

Bis(phosphine)bis(tellurocarboxylato)-palladium(II) and -platinum(II) complexes: synthesis and crystal structure

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Bis(phosphine)bis(tellurocarboxylato)-palladium(II) and -platinum(II), $[M(RCOTe)_2(PR'_3)_2]$ ($M = Pd$ or Pt ; $R = Bu^t, Ph, 4-MeC_6H_4, etc.$; $R' = Et$ or Ph), were synthesized in moderate to good yields by treating sodium tellurocarboxylates or *O*-trimethylsilyl telluroesters with $[MCl_2(PR'_3)_2]$. The platinum complexes with 2-methoxybenzenecarbotelluroato ligands also were synthesized from $[Pt(PR'_3)_4]$ with the corresponding diacyl ditelluride. The tellurocarboxylato complexes are yellow to orange or red crystals, and labile thermally and toward oxygen. The nickel analogues $[Ni(RCOTe)_2(PR'_3)_2]$ ($R' = Et$ or Ph) were obtained by similar fashion, but were too labile to isolate. X-Ray diffraction analysis of *trans*- $[Pt(4-MeC_6H_4COTe)_2(PEt_3)_2]$ was carried out, and compared with those of the corresponding thio- and seleno-carboxylato complexes. These complexes crystallized in the same space group ($P2_1/c$) and are isostructural having a square-planar co-ordination geometry with thio- or telluro-carboxylato ligands which are unidentate.

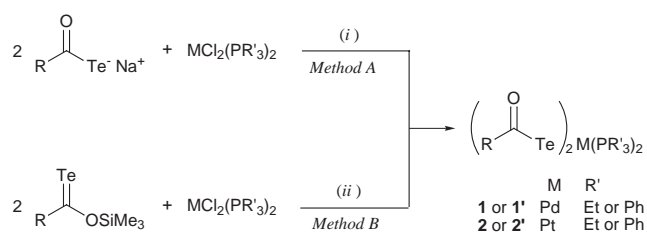
Introduction

There have been extensive studies of certain platinum complexes as antitumor agents and organo-selenium and -tellurium compounds in part because of their relevance in organic synthesis and their role as biologically active reaction centers.¹ Since the first synthesis in 1978 by Chai and McWhinnie,² who synthesized $[Pt(PhTe)_2(PPh_3)_2]$, some complexes with organotellurium ligands have been reported: $[Pt(1,2-Te_2C_6H_4)(PPh_3)_2]$,³ $[Pd(PhTe)_2L_2]$ and $[Pd(PhTe)ClL_2]$ ($L = PPh_3$ or COD).^{4,5} The syntheses of complexes with seleno- ($RCOSe^-$) and telluro-carboxylato ligands ($RCOTe^-$) are quite limited, although the fundamental importance of metal complexes containing thio- ($RCOS^-$) and dithio-carboxylato ligands ($RCSS^-$) has been well documented.^{6,7} This is most likely due to the difficulty of obtaining the starting compounds, such as seleno- and telluro-carboxylic acids and their alkali metal salts. Recently, we established methods for preparing a series of selenocarboxylic acids^{8,9} and their alkali metal salts,¹⁰⁻¹³ and *O*-triorganosilyl esters.¹⁴ In addition, we have succeeded in isolating the first transition-metal complexes with selenocarboxylato ligands; *i.e.* bis(phosphine)bis(selenocarboxylato)-nickel(II), -palladium(II) and -platinum(II) complexes.¹⁵ Two selenocarboxylato manganese $[Mn(CO)_2(\mu-PhCOSe)]_2$ ¹⁶ and ruthenium complexes $[Ru(Bu^tC_3H_7)(CO)_2(PhCOSe)]$ ¹⁷ have been reported by other groups. Our continuous effort led to the synthesis of tellurocarboxylic acids⁹ and their alkali metal salts.¹⁸⁻²⁰ In addition, the reaction of the latter with triorganosilyl halides has been found to give *O*-triorganosilyl tellurocarboxylates^{20,21} (hereafter called *O*-silyl telluroesters), which act as effective tellurocarboxylating agents in aprotic solvents. These findings have prompted us to study the first synthesis of transition-metal complexes bearing tellurocarboxylato ligands.²² A very recent report concerning the isolation of $[M(TeR)R(PEt_3)_2]$ ($M = Ni, Pd$ or Pt) by Tanaka and his co-workers^{23,24} stimulated us to reveal our results.²² We describe here the first synthesis and structural analysis of bis(phosphine)bis(tellurocarboxylato)-palladium(II) and -platinum(II) complexes.

Results and discussion

Synthesis

Initially, the synthesis of $[Pt(RCOTe)_2(PR'_3)_2]$ **2** was examined



Scheme 1 (i) Et_2O or CH_2Cl_2 , $0^\circ C$, 1 h; (ii) Et_2O , $0^\circ C$, 1 h.

using sodium tellurocarboxylates (Method A in Scheme 1), since these were expected to be the most stable complexes. In fact, the sodium salts were found readily to react with *trans*-dichlorobis(triethylphosphine)platinum(II) to give the expected bis(phosphine)bis(tellurocarboxylato)platinum complexes **2** in good yields. For example, *trans*-dichlorobis(triethylphosphine)platinum(II) was added to a suspension of sodium 4-methylbenzenecarbotelluroate in dichloromethane at $0^\circ C$ and the mixture was stirred for 1 h. The reaction mixture rapidly changed from yellow to deep orange. Filtration of the precipitates, removal of the solvent under reduced pressure and subsequent recrystallization of the residue from dichloromethane gave *trans*-bis(4-methylbenzenecarbotelluroato)bis(triethylphosphine)platinum(II) **2c** in 74% yield as yellow micro crystals. Under similar conditions, the reaction with other sodium tellurocarboxylates led to the corresponding tellurocarboxylatoplatinum(II) complexes **2** in yields of 46–66%. Notably, the reaction with *cis*-dichlorobis(triethylphosphine)platinum(II) also gave *trans* isomer **2** (Table 1, entries 8, 12 and 13; the yields are given in parentheses). Previously, *O*-trimethylsilyl selenocarboxylates $[RC(Se)OSiMe_3]$ have been found to react with $[MCl_2(PR'_3)_2]$ ($M = Ni, Pd$ or Pt) to give selenocarboxylato complexes $[M(RCOSe)_2(PR'_3)_2]$.¹⁵ Expecting an increase in yield, the reaction with *O*-trimethylsilyl 4-methylbenzene tellurocarboxylate instead of the sodium salt was examined under several conditions (Method B). However, the highest yield of *o*-silyl telluroester was limited to 51% due to the low reactivity and decomposition of **2c** in this reaction. Attempts to isolate the triphenylphosphine complexes **2'd** ($R' = Ph$) from 2-MeOC₆H₄COTeNa and $[PtCl_2(PPh_3)_2]$ failed due to their poor solubility. However, a yellow solid, which appeared to be the expected triphenylphosphine complex of 2-methoxybenzenetellurocarboxylic acid based on comparison with the

