FULL PAPER

Dalton
www.rsc.org/dalton

Organomercury-based imino-bis(diisopropylphosphine chalcogenide) complexes: synthesis and characterisation of novel hybrid "*single-source precursors*" for mercury chalcogenide solid-state materials

David J. Crouch,[a] Paul M. Hatton,[b] Madeleine Helliwell,[b] Paul O'Brien *[a] and James Raftery [a]

[a] *Department of Chemistry, University of Manchester, Oxford Road, Manchester, UK M13 9PL*

[b] *Materials Research Institute, Sheffield Hallam University, Pond Street, Sheffield, UK S1 1WB*

Received 20th March 2003, Accepted 20th May 2003
First published as an Advance Article on the web 9th June 2003

The synthesis and characterisation of the mercury(II) complexes [RHg{(SeP^iPr_2)$_2$N}] [R = methyl (**2a**), ethyl (**3a**), thienyl (T) (**4a**), 2-selenyl (SL) (**5a**) and phenyl (**6a**)], prepared by the reaction of the sodium salt of NH(SeP^iPr_2)$_2$ (**1a**) with the appropriate alkyl/aryl mercury halide in methanol are reported. Results are compared and contrasted to the corresponding sulfur analogues [RHg{(SP^iPr_2)$_2$N}] [R = T (**4b**), SL (**5b**) and Ph (**6b**)], and these new compounds have been evaluated, by thermogravimetric analysis and mass spectrometry as potential precursors and powder X-ray diffraction used to identify solid-state products. The solid-state structure of the symmetrical complex Hg[(SeP^iPr_2)$_2$N]$_2$ **7a**, and di(2-selenyl)mercury, one of the symmetrisation products of [SLHg{(SeP^iPr_2)$_2$N}] **5a** in solution, have been determined by single crystal X-ray crystallography.

Introduction

The last few decades has seen considerable interest in the synthesis of molecular "*single-source*" precursors for solid-state materials.[1–3] Generally the electrical and optical properties of solid-state materials grown by chemical vapour deposition (CVD) and solution thermolysis are critically dependant on the nature and purity of the precursors used. However traditional materials utilise gaseous and hazardous organometallic compounds for fabrication of the solid-state material.[3] Such properties are obviously disadvantageous when considering industrial applications. For example II–VI semiconductors, such as group 12 chalcogenides, are one of the more important classes of solid-state materials as species such as CdHgTe and HgSe have demonstrated various potential applications, ranging from integration in display devices,[4] and optoelectronic devices[5] to infrared detectors and thermal imaging systems.[6] Alternative "*single-source*" precursors of materials incorporating group 12 and 16 elements have therefore been sought resulting in various examples being reported.[7–9]

As part of our studies into cleaner forms of single-source precursors, we have demonstrated numerous alternative chalcogenide-sources for the preparation of solid-state materials. For example, asymmetrical four coordinate dithio- and diselenocarbamates M($E_2CNR^1R^2$)$_2$ have proved sufficiently volatile for the growth of zinc and cadmium chalcogenide films and nanoparticles.[10] More recently we have demonstrated that imino-bis(dialkylphosphine chalcogenide) [$R_2P(E)–N–P(E)R_2$] complexes[11] can be utilised to prepare CdSe quantum dots using solution thermolysis.[12]

Dichalcogenoimidodiphosphinato anions [$R_2P(E)–N–P(E)R_2$]$^-$ (E = O, S or Se) are versatile ligands, with a strong tendency to form inorganic (carbon free) chelate rings.[11] Transition-metal complexes incorporating such ligands have demonstrated improved thermal and chemical stability over traditional organic based ligands such as β-diketonate complexes.[13]

Nevertheless, while numerous zinc and cadmium single-source precursors have been utilised to prepare various materials, *via* CVD[2,7–9] and solution thermolysis,[10,12] there have been few examples reported on corresponding mercury complexes.[14]

Mercury(II) chalcogenides are important species as HgE solid-state materials (E = S, Se or Te) have demonstrated, amongst other phenomena, strong room-temperature infrared luminescence.[15] Such behaviour makes these semiconductor nanocrystals attractive candidates for integration into light-emitting devices.[16] However, to date, the majority of methods utilised for fabricating such materials have involved aqueous solution growth techniques[16,17] due to the non-volatile nature of the chalcogenide-releasing agents used. The general requirements for successful precursors are a low degree of association and adequate volatility, at least sufficient for low-pressure deposition and solution thermolysis techniques. In terms of the dichalcogenoimidodiphosphinato compounds, the volatility associated with these phopshine-based ligands can be drastically altered by the correct choice of alkyl functionality. For example introduction of isopropyl moieties [R = $CH(CH_3)_2$] into the core framework drastically increases volatility when compared to the aryl analogue HN($EPPh_2$)$_2$.[11]

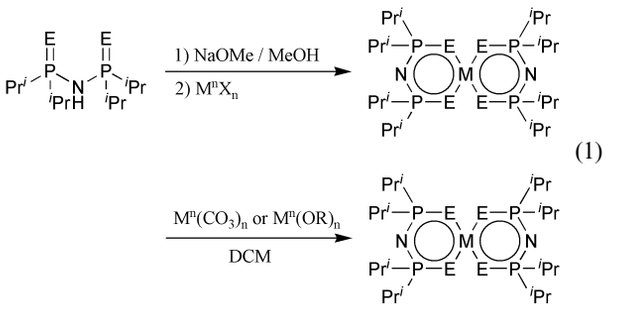
In this paper we report on the synthesis and structural characterisation of organomercury dichalcogenideimidodiphosphinato complexes. Formed by the reaction of NH(EP^iPr_2)$_2$ (**1**) [E = Se (**a**) and S (**b**)] with the appropriate alkyl/aryl mercuric chloride, under basic conditions, examples of methyl (**2**), ethyl (**3**), 2-thienyl (T) (**4**), 2-selenyl (SL) (**5**) and phenyl (**6**) mercury iminobis(diisopropylphosphinechalcogenide) coordination complexes [RHg{(EP^iPr_2)$_2$N}] are described along with their structural characterisation. Compared and contrasted with the symmetrical dichalcogenideimidodiphosphinato analogue, Hg[N(SeP^iPr_2)$_2$]$_2$, **7a**, these new compounds have been characterised by microanalysis, multi-element NMR, IR, positive-ion APCI mass spectrometry and thermogravimetric (TGA) analysis. Single-crystal X-ray diffraction crystallography has been carried on the symmetrical analogue **7a** and the symmetrisation product of **5a**, di(2-selenyl)mercury.

