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Isolation and characterization of Se-organolead selenocarboxylates

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Abstract

Se-organolead selenocarboxylates were characterized after they were obtained from the reactions of alkali metal or piperidinium selenocarboxylates with organolead chlorides in moderate to good yields. The reactions of triphenyllead selenocarboxylates with benzeneselenenyl bromide afforded acyl phenyl diselenides.

In contrast with thio- and dithiocarboxylic acid derivatives [1–7], up to now little was known about the chemistry of selenocarboxylic acid ones [8,9]. Previously, we

Table 1

Yields of triphenyllead selenocarboxylates (**4**) and diphenyllead bis(selenocarboxylate)s (**5**)

No.	$(RCOSe)_xPbPh_{4-x}$		Yield [a] (%)	m.p. [b] (°C)
	R	x		
4a	CH_3	1	39	94– 96
4b	t-C_4H_9	1	59	124–127
4c	C_6H_5	1	99	95– 97
4d	4-$CH_3C_6H_4$	1	89 87 [c] 84 [d]	108–110
4e	4-$CH_3OC_6H_4$	1	96	99–100
4f	4-ClC_6H_4	1	97	86– 88
5a	CH_3	2	45	85– 88
5b	t-C_4H_9	2	59	57– 59
5c	C_6H_5	2	95 [c]	123–125
5d	4-$CH_3C_6H_4$	2	97 [c]	144–146
5e	4-$CH_3OC_6H_4$	2	78 [c]	116–118
5f	4-ClC_6H_4	2	84 [c]	123–125

[a] Yield of isolated product. Unless cited, the relevant sodium selenocarboxylates were used. [c] Decomposition. [c] Using the relevant potassium selenocarboxylates. [d] Using piperidinium 4-methylbenzenecarboselenoate.

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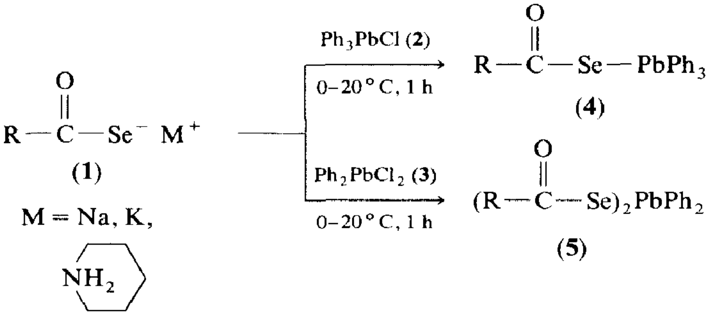
reported that potassium selenocarboxylates react with trimethylsilyl chloride to produce *O*-trimethylsilyl selenocarboxylates [RC(Se)OSiMe$_3$], whereas the reaction with trimethylgermyl and trimethylstannyl chlorides gave exclusively the corresponding Se-trimethylgermyl [RC(O)SeGeMe$_3$] and Se-trimethylstannyl selenocarboxylates [RC(O)SeSnMe$_3$] [10]. Owing to their instability and difficulty in purification no organolead selenocarboxylates have been described in the literature. We recently established a convenient preparation of sodium and potassium selenocarboxylates [11,12]. Here we report the first, characterized Se-organolead selenocarboxylates (**4**, **5**) obtained from the reaction of alkali-metal or piperidinium selenocarboxylates (**1**) with organolead halides (eq. 1).



(1)

No.	R
4a, **5a**	CH_3
4b, **5b**	t-C_4H_9
4c, **5c**	C_6H_5
4d, **5d**	4-$CH_3C_6H_4$
4e, **5e**	4-$CH_3OC_6H_4$
4f, **5f**	4-ClC_6H_4

When an ether solution of triphenyllead chloride was added to a suspension of an equivalent of sodium 4-methylbenzenecarboselenoate in the same solvent at 20 °C, the pale-yellow color of the mixture quickly disappeared. The insoluble NaCl was filtered off, and the usual work-up of the filtrate gave Se-triphenyllead 4-methylbenzenecarboselenoate (**4d**) as slightly yellow needles in 89% yield. Under similar conditions, the stoichiometric reaction of other sodium, potassium, or piperidinium selenocarboxylates (**1**) with triphenyllead chloride or diphenyllead dichloride gave the corresponding Se-triphenyllead selenocarboxylates (**4a**–**4c**, **4e**–**4f**) and Se-diphenyllead bis(selenocarboxylate)s (**5a**–**5f**) in 39–99% yields. The structures of **4** and **5** were established from the IR, mass and ^1H and ^{13}C NMR spectra and the microanalyses (Table 1).

