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Mercuriation of 3,4,5-trimethoxybenzoic acid. Synthesis of derivatives of the mercuriation product and crystal and molecular structure of $[PPh_3(CH_2Ph)][HgCl\{C_6H(CO_2)\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}]$

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Abstract

The mercuriation of 3,4,5-trimethoxybenzoic acid has been re-investigated and the product $[HgCl\{C_6H(CO_2H)\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}]$ (**1**) characterized. It is deprotonated by Na_2CO_3 to give $[Hg\{C_6H(CO_2)\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}]_n$ (**2**) which, in turn, reacts with benzyltriphenylphosphonium chloride or triphenylphosphine to give $[PPh_3(CH_2Ph)][HgCl\{C_6H(CO_2)\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}]$ (**3**) or $[Hg\{C_6H(CO_2)\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}(PPh_3)]$ (**4**), respectively. The reaction of **2** with MeI in the presence of $[NMe_4]Cl$ affords $[Hg\{C_6H(CO_2Me)\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}_2]$ (**5**), which reacts with $HgCl_2$ or HgI_2 to give $[HgX\{C_6H(CO_2Me)\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}]$ [X = Cl (**6**), I (**7**)]. The crystal structure of **3** shows a linear geometry at the mercury atom [Cl–Hg–C 178.0(2)°, Hg–Cl 2.315(2), Hg–C 2.060(5) Å], with an additional long Hg · · · O contact [2.573(4) Å].

The organometallic chemistry of mercury has been studied for more than a century, giving rise not only to the synthesis of a great number of organomercurials [1] but also to the discovery of important applications in organic synthesis [2]. A further use of these compounds is as transmetallating agents in the synthesis of organometallic compounds [1b,3]; we are currently using this method for the synthesis of functionalized aryl complexes that are not readily accessible from Grignard or lithium derivatives [3b]. In particular, we are now interested in the use of mercurials containing aryl groups $6\text{-X-}2,3,4\text{-}(OMe)_3C_6H$ (X = CHO, NH_2, NO_2 or CO_2H) because the three electron-releasing methoxy groups confer interesting properties on the corresponding aryl derivatives [4]. Furthermore, the 2,3,4-tri-

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methoxyphenyl moiety is present in several molecules of pharmaceutical interest, *e.g.* the antileukaemic lactones steganacin and steganangin [5], the antibacterial agent trimethoprim [6] and the cytotoxin colchicine [7]; this provides a further context in which the synthesis and use of organomercury derivatives containing 2,3,4-trimethoxyphenyl groups is of interest [2].

A report in 1937 [8] described the mercuriation of 3,4,5-trimethoxybenzoic acid by mercuric acetate to give a solid that dissolved in aqueous sodium hydroxide. When the solution was treated with HBr the compound $[HgBr\{C_6H(CO_2H)\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}]$ separated out. However, the addition of HCl did not give the corresponding chloro-derivative but a compound formulated as a "basic salt" [8]. The account did not present spectroscopic data and so we decided to re-investigate the formation of these organomercurials and study their reactivity. Our results are shown below.