Such single-source precursors are of viable interest for the generation of mercuric chalcogenide materials as we have recently demonstrated the ability to generate CdSe thin films from a related [MeCd(SeP^iPr_2)$_2$N]$_2$ compound *via* LP-MOCVD.[18] This demonstration make the use of compounds **2**–**7**, a potentially interesting area of endeavour as, to our knowledge, mercury sulfide and selenides produced *via* thermolytic reactions have received scant attention.

DOI: 10.1039/b303200k

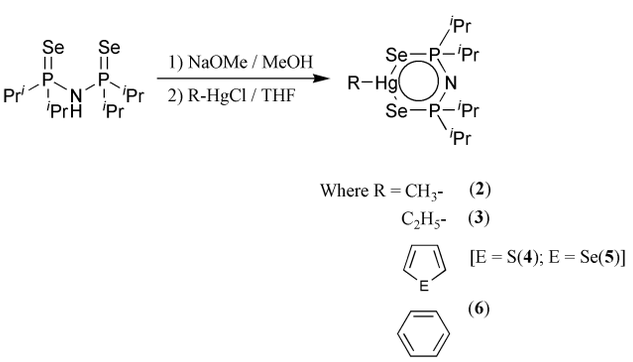
Results and discussion

Organomercury dichalcogenideimidodiphosphinato complexes are generally accessible *via* methods analogous to those for symmetrical dichalcogenideimidodiphosphinato species, $M^n[N(EPR_2)_2]_n$ [eqn. (1); E = S or Se].[11,19] The interaction of organomercury halides with the corresponding ligand under basic methanolic conditions ($NaOCH_3/CH_3OH$) has the advantage of yielding compounds free of ionic impurities under very mild conditions.[19] The dichalcogenoimidodiphosphinato ligands employed in this study are $NH(SeP^iPr_2)_2$ **1a** and $NH(SP^iPr_2)_2$ **1b**. The generation of **1a** or **1b**, in a one-pot synthesis from chlorodiisopropylphosphine, is relatively straightforward and has been documented elsewhere.[11,19]



(1)

We have studied the reactions of **1a** and **1b** and their salts with various organomercury halides.[20] Improved complex formation was observed by reaction of **1a** or **1b** with sodium methoxide in anhydrous methanol yielding the sodium salt $NaN(EP^iPr_2)_2$. As *in-situ* treatment of $NaN(EP^iPr_2)_2$, with the appropriate organomercury halide yields compounds **2**–**6** in good-to-excellent yields (Scheme 1). For example, the reaction of 2-thienylmercuric chloride with $NaN(SeP^iPr_2)_2$ directly produces $THg[(^iPr_2PSe)_2N]$ **4a** as a *white* powder in 82% yield. The analogous reaction of **1b** with 2-thienylmercury chloride gave **4b** as a *pale cream* powder in 54% yield. Compound **7a** is obtained in excellent yields under similar conditions using mercury(II) chloride. Attempts to obtain methyl- (**2b**) and ethyl- (**3b**) sulfide-precursors using the above method were generally unsuccessful.



Scheme 1 Synthesis of various mercury complexes.

Complexes **2**–**7** all show good solubility in common organic solvents and are air-stable in the solid state for prolonged periods. The volatility characteristics of the precursors were determined by thermogravimetric analysis (TGA), showing clean sublimation without any residues, which is desirable for use as precursors for MOCVD studies.

Solid-state decomposition

Mercury chalcogenides are widely used in LED technology, especially the selenides and tellurides.[4–6,16] We have investigated the behaviour of some of the new organo-mercury sulfide and selenide *single-source* precursors under thermolysis conditions at low pressure. Due to the extreme biotoxicity and potential for *trans*-alkylation, resulting in the formation of extremely toxic dimethylmercury and diethylmercury,[21,22] the simple alkyl derivatives **2** and **3** were not studied. Thermolytic reactions were studied on compounds **4**–**7** at two different temperatures, 300 and 350 °C *in vacuo*. The results are summarised in Table 1. Thermolysis of the selenide compounds **4a**, **5a**, **6a** and **7a** under the conditions given in the Table 1 results in the clean formation of mercury(II) selenide at the higher temperature. Evidently the P–E bonds rupture under these conditions in preference to Hg–E. This conjecture is supported by the powder X-Ray diffraction (PXRD) patterns obtained from the isolated inorganic residues. Comparison of the observed diffraction peaks with the standards [JCPDS powder diffraction data sets no. 15-1554 (HgSe) and 75-1538/1589 (HgS) from the 1-46 database] confirm that most of the deposited material is the corresponding mercury chalcogenide. For example the diffraction pattern (Fig. 1) obtained from the thermolysis products for **5a** at 350 °C clearly illustrate the cubic form of mercury(II) selenide (known as tiemannite). The Miller indices in the diffractograms were taken from the previously mentioned database. As illustrated in Fig. 1, the resulting HgSe material shows strong {111} texturing. All of the diselenideimidodiphosphinato complexes **4a**–**6a** were found to decompose cleanly at 350 °C yielding cubic HgSe. The PXRD patterns obtained from reactions conducted at 300 °C showed in some cases HgSe formation along with considerable unidentified inorganic/organic contaminates, as neither elemental selenium/sulfur or mercury were observed in the PXRD spectra. The symmetrical analogue **7a** showed similar behaviour to **4a**–**6a**, but required a higher temperature of 400 °C to afford clean decomposition and HgSe formation. This demonstrates the effect, that with correct choice of functionality within the precursor, the decomposition temperature and that required for HgE formation can be significantly lowered.