The organolead selenocarboxylates (**4** and **5**) obtained are fairly stable to heat, but not towards oxygen. In general, the aliphatic esters (**4**, **5**, R = alkyl) are less stable than the aromatic ones. For example, triphenyllead selenoacetate (**4a**) decomposes quickly in air at 20 °C to give the corresponding carboxylic acid with liberation of red selenium.

In general, organotin [13] and -lead carboxylates [14], which in the solid state exhibit the bands around 1500–1520 cm^{-1} due to the carbonyl stretching frequencies, occur as co-ordination polymers with planar organotin and -lead groups, and

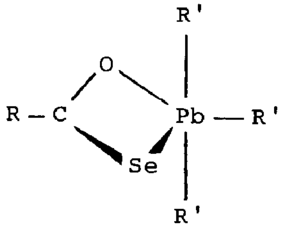
Table 2

Carbonyl stretching frequencies of Se–organolead (**4** and **5**) and Se–organotin selenocarboxylates [16]

No.	$(RCOSe)_xEPh_{4-x}$		ν(C=O) (cm^{-1})	
	R	x	E = Pb	E = Sn
4c	C_6H_5	1	1642	1642
4d	$4\text{-}CH_3C_6H_4$	1	1640	1638
4e	$4\text{-}CH_3OC_6H_4$	1	1630	1640
4f	$4\text{-}ClC_6H_4$	1	1650	1640
5c	C_6H_5	2	1620	1630
5d	$4\text{-}CH_3C_6H_4$	2	1625	1630
5e	$4\text{-}CH_3OC_6H_4$	2	1615	1625
5f	$4\text{-}ClC_6H_4$	2	1635	1642

having bridging carboxylate groups. For the common thio- and selenocarboxylic acid esters which exist in monomeric form, the ν(C=O) bands appear in the region 1650–1700 cm^{-1} [8]. As shown in Table 2, the carbonyl stretching frequencies of **4** and **5** are observed in the region 1620–1650 cm^{-1} which are close to those of the thio- and seleno-esters and the organolead thiocarboxylates [15*] and organotin selenocarboxylates [16]. On the basis of these data, the organolead selenocarboxylates **4** and **5** seem to be monomers e.g. I and II, in which the carbonyl oxygen is coordinated to the lead atom, rather than linear polymers, in which the OCSe group bridges the lead atoms.

In a previous paper, we described the preparation of acyl phenyl diselenides (**7**) from the reaction of potassium selenocarboxylates with benzeneselenenyl bromide [17]. However, their yields were below 60%, because of the formation of by-products such as bis(acyl) and diphenyl diselenides. In earlier work on new thiocarboxylic acid derivatives, we found that the Sn–S bond of organotin thiocarboxylates can be readily cleaved by halogen or pseudohalogen to give acylsulfenyl halogenides in good yields [15*]. In addition, the reaction with benzenesulfenyl chloride gives acyl aryl disulfides in good yields [18]. Therefore, the reactions of the lead esters (**4**) with benzeneselenenyl bromide were carried out, in the expectation that acyl phenyl diselenides (**7**) would be formed. The outcome was satisfactory, the organolead



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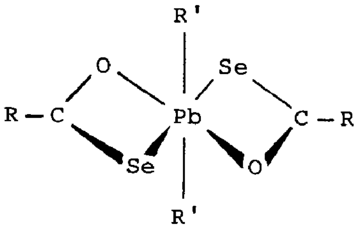

II

Fig. 1.