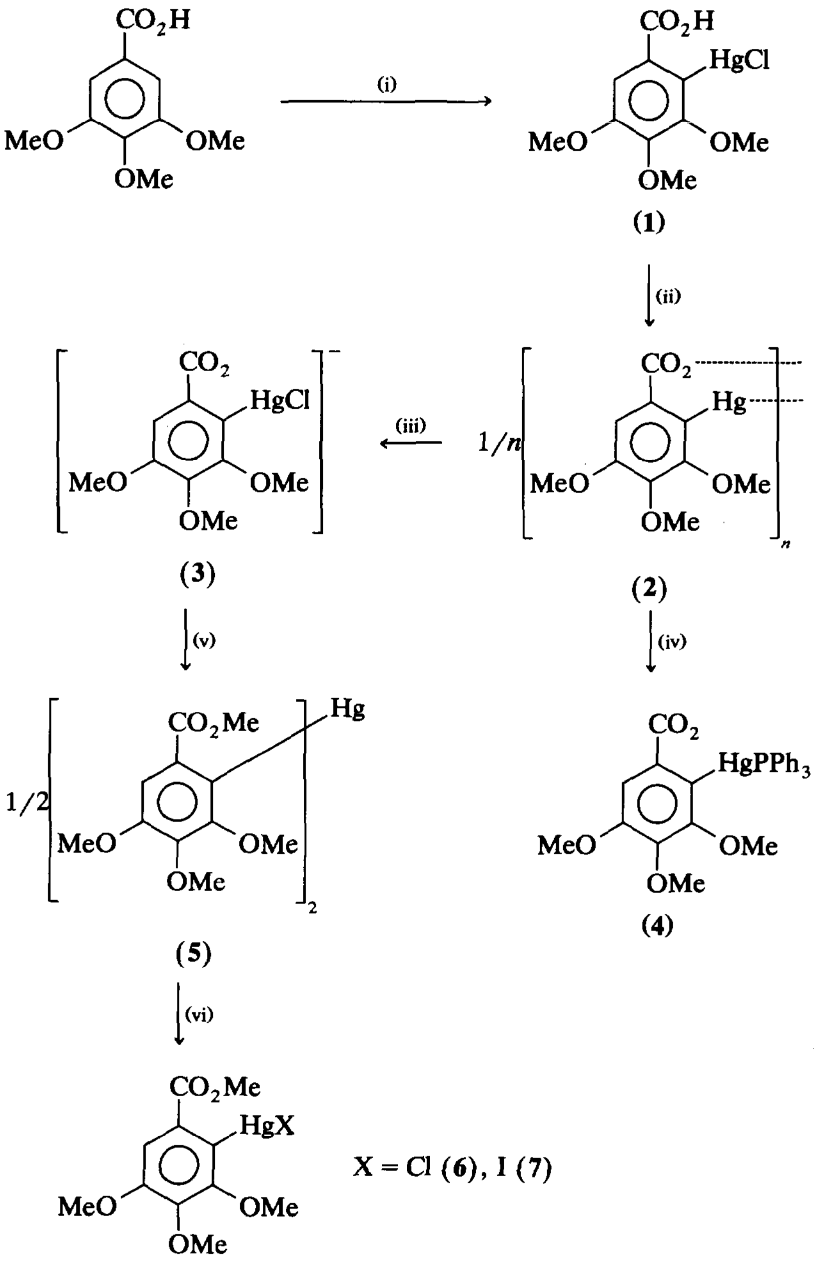
Results and discussion

Synthesis

The mercuriation of 3,4,5-trimethoxybenzoic acid was carried out under the conditions previously described [8], namely by refluxing an ethanol/acetic acid and solution of equimolar amounts of $HgAc_2$ and the arene. The resulting suspension, probably containing the acetoxymercury derivative, was poured into saturated aqueous NaCl and $[HgCl\{C_6H(CO_2H)\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}]$, **1** separated out.

The reaction of **1** with Na_2CO_3 in acetone proceeded in good yield to give the internal salt $[Hg\{C_6H(CO_2)\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}]_n$ (**2**), see Scheme 1. Ortho-mercuriated salts of this type have been described previously, being accessible through mercuriation of aryl-carboxylic acids (*e.g.* benzoic acid [1a]) or by decarboxylation of arylmono- or di-carboxylates of mercury [1a,2b,9]. However, no studies of their structures and reactivity have so far been reported. We have succeeded in preparing some complexes of this internal salt soluble enough for characterization. The reaction of **2** with QCl $[Q = PPh_3(CH_2Ph)]$ (1:1 in CH_2Cl_2), allowed the isolation of the complex $Q[HgCl\{C_6H(CO_2)\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}]$ (**3**), whose structure was elucidated by an X-ray diffraction study (see below). Similarly, the reaction of **2** with PPh_3 (1:1 in CH_2Cl_2) yielded $[Hg\{C_6H(CO_2)\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}(PPh_3)]$ (**4**). As far as we are aware, compound **3** is the first example of an anionic chloro-(aryl)mercurial to be prepared and structurally characterized [1,10]. Only two complexes of mercury related to **4** are known [10] namely $[Hg(Ph)PEt_3]NO_3$ [11] and $[Hg(Ph)PPh_3]NO_3$ [12]. Only IR data are reported for the former; the latter was structurally characterized by X-ray methods.