Table 1 Synthesis of tellurocarboxylato-palladium **1** and -platinum complexes **2** [M(RCOTe)₂(PR'₃)₂] (M = Pd or Pt)

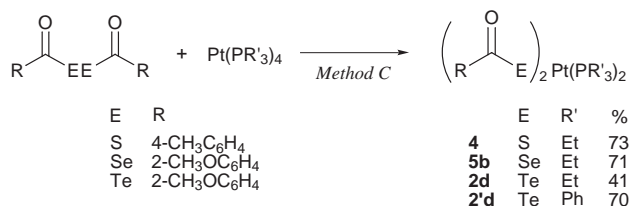
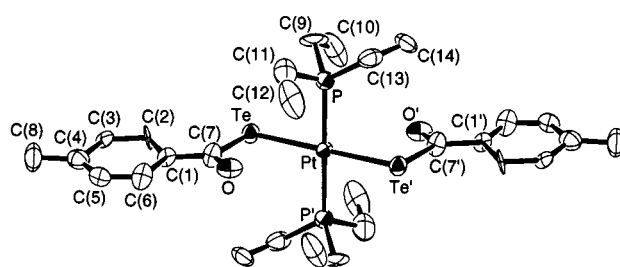
Entry	M	R	R'	Method	Solvent	Product	Yield (%)	mp (decomp.)
1	Pd	Bu ^t	Et	A	Et ₂ O	1a	34	45–52
2		Ph	Et	A	Et ₂ O	1b	50	59–63
3		4-MeC ₆ H ₄	Et	A	Et ₂ O	1c	54	102–105
4		4-MeOC ₆ H ₄	Et	A	Et ₂ O	1e	72	82–83
5		4-ClC ₆ H ₄	Et	A	Et ₂ O	1f	65	98–104
6		Pt	Bu ^t	Et	A	CH ₂ Cl ₂	2a	46
7	Ph		Et	A	CH ₂ Cl ₂	2b	64	77–80
8	4-MeC ₆ H ₄		Et	A	CH ₂ Cl ₂	2c	74 (66) ^a	118–120
9			Et	B	Et ₂ O	2c	51	
10	2-MeOC ₆ H ₄		Et	A	CH ₂ Cl ₂	2d	56	105–107
11	Ph		Et	A	CH ₂ Cl ₂	2'd	37	175–178
12	4-MeOC ₆ H ₄		Et	A	CH ₂ Cl ₂	2e	66 (42) ^a	104–106
13	4-ClC ₆ H ₄	Et	A	CH ₂ Cl ₂	2f	48 (40) ^a	115–117	

^a *cis*-[PtCl₂(PEt₃)₂] was used, and the yield of the products **2** is in parentheses.

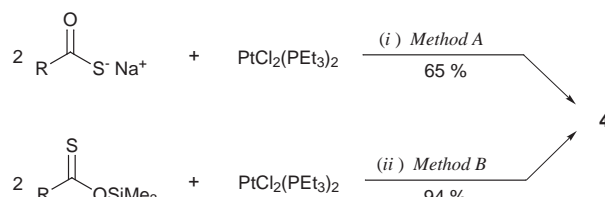
IR spectra of the corresponding ditelluride with platinum(0) complex (Method C, see below), was obtained. Next, the synthesis of the palladium complexes **1** was carried out. As expected, the reactions of the alkali metal salts with [PdCl₂(PEt₃)₂] under similar conditions led to *trans*-bis(tellurocarboxylato)bis(triethylphosphine)palladium(II) **1a–1c**, **1e** and **1f** in isolated yields of 34–72% (Table 1). However, attempts to isolate the triphenylphosphine complexes [Pd(RCOTe)₂(PPh₃)₂] failed due to the difficulty of purification, although yellow-brown solids formed, which appeared to be the expected complexes. In addition, the same reaction with the silyl telluroester 4-MeC₆H₄C(Te)OSiMe₃ resulted in the recovery of [PdCl₂(PPh₃)₂].

Next, the reaction of sodium 4-methylbenzenecarboxylate with [NiCl₂(PR'₃)₂] (R' = Et or Ph) were carried out under several conditions. The reactions immediately occurred and produced a dark brown oil (for R' = Et) or solid (for R' = Ph). However, the expected bis(phosphine)bis(tellurocarboxylato)nickel(II) complexes **3c** (for R' = Et) and **3'e** (for R' = Ph) were too unstable to isolate. On the other hand, the reaction of the silyl ester 4-MeC₆H₄C(Te)OSiMe₃ with [NiCl₂(PR'₃)₂] resulted in a complex mixture.

It is known that the Te–Te bond of dialkyl and diaryl ditellurides are cleaved by complexes of transition metals such as Cr, Mo, Fe, and Pd to give the corresponding metal complexes with organotellurium ligands, [M(TeR)_mL_n]_x (M = Cr, Mo, Fe, etc., L = Cp, CO or PPh₃).²⁵ Previously, we reported that piperidinium tellurocarboxylates were readily oxidized in methanol to give diacyl ditellurides.²⁶ Expecting the formation of **2**, the reaction of bis(2-methoxybenzoyl) ditelluride with [Pt(PEt₃)₄] was carried out. In fact, the reaction readily occurred at room temperature to give the expected *trans*-[Pt(2-MeOC₆H₄COTe)₂(PEt₃)₂] **2d** in 41% yield. In addition, the reaction with [Pt(PPh₃)₄] gave the corresponding triphenylphosphine platinum complex **2'd** in 70% yield. Similarly, the reaction of bis(4-methylbenzoyl) disulfide and bis(2-methoxybenzoyl) diselenide with [Pt(PEt₃)₄] afforded the corresponding complexes, *trans*-[Pt(4-MeC₆H₄COS)₂(PEt₃)₂] **4**²⁷ and *trans*-[Pt(2-MeOC₆H₄COSe)₂(PEt₃)₂] **5b** as colorless and pale yellow micro crystals, respectively, in good yields (Scheme 2). The oxidative addition of dialkyl and diaryl disulfides and diselenides to transition metals is well known. To our knowledge, these are the

**Scheme 2** Benzene, r.t., 1 or 2 h.**Fig. 1** An ORTEP drawing of *trans*-[Pt(4-MeC₆H₄COTe)₂(PEt₃)₂] **2c**.

first examples of the oxidative addition of diacyl dichalcogenide [(RCOE)₂, E = S, Se or Te] to transition metals. We have found that **4** was obtained in moderate to good yields by treating sodium and *O*-trimethylsilyl 4-methylbenzenecarboxylate with [PtCl₂(PEt₃)₂] (Scheme 3).