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[*] Reference number with asterisk indicates a note in the list of references

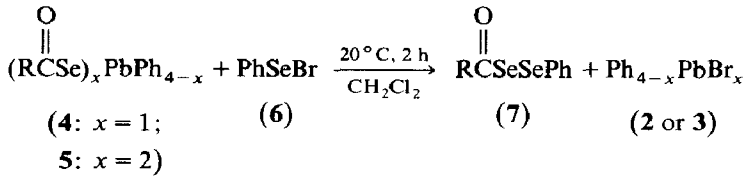
Table 3

Yields of acyl phenyl diselenides (**7**)

No.	RC(O)SeSePh R	Yield (%)	m.p. (°C)
7a	C_6H_5	78 [a] 71 [b]	oil
7b	4-$CH_3C_6H_4$	75 [a] 60 [b]	84–86
7c	4-$CH_3OC_6H_4$	67 [a] 77 [b]	45–47
7d	4-ClC_6H_4	75 [a] 80 [b]	77–78

[a] Using triphenyllead selenocarboxylates (**4**). [b] Using diphenyllead bis(selenocarboxylate)s (**5**).

selenocarboxylates (**4** and **5**) react readily with benzeneselenenyl bromide at room temperature to give the corresponding acyl phenyl diselenides (**7**) in 60–80% yields (eq. 2, Table 3).



$$(\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Se})_x\mathrm{PbPh}_{4-x} + \mathrm{PhSeBr} \xrightarrow[\mathrm{CH_2Cl_2}]{20\,^\circ\mathrm{C},\ 2\ \mathrm{h}} \mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{SeSePh} + \mathrm{Ph}_{4-x}\mathrm{PbBr}_x \qquad (2)$$

(**4**: $x = 1$; **5**: $x = 2$) (**6**) (**7**) (**2** or **3**)

No.	R
7a	C_6H_5
7b	4-$CH_3C_6H_4$
7c	4-$CH_3OC_6H_4$
7d	4-ClC_6H_4

Experimental

Melting points were determined by use of a Yanagimoto micromelting point apparatus and are uncorrected. The IR spectra were measured on JASCO IR spectrometers IR-G and IRA-2. The ^1H and ^{13}C NMR spectra were recorded on a JEOL-JNM-GX270 (270 MHz) spectrometer with tetramethylsilane as an internal standard. High resolution mass spectra were taken by a Shimadzu 9020-DF mass spectrometer at an ionizing energy of 20 eV. Elemental analyses were carried out by the Analytical Center of Kyoto University.

Sodium (**1**, M = Na) [12], potassium (**1**, M = K) [11], piperidinium arenecarboselenoates (**1**, $\overset{+}{N}H_2C_5H_{10}$) [19], triphenyllead chloride [20], diphenyllead dichloride [20], and benzeneselenenyl bromide [21] were prepared by published procedures. Solvents were dried with sodium metal or calcium dichloride and carefully degassed.

The preparations of triphenyllead selenoacetate (**4a**), 4-methylbenzenecarboselenoate (**4d**), diphenyllead bis(selenoacetate) (**5a**) and bis(benzenecarboselenoate) (**5c**) are described in detail as typical procedures for preparation of organolead selenocarboxylates (**4**, **5**). All manipulations were carried out under argon.

Triphenyllead selenoacetate (4a)

Triphenyllead chloride (237 mg, 0.5 mmol) was added to a suspension of sodium selenoacetate **1a** (M = Na) (145 mg, 1.0 mmol) and triphenyllead chloride (474 mg, 1.0 mmol) in ether (20 ml), and the mixture was stirred at 0 ° C for 1 h. Filtration of the precipitates, evaporation of the solvent under reduced pressure and recrystallization from ether/hexane (1 : 4, 10 ml) gave 219 mg (39%) of **4a** as a colorless crystal, m.p. 94–96 ° C (dec.). Anal. Found: C, 43.01; H, 3.18. $C_{20}H_{18}OSePb$ calcd.: C, 42.86; H 3.24%. IR (KBr, cm^{-1}) 3050, 1662 (C=O), 1600, 1565, 1470, 1425, 1325, 1295, 1182, 1155, 1095, 1055, 1010, 990, 940, 720, 685, 570, 430. ^1H NMR ($CDCl_3$, δ) 2.51 (s, 3H, CH_3), 7.3–7.7 (m, 15H, Ar). ^{13}C NMR ($CDCl_3$, δ) 198.7 (C=O), 152.6, 138–128 (Ar), 38.1 (CH_3). MS (EI, 20 eV, m/z) 43, 122, 77 (100), 105, 154, 208 (Pb^+), 284, 438, 485, 560 (M^+, 1.0).