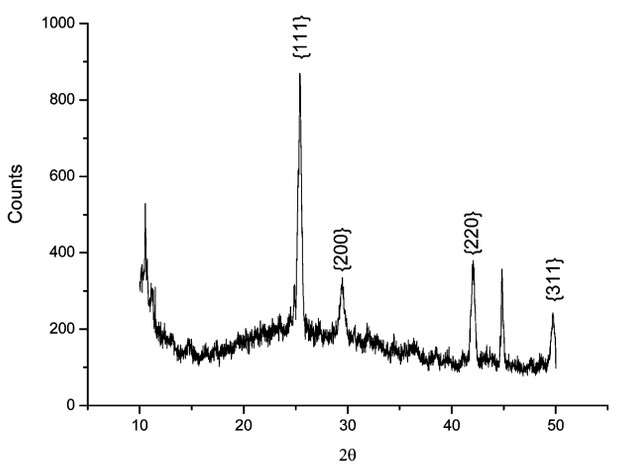


Fig. 1 PXRD of cubic mercury selenide obtained from thermolysis of compound **5a**.

The corresponding sulfur analogues showed similar behaviour with clean decomposition being observed only at the higher temperature of 350 °C. Again unidentifiable inorganic/organic species were observed in the PXRD patterns from the residues obtained at 300 °C. A typical example is illustrated in Fig. 2, with the PXRD pattern obtained from the decomposition products of **5b** at 350 °C. The resulting HgS material was found to be hexagonal (known as cinabar) in nature with {101} and {012} texturing.

Mass spectral analysis of the organic by-products, condensed in the cooler part of the Schlenk tube, using chemical ionisation revealed that thermolytic decomposition of the complexes is relatively clean (Table 1). At the lower temperature of 300 °C, the major products isolated were mono- and bis-dechalco-

Table 1 Thermal decomposition data of organomercuric dichalcogenideimidodiphosphinato complexes

	Compound	Reactor pressure/mm Hg	T/°C	Inorganic residue[a]	Main organic by-product[b]
	4a	0.61	300	HgSe + other	$^{i}Pr_2P(E)NP^{i}Pr_2$
	4a	0.58	350	HgSe	$(^{i}Pr_2P)_2NH$
	4b	0.52	300		$^{i}Pr_2P(E)NP^{i}Pr_2$
	4b	0.71	350	HgS	$(^{i}Pr_2P)_2NH$
	5a	0.48	300	HgSe + other	$(^{i}Pr_2P)_2NH$
	5a	0.44	350	HgSe	$^{i}Pr_2P{=}N$
	5b	0.52	300	HgS + other	$^{i}Pr_2P{=}N$
	5b	0.54	350	HgS	$^{i}Pr_2P{=}N$
	6a	0.63	300	HgSe + other	$^{i}Pr_2P{=}N$
	6a	0.54	350	HgSe	$^{i}Pr_2P{=}N$
	6b	0.53	300	HgS + other	$^{i}Pr_2P{=}N$
	6b	0.68	350	HgS	$^{i}Pr_2P{=}N$
	7a	0.48	300	HgSe + other	$^{i}Pr_2P(E)NP^{i}Pr_2$
	7a	0.52	400	HgSe	$^{i}Pr_2P{=}N$

[a] As determined by powder X-Ray diffraction. [b] By mass spectrometry (CI).

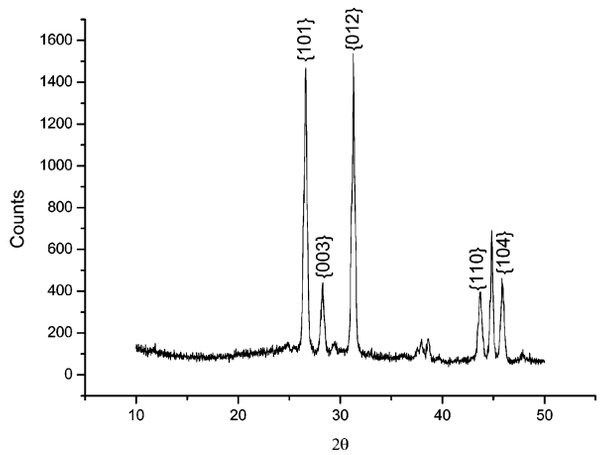


Fig. 2 PXRD of hexagonal mercury sulfide obtained from thermolysis of compound **4b**.

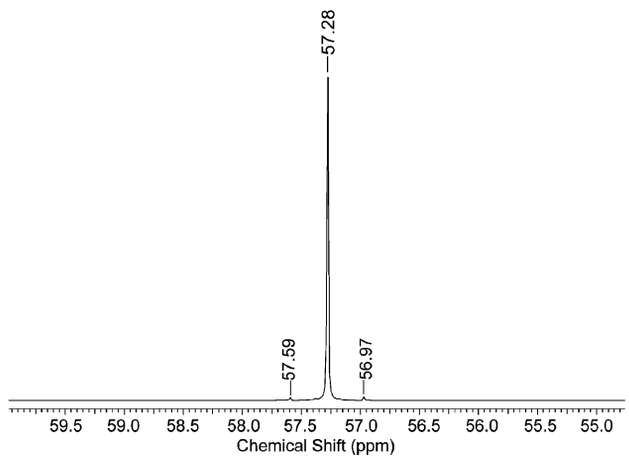


Fig. 3 ^{31}P NMR Spectrum of compound **5a**.

genated species, $^{i}Pr_2P(E)NP^{i}Pr_2$ and $(^{i}Pr_2P)_2NH$. Thus further demonstrating cleavage of the P–E bonds and HgE formation. At the higher reaction temperature of 350 °C the major product isolated for almost all of the analogues is the amino-phosphonium fragment, $[(^{i}Pr_2P{=}N) + H]^{+}$, thus further illustrating degradation of the imidodiphosphinato framework and the clean decomposition of the precursor.

NMR Spectroscopy studies

Among the several elements that have at least one nuclide suitable for NMR studies, mercury has two magnetically active isotopes, ^{201}Hg and ^{199}Hg. The latter has nuclear spin $I = ½$ and its natural abundance (16.84%) and receptivity (5.42 with respect to ^{13}C) make its detection easy by NMR. Also, relaxation rates are very high, so that a large number of transients can be acquired in a very short time. Chemical shifts are spread over a very large range and, as a consequence, are very sensitive to the electronic environment and geometry at the mercury centre.[23] We have investigated the NMR properties of compounds **2**–**7** using ^{199}Hg NMR spectroscopy. To complement these studies ^{1}H and ^{31}P NMR studies were also conducted. ^{1}H, ^{31}P and ^{199}Hg NMR studies were not conducted on the phenyl analogues **6a** and **6b** due to their insolubility in almost all deuterated solvents.