**Scheme 3** R = 4-MeC₆H₄. (i) Et₂O, r.t., 20 h; (ii) Et₂O, r.t., 20 h.

The tellurocarboxylato-palladium(II) **1** and -platinum(II) complexes **2** melt at around 45–120 °C with decomposition. The platinum complexes **2** were stable compared with the corresponding palladium complexes **1** {stability of [M(RCOTE)₂(PR'₃)₂]; M = Pt (**2**) > Pd (**1**) ≫ Ni (**3**)}. Upon exposure of **2** to air at room temperature for a week no appreciable change was observed. Similar exposure of **1** for 1 d resulted in decomposition. On the other hand, the stability of platinum complexes with the chalcogenocarboxylato ligands is in the following order; [Pt(RCOE)₂(PR'₃)₂] E = S > Se ≫ Te. The aromatic derivatives **1** and **2**, (R = aryl) were soluble in dichloromethane, chloroform and benzene, but insoluble in diethyl ether and hexane, whereas the aliphatic derivatives **1a** and **2a** (R = Bu^t) dissolved in dichloromethane, chloroform, benzene and ether.

Structure

The ORTEP²⁸ drawing of *trans*-bis(4-methylbenzenecarboxylato)bis(triethylphosphine)platinum(II) **2c** is shown in Fig. 1. Selected bond lengths, angles and torsion angles are listed in Table 2.

Complex **2c** adopts a square-planar co-ordination geometry with two *trans* phosphine ligands. The value [1.23(2) Å] of the

C–O bond lengths is slightly longer than that of *Te*-methyl arenecarbotelluroate¹⁹ and the C–Te distance is 2.15(2) Å, which is almost identical to that of a typical C sp²–Te single bond. Little information is available in the literature regarding Pt–Te bond distances. The present value of 2.632(2) Å is longer than those of the ditellurene complex [Pt(1,2-Te₂C₆H₄)(PPh₃)₂] [2.636(3), 2.630(3) and 2.621(1), 2.618(1) Å]³ and shorter than those of the PhTe terminal complexes *trans*-[Pt(TePh)Ph-(PEt₃)₂] [2.693(2) Å]²³ and *trans*-[Pt(TeC₆H₄Ph-4)(SiMe₃)-(PEt₃)₂] [2.764(2) Å],²⁴ but is somewhat consistent with those [2.586(1), 2.592(1) Å] of the *Te*-bridged complexes [{Pt(Ph₂-PCH₂CH₂PPh₂)₂(μ-Te)₂} and [{Pt(PEt₃)₂}(μ-Te)₂].³⁰ The distance between the carbonyl oxygen and the platinum center is 3.50(2) Å, which indicates no interaction between these atoms.

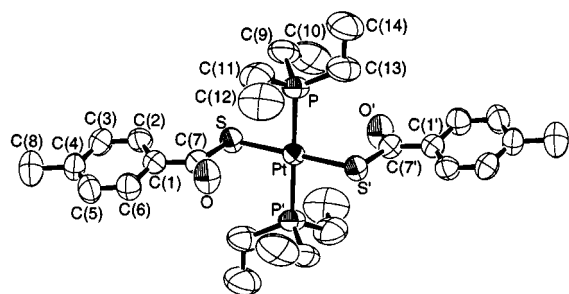


Fig. 2 An ORTEP drawing of *trans*-[Pt(4-MeC₆H₄COS)₂(PEt₃)₂] **4**.

Table 2 Selected bond lengths (Å), angles (°) and torsion angles (°) for complexes **2c** and **4**

	E = Te (2c)	E = S (4)
Pt–E	2.632(2)	2.331(2)
Pt–P	2.313(6)	2.310(2)
E–C(7)	2.15(2)	1.753(8)
P–C(9)	1.87(3)	1.846(9)
P–C(11)	1.78(2)	1.81(1)
P–C(13)	1.86(3)	1.849(9)
O–C(7)	1.23(2)	1.219(7)
C(1)–C(7)	1.48(3)	1.50(1)
E–Pt–E'	180.0	180.0
E–Pt–P	86.9(1)	87.09(7)
E–Pt–P'	93.1(1)	92.91(7)
P–Pt–P'	180.0	180.0
Pt–E–C(7)	99.3(6)	105.1(3)
Pt–P–C(9)	115.2(9)	113.0(3)
Pt–P–C(11)	110.2(8)	111.3(3)
Pt–P–C(13)	121.3(7)	116.7(3)
E–C(7)–O	117(1)	122.4(6)
E–C(7)–C(1)	120(1)	116.0(5)
O–C(7)–C(1)	121(1)	121.6(7)
Pt–E–C(7)–O	2(1)	7.0(8)
P–Pt–E–C(7)	–94.8(6)	–104.5(3)
O–C(7)–C(1)–C(2)	173(2)	167.9(8)

Table 3 Spectroscopic data of [M(RCOTe)₂(PEt₃)₂] (M = Pd **1** or Pt **2**)

Compound	M	R	$\tilde{\nu}(\text{C=O})^a/\text{cm}^{-1}$	$\delta_{\text{C=O}}^b$	$\delta_{\text{P}}^c (J_{\text{PPt}}/\text{Hz})$	$\delta_{\text{Te}}^d (J_{\text{TePt}}/\text{Hz})$
1a	Pd	Bu ^t	1642 ^e	214.1	5.7	362.1
1b		Ph	1624	198.3	6.9	438.2
1c		4-MeC ₆ H ₄	1618	197.5	6.7	426.2
1e		4-MeOC ₆ H ₄	1617	195.7	6.4	407.1
1f		4-ClC ₆ H ₄	1616	196.5	7.1	443.8
2a	Pt	Bu ^t	1635 ^e	213.7	–1.1 (2435)	329.4(681)
2b		Ph	1627	197.7	–0.3 (2397)	404.9 (711)
2c		4-MeC ₆ H ₄	1621	196.9	–0.4 (2403)	392.6 (717)
2d		2-MeOC ₆ H ₄	1623	196.0	0.0 (2415)	532.2 (812)
2e		4-MeOC ₆ H ₄	1616	195.2	–0.8 (2406)	373.2 (711)
2f		4-ClC ₆ H ₄	1619	195.9	–0.3 (2385)	410.3 (696)

^a In KBr. ^b In CDCl₃. ^c In CDCl₃, standard H₃PO₄. ^d In CDCl₃, standard Me₂Te. ^e Nujol.