Triphenyllead 1,1-dimethylethanecarboselenoate (4b)

As described for **4a**, the reaction of sodium 1,1-dimethylethanecarboselenoate **1b** (M = Na) (187 mg, 1.0 mmol) with triphenyllead chloride (474 mg, 1.0 mmol), followed by recrystallization from ether/hexane (1 : 4, 10 ml), gave 355 mg (59%) of **4b** as colorless crystals, m.p. 124–127 ° C (dec.). Anal. Found: C, 45.72; H, 4.09. $C_{23}H_{24}OSePb$ calcd.: C, 45.84 H, 4.01%. IR (KBr, cm^{-1}) 3050, 2960, 1660 (C=O), 1600, 1560, 1480, 1428, 1320, 1290, 1179, 1148, 1052, 1010, 990, 900, 830, 790, 730, 720, 685, 590, 430. ^1H NMR ($CDCl_3$, δ) 1.12 (s, 9H), 7.2–7.7 (m, 15H). ^{13}C NMR ($CDCl_3$, δ) 213.0 (C=O), 153.0, 137–129, 28.1 (CH_3). MS (EI, 20 eV, m/z) 43, 57, 77, 85, 154, 208, 284, 361, 438, 527 (M^+ – Ph)

Triphenyllead benzenecarboselenoate (4c)

As described for **4a**, the reaction of sodium benzenecarboselenoate, **1c** (M = Na) (104 mg, 0.5 mmol), with triphenyllead chloride (237 mg, 0.5 mmol), followed by recrystallization from ether/hexane (1 : 3, 20 ml), gave 273 mg (88%) of **4c** as slightly yellow crystals, m.p. 95–97 ° C (dec.). Anal. Found: C, 48.33; H. 3.21, $C_{25}H_{20}OSePb$ calcd.: C, 48.23; H, 3.24%. IR (KBr, cm^{-1}) 3040, 1642 (C=O), 1598. 1568, 1474, 1443, 1425, 1325, 1300, 1198, 1165, 1058, 1012, 994, 880 (CO–Se), 768, 726, 722, 695, 682, 668, 620, 442. ^1H NMR ($CDCl_3$, δ) 7.1–8.1 (m, Ar). ^{13}C NMR ($CDCl_3$, δ) 196.1 (C=O), 155.8, 138–128 (Ar.).

Triphenyllead 4-methylbenzenecarboselenoate (4d)

Triphenyllead chloride (237 mg, 0.5 mmol) was added to a suspension of sodium 4-methylbenzenecarboselenoate, **1d** (M = Na) (111 mg, 0.5 mmol), in ether (20 ml) at 20 ° C and the mixture was stirred for 1 h. (The brown color of the mixture quickly changed to a pale yellow and a gray precipitate formed.) The precipitate was filtered off, and the filtrate was evaporated off under reduced pressure (20 Torr). Recrystallization from ether/hexane (1 : 3, 20 ml) at – 15 ° C gave 283 mg (89%) of chemically pure **4d** as slightly yellow crystals, m.p. 108–110 ° C (dec.). Anal. Found: C, 49.00; H, 3.40. $C_{26}H_{22}OSePb$ calcd.: C, 49.05; H, 3.48%. IR (KBr, cm^{-1}) 3030, 1640 (C=O), 1600, 1572, 1470, 1426, 1315, 1302, 1198, 1164, 1055, 1014, 990, 878 (CO–Se), 817, 780, 722, 693, 620, 615, 437. ^1H NMR ($CDCl_3$, δ) 2.34 (s, 3H, CH_3), 7.0–8.0 (m, 19H, Ar). ^{13}C NMR ($CDCl_3$, δ) 195.4 (C=O), 152.8, 138–129 (Ar), 21.6 (CH_3). MS (EI, 20 eV, m/z) 51, 65, 77 (100), 91 (87), 119, 154, 208 (Pb^+, 47), 434, 638 (M^+, 1.2).