The proton decoupled phosphorus-31 NMR spectra of compounds, **2a**–**5a** and **7a**, at room temperature, all consist of a triplet with selenium-77 satellites ($J(^{31}P–^{77}Se)$ = 461–566 Hz). A representative example is illustrated in Fig. 3, with the ^{31}P spectrum for **5a** The phosphorus–selenium coupling constants (J(P–Se)) are less than that in the free ligand ($J(^{31}P–^{77}Se)$ for **1a** = 757 Hz).[11] The phosphorus resonance (57.28 ppm) is also well shifted from that observed in the free ligand (89.5 ppm).[11] This has been shown[24] in other systems to be indicative of selenium coordination. The corresponding sulfur analogues, **4a**, **5a**, showed no such behaviour, with single ^{31}P peaks being observed in both cases, due to the distinct absence of coupling between phosphorus and the non-NMR active sulfur nuclei. (Note: ^{33}S is NMR active with a nuclear spin (I) of 3/2. However it has a very low receptivity of 0.0972 with respect to ^{13}C.)

As expected, the ^{199}Hg chemical shifts are sensitive to the electronic effects of the substituents around the metal centre. The aryl substituted analogues **4**–**5** show increased nuclear shielding compared to the simple alkyl analogues **2**–**3**. Analogues prepared from **1a** also show increased shielding and thus larger chemical shifts, resulting from the more effective overlap of the selenium–mercury orbitals, when compared to the corresponding sulfur species prepared from **1b**. For example Fig. 4 shows the ^{199}Hg NMR spectrum of $C_4H_3Se–Hg[(^{i}Pr_2PSe)_2N]$

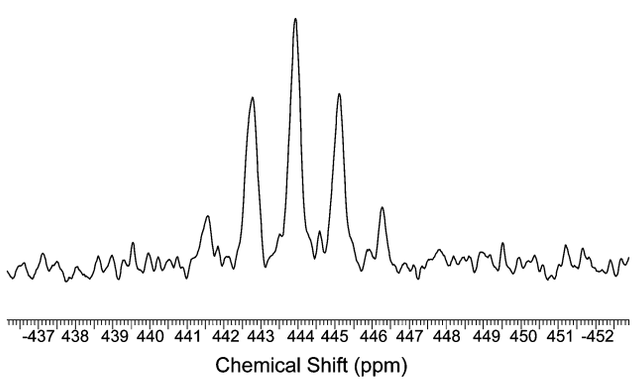


Fig. 4 ^{199}Hg NMR Spectrum of compound **5a**.

5a. The ^{199}Hg spectrum of **5a** in d_8-THF is a multiplet with phosphorus-31 and selenium-77 satelittes (J(Se–Hg) = 737 Hz and J(P–Hg) = 179 Hz), which compare well with the J(Se–Hg) and J(P–Hg) values of 642–737 and 127–179 Hz, observed for the other mercury selenide precursors and reported examples.[23]

Solid-state structure

The monomeric nature of the dichalcogenideimidodiphosphinato materials in the solid state has been confirmed by single-crystal X-ray analyses. X-Ray crystallographic studies carried out on the symmetrical **7a** analogue revealed each metal centre to be tetrahedrally coordinated by two ligands through the selenium atoms of the diselenoimidodiphosphinate moiety. The structure of **7a**, illustrated in Fig. 5, is isostructural with the analogous cadmium(II) complex,[11] revealing a distorted mercury centre with Se–Hg–Se angles ranging from 106.830 to 113.202°. Shortening of the P–N bonds to ~1.58–1.59 Å and the subsequently extended P–Se bonds (2.18–2.19 Å) clearly illustrate delocalisation within the diselenoimidodiphosphinate architecture.[11]

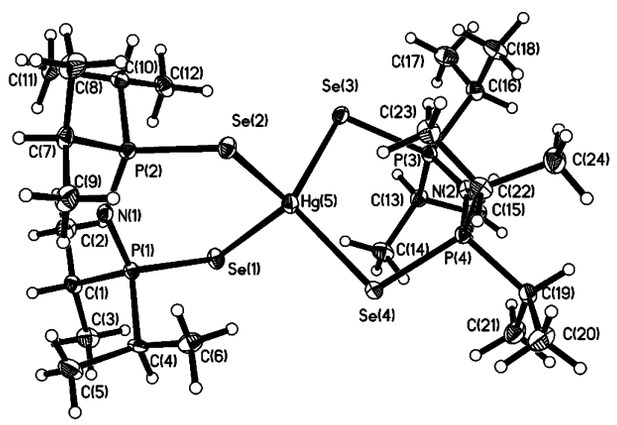


Fig. 5 X-Ray crystal structure of Hg[(^{i}Pr$_2$PSe)$_2$N]$_2$, **7a**.

The organomercuric dichalcogenideimidodiphosphinate compounds **2**–**6**, on the other hand, were found to be unstable in solution and over time undergo rearrangement reactions yielding dialkyl/aryl mercury compounds. Such behaviour is common in organomercuric sulfides and selenides[22] and is demonstrated again here in the attempted slow growth of crystals of **2**–**6** from dichloromethane–hexane solution. Thus prolonged periods in solution at room temperature resulted in the rearrangement of the organomercuric dichalcogenide-imidodiphosphinato complexes to the corresponding dialkyl/aryl mercury compound. For example the attempted growth of crystals of **5a** from dichloromethane–hexane results in the isolation of crystals of the hitherto unknown di(2-selenyl)-mercury compound, $(C_4H_3Se)_2Hg$ (Fig. 6). This rearranged product crystallises in the *C*2/*c* space group with the Hg atom on a centre of symmetry, consequently the C–Hg–C bond angle is exactly 180° and the selenium atoms in the *anti* conformation. The Hg–C bond lengths (2.051 Å) are typically similar to those reported by Grdenic *et al*.[25] for the related $(C_4H_3S)_2Hg$. The