Thus, the tellurocarboxylato ligands act as unidentate ligands. The dihedral angle between the tellurocarboxyl group (COTe) and the benzene ring is 8.3°. The plane including tellurocarboxylato ligands is nearly perpendicular (86.1°) to the Te–P–Te'–P' square plane including the metal. The bond angle around the Te atom [Pt–Te–C(7)] is 99.3(6)°, which is somewhat greater than that of the telluroester 4-ClC₆H₄COTeMe [C–Te–C 92.3(2)°].¹⁹

For comparison, the structure of the corresponding sulfur isologue **4** is also shown in Fig. 2. Selected bond lengths, angles and torsion angles are listed in Table 2 together with those of **2c**.

The C=O bond length [1.219(7) Å] is similar to those of common thioesters (1.20 ± 0.01 Å). The C–S bond is a normal single bond. No interaction between the carbonyl oxygen and central metal is observed, indicating that the thiocarboxylate ligands are unidentate. Such unidentate thiocarboxylato ligands in palladium and platinum complexes have been suggested on the basis of their IR spectra.²⁷ Complexes **2c** and **4** are isostructural with the previously reported selenium isologue [Pt(4-MeC₆H₄COSe)₂(PEt₃)₂] **5a**.¹⁵ These three complexes crystallize in the same space group (*P2₁/c*), and their lattice parameters are similar to each other. The dihedral angle between the benzene ring and tellurocarboxyl group of **2c** is 8.3°, nearly equal to those of the sulfur **4** (13.8°) and selenium isologues **5a** (11.8°). It is well known that the H–E–H (E = S, Se or Te) bond angles approach 90° upon descending in this group, which implies that the lone pairs of the chalcogens (E = S, Se or Te) exert a large stereochemical effect.³¹ As expected, the angles of C–E–Pt in **4**, **5a** and **2c** decrease in the order E = S [105.1(3)] > Se [101.7(2)] > Te [99.3(6)].

Spectra

The spectroscopic data for [M(RCOTe)₂(PEt₃)₂] (M = Pd **1** or Pt **2**) are summarized in Table 3. The carbonyl stretching frequencies appear at *ca.* 1640 (for R = Bu^t) and at *ca.* 1620 cm^{–1} (for R = aryl), respectively, regardless of the central metals, which are lower values than those of the corresponding *Te*-alkyl telluroesters. Such shifts are consistent with the fact that the C–O bond length in these complexes is greater than those in the corresponding *Te*-alkyl telluroesters.¹⁹ The ¹³C NMR spectra show ¹³C=O resonances at δ 213.9 ± 0.2 (for R = Bu^t) and 196.8 ± 1.6 (for R = aryl). The ¹²⁵Te NMR spectra show only a single peak at δ 329–532, which reflects lower field shifts than those of the corresponding alkali metal salts (RCOTe[–] M⁺: M = Li, Na, K, Rb or Cs),^{18–20} but higher field shifts than those of the corresponding *Te*-methyl telluroesters.¹⁹ For the platinum complexes **2** the ¹²⁵Te resonances [with ¹J(PPTe) = 681–812 Hz] show upper field shifts by 33.6 ± 0.3 ppm compared with those of the corresponding palladium complexes **1**. In the ³¹P NMR spectra, the signals of the platinum complexes **2** (δ –1.1–0.0) are shifted to somewhat higher fields than those of the corresponding palladium complexes **1** (δ 5.7–7.1). The coupling

Table 4 Spectroscopic data and structural parameters of [Pt(4-MeC₆H₄COE)₂(PEt₃)₂] (E = S, Se or Te)

	E = S (4)	E = Se (5a) ^d	E = Te (2c)
$\nu(\text{C}=\text{O})/\text{cm}^{-1}$	1609	1619	1621
$\delta_{\text{C}=\text{O}}^b$	197.8	199.6	196.9
δ_{P}^c	12.0	7.6	-0.4
J_{PPt}/Hz	2465	2454	2403
Pt–P/Å	2.310(2)	2.304(2)	2.313(6)
C(7)–O/Å	1.219(7)	1.212(6)	1.23(3)
Pt···O/Å	3.256(6)	3.362(5)	3.50(2)

^a In KBr. ^b In CDCl₃. ^c In CDCl₃, standard H₃PO₄. ^d Ref. 15.

constants [$J(\text{PPt})$] of **2** are *ca.* 2400 Hz, indicating that these complexes are *trans* isomers.³²

In Table 4 the spectroscopic data of the chalcogenocarboxylic acid platinum complexes [Pt(4-MeC₆H₄COE)₂(PEt₃)₂] [E = S (**4**), Se (**5a**) or Te (**2c**)] are shown together with selected structural parameters. The C(7)–O distances suggest C=O double bonds. There are no great differences between $\nu(\text{C}=\text{O})$ and $\delta(\text{C}=\text{O})$ in these complexes. The ³¹P NMR signals which can be observed in the range δ 12.0 to -0.4 show an upfield shift with a change from S to Te. The coupling constants [$J(\text{PPt})$] decrease in this order, but there is no correlation between these values and the Pt–P distances.

Conclusion

The first synthesis and characterization of transition-metal complexes containing tellurocarboxylato ligands, *i.e.* bis(phosphine)bis(tellurocarboxylato)-palladium(II) **1** and -platinum(II) **2**, have been demonstrated. These complexes are obtained in moderate to good yields by treating sodium tellurocarboxylates or *O*-trimethylsilyl telluroesters with [MCl₂(PR')₂] (M = Pd or Pt), or by treating diacyl ditelluride with [Pt(PR')₄]. The obtained tellurocarboxylato complexes are yellow to orange or red crystals, and the platinum complexes **2** are much more thermally- and air-stable than the palladium complexes **1**. In contrast, the corresponding nickel complexes [Ni(RCOTe)₂(PR')₂] **3** appeared to be too labile to isolate. An X-ray diffraction analysis of the platinum complex *trans*-[Pt(4-MeC₆H₄COTe)₂(PEt₃)₂] **2c** revealed that it has a square-planar co-ordination geometry with *trans* tellurocarboxylato ligands which are unidentate. A series of chalcogenocarboxylato complexes [Pt(4-MeC₆H₄COE)₂(PEt₃)₂] [E = S (**4**), Se (**5a**) or Te (**2c**)] crystallized in the same space group and are isostructural.