Complex **2** reacts with MeI only in the presence of $[NMe_4]Cl$. Treatment of **2** with $[NMe_4]Cl$ in refluxing acetone gives rise to solutions from which only ill-defined oily materials, probably containing the analogous $[NMe_4]^+$ salt of **3**, were isolated. However, we used these solutions as starting materials in the reaction with MeI, to give $[Hg\{C_6H(CO_2Me)\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}_2]$ (**5**) (see Scheme 1). It is probable that an intermediate, such as $[HgX\{C_6H(CO_2Me)\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}]$ ($X = Cl$ or I), undergoes symmetrization in the presence of X^- ($2[Hg(R)X] + X^- \rightarrow [HgR_2] + [HgX_3]^-$) [1]. Compound **5** reacts with $HgCl_2$ or HgI_2 to give the corresponding chloro- or iodo-(aryl)mercurials $[HgX\{C_6H(CO_2Me)\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}]$ [$X = Cl$ (**6**), I (**7**)].



Scheme 1. Synthesis of complexes **1**–**7**. (i)+$HgAc_2$+NaCl−AcH−NaAc; (ii)+$\frac{1}{2}Na_2CO_3$−NaCl −$\frac{1}{2}CO_2$−$\frac{1}{2}H_2O$; (iii)+Cl^-; (iv)+PPh_3; (v)+$\frac{1}{2}$MeI−$\frac{1}{2}[HgCl_2I]^-$; (vi)+$\frac{1}{2}HgX_2$.

IR and NMR spectra

Solid **1** shows IR absorptions at 3510w and 3000s br cm^{-1}, due to ν(OH) modes that are absent in its derivatives **2**–**6**. The band corresponding to $\nu_{asym}(CO_2)$ appears at approx. 1670 cm^{-1} for complexes **1** (1660 cm^{-1}), **5** (1685 cm^{-1}), and **6** (1675 cm^{-1}). In the carboxylato complexes **2**, **3**, and **4** this absorption, as expected, shifts to lower energy near the ν(CC) ring modes (range 1550–1590 cm^{-1}). In the chloro-complexes **1**, **3**, and **6** ν(Hg–Cl) appears at 340, 330, and 335 cm^{-1}, respectively.

The ^{1}H NMR spectrum of **1** shows the expected signals (see Experimental), but two of the three inequivalent MeO groups accidentally coincide; the ^{13}C NMR spectrum shows three signals for the MeO groups, two of them very close. The low solubility of **2** in organic solvents, probably due to its polymeric nature, prevented its characterization by NMR spectroscopy. The ^{1}H, ^{13}C and ^{31}P NMR spectra of **4** show a broadening of all signals at room temperature, except for the methoxy resonances in the ^{13}C NMR spectrum. Furthermore, the ^{31}P NMR spectrum shows two broad signals at 27 and 35 ppm; on cooling to −40°C, the first one disappears while the second becomes stronger and sharper, showing P–Hg coupling. This may be due to some kind of dynamic equilibrium in solution. Because this compound is monomeric, as shown by molecular weight measurements (see Experimental), the equilibrium could be between the two- and three-coordinate species resulting from monodentate or chelating aryl groups.

Crystal structure determination of complex 3

The structure of **3** consists of a monomer in which the Hg atom exhibits an almost linear coordination [C–Hg–Cl 178.0(2)°] with bond lengths C–Hg 2.060(5) and Cl–Hg 2.315(2) Å, similar to those in other mercury derivatives [1b], *e.g.* C–Hg 2.085 Å in [$HgPh_2$] [13] and Cl–Hg 2.283 Å in [HgMeCl] [14]. The carboxylate group is rotated by 10° with respect to the plane of the aromatic ring.