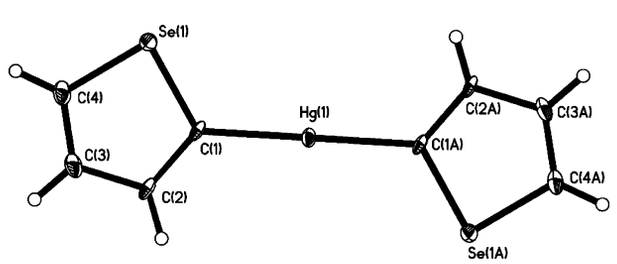


Fig. 6 X-Ray Structure of SL–Hg–SL.

shortening of the carbon-to-metal bond is attributed to the electron donating character of the selenyl ring.[26] This analogy is also seen in the C–C bonds in the selenyl ring where the C(1)–C(2) (1.412 *cf*. 1.370 Å) bond is longer and the C(2)–C(3) (1.416 *cf*. 1.423 Å) bond shorter than the corresponding bond in the selenophene molecule.[26]

Experimental

Unless, otherwise stated all reactions were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques. All glassware was flame dried under vacuum prior to use. All solvents and reagents were purchased from Sigma–Aldrich chemical company and used as received. ^{i}Pr$_2$P(Se)-NHP(Se)^{i}Pr$_2$ **1a** and ^{i}Pr$_2$P(S)NHP(S)^{i}Pr$_2$ **1b** were synthesised from 1,1,1,3,3,3-hexamethyldisilazane according to literature methods.[19] 2-Thienyl- and 2-selenyl-mercury chloride were prepared *via* standard literature methods.[22] ^{1}H and ^{31}P NMR studies were carried out using a Bruker AC300 FTNMR instrument operating at room temperature (300 MHz for ^{1}H, 162 MHz for ^{31}P). ^{199}Hg NMR studies were carried out using a Bruker AC500 FTNMR instrument operating at room temperature (71.63 MHz for ^{199}Hg). All ^{199}Hg-NMR chemical shifts are given in ppm and referenced to mercury perchlorate [1 M $Hg(ClO_4)_2$ in 1 M $DClO_4$; δ(^{199}Hg) −2250 ppm] standard.[23] Mass spectra were recorded on a Kratos concept 1S instrument. Infrared spectra were recorded on a Specac single reflectance ATR instrument (4000–400 cm^{-1}, resolution 4 cm^{-1}). X-Ray powder diffraction patterns were determined on a Phillips 3710 powder diffractometer using nickel-filtered monochromated Cu-Kα radiation (λ = 1.5418 Å) and were indexed using the JCPDS programs.[27] Elemental analysis was performed by the University of Manchester micro-analytical laboratory. Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. Compounds **2**–**6** were all prepared in an analogous manner. A generic method is illustrated below for the synthesis of CH$_3$–Hg[(^{i}Pr$_2$PSe)$_2$N] **2a**. Compound **7a** was prepared in a similar fashion using mercury(II) chloride.

CH$_3$–Hg[(^{i}Pr$_2$PSe)$_2$N] (2a)

Sodium methoxide (0.42 g, 7.36 mmol) was added to a stirred solution of **1a** (3.00 g, 7.36 mmol) in anhydrous methanol (100 cm^3). The resulting pink solution was stirred at room temperature for 10 min. The solution was then added dropwise over a period of 45 min to a stirred solution of methylmercury chloride (1.84 g, 7.36 mmol) in anhydrous tetrahydrofuran (10 cm^3). After complete addition the reaction was stirred at room temperature for 2 h. The resulting white suspension was filtered and the recovered solid washed with methanol (100 cm^3) before drying under vacuum. Recrystallisation from tetrahydrofuran–methanol yielded 3.58 g (79%) of rose pink powder (mp 81–84 °C); FT-IR (KBr)/cm^{-1}: 2959, 2858 (C–H str.) 1263, 1224, 751 (ν(P–N–P)), 541 (Hg–C str.) 422 (P–Se str.); ^{1}H NMR ($CDCl_3$): δ 0.85 (s, 3H, CH_3–Hg), 1.27 (m, 24H, CH_3R), 2.14 (m, 4H, CHR); ^{31}P{^{1}H} NMR ($CDCl_3$): δ 55.670 [m, 2SeP, ^1J(^{31}P–^{77}Se) 461 Hz]; ^{199}Hg{^{1}H} NMR ($CDCl_3$): δ −246 [m, HgSe, ^1J(^{199}Hg–^{77}Se) 686 Hz, ^2J(^{199}Hg–^{31}P) 135 Hz]; MS (APCI): m/z = 1643 (26%, 2M + 2Hg), 624 (21%, M + H), 408 (100%, M − MeHg) (Found: C 25.30, H 5.39, N 2.42, P 10.56. $C_{13}H_{31}N_1P_2Se_2Hg$ requires C 25.11, H 5.02, N 2.25, P 9.96%).

C$_2$H$_5$–Hg[(^{i}Pr$_2$PSe)$_2$N] (3a)

Yield = 42% (mp 169–172 °C); FT-IR (KBr)/cm^{-1}: 2961, 2956 (C–H str.) 1229, 1222, 750 (ν(P–N–P)), 530 (Hg–C str.), 427 (ν(P–Se)); ^{1}H NMR ($CDCl_3$): δ 1.21–1.28 (m, 29H, 8CH_3R, CH_3CH$_2$–Hg and CH_3CH_2–Hg), 2.17 (m, 4H, CHR); ^{31}P{^{1}H} NMR ($CDCl_3$): δ 55.930 [m, 2SeP, ^1J(^{31}P–^{77}Se) 468 Hz]; ^{199}Hg–{^{1}H} NMR ($CDCl_3$): δ −317 [m, HgSe, ^1J(^{199}Hg–^{77}Se) 642 Hz, ^2J(^{199}Hg–^{31}P) 138 Hz]; MS (APCI): m/z = 637 (46%, M + H),

408 (100%, M − HgEt) (Found: C 26.30, H 5.37, N 2.69, P 9.94. $C_{14}H_{33}N_1P_2Se_2Hg$ requires C 26.44, H 5.23, N 2.20, P 9.74%).