Experimental

Melting points were determined with a Yanagimoto micromelting point apparatus, and are uncorrected. The IR spectra were recorded on a Perkin-Elmer FT-IR 1640 spectrophotometer, ¹H, ¹³C, ³¹P, ⁷⁷Se and ¹²⁵Te NMR recorded on a JEOL JNM-α400 instrument at 399.7, 100.4, 161.7, 76.2 and 126.0 MHz, respectively; CDCl₃ was employed as a solvent with tetramethylsilane as internal standard; for ¹H NMR, CDCl₃ for ¹³C NMR as internal standard, H₃PO₄ for ³¹P NMR, dimethyl selenide for ⁷⁷Se NMR and dimethyl telluride for ¹²⁵Te NMR as external standard. The UV-VIS spectra were measured on a JASCO U-Best 55 instrument. Elemental analyses were performed by the Elemental Analysis Center of Kyoto University.

Materials

Sodium tellurocarboxylates,¹⁹ sodium and potassium thio-carboxylates,³³ bis(2-methoxybenzoyl) ditelluride²⁶ and diselenide,³⁴ bis(4-methylbenzoyl) disulfide (mp 117–119 °C; lit.,³⁵ 116 °C), tetrakis(triethylphosphine)platinum(0)³⁶ and

dichlorobis(triethylphosphine)-^{37a} and dichlorobis(triphenylphosphine)-nickel(II)^{37b} were synthesized according to the literature. Tetrakis(triphenylphosphine)platinum(0), dichlorobis(triethylphosphine)- and dichlorobis(triphenylphosphine)-palladium(II), and *trans*- and *cis*-dichlorobis(triethylphosphine)- and dichlorobis(triphenylphosphine)-platinum(II) were purchased from Aldrich or Nacalai Tesque. All solvents were dried, distilled and degassed before use. All manipulations were carried out under argon.

Attempted syntheses of nickel(II) complexes 3

trans-[Ni(4-MeC₆H₄COTe)₂(PEt₃)₂] **3c**. *Method A*. To a suspension of sodium 4-methylbenzenecarbotelluroate (0.192 g, 0.712 mmol) in ether (10 cm³), dichlorobis(triethylphosphine)nickel(II) (0.129 g, 0.353 mmol) was added in a 10 cm³ two necked round bottom flask at 0 °C under an argon atmosphere. The mixture was stirred at the same temperature for 1 h. It immediately changed from yellow-brown to black. Filtration of the insoluble parts and removal of the solvent from the filtrate under reduced pressure (18 °C, 0.3 Torr) gave a yellow solid containing black tellurium and a small amount of bis(4-methylbenzoyl) telluride ($\delta_{\text{C}=\text{O}}$ 191.5; δ_{Te} 1039.4). Use of various conditions failed to isolate the desired complex **3c**. The signals attributable to the carbonyl carbon and tellurium are as follows; δ_{C} (100.4 MHz, CDCl₃) 202.2 (C=O); δ_{P} (161.7 MHz, CDCl₃) 9.0; δ_{Te} (126.0 MHz, CDCl₃) 923.2.

trans-[Ni(4-MeC₆H₄COTe)₂(PPh₃)₂] **3c**. *Method A*. To a suspension of sodium 4-methylbenzenecarbotelluroate (0.104 g, 0.386 mmol) in ether (10 cm³), dichlorobis(triphenylphosphine)nickel(II) (0.128 g, 0.196 mmol) was added in a 10 cm³ two necked round bottom flask at 0 °C under an argon atmosphere. The mixture was stirred at the same temperature for 50 min. It immediately changed from brown to dark reddish brown. Filtration of the insoluble parts and removal of the solvent from the filtrate under reduced pressure (32 °C, 0.3 Torr) gave a yellow-brown solid containing a trace amount of bis(4-methylbenzoyl) telluride. Use of various conditions failed to isolate the desired complex **3c**. The signals attributable to the carbonyl carbon and tellurium are as follows; δ_{C} (100.4 MHz, CDCl₃) 199.3 (C=O); δ_{P} (161.7 MHz, CDCl₃) -4.9; δ_{Te} (126.0 MHz, CDCl₃) 924.1.

Syntheses of the palladium(II) complexes 1

trans-[Pd(Bu'COTe)₂(PEt₃)₂] **1a**. *Method A*. To a suspension of sodium 1,1-dimethylethanecarbotelluroate (0.216 g, 0.916 mmol) in ether (12 cm³), dichlorobis(triethylphosphine)palladium(II) (0.188 g, 0.455 mmol) was added in a 10 cm³ two necked round bottom flask at 0 °C under an argon atmosphere. The mixture was stirred at the same temperature for 1 h. It immediately changed from dark green to dark red. Filtration of the insoluble parts (NaCl) and removal of the solvent from the filtrate under reduced pressure (25 °C, 0.3 Torr) gave a reddish brown–orange wet solid of *trans*-bis(1,1-dimethylethanecarbotelluroato)bis(triethylphosphine)-palladium(II) **1a** (0.328 g, yield 94%). Recrystallization from hexane (1 cm³) at -20 °C for 17 h yielded chemically pure **1a** as dark red prisms (0.120 g, 34%), mp 45–52 °C (decomp.) (Found: C, 34.3; H, 6.05. C₂₂H₄₈O₂P₂PdTe₂ requires C, 34.4; H, 6.30%); $\lambda_{\text{max}}/\text{nm}$ (Et₂O) 227 (log ϵ 4.21), 244 (4.38), 247 (4.40), 254 (4.44), 256 (4.44), 341 (4.35) and 447 (3.72); IR/cm⁻¹ 2932, 1770, 1680, 1642 (C=O), 1455, 1412, 1378, 1359, 1249, 1031, 1002, 886, 787, 764, 716, 627 and 591 (Nujol); δ_{H} (399.7 MHz, CDCl₃) 0.99 [18 H, td, $J(\text{HH})$ 7.9, $J(\text{HP})$ 15.8 Hz, 6 PCH₂CH₃], 1.08 [18 H, s, 2 (CH₃)₃C] and 2.22–2.29 (12 H, m, 6 PCH₂CH₃); δ_{C} (100.4 MHz, CDCl₃) 9.4 (PCH₂CH₃), 20.6 [dd, $J(\text{CP})$ + $^3J(\text{CP})$ 30.2 Hz, PCH₂CH₃], 27.8 [(CH₃)₃C], 54.7 [(CH₃)₃C] and 214.1 (C=O); δ_{P} (161.7 MHz, CDCl₃) 5.7; δ_{Te} (126.0 MHz, CDCl₃) 362.1.