The distance between the carboxylate oxygen O(1) and the mercury atom [2.573(4) Å] is longer than expected for a coordinated carboxylato group, *cf.* 2.11 Å in [$HgPh(O_2CMe_3)$] [15]. If we consider this secondary O–Hg interaction [1b] as significant, it extends the coordination number at the metal atom to three, with a T-shaped geometry; this should result in different carboxylate C–O bond lengths, which are however identical [1.244(6) Å]. Recently the molecular structures of (2-phenylazophenyl)mercury(II) chloride [16] and (2-pyridyl-phenyl)mercury(II) chloride [17] have been determined. In both cases only two clearly bonding distances Hg–C and Hg–Cl are observed, giving a linear geometry (178.1° in [17], no angle given in [16]). Additionally, there are longer contacts to nitrogen donor atoms (2.63–2.70 Å) and much longer contacts to chlorine donor atoms (3.41–3.44 Å). The authors claim that these organomercurials are dimeric and tetrameric, respectively, although the very long Hg · · · Cl contacts, such as are often observed in organomercurials [1b], can scarcely be regarded as bonds. Similar weak interactions, *e.g.* 2.87, 2.98 Å between mercury and two nitrato oxygen atoms in [$Hg(Ph)PPh_3]NO_3$ [12], can lead to a more distorted linear geometry [167.5(2)°]. There appears to be no clear correlation between the strength of secondary interactions and the influence on bond lengths and angles.

There are no further significant non-bonded interactions involving the mercury atom; the shortest is 3.65 Å to C(33) at $1-x$, $1-y$, $1-z$.

Experimental

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin–Elmer spectrophotometer using Nujol mulls between polyethylene sheets; ^{1}H, ^{13}C, ^{31}P

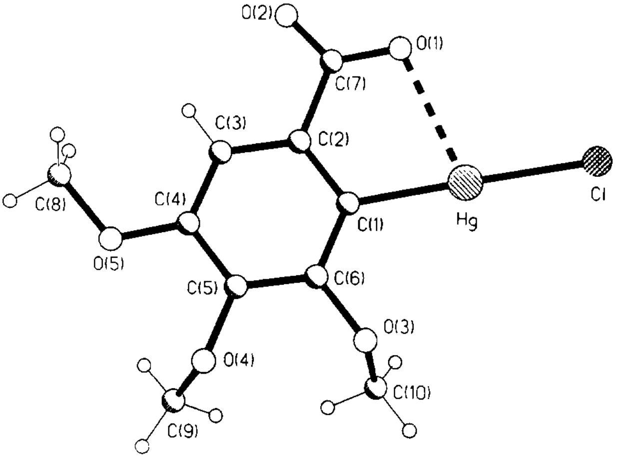


Fig. 1. The anion of compound **3** in the crystal. Radii are arbitrary. The secondary Hg ··· O contact (see text) is shown as a broken line.

NMR spectra [δ with respect to $SiMe_4$ (^1H, ^{13}C) or to external H_3PO_4] in $CDCl_3$ or dmso-d_6 solutions, on Bruker AC 200 (^1H, ^{13}C) and Varian FT-300 (^{31}P) spectrometers. Conductivities were measured with a Philips 9501 conductimeter and acetone solutions. Melting points were determined on a Reichert apparatus and are uncorrected. C, H, and N analyses were carried out by Centro de Investigación y Desarrollo, Barcelona). The molecular weight of complex **4** was determined with a Knauer vapour pressure osmometer in chloroform.

Reactions were carried out with magnetic stirring, without special precautions against light or atmospheric moisture unless otherwise stated. Single crystals of **3** were obtained by slow diffusion of n-hexane into solutions of the complex in dichloromethane.