C_4H_3S–Hg[(^{i}Pr$_2$PSe)$_2$N] (4a)

Yield = 82% (mp 146–149 °C); FT-IR (KBr)/cm^{-1}: 2957 (C–H str.) 1222, 753 (ν(P–N–P)), 538 (Hg–C str.) 429 (P–Se str.); ^{1}H NMR (CD_2Cl_2): δ 1.25 (m, 24H, CH_3R), 2.18 (m, 4H, C*H*R), 7.30 (d, 1H, T-H), 7.55 (m, 1H, T-H), 7.81 (d, 1H, T-H); ^{31}P{^{1}H} NMR ($CDCl_3$): δ 56.816 [m, 2SeP, ^1J(^{31}P–^{77}Se) 534 Hz]; ^{199}Hg{^{1}H} NMR ($CDCl_3$): δ −587 [m, HgSe, ^1J(^{199}Hg–^{77}Se) 672 Hz, ^2J(^{199}Hg–^{31}P) 152 Hz]; MS (APCI): *m*/*z* = 692 (41%, M + H), 409 (100%, M − HgT) (Found: C 28.02, H 4.37, N 2.09, P 9.37, S 3.87. $C_{16}H_{31}N_1P_2Se_2SHg$ requires C 27.85, H 4.53, N 2.03, P 8.98, S 4.65%).

C_4H_3S–Hg[(^{i}Pr$_2$PS)$_2$N] (4b)

Yield = 54% (mp 136–139 °C); FT-IR (KBr)/cm^{-1}: 2959 (C–H str.) 1259, 1223, 759 (ν(P–N–P)), 673, 634 (N–P–S str.) 538 (ν(P–S) and Hg–C str.); ^{1}H NMR (CD_2Cl_2): δ 1.25 (m, 24H, CH_3R), 2.15 (m, 4H, C*H*R), 7.27 (d, 1H, T-H), 7.50 (m, 1H, T-H), 7.80 (d, 1H, T-H); ^{31}P{^{1}H} NMR ($CDCl_3$): δ 63.085 [s, 2SP]; ^{199}Hg{^{1}H} NMR ($CDCl_3$): δ −464 [t, HgS, ^2J(^{199}Hg–^{31}P) 144 Hz]; MS (APCI) *m*/*z* = 599 (15%, M + H) 408 (100%, M − HgT) (Found: C 32.45, H 5.50, N 2.42, P 10.55, S 15.86. $C_{16}H_{31}N_1P_2S_3Hg$ requires C 32.24, H 5.24, N 2.35, P 10.39, S 16.13%).

C_4H_3Se–Hg[(^{i}Pr$_2$PSe)$_2$N] (5a)

Yield = 61% (mp 158–161 °C); FT-IR (KBr)/cm^{-1}: 2954 (C–H str.) 1217, 753 (ν(P–N–P)), 538 (Hg–C str.) 554, 429 (P–Se str.); ^{1}H NMR (d$_8$-THF): δ 1.23 (m, 24H, CH_3R), 2.18 (m, 4H, C*H*R), 7.50 (d, 1H, SL-H), 7.65 (m, 1H, SL-H), 8.41 (d, 1H, SL-H);^{31}P{^{1}H} NMR (d$_8$-THF): δ 57.276 [m, 2SeP, ^1J(^{31}P–^{77}Se) 566 Hz]; ^{199}Hg{^{1}H} NMR (d$_8$-THF): δ −443 [m, HgSe, ^1J(^{199}Hg–^{77}Se) 737 Hz, ^2J(^{199}Hg–^{31}P) 179 Hz]; MS (APCI): *m*/*z* = 1337 (100%, 2M − SL), 809 (60%, M + THF), 741 (30%, M + H) (Found: C 26.14, H 3.97, N 1.80, P 7.93. $C_{16}H_{31}NP_2Se_3Hg$ requires C 26.08, H 4.08, N 1.90, P 8.40%).

C_4H_3Se–Hg[(^{i}Pr$_2$PS)$_2$N] (5b)

Yield = 76% (mp 150–153 °C); FT-IR (KBr)/cm^{-1}: 2967, 2960 (C–H str.) 1222, 1217, 761 (ν(P–N–P)), 540 (Hg–C str.) 638 (P–S str.); ^{1}H NMR [(CD$_3$)$_2$CO]: δ 1.25 (m, 24H, CH_3R), 2.18 (m, 4H, C*H*R), 7.58 (d, 1H, SL-H), 7.65 (t, 1H, SL-H), 8.50 (d, 1H, SL-H); ^{31}P{^{1}H} NMR ($CDCl_3$): δ 63.459 [s, 2SP]; ^{199}Hg{^{1}H} NMR (d$_8$-THF): δ −355 [t, HgS, ^2J(^{199}Hg–^{31}P) 165 Hz]; MS (APCI): *m*/*z* = 824 (100%, M + 2THF + MeCN), 643 (25%, M + H) (Found: C 29.96, H 4.78, N 2.11, P 9.44, S 9.90. $C_{16}H_{31}NP_2SeS_2Hg$ requires C 29.88, H 4.86, N 2.18, P 9.90, S 9.97%).

C_6H_5–Hg[(^{i}Pr$_2$PSe)$_2$N] (6a)

Yield = 47% (mp 130–132 °C); FT-IR (KBr)/cm^{-1}: 2957 (C–H str.) 1251, 1222, 752 (ν(P–N–P)), 538 (Hg–C str.) 429 (P–Se str.); MS (APCI): *m*/*z* = 829 (76%, M + THF), 685 (20%, M + H) (Found: C 31.27, H 4.99, N 2.37, P 9.05. $C_{18}H_{33}NP_2Se_2Hg$ requires C 31.61, H 4.86, N 2.05, P 9.06%).