trans-[Pd(PhCOTe)₂(PEt₃)₂] 1b. *Method A.* Similarly to the above, to a suspension of sodium benzenecarbotelluroate (0.378 g, 1.48 mmol) in ether (9 cm³), dichlorobis(triethylphosphine)palladium(II) (0.306 g, 0.740 mmol) was added in a 20 cm³ two necked round bottom flask at 0 °C under an argon atmosphere. The mixture was stirred at the same temperature for 1 h. It gradually changed from dark red to orange. Filtration of the precipitates by a glass filter (G4) gave an orange solid (0.592 g) containing sodium chloride. The solid was dissolved in dichloromethane (10 cm³). Filtration of the insoluble parts (NaCl) and removal of the solvent from the filtrate under reduced pressure (23 °C, 0.3 Torr) gave an orange-brown solid (0.447 g). Ether (5 cm³) was added and the mixture stirred at room temperature for 10 min (ether washing). Filtration of the insoluble parts gave *trans*-bis(benzenecarbotelluroato)bis(triethylphosphine)palladium(II) **1b** as orange microfine crystals (0.299 g, 50%). The crystals (0.236 g) was dissolved in dichloromethane-hexane (0.6:1.0, 1.6 cm³); and the dark red solution was allowed to stand at -20 °C for 20 min. Filtration of the resulting precipitates yielded chemically pure **1b** as red prisms (0.127 g, 27%), mp 59–63 °C (decomp.) (Found: C, 38.4; H, 4.9. C₂₂H₄₈O₂P₂PdTe₂ requires C, 38.6; H, 5.0%); IR/cm⁻¹ 3448, 2956, 2362, 2344, 1719, 1654, 1624(C=O), 1577, 1560, 1458, 1444, 1414, 1376, 1299, 1248, 1196, 1161, 1070, 1032, 857, 760, 716, 685, 662, 616 and 597 (KBr); δ_H(399.7 MHz, CDCl₃) 1.08 [18 H, td, *J*(HH) 8.2, *J*(HP) 16.0, 6 PCH₂CH₃], 2.30–2.37 (12 H, m, 6 PCH₂CH₃), 7.37 [4 H, t, *J*(HH) 7.8, *m*-H], 7.51 [2 H, t, *J*(HH) 7.8, *p*-H] and 7.96 [4 H, d, *J*(HH) 7.8 Hz, *o*-H]; δ_C(100.4 MHz, CDCl₃) 9.5 (PCH₂CH₃), 20.6 [dd, ¹*J*(CP) + ³*J*(CP) 30.2 Hz, PCH₂CH₃], 127.5, 128.2, 132.1, 146.4 (aryl) and 198.3 (C=O); δ_P(161.7 MHz, CDCl₃) 6.9; δ_{Te}(126.0 MHz, CDCl₃) 438.2.

trans-[Pd(4-MeC₆H₄COTe)₂(PEt₃)₂] 1c. *Method A.* Similarly to complex **1b**, reaction of 4-MeC₆H₄COTeNa and [PdCl₂(PEt₃)₂] gave **1c** as orange microfine crystals (54%). The crystals (0.124 g) were dissolved in dichloromethane (1.7 cm³) and the dark red solution was allowed to stand at -20 °C for 19 h. Filtration of the resulting precipitates yielded chemically pure **1c** as dark red prisms (0.037 g, 16%), mp 102–105 °C (decomp.) (Found: C, 40.05; H, 5.25. C₂₈H₄₄O₂P₂PdTe₂ requires C, 40.22; H, 5.30%); IR/cm⁻¹ 2960, 1654, 1648, 1618 (C=O), 1560, 1543, 1508, 1459, 1196, 1159, 1030, 864, 821, 777, 716 and 609 (KBr); δ_H(399.7 MHz, CDCl₃) 1.07 [18 H, td, *J*(HH) 8.1, *J*(HP) 16.0, 6 PCH₂CH₃], 2.29–2.36 (12 H, m, 6 PCH₂CH₃), 2.33 (6 H, s, 2 CH₃-C₆H₄), 7.16 [4 H, d, *J*(HH) 8.1, aryl] and 7.87 [4 H, d, *J*(HH) 8.1 Hz, aryl]; δ_C(100.4 MHz, CDCl₃) 9.4 (PCH₂CH₃), 20.6 [dd, ¹*J*(CP) + ³*J*(CP) 29.3 Hz, PCH₂CH₃], 21.6 (CH₃C₆H₄), 127.7, 128.8, 142.7, 144.0 (aryl) and 197.5 (C=O); δ_P(161.7 MHz, CDCl₃) 6.7; δ_{Te}(126.0 MHz, CDCl₃) 426.2.

trans-[Pd(4-MeOC₆H₄COTe)₂(PEt₃)₂] 1e. *Method A.* Similarly to complex **1b**, reaction of 4-MeOC₆H₄COTeNa and [PdCl₂(PEt₃)₂] gave **1e** as brown-orange microfine crystals (72%). The solid (0.201 g) was dissolved in dichloromethane (1.2 cm³) and the dark red solution was allowed to stand at -20 °C for 11 h. Filtration of the resulting precipitates yielded chemically pure **1e** as orange microcrystals (0.068 g, 27%), mp 82–83 °C (decomp.) (Found: C, 38.7; H, 5.05. C₂₈H₄₄O₂P₂PdTe₂ requires C, 38.7; H, 5.11%); IR/cm⁻¹ 3448, 2960, 2367, 2346, 1654, 1648, 1617 (C=O), 1596, 1572, 1560, 1543, 1500, 1458, 1414, 1307, 1263, 1200, 1182, 1155, 1028, 864, 837, 762, 717, 644 and 612 (KBr); δ_H(399.7 MHz, CDCl₃) 1.06 [18 H, td, *J*(HH) 7.8, *J*(HP) 15.6, 6 PCH₂CH₃], 2.30–2.36 (12 H, m, 6 PCH₂CH₃), 3.84 (6 H, s, CH₃O), 6.86 [4H, d, *J*(HH) 8.9, aryl] and 7.97 [4H, d, *J*(HH) 8.9 Hz, aryl]; δ_C(100.4 MHz, CDCl₃) 9.4 (PCH₂CH₃), 20.6 [dd, ¹*J*(CP) + ³*J*(CP) 30.2 Hz, PCH₂CH₃], 55.5 (CH₃O), 113.2, 129.9, 139.4, 162.9 (aryl) and 195.7 (C=O); δ_P(161.7 MHz, CDCl₃) 6.4; δ_{Te}(126.0 MHz, CDCl₃) 407.1.