$[HgCl\{C_6H(CO_2H)\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}]$ (*1*)

Mercuric acetate (5.1 g, 16 mmol) and acetic acid (4 cm^3) were added to a solution of 3,4,5-trimethoxybenzoic acid (3.4 g, 16 mmol) in ethanol (50 cm^3) and the mixture was refluxed for 4 h then poured into a saturated aqueous NaCl solution (300 cm^3). The mixture was stirred for 1 h and the suspended **1** then filtered off. This material was pure enough for most purposes. Yield: 82%. Analytically pure samples were obtained by cooling of the solution obtained by extraction of the crude product with acetone in a Soxhlet apparatus; m.p. > 300°C. $\Lambda_M = 0\ \Omega^{-1}\ cm^2\ mol^{-1}$. Anal. Found: C, 26.40; H, 2.30. $C_{10}H_{11}ClHgO_5$ calc.: C, 26.90; H, 2.50%. δ (^1H, dmso-d_6): 3.83 (s, 6 H, 2 × MeO), 3.85 (s, 3 H, MeO), 5.3 (br, 1 H, CO_2H) and 7.53 (s, 1 H, aryl proton). δ (^{13}C, dmso-d_6): 56.1 (s, MeO), 60.4 (s, MeO), 60.9 (s, MeO), 110.5 (s, C–H), 129.6 (s, C–Hg), 138.8 (s, *C*–CO_2H), 145.9 (s, *C*–OMe-3), 153.3 (s, *C*–OMe-4), 154.8 (s, *C*–OMe-2) and 169.8 (s, CO_2H).

$[Hg\{C_6H(CO_2)\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}]_n$ (*2*)

A mixture of Na_2CO_3 (51 mg, 0.48 mmol) and **1** (427 mg, 0.95 mmol) in acetone was stirred for 24 h at room temperature. The precipitate of **2** was filtered off, washed with water, acetone, and diethyl ether, then dried. Yield: 87%, m.p. > 300°C. Anal. Found: C, 28.70; H, 2.20. $C_{10}H_{10}HgO_5$ calc.: C, 29.20; H, 2.45%.

[PPh$_3$(CH$_2$Ph)][HgCl{C$_6$H(CO$_2$)-6-(OMe)$_3$-2,3,4}] (3)

Benzyltriphenylphosphonium chloride (95 mg, 0.24 mmol) was added to a suspension of **2** (100 mg, 0.24 mmol) in dichloromethane (12 cm^3) and the mixture was stirred at room temperature for 1 h. The resulting solution was concentrated to approx. 3 cm^3, and diethyl ether was added to the precipitate (**3**). Yield: 78%; m.p. 169°C. $\Lambda_M = 94\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$. Anal. Found: C, 52.70; H, 3.95. $C_{35}H_{32}ClHgO_5P$ calc.: C, 52.60; H, 4.05%. δ (^{1}H, CDCl$_3$): 3.78 (s, 3 H, MeO), 3.82 (s, 3 H, MeO), 3.83 (s, 3 H, MeO), 5.26 [d, 2 H, P–CH$_2$, J(PH) = 16 Hz] and 6.5–8 (m, 21 H, PPh$_3$ (CH$_2$Ph) and aryl proton). δ (^{13}C, CDCl$_3$): 30.0 (d, P–CH$_2$, J(PC) = 47 Hz), 55.7 (s, MeO), 60.3 (s, MeO), 60.6 (s, MeO), 109.9 (s, C–H), 135.2 (s, C–Hg), 138.7 (s, *C*–CO$_2$H), 143.0 (s, *C*–OMe-3), 152.8 (s, *C*–OMe-4), 153.3 (s, *C*–OMe-2), and 171.0 (s, CO$_2$). δ [^{31}P{^{1}H}, CDCl$_3$]: 23.3.

