972; 42:267–275. (b) Banney PJ, Wells PR. *Aust J Chem*. 1971; 24:317–324. (c) Wrackmeyer B, Contreras R. *Annu Rep NMR Spectrosc*. 1992; 24:267–329. (d) Bebout DC, Garland MM, Murphy GS, Bowers EV, Abelt CJ, Butcher RJ. *Dalton Trans*. 2003:2578–2584.
50. (a) Bach RD, Weibel AT. *J Am Chem Soc*. 1976; 98:6241–6249. [PubMed: 965642] (b) Bach RD, Weibel AT. *J Am Chem Soc*. 1975; 97:2575–2576.
51. Murrell LL, Brown TL. *J Organomet Chem*. 1968; 13:301–311.

52. Bruch, M. NMR Spectroscopy Techniques. 2nd. Marcel Dekker; New York: 1996.
53. Simpson RB. J Chem Phys. 1967; 46:4775–4783.
54. Gottlieb HE, Kotlyar V, Nudelman A. J Org Chem. 1997; 62:7512–7515. [PubMed: 11671879]
55. (a) Harris RK, Becker ED, De Menezes SMC, Goodfellow R, Granger P. Pure Appl Chem. 2001; 73:1795–1818. (b) Harris RK, Becker ED, De Menezes SMC, Granger P, Hoffman RE, Zilm KW. Pure Appl Chem. 2008; 80:59–84.
56. (a) Sheldrick, GM. SHELXTL, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data. University of Göttingen, Göttingen; Federal Republic of Germany: 1981. (b) Sheldrick GM. Acta Cryst. 2008; A64:112–122.

The phenylselenolate mercury alkyl compounds, PhSeHgR (R = Me, Et), have been structurally characterized by X-ray diffraction. Both compounds undergo rapid exchange with RHgX (X = SPh, Cl) on the NMR timescale, while PhSeHgEt also undergoes facile protolytic cleavage of the Hg–C bond by PhSH.

Figure 1.
Molecular structure of PhSeHgEt (only one of the crystallographically independent molecules is shown).

Figure 2.
Molecular structure of PhSeHgMe.

Figure 3.
Chain-type structure of PhSeHgR.

Figure 4.
Correlation between $^2J_{\text{Hg-H}}$ and $^3J_{\text{Hg-H}}$ for mercury ethyl compounds listed in Table 3.

Figure 5. Non first-order ^1H NMR spectra of the ethyl group of PhSeHgEt in benzene: (a) 300 MHz (top), (b) 400 MHz (middle) and (c) 500 MHz (bottom).

Figure 6. Correlation between $\Delta\delta$ and $^nJ_{\text{Hg-H}}$ ($n = 2, 3$) for mercury ethyl compounds listed in Table 3, where $\Delta\delta = \delta(\text{CH}_2) - \delta(\text{CH}_3)$.

Figure 7. ^1H NMR spectra (400 MHz) of the methyl region of (a) PhSeHgMe (top), (b) a mixture of PhSeHgMe and MeHgCl (middle) and (c) MeHgCl (bottom)

Figure 8. ^1H NMR spectra (400 MHz) of the methyl region of (a) PhSeHgMe (top), (b) a mixture of PhSeHgMe and PhSHgMe (middle) and PhSHgMe (bottom).

Figure 9. ^1H NMR spectra (400 MHz) of the ethyl region of (a) PhSeHgEt (top), (b) a mixture of PhSeHgEt and EtHgCl (middle) and (c) EtHgCl (bottom).

Figure 10.
 $^{199}\text{Hg}\{^1\text{H}\}$ NMR spectra of a mixture of PhSeHgMe and PhSeHgEt.

Scheme 1.
Synthesis of PhSeHgEt.

Scheme 2.

Two mechanisms for degenerate exchange of R groups.

Table 1

Bond length and angle data for selected two coordinate mercury alkyl compounds with selenium co-ligands.