trans-[Pd(4-ClC₆H₄COTe)₂(PEt₃)₂] 1f. *Method A.* Similarly to complex **1b**, reaction of 4-ClC₆H₄COTeNa and [PdCl₂(PEt₃)₂] gave **1f** as orange microfine crystals (65%). The solid (0.280 g) was dissolved in dichloromethane (6 cm³) and the insoluble parts were filtered off by a glass filter (G4). The dark red filtrate was allowed to stand at -20 °C for 16 h. Filtration of the resulting precipitates yielded chemically pure **1f** as orange needles and prisms (0.108 g, 25%), mp 98–104 °C (decomp.) (Found: C, 35.6; H, 4.4. C₂₆H₃₈Cl₂O₂P₂PdTe₂ requires C, 35.6; H, 4.4%); IR/cm⁻¹ 2956, 1616 (C=O), 1566, 1456, 1413, 1377, 1186, 1154, 1082, 1033, 1008, 860, 830, 761, 716, 629, 587, 547 and 462 (KBr); δ_H(399.7 MHz, CDCl₃) 1.07 [18 H, td, *J*(HH) 8.2, *J*(HP) 15.9, 6 PCH₂CH₃], 2.28–2.35 (12 H, m, 6 PCH₂CH₃), 7.34 [4 H, d, *J*(HH) 8.5, aryl] and 7.91 [4 H, t, *J*(HH) 8.5 Hz, aryl]; δ_C(100.4 MHz, CDCl₃) 9.4 (PCH₂CH₃), 20.6 [dd, ¹*J*(CP) + ³*J*(CP) 30.2 Hz, PCH₂CH₃], 128.3, 128.8, 138.5, 144.7 (aryl) and 196.5 (C=O); δ_P(161.7 MHz, CDCl₃) 7.1; δ_{Te}(126.0 MHz, CDCl₃) 443.8.

Syntheses of the platinum(II) complexes 2

trans-[Pt(Bu'COTe)₂(PEt₃)₂] 2a. *Method A.* To a suspension of sodium 1,1-dimethylethanecarbotelluroate (0.209 g, 0.887 mmol) in dichloromethane (9 cm³), *trans*-dichlorobis(triethylphosphine)platinum(II) (0.222 g, 0.442 mmol) was added in a 10 cm³ two necked round bottom flask at 0 °C under an argon atmosphere. The mixture was stirred at the same temperature for 1 h. It gradually changed from dark green to dark green-brown. Filtration of the insoluble parts (NaCl) and removal of the solvent from the filtrate under reduced pressure (22 °C, 0.3 Torr) gave a yellow solid (0.301 g, yield 79%) of crude *trans*-bis(1,1-dimethylethanecarbotelluroato)bis(triethylphosphine)platinum(II) **2a**. Recrystallization from ether (0.7 cm³) at -20 °C for 17 h yielded chemically pure **2a** as yellow prisms (0.174 g, 46%), mp 62–68 °C (decomp.) (Found: C, 30.55; H, 5.51. C₂₂H₄₈O₂P₂PtTe₂ requires C, 30.84; H, 5.65%); λ_{max}/nm (Et₂O) 259 (log ε 4.42) and 261 (4.42); IR/cm⁻¹ 2966, 1770, 1678, 1635 (C=O), 1472, 1453, 1410, 1385, 1358, 1253, 1231, 1033, 885, 786, 763, 722, 632 and 589 (Nujol); δ_H(399.7 MHz, CDCl₃) 0.99 [18 H, td, *J*(HH) 8.0, *J*(HP) 15.9, 6 PCH₂CH₃], 1.08 [18 H, s, 2 (CH₃)₂C] and 2.23–2.36 (12 H, m, 6 PCH₂CH₃); δ_C(100.4 MHz, CDCl₃) 9.2 [satellite ³*J*(Cpt) 22.4, PCH₂CH₃], 19.0 [dd, ¹*J*(CP) + ³*J*(CP) 37.1, satellite ²*J*(Cpt) 31.2, PCH₂CH₃], 27.7 [(CH₃)₂C], 54.3 [(CH₃)₂C] and 213.7 [satellite ²*J*(Cpt) 22.4 Hz, C=O]; δ_P(161.7 MHz, CDCl₃) -1.1 [¹*J*(PPt) 2435 Hz]; δ_{Te}(126.0 MHz, CDCl₃) 329.4 [¹*J*(TePt) 681 Hz].

trans-[Pt(PhCOTe)₂(PEt₃)₂] 2b. *Method A.* Similarly to complex **2a**, to a suspension of sodium benzenecarbotelluroate (0.215 g, 0.849 mmol) in dichloromethane (15 cm³), *trans*-dichlorobis(triethylphosphine)platinum(II) (0.209 g, 0.416 mmol) was added in a 20 cm³ two necked round bottom flask at 0 °C under an argon atmosphere. The mixture was stirred at the same temperature for 1 h. It rapidly changed from pale yellow to dark orange with precipitation of a yellow-brown solid. The precipitates were filtered off by a glass filter (G4). Removal of the solvent from the filtrate under reduced pressure (24 °C, 0.3 Torr) gave a yellow-brown solid (0.211 g). Ether (5 cm³) was added and the mixture stirred at room temperature for 15 min (ether washing). Filtration of the insoluble parts gave *trans*-bis(benzenecarbotelluroato)bis(triethylphosphine)platinum(II) **2b** as yellow microfine crystals (0.239 g, 64%), mp 77–80 °C (decomp.); IR/cm⁻¹ 2960, 1627 (C=O), 1560, 1542, 1508, 1459, 1195, 1162, 1033, 858, 760, 720, 685 and 662 (KBr); δ_H(399.7 MHz, CDCl₃) 1.09 [18 H, td, *J*(HH) 8.1, *J*(HP) 15.7, 6 PCH₂CH₃], 2.32–2.45 (12 H, m, 6 PCH₂CH₃), 7.37 [4 H, t, *J*(HH) 7.7, *m*-H], 7.51 [2 H, t, *J*(HH) 7.7, *p*-H] and 7.96 [4 H, d, *J*(HH) 7.7 Hz, *o*-H]; δ_C(100.4 MHz, CDCl₃) 9.2 [satellite ³*J*(Cpt) 21.5, PCH₂CH₃], 19.1 [dd, ¹*J*(CP) + ³*J*(CP)

36.1, $^2J(\text{CPt})$ 32.2, PCH_2CH_3], 127.3 [satellite $^3J(\text{CPt})$ 11.7, aryl], 128.2, 132.1, 146.0 (aryl) and 197.7 [satellite $^2J(\text{CPt})$ 25.4 Hz, C=O]; $\delta_{\text{p}}(161.7 \text{ MHz, CDCl}_3)$ -0.3 [satellite $^1J(\text{PPt})$ 2397 Hz]; $\delta_{\text{Te}}(126.0 \text{ MHz, CDCl}_3)$ 404.9 [satellite $^1J(\text{TePt})$ 711 Hz].