C_6H_5–Hg[(^{i}Pr$_2$PS)$_2$N] (6b)

Yield = 52% (mp 142–144 °C); FT-IR (KBr)/cm^{-1}: 2959, 2926, 2867 (C–H str.) 1259, 1224, 761 (ν(P–N–P)), 673, 634 (N–P–S str.), 540 (ν(P–S) and Hg–C str.); MS (APCI): *m*/*z* = 663 (90%, M + THF), 591(35%, M + H) (Found: C 36.26, H 5.57, N 2.31, P 10.00, S 10.27. $C_{18}H_{33}NP_2S_2Hg$ requires C 36.64, H 5.64, N 2.37, P 10.49, S 10.86%).

Hg[(^{i}Pr$_2$PSe)$_2$N]$_2$ (7a)

Yield = 86% (mp 181–184 °C); FT-IR (KBr)/cm^{-1}: 2967 (C–H str.) 1259, 1222, 762 (ν(P–N–P)), 427 (P–Se str.); ^{1}H NMR ($CDCl_3$): δ 1.25 (m, 48H, CH_3R), 2.18 (m, 8H, C*H*R); ^{31}P{^{1}H} NMR ($CDCl_3$): δ 56.80 [m, 4SeP, ^1J(^{31}P–^{77}Se) 518 Hz]; ^{199}Hg{^{1}H} NMR ($CDCl_3$): δ −859 [m, 2HgSe, ^1J(^{199}Hg–^{77}Se) 855 Hz, ^2J(^{199}Hg–^{31}P) 127 Hz]; MS (APCI): *m*/*z* = 1015 (85%, M + H) 608 (100% M − L) (Found: C 28.47, H 5.52, N 2.72, P 12.29. $C_{24}H_{56}N_2P_4Se_4Hg$ requires C 28.45, H 5.57, N 2.76, P 12.23%).

Bulk decomposition studies

Typically, about 100 mg of the compound were placed in the bottom of a Schlenk tube connected to a high vacuum line. The tube was then evacuated to ~0.5 mm Hg before its tap was closed. The bottom two-thirds of the Schlenk tube were then inserted into a tube furnace. The decomposition temperatures are given in Table 1. The organic by-products condensed in the cooler part of the Schlenk tube and were analysed by mass spectrometry using chemical ionisation (NH_3 carrier gas) and the remaining inorganic matter by powder X-ray diffraction (PXRD). PXRD samples were prepared by slow evaporation from dichloromethane solution onto clean glass substrates.

X-Ray crystallography

Crystals suitable for X-ray diffraction studies were obtained by slow diffusion of hexane into dichloromethane solutions of the appropriate compound. Single-crystal structure determination of **7a** and one of the rearrangement products of **5a**, $(C_4H_3Se)_2Hg$, was carried out from data collected using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) on an Bruker APEX diffractometer. The structures were solved by Direct Methods[28] and refined by full-matrix least squares on F^2.[29] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters and allowed to ride on their parent carbon atoms.

Crystal data. $C_{24}H_{56}N_2P_4Se_4Hg$ **7a**, M = 1013.02, triclinic, space group $P\bar{1}$, a = 9.3488(11), b = 12.9314 (15), c = 16.2877 (19) Å, α = 79.110(2), β = 77.862(2), γ = 70.473(2)°, V = 1799.2(4) Å^3, T = 100(2) K, Z = 2 μ(Mo-Kα) = 8.518 mm^{-1}, 7239 reflections measured, 6281 unique (R_{int} = 0.0222) which were used in all calculations. The final $wR(F^2)$ was 0.0578 (all data) and final $R(F)$ was 0.0265 (observed data, $I > 2\sigma(I)$).

Di(2-selenyl)mercury: C_4H_3SeHg, M = 230.31, monoclinic, space group $C2/c$, a = 21.847(6), b = 5.3593(14), c = 7.761(2) Å, β = 104.845(4), V = 878.3(4) Å^3, T = 100(2) K, Z = 8 μ(Mo-Kα) = 25.738 mm^{-1}, 3049 reflections measured, 888 unique (R_{int} = 0.0477) which were used in all calculations. The final $wR(F^2)$ was 0.0966 (all data) and final $R(F)$ was 0.0377 (observed data, $I > 2\sigma(I)$).

CCDC reference numbers 206589 and 206590.

See http://www.rsc.org/suppdata/dt/b3/b303200k/ for crystallographic data in CIF or other electronic format.

Conclusion

This paper describes the synthesis and characterisation of organo-mercury imino-bis(diisopropylphosphine chalcogenide) complexes. The symmetrical complex **7a** has been shown to be monomeric in the solid state by single crystal X-ray diffraction possessing a distorted tetrahedral configurations with extended P–Se bonds. The air stable complexes **2**–**6** demonstrate unstable behaviour in solution rearranging to dialkyl/diaryl mercury species. Thermolytic decomposition of the aryl-susbtituted precursors has been carried in the solid state using simple pyrolysis studies, affording HgE, thus illustrating that such dichalco-

genoimidodiphosphinato compounds are excellent candidates as molecular single-source precursors for the preparation of mercury chalcogenide solid-state materials

Acknowledgements

We would like to thank Mr J. Friend for experimental assistance. This work was supported by the Engineering and Physical Sciences Research Council.