[Hg{C$_6$H(CO$_2$)-6-(OMe)$_3$-2,3,4}(PPh$_3$)] (4)

Triphenylphosphine (150 mg, 0.61 mmol) was added to a suspension of (**2**) (250 mg, 0.61 mmol) in dichloromethane and the mixture was refluxed for 2 h. The solution was filtered through anhydrous MgSO$_4$ and then evaporated to approx. 3 cm^3 and hexane was added to precipitate compound **4**. Yield: 56%; m.p. 118°C. $\Lambda_M = 0\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$. Anal. Found: C, 49.25; H, 3.60, M. 632. $C_{10}H_{11}ClHgO_5$ calc.: C, 49.95; H, 3.75%. M = 673 g mol^{-1}. δ (^{1}H, CDCl$_3$): 3.76 (br, 3H, MeO), 3.89 (br, 6H, 2 × MeO) and 7–8 (m, 16H, PPh$_3$ and aryl proton). δ (^{13}C, CDCl$_3$): 55.9 (s, MeO), 60.5 (s, MeO), 61.0 (s, MeO). δ [^{31}P{^{1}H}, CDCl$_3$]: (see Discussion). δ (CDCl$_3$, −40°C) 35.9 (s, J(PHg) = 5507 Hz).

[Hg{C$_6$H(CO$_2$Me)-6-(OMe)$_3$-2,3,4}$_2$] (5)

A mixture of **2** (150 mg, 0.37 mmol) and [NMe$_4$]Cl (40 mg, 0.37 mmol) in acetone (12 cm^3) was refluxed for 1 h then cooled to room temperature. An excess of MeI was added and the mixture stirred for a further 4 h. The solution was filtered then evaporated to dryness, and the residue was recrystallized from dichloromethane/n-hexane. Yield: 48%; m.p. 139°C. $\Lambda_M = 1\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$. Anal. Found: C, 39.59; H, 3.94. $C_{22}H_{26}HgO_{10}$ calc.: C, 40.59; H, 4.05%. δ (^{1}H, CDCl$_3$): 3.88 (s, 3H, MeO) 3.92 (s, 6H, 2 × MeO), 3.96 (s, 3H, MeO), and 7.57 (s, 1H, aryl proton). δ (^{13}C, CDCl$_3$): 52.3 (s, CO$_2$*C*H$_3$), 56.2 (s, MeO), 60.7 (s, MeO), 61.1 (s, MeO), 110.9 (s, C–H), 129.0 (s, C–Hg), 131.3 (s, *C*–CO$_2$H), 146.7 (s, *C*–OMe-3), 152.9 (s, *C*–OMe-2), 157.7 (s, *C*–OMe-4) and 170.3 (s, CO$_2$).

[HgCl{C$_6$H(CO$_2$Me)-6-(OMe)$_3$-2,3,4}] (6)

A dichloromethane solution of compound **5**, prepared from **2** (300 mg, 0.73 mmol), [NMe$_4$]Cl (80 mg, 0.73 mmol) and MeI as above, was evaporated to dryness. Ethanol (7 cm^3) and HgCl$_2$ (198 mg, 0.78 mmol) were added and the mixture was stirred for 45 min. The precipitate of **6** was filtered off. Yield: 81%; m.p. 207°C. $\Lambda_M = 0\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$. Anal. Found: C, 28.80; H, 2.80. $C_{11}C_{13}ClHgO_5$ calc.: C, 28.65; H, 2.85%. δ (^{1}H, CDCl$_3$): 3.90 (s, 3H, MeO), 3.92 (s, 3H, MeO), 3.93 (s, 3H, MeO), 3.94 (s, 3H, MeO) and 7.50 (s, 1H, aryl proton). δ (^{13}C, CDCl$_3$):