The reaction of potassium 4-methylbenzenecarboselenoate, **1d** (M = K) (158 mg, 0.5 mmol), with triphenyllead chloride (237 mg, 0.5 mmol), followed by recrystallization from ether/hexane (1 : 3) gave 277 mg (87%) of **4d**.

The reaction of piperidinium 4-methylbenzenecarboselenoate, **1d** (M = $^{+}NH_2C_5H_{10}$) (284 mg, 1.0 mmol), with triphenyllead chloride (474 mg, 1.0 mmol) gave 534 mg (84%) of **4d**.

*Triphenyllead 4-methoxybenzenecarboselenoate (**4e**)*

As described for **4d**, the reaction of sodium 4-methoxybenzenecarboselenoate, **1e** (M = Na) (119 mg, 0.5 mmol), with triphenyllead chloride (237 mg, 0.5 mmol), followed by recrystallization from ether/hexane (1 : 3, 40 ml), gave 314 mg (96%) of **4e** as slightly yellow crystals, m.p. 99–100 ° C (dec.). Anal. Found: C, 47.73; H, 3.48. $C_{26}H_{22}O_2SePb$ calcd.: C, 47.85; H, 3.40%. IR (KBr, cm^{-1}) 3050, 1630 (C=O), 1595, 1564, 1502, 1470, 1424, 1313, 1298, 1258, 1205, 1158, 1052, 1010, 992, 882 (CO–Se), 830, 782, 722, 690, 604, 435. ^1H NMR ($CDCl_3$, δ) 3.81 (s, 3H, CH_3O), 6.6–7.9 (m, 19H, Ar). ^{13}C NMR ($CDCl_3$, δ) 193.9 (C=O), 163.8, 152.9, 138–128, 113.5 (Ar), 55.5 (CH_3O).

*Triphenyllead 4-chlorobenzenecarboselenoate (**4f**)*

As described for **4d**, the reaction of sodium 4-chlorobenzenecarboselenoate, **1f** (M = Na) (121 mg, 0.5 mmol), with triphenyllead chloride (237 mg, 0.5 mmol), followed by recrystallization from ether/hexane (1 : 3, 40 ml), gave 316 mg (97%) of **4f** as slightly yellow crystals, m.p. 86–88 ° C (dec.). Anal. Found: C, 45.55; H, 2.91. $C_{25}H_{19}OClSePb$ calcd.: C, 45.70; H, 2.91%. IR (KBr, cm^{-1}) 3055, 1650 (C=O), 1590, 1575, 1480, 1433, 1400, 1332, 1300, 1192, 1165, 1084, 1060, 1014, 998, 876 (CO–Se), 838, 818, 722, 696, 616, 550, 437. ^1H NMR ($CDCl_3$, δ) 7.8–8.1 (m, Ar). ^{13}C NMR ($CDCl_3$, δ) 194.9 (C=O), 152.8, 139.7–128.6 (Ar).

*Diphenyllead bis(selenoacetate) (**5a**)*

Diphenyllead dichloride (216 mg, 0.5 mmol) was added to a suspension of sodium selenoacetate **1a** (M = Na) (145 mg, 1.0 mmol) in dry ether (20 ml) and the mixture was stirred at 20 ° C for 1 h. The precipitate of NaCl was filtered off, and the solvent was evaporated in vacuo. Recrystallization of the residue from a mixed solvent of ether/hexane (1 : 3, 10 ml) yielded 135 mg (45%) of **5a** as colorless plates, m.p. 85–88 ° C (dec.). Anal. Found: C, 31.62; H, 2.73. $C_{16}H_{16}O_2Se_2Pb$ calcd.: C, 31.74; H, 2.66%. IR (KBr, cm^{-1}) 3050, 1670 (C=O), 1598, 1573, 1472, 1431, 1332, 1303, 1100, 1060, 1010, 990, 940, 735, 689, 520, 440, 430. ^1H NMR ($CDCl_3$, δ) 2.32 (s, 6H, CH_3), 7.2–7.6 (m, 10H, Ar). ^{13}C NMR ($CDCl_3$, δ) 198.7 (C=O), 152.5, 138–129 (Ar), 38.0 (CH_3).