References

1 P. O'Brien, in *Inorganic Materials*, ed. D. W. Bruce and D. O'Hare, Wiley, Chichester, 1992, p. 491.
2 A. N. Gleizes, *Chem. Vap. Deposition*, 2000, **6**, 155 and references therein.
3 (*a*) N. L. Pickett, S. Lawson, W. Gregor-Thomas, F. G. Riddell, D. F. Foster, D. J. Cole-Hamilton and J. R. Fryer, *J. Mater. Chem.*, 1998, **8**, 2769; (*b*) N. L. Pickett, F. G. Riddell, D. F. Foster, D. J. Cole-Hamilton and J. R. Fryer, *J. Mater. Chem.*, 1997, **7**, 1885.
4 S. K. Dhawan and D. C. Trivedi, *J. Appl. Electrochem.*, 1992, **22**, 563.
5 G. Gustaffson, Y. Cao, G. M. Treacy, F. Clavetter, M. Colaneri and A. J. Heeger, *Nature*, 1992, **357**, 477.
6 (*a*) A. Rogalski, *Opt. Eng.*, 1994, **33**, 1395; (*b*) R. Balcerak, J. F. Gibson, W. Guiterrez and J. H. Pollard, *Opt. Eng.*, 1987, **26**, 191.
7 M. Bochmann, K. Webb, M. Harman and M. B. Hursthouse, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 638.
8 H. S. Park, M. Mokhatari and H. W. Roesky, *Chem. Vap. Deposition*, 1996, **2**, 135.
9 (*a*) M. Afzaal, S. M. Ascott, D. Crouch, P. O'Brien, J. D. Woollins and J.-H. Park, *Chem. Vap. Deposition*, 2002, **8**, 187; (*b*) M. Green and P. O'Brien, *Chem. Commun.*, 1999, 2235; (*c*) N. L. Pickett and P. O'Brien, *Chem. Rec.*, 2001, **1**, 467.
10 (*a*) N. Revaprasadu, M. A. Malik, P. O'Brien, M. M. Zulu and M. Wakefield, *J. Mater. Chem.*, 1998, **8**, 1885; (*b*) B. Ludolph, M. A. Malik, P. O'Brien and N. Revaprasadu, *Chem. Commun.*, 1998, 1849.
11 (*a*) J. D. Woollins, *J. Chem. Soc. Dalton Trans.*, 1996, 2893 and references therein; (*b*) D. Cupertino, D. J. Birdsall, A. M. Z. Slawin and J. D. Woollins, *Inorg. Chim. Acta*, 1999, **290**, 1 and references therein; (*c*) P. Bhattacharyya, A. M. Z. Slawin and M. B. Smith, *J. Chem. Soc., Dalton Trans.*, 1998, 2467.
12 D. J. Crouch, P. O'Brien, M. A. Malik, P. J. Skabara and S. Wright, *Chem. Commun.*, 2003, 1994.
13 R. C. Mehrotra, R. Bohra and D. P. Gaur, *Metal β-Diketonates and Allied Derivatives*, Academic Press, London, 1978.
14 (*a*) Y. Cheng, T. J. Emge and J. G. Bernnan, *Inorg. Chem.*, 1994, **33**, 3711; (*b*) V. Garcia-Montalvo, J. Novosad, P. Kilian, J. D. Woollins, A. M. Z. Slawin, P. G. Y. Garcia, M. Lopez-Cardoso, G. Espinosa-Perez and R. Cea-Olivares, *J. Chem. Soc., Dalton Trans.*, 1997, 1025; (*c*) A. L. Seligson, P. J. Bonasia, J. Arnold, K.-M. Yu, J. M. Walker and E. D. Bourret, *Mater. Res. Soc. Symp. Proc.*, 1993, **282**, 665.
15 A. L. Rogach, D. S. Koktysh, M. Harrsion and N. A. Kotov, *Chem. Mater.*, 2000, **12**, 1526.
16 (*a*) Z. Yu, J. Ren, J. W. Cook and J. F. Schedzina, *Physica B (Amsterdam)*, 1993, **119**, 119; (*b*) M. Green, G. Wakefield and P. J. Dobson, *J. Mater. Chem.*, 2003, **13**, 1076.
17 (*a*) A. L. Rogach, S. V. Kershaw, M. Burt, M. Harrison, A. Kornowski, A. Eychmüller and H. Weller, *Adv. Mater.*, 1999, **11**, 552; (*b*) M. T. Harrison, S. V. Kershaw, M. G. Burt, A. L. Rogach, A. Eychmüller and H. Weller, *J. Mater. Chem.*, 1999, **9**, 2721; (*c*) P. Pramanic and S. Bhattacharya, *Mater. Res. Bull.*, 1989, **24**, 945.
18 M. Afzaal, D. Crouch, M. A. Malik, M. Motevalli and P. O'Brien and J-H. Park, *J. Mater. Chem.*, 2003, **13**, 1.
19 For example see. (*a*) Q.-F. Zhang, K.-K. Lau, J. L. C. Chim, T. K. T. Wong, W.-T. Wong, I. D. Williams and W.-H. Leung, *J. Chem. Soc., Dalton Trans.*, 2000, 3027; (*b*) D. C. Cupertino, R. W. Keyte, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *Inorg. Chem.*, 1996, **35**, 2695; (*c*) L. M. Gilby and B. Piggott, *Polyhedron*, 1999, **18**, 1077; (*d*) P. Bhattacharyya and J. D. Woollins, *Polyhedron*, 1995, **14**, 3367.
20 D. J. Crouch and P. O'Brien, unpublished work.
21 T. W. Clarkson, *Annu. Rev. Pharm.*, 1972, **12**, 375 and references therein.
22 (*a*) F. C. Whitmore, *Organic Compounds of Mercury*, The Chemical Catalog Company, Inc, New York, 1921; (*b*) W. Steinkopf and M. Bauermeister, *Ann. Chem.*, 1914, **403**, 59; (*c*) N. A. Bell and R. M. King, *J. Organomet. Chem.*, 1979, **179**, 133; note: 2-selenylmercury chloride was prepared in a 72% yield (mp 197–200 °C) in an analogous manner to 2-thienylmercury chloride.
23 (*a*) B. Wrackmeyer and R. Contreras, *Annu. Rep. NMR Spectrosc.*, 1992, **24**, 267; (*b*) P. L. Goggin, R. J. Goodfellow and N. W. Hurst, *J. Chem. Soc., Dalton Trans.*, 1978, 561.
24 (*a*) R. Colton and P. Panagiotidou, *Aust. J. Chem.*, 1987, **40**, 13; (*b*) A. M. Bond, R. Colton and J. Ebner, *Inorg. Chem.*, 1988, **27**, 1697.
25 D. Grdenic, B. Kamenar and V. Zezelj, *Acta Crystallogr., Sect B.*, 1979, **35**, 1889.
26 R. D. Brown, F. R. Burden and P. D. Godfrey, *J. Mol. Spectrosc.*, 1968, **25**, 415.
27 JCPDS, International Centre for Diffraction Data, 2000.
28 G. M. Sheldrick, SHELXS-97, program for crystal structure determination, University of Göttingen, Germany, 1990.
29 G. M. Sheldrick, SHELXL-97, program for crystal structure refinement, University of Göttingen, Germany, 1997.