Table 1

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^4$) for compound **3**

	x	y	z	U_{eq} [a]
Hg	5571.3(2)	7216.2(2)	3818.5(2)	366(1)
Cl	5877(1)	8087(2)	1911(1)	575(7)
C(1)	5300(4)	6389(4)	5506(4)	317(21)
C(2)	4099(5)	6892(3)	6060(4)	307(21)
C(3)	3855(5)	6371(5)	7193(4)	335(22)
C(4)	4806(5)	5370(5)	7791(4)	368(23)
C(5)	6037(5)	4880(4)	7244(4)	346(22)
C(6)	6265(5)	5378(4)	6111(4)	310(21)
C(7)	3024(5)	8028(4)	5433(5)	349(23)
C(8)	3506(6)	5397(7)	9526(5)	589(35)
C(9)	7001(7)	2788(5)	8277(6)	565(30)
C(10)	7736(7)	3850(6)	5330(6)	575(34)
O(1)	3316(4)	8589(3)	4460(3)	501(18)
O(2)	1931(3)	8315(3)	5956(3)	430(17)
O(3)	7475(3)	4912(3)	5574(3)	409(16)
O(4)	7048(3)	3972(3)	7838(3)	445(17)
O(5)	4666(4)	4816(4)	8913(3)	528(20)
P	1606(1)	2091(1)	3316(1)	233(5)
C(11)	3292(4)	1785(4)	2800(4)	289(19)
C(12)	4243(5)	1210(5)	3540(5)	374(23)
C(13)	5539(5)	931(6)	3119(6)	503(30)
C(14)	5884(6)	1213(6)	1999(6)	536(30)
C(15)	4949(6)	1770(5)	1266(5)	519(29)
C(16)	3654(5)	2060(5)	1654(4)	392(23)
C(21)	654(4)	3592(4)	2497(4)	266(19)
C(22)	1208(5)	4464(4)	1934(4)	356(21)
C(23)	452(5)	5621(5)	1372(5)	424(24)
C(24)	−883(5)	5938(5)	1387(4)	392(23)
C(25)	−1439(5)	5089(4)	1971(4)	358(22)
C(26)	−679(5)	3901(4)	2530(4)	307(20)
C(31)	1355(4)	2119(4)	4731(4)	248(18)
C(32)	1354(5)	3135(4)	4920(4)	319(21)
C(33)	1096(6)	3209(5)	6003(4)	403(25)
C(34)	849(6)	2287(5)	6874(5)	471(28)
C(35)	866(6)	1267(5)	6685(4)	447(26)
C(36)	1115(5)	1180(4)	5619(4)	333(21)
C(41)	1170(5)	867(4)	2123(4)	302(20)
C(42)	2353(6)	282(5)	1600(5)	420(25)
C(43)	2436(7)	210(5)	545(5)	565(32)
C(44)	1323(9)	692(6)	10(5)	659(38)
C(45)	120(8)	1260(5)	529(5)	575(33)
C(46)	44(6)	1368(4)	1581(4)	385(23)
C(47)	1089(4)	942(4)	3279(4)	260(18)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

52.9 (s, CO_2CH_3), 56.1 (s, MeO), 60.4 (s, MeO), 60.8 (s, MeO), 110.1 (s, C–H), 128.0 (s, *C*–CO_2H), 139.5 (s, C–Hg), 146.2 (s, *C*–OMe-3), 153.3 (s, *C*–OMe-2), 154.7 (s, *C*–OMe-4) and 166.8 (s, CO_2).

$[HgI\{C_6H(CO_2Me)\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}]$ (7)

This compound was prepared in the same way as **6** but from HgI_2 (332 mg, 0.73 mmol). Yield: 71%; m.p. 181°C. $\Lambda_M = 0\ \Omega^{-1}\ cm^2\ mol^{-1}$. Anal. Found: C, 23.88; H, 2.31. $C_{11}H_{13}IHgO_5$ calc.: C, 23.90; H, 2.37%. δ (^1H, $CDCl_3$): 3.91 (s, 3H, MeO), 3.92 (s, 3H, MeO), 3.94 (s, 6H, 2 × MeO), and 7.50 (s, 1H, aryl proton). δ (^{13}C, $CDCl_3$): 52.9 (s, $CO_2\mathit{C}H_3$), 56.3 (s, MeO), 60.8 (s, MeO), 61.2 (s, MeO), 110.2 (s, C–H), 129.0 (s, *C*–CO_2H), 146.9 (s, *C*–OMe-3), 148.1 (s, C–Hg), 153.9 (s, *C*–OMe-2), 155.5 (s, *C*–OMe-4) and 169.9 (s, CO_2).