*Diphenyllead bis(1,1-dimethylethanecarboselenoate) (**5b**)*

As described for **5a**, the reaction of sodium 1,1-dimethylethanecarboselenoate **1b** (M = Na) (187 mg, 1.0 mmol) with diphenyllead dichloride (216 mg, 0.5 mmol), followed by recrystallization from ether/hexane (1 : 3, 10 ml), gave 204 mg (59%) of **5b** as colorless plates, m.p. 57–59 ° C (dec.). Anal. Found: C, 38.44; H, 4.11. $C_{22}H_{28}O_2Se_2Pb$ calcd.: C, 38.32; H, 4.09%. IR (KBr, cm^{-1}) 3050, 2970, 1655 (C=O), 1598, 1568, 1470, 1430, 1360, 1323, 1220, 1180, 1029, 1010, 990, 905, 795, 720, 682, 590, 430. ^1H NMR ($CDCl_3$, δ) 1.20 (s, 18H, CH_3), 7.4–7.8 (m, 10H, Ar).

^{13}C NMR ($CDCl_3$, δ) 213.5 (C=O), 154.1, 137–128.1 (Ar), 51.3 (CCH_3), 28.1 (CH_3), MS (EI, 20 eV, m/z) 77, 85, 154, 208, 285, 362, 527, 692 (M^+).

Diphenyllead bis(benzenecarboselenoate) (5c)

Diphenyllead dichloride (216 mg, 0.50 mmol) was added to a suspension of potassium benzenecarboselenoate **1c** (M = K) (302 mg, 1.0 mmol) in ether (20 ml) and the mixture was stirred at 20 ° C for 1 h. The precipitates of KCl and Se were filtered off and the solvent was evaporated in vacuo. Recrystallization of the resulting residue from a mixed solvent of ether/hexane (1 : 3, 40 ml) yielded 346 mg (95%) of **5c** as colorless plates, m.p. 123–125 ° C (dec.). Anal. Found: C, 42.85; H, 2.80. $C_{26}H_{20}O_2Se_2Pb$ calcd.: C, 42.80; H, 2.76%. IR (KBr, cm^{-1}) 3030, 1620 (C=O), 1598, 1577, 1480, 1438, 1330, 1326, 1302, 1204, 1180, 1072, 1014, 996, 927, 886 (CO–Se), 772, 734, 686, 677, 628, 442. ^{1}H NMR ($CDCl_3$, δ) 7.2–8.0 (m, Ar). ^{13}C NMR ($CDCl_3$, δ) 196.2 (C=O), 154.5, 140.2, 136–128 (Ar).

Diphenyllead bis(4-methylbenzenecarboselenoate) (5d)

As described for **5c**, the reaction of potassium 4-methylbenzenecarboselenoate, **1d** (M = K) (316 mg, 1.0 mmol), with diphenyllead dichloride (216 mg, 0.50 mmol), followed by recrystallization from ether/hexane (1 : 3, 40 ml), gave 367 mg (97%) of **5d** as slightly yellow crystals, m.p. 144–146 ° C (dec.). Anal. Found: C, 44.30; H, 3.18. $C_{28}H_{24}O_2Se_2Pb$ calcd.: C, 44.39; H, 3.19%. IR (KBr, cm^{-1}) 3040, 1625 (C=O), 1602, 1572, 1478, 1437, 1312, 1212, 1177, 1018, 996, 887 (CO–Se), 818, 786, 738, 696, 626, 446. ^{1}H NMR ($CDCl_3$, δ) 2.29 (s, 6H, CH_3), 7.0–8.0 (m, 18H, Ar). ^{13}C NMR ($CDCl_3$, δ) 195.3 (C=O), 154.5, 137.6–129 (Ar), 21.8 (CH_3).