	Hg–C/Å	Hg–Se/Å	Se–Hg–C/°	Reference
PhSeHgCH ₃	2.087(6)	2.4990(13)	177.03(19)	this work
PhSeHgCH ₂ CH ₃	2.083(9)	2.4955(14)	173.6(2)	this work
	2.111(10)	2.4940(14)	174.7(3)	
(2,4,6-Pr ⁱ ₃ C ₆ H ₂)SeHgMe	2.039(35)	2.460(3)	175.7(9)	25
{(H ₂ N) ₂ CSeHgMe}[NO ₃]	2.13(3)	2.477(3)	177.0(8)	26
[O ₂ C(H ₃ N)CHCH ₂ Se]HgMe	2.10(4)	2.469(4)	177.8(11)	27

Table 2

^{199}Hg NMR data for two-coordinate organomercury compounds with sulfur and selenium co-ligands.

	δ/ppm	Reference
PhSeHgMe	-688^a	21a
	-658^b	this work
PhSeHgEt	-815^b	this work
$[\text{O}_2\text{C}(\text{H}_3\text{N})\text{CHCH}_2\text{Se}]\text{HgMe}$	-644^c	21a,27
PhSHgMe	-620^a	21a
	-557^b	19e
PhSHgEt	-730^b	19e
	-784^c	17
$\left[\left(\text{Ar}^{\text{CO}_2} \right) \text{SHgEt} \right] \text{Na}_{(\text{thimerosal})}$	-788^d	18
$(\text{Ar}^{\text{CO}_2\text{H}}) \text{SHgEt}$		
$(3\text{-H}_2\text{NC}_6\text{H}_4\text{S})\text{HgMe}$	-613^d	19c
$(4\text{-H}_2\text{NC}_6\text{H}_4\text{S})\text{HgMe}$	-645	19c

a DMF

b Benzene

c D_2O

d DMSO

Table 3¹H NMR chemical shift and ⁿJ_{Hg-H} (n = 2, 3) coupling constant data for mercury ethyl complexes.^a

	$\Delta\delta = \delta(\text{CH}_2) - \delta(\text{CH}_3)$	$ ^2J_{\text{Hg-H}} ^a/\text{Hz}$	$ ^3J_{\text{Hg-H}} ^a/\text{Hz}$	Reference
Et ₂ Hg	-0.29	91 ^b	120 ^b	40
PhSeHgEt	0.14	159	232	this work ^d
PhSHgEt	0.20	162	228	18
$[(\text{Ar}^{\text{CO}_2})\text{SHgEt}]\text{Na}$	0.39	176	250	17
$[(\text{Ar}^{\text{CO}_2\text{HgEt}})\text{SHgEt}]_2$	0.51	193	273	18
$(\text{Ar}^{\text{CO}_2\text{H}})\text{SHgEt}$	0.54	168	252	18
EtHgCl	0.63	202	292	18
EtHgBr	0.65	214	301	39a
EtHgI	0.66	— ^c	— ^c	39a
EtHgClO ₄	0.98	— ^c	— ^c	39a

^a In cases where the signs of the coupling constants have been measured, ²J_{Hg-H} are negative, whereas ³J_{Hg-H} are positive. See reference 36.^b Values of ²J_{Hg-H} = 100 Hz and ³J_{Hg-H} = 128 Hz have also been reported. See reference 37.^c Values not reported^d Benzene

Table 4

Crystal, intensity collection and refinement data.

	PhSeHgMe	PhSeHgEt
lattice	Orthorhombic	Monoclinic
formula	C ₇ H ₈ HgSe	C ₈ H ₁₀ HgSe
formula weight	371.68	385.71
space group	<i>Pbcn</i>	<i>P2₁/c</i>
<i>a</i> /Å	24.803(12)	14.275(5)
<i>b</i> /Å	9.758(5)	17.858(7)
<i>c</i> /Å	7.041(3)	7.239(3)
α /°	90	90
β /°	90	91.743(6)
γ /°	90	90
<i>V</i> /Å ³	1704.2(14)	1844.7(12)
<i>Z</i>	8	8
temperature (K)	200(2)	200(2)
radiation (λ , Å)	0.71073	0.71073
ρ (calcd.), g cm ⁻³	2.897	2.778
μ (Mo K α), mm ⁻¹	22.249	20.559
θ max, deg.	30.71	29.61
no. of data collected	24879	27354
no. of data used	2631	5165
no. of parameters	82	181
R_I [$I > 2\sigma(I)$]	0.0297	0.0372
wR_2 [$I > 2\sigma(I)$]	0.0549	0.0570
R_I [all data]	0.0682	0.1059
wR_2 [all data]	0.0653	0.0726
GOF	1.008	1.007
R_{int}	0.0836	0.0653