X-Ray structure determination of compound 3

Crystal data. $C_{35}H_{32}ClHgO_5P$, $M = 799.6$. Triclinic, space group $P\bar{1}$, $a = 11.365(4)$, $b = 12.659(4)$, $c = 12.929(4)$ Å, $\alpha = 68.63(2)$, $\beta = 76.57(2)$, $\gamma = 65.33(2)°$, $U = 1566.8$ Å^3, $Z = 2$, $D_x = 1.695$ mg m^{-3}, $\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å, $\mu = 5.1$ mm^{-1}, $T = 178$ K, $F(000) = 788$.

Data collection and refinement. Colourless prism $0.5 \times 0.3 \times 0.2$ mm^3 was mounted on a glass fibre in inert oil and transferred to the cold gas stream of the diffractometer (Siemens R3 with LT-2 low-temperature attachment). Data were collected to $2\theta_{max} = 50°$ with monochromated Mo-K_α radiation. Of 6456 reflections, 5503 were unique ($R_{in} = 0.028$) and $4817 > 4\sigma(F)$ used for all calculations (program system Siemens SHELXTL PLUS).

Structure solution and refinement. The structure was solved by the heavy atom method. After isotropic refinement, an absorption correction was applied using the program DIFABS [18]; transmission factors varied from 0.76 to 1.35. Anisotropic refinement proceeded to $R = 0.033$, $R_w = 0.040$. Hydrogen atoms were included

Table 2

Bond lengths (Å) and angles (°) in the anion of compound **3**

Hg–Cl	2.315(2)	Hg–C(1)	2.060(5)
Hg–O(1)	2.573(4)	C(1)–C(2)	1.391(6)
C(1)–C(6)	1.396(6)	C(2)–C(3)	1.385(7)
C(2)–C(7)	1.536(6)	C(3)–C(4)	1.379(6)
C(4)–C(5)	1.406(7)	C(4)–O(5)	1.366(6)
C(5)–C(6)	1.377(7)	C(5)–O(4)	1.377(6)
C(6)–O(3)	1.379(5)	C(7)–O(1)	1.244(6)
C(7)–O(2)	1.244(6)	C(8)–O(5)	1.428(7)
C(9)–O(4)	1.416(8)	C(10)–C(3)	1.388(10)
Cl–Hg–C(1)	178.0(2)	Cl–Hg–O(1)	106.0(1)
C(1)–Hg–O(1)	74.9(1)	Hg–C(1)–C(2)	117.5(3)
Hg–C(1)–C(6)	123.3(3)	C(2)–C(1)–C(6)	119.2(4)
C(1)–C(2)–C(3)	120.1(4)	C(1)–C(2)–C(7)	120.9(4)
C(3)–C(2)–C(7)	119.0(4)	C(2)–C(3)–C(4)	120.7(4)
C(3)–C(4)–C(5)	119.6(4)	C(3)–C(4)–O(5)	124.7(4)
C(5)–C(4)–O(5)	115.7(4)	C(4)–C(5)–C(6)	119.7(4)
C(4)–C(5)–O(4)	120.8(4)	C(6)–C(6)–O(4)	119.3(4)
C(1)–C(6)–C(5)	120.7(4)	C(1)–C(6)–O(3)	119.3(4)
C(5)–C(6)–O(3)	119.9(4)	C(2)–C(7)–O(1)	118.1(4)
C(2)–C(7)–O(2)	116.4(4)	O(1)–C(7)–O(2)	125.6(4)
Hg–O(1)–C(7)	107.2(3)	C(6)–O(3)–C(10)	115.8(5)
C(5)–O(4)–C(9)	117.1(5)	C(4)–O(5)–C(8)	117.3(4)

using a riding model; the methyl group at C(9) converged slowly, probably indicating rotational disorder. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0003F^2$. $S = 1.5$; max $\Delta/\sigma = 0.86$ for C(9), otherwise 0.04; max $\Delta\rho = 1.2$ e Å^{-3}.

Final atom coordinates are given in Table 1, with selected bond lengths and angles in Table 2. Further details of the structure determination (complete bond lengths and angles, H atom coordinates, structure factors, temperature factors) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, Germany. Any request for this material should quote a full literature citation and the reference number CSD-56072.

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