Diphenyllead bis(4-methoxybenzenecarboselenoate) (5e)

As described for **5c**, the reaction of potassium 4-methoxybenzenecarboselenoate, **1e** (M = K) (328 mg, 1.0 mmol), with diphenyllead dichloride (216 mg, 0.5 mmol), followed by recrystallization from ether/hexane (1 : 3, 40 ml), gave 308 mg (78%) of **5e** as slightly yellow crystals, m.p. 116–118 ° C (dec.). Anal. Found: C, 42.48; H, 3.12. $C_{28}H_{24}O_4Se_2Pb$ calcd.: C, 42.60 H, 3.06%. IR (KBr, cm^{-1}) 3030, 2820, 1615 (C=O), 1598, 1578, 1510, 1438, 1324, 1308, 1270, 1215, 1180, 1163, 1117, 1025, 996, 886 (CO–Se), 837, 783, 730, 690, 640, 622, 608, 520, 500, 440. ^{1}H NMR ($CDCl_3$, δ) 3.72 (s, 6H, CH_3). 6.6–7.9 (m, 18H, Ar). ^{13}C NMR ($CDCl_3$, δ) 193.7 (C=O), 164.1, 135.5–129.4, 113.6 (Ar), 55.4 (CH_3O).

Diphenyllead bis(4-chlorobenzenecarboselenoate) (5f)

As described for **5c**, the reaction of potassium 4-chlorobenzenecarboselenoate, **1f** (M = K) (318 mg, 1.0 mmol), with diphenyllead dichloride (216 mg, 0.5 mmol), followed by recrystallization from ether/hexane (1 : 3, 40 ml), gave 335 mg (84%) of **5f** as slightly yellow crystals: m.p. 123–125 ° C (dec.). Anal. Found: C, 39.12; H, 2.22. $C_{26}H_{18}O_2Cl_2Se_2Pb$ calcd.: C, 39.11; H, 2.27%. IR (KBr, cm^{-1}) 3040, 1635 (C=O), 1690, 1570, 1483, 1477, 1438, 1400, 1332, 1302, 1202, 1175, 1095, 1020, 996, 878 (CO–Se), 840, 818, 737, 696, 630, 620, 558, 442, 430. ^{1}H NMR ($CDCl_3$, δ) 7.1–8.1 (m, Ar). ^{13}C NMR ($CDCl_3$, δ) 194.2 (C=O), 152.8, 139.7–128.6 (Ar).

Benzoyl phenyl diselenide (7a)

Benzeneselenenyl bromide (118 mg, 0.5 mmol) was added to a solution of triphenyllead benzenecarboselenoate, **4c** (311 mg, 0.5 mmol), in ether (20 ml) and the mixture was stirred at 20 °C for 2 h. The solvent was evaporated in vacuo (10 °C/15 torr). Hexane (20 ml) was added to the residue, and the mixture was cooled at −20 °C for 40 h. After filtration of the resulting precipitates (Ph_3PbBr, 235 mg, 91%), the filtrate was evaporated in vacuo to give 133 mg (78%) of **7a** as a yellow oil. (Lit. [16] oil)

4-Methylbenzoyl phenyl diselenide (7b)

To a solution of triphenyllead bis(4-methylbenzenecarboselenoate), **5d** (378 mg, 0.5 mmol), in ether (20 ml) was added benzeneselenenyl bromide (236 mg, 1.0 mmol) and the mixture was stirred at 20 °C for 1 h. The mixture was concentrated to ca. 5 ml, then hexane (10 ml) was added, and the mixture was left to stand at −20 °C for 5 h. Filtration of the resulting yellow crystals afforded 212 mg (60%) of **7b**, m.p. 84–86 °C (Lit. [16] 85–86 °C).

4-Methoxybenzoyl phenyl diselenide (7c)

The reaction of diphenyllead 4-methoxybenzenecarboselenoate **4e** (326 mg, 0.5 mmol) with benzeneselenenyl bromide (118 mg, 0.5 mmol) yielded 124 mg (67%) of **7c** as light yellow crystals, m.p. 45–47 °C (Lit. [16] 43–44 °C).

4-Chlorobenzoyl phenyl diselenide (7d)

The reaction of triphenyllead 4-chlorobenzenecarboselenoate **4f** (284 mg, 0.5 mmol) with benzeneselenenyl bromide (118 mg, 0.5 mmol) yielded 140 mg (75%) of **7d** as light yellow crystals, m.p. 77–78 °C (Lit. [16] 76–78 °C).

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