trans-[Pt(4-MeC₆H₄COTe)₂(PEt₃)₂] 2c. *Method A.* Similarly to complex **2b**, reaction of 4-MeC₆H₄COTeNa and *trans*-[PtCl₂(PEt₃)₂] gave **2c** as yellow microfine crystals (74%). The solid (0.182 g) was dissolved in dichloromethane (2 cm³) and the dark brown solution was allowed to stand at -20°C for 12 h. Filtration of the resulting precipitates yielded chemically pure **2c** as orange prisms (0.093 g, 38%), mp 118–120 °C (decomp.) (Found: C, 36.1; H, 4.75. C₂₈H₄₄O₂P₂PtTe₂ requires C, 36.4; H, 4.79%); $\lambda_{\text{max}}/\text{nm}$ (Et₂O) 224 (log ϵ 4.26), 259 (4.48), 261 (4.48) and 378 (3.64); IR/cm⁻¹ 2961, 1648, 1621 (C=O), 1597, 1560, 1458, 1412, 1376, 1196, 1160, 1033, 864, 820, 778, 720, 609, 594 and 464 (KBr); $\delta_{\text{H}}(399.7 \text{ MHz, CDCl}_3)$ 1.08 [18 H, td, $J(\text{HH})$ 7.6, $J(\text{HP})$ 15.8, 6 PCH₂CH₃], 2.32 (6 H, s, 2 CH₃-C₆H₄), 2.34–2.41 (12 H, m, 6 PCH₂CH₃), 7.16 [4 H, d, $J(\text{HH})$ 7.9, aryl] and 7.87 [4 H, d, $J(\text{HH})$ 7.9 Hz, aryl]; $\delta_{\text{C}}(100.4 \text{ MHz, CDCl}_3)$ 9.2 [satellite $^3J(\text{CPt})$ 21.5, PCH₂CH₃], 19.1 [dd, $^1J(\text{CP}) + ^3J(\text{CP})$ 36.1 satellite $^2J(\text{CPt})$ 32.2, PCH₂CH₃], 21.6 (CH₃-C₆H₄), 127.5 [satellite $^3J(\text{CPt})$ 12.7, aryl], 128.9, 142.7, 143.6 (aryl) and 196.9 [satellite $^2J(\text{CPt})$ 26.3 Hz, C=O]; $\delta_{\text{p}}(161.7 \text{ MHz, CDCl}_3)$ -0.4 [satellite $^1J(\text{PPt})$ 2403 Hz]; $\delta_{\text{Te}}(126.0 \text{ MHz, CDCl}_3)$ 392.6 [satellite $^1J(\text{TePt})$ 717 Hz].

Similarly, the reaction of sodium salt 4-MeC₆H₄COTeNa and *cis*-[PtCl₂(PEt₃)₂] gave complex **2c** as yellow microfine crystals (66%). The IR and NMR spectra were consistent with *trans*-**2c**.

Method B. To a suspension of sodium 4-methylbenzenecarbotelluroate (0.091 g, 0.337 mmol) in ether (5 cm³), trimethylsilyl chloride (1 cm³, 8 mmol) was added at 0 °C followed by stirring at the same temperature for 10 min. The mixture changed from dark brown to dark green, indicating the formation of *O*-trimethylsilyl 4-methylbenzenecarbotelluroate. Filtration of the precipitates (black tellurium and sodium chloride) gave a deep green solution of the latter. *cis*-Dichlorobis(triethylphosphine)platinum(II) (0.044 g, 0.088 mmol) was added and stirred at 0 °C for 1 h. The solution gradually changed from deep green to yellow with precipitation of a yellow solid. Filtration of the insoluble parts gave *trans*-bis(4-methylbenzenecarbotelluroato)bis(triethylphosphine)platinum(II) **2c** as a yellow microfine solid (0.041 g, 51%). The IR and NMR spectra were consistent with *trans*-**2c**.

trans-[Pt(2-MeOC₆H₄COTe)₂(PEt₃)₂] 2d. *Method A.* Similarly to complex **2b**, reaction of 2-MeOC₆H₄COTeNa and *trans*-[PtCl₂(PEt₃)₂] gave **2d** as yellow microfine crystals (56%). The solid (0.133 g) was dissolved in dichloromethane (4 cm³) and the dark reddish brown solution was allowed to stand at -20°C for 17 h. Filtration of the resulting precipitates yielded chemically pure **2d** as yellow prisms (0.069 g, 29%), mp 105–107 °C (decomp.) (Found: C, 34.85; H, 4.6. C₂₈H₄₄O₄P₂PtTe₂ requires C, 35.15; H, 4.6%); IR/cm⁻¹ 2960, 1646, 1623 (C=O), 1592, 1572, 1560, 1480, 1458, 1433, 1406, 1376, 1278, 1245, 1186, 1164, 1118, 1035, 870, 855, 768, 718, 653, 603 and 544 (KBr); $\delta_{\text{H}}(399.7 \text{ MHz, CDCl}_3)$ 1.13 [18 H, td, $J(\text{HH})$ 8.1, $J(\text{HP})$ 15.8, 6 PCH₂CH₃], 2.42–2.49 (12 H, m, 6 PCH₂CH₃), 3.84 (6 H, s, CH₃O), 6.86 [2 H, d, $J(\text{HH})$ 7.7, aryl], 6.95 [2 H, t, $J(\text{HH})$ 7.7, aryl], 7.34 [2 H, t, $J(\text{HH})$ 7.7, aryl] and 7.62 [2 H, d, $J(\text{HH})$ 7.7 Hz, aryl]; $\delta_{\text{C}}(100.4 \text{ MHz, CDCl}_3)$ 9.3 [satellite $^3J(\text{CPt})$ 22.3, PCH₂CH₃], 19.0 [dd, $^1J(\text{CP}) + ^3J(\text{CP})$ 36.4, satellite $^2J(\text{CPt})$ 31.4 Hz, PCH₂CH₃], 55.7 (CH₃O), 111.8, 119.7, 127.7, 131.2, 137.9, 153.1 (aryl), 196.0 [satellite $^2J(\text{CPt})$ 26.5 Hz, C=O]; $\delta_{\text{p}}(161.7 \text{ MHz, CDCl}_3)$ 0.0 [satellite $^1J(\text{PPt})$ 2415 Hz]; $\delta_{\text{Te}}(126.0 \text{ MHz, CDCl}_3)$ 532.2 [satellite $^1J(\text{TePt})$ 812 Hz].

Method C. To a solution of tetrakis(triethylphosphine)platinum(0) (0.105 g, 0.157 mmol) in benzene (1 cm³), a benzene

(10 cm³) solution of bis(2-methoxybenzoyl) ditelluride (0.087 g, 0.166 mmol) was added in a 20 cm³ two necked round bottom flask at 0 °C under an argon atmosphere. The mixture was stirred at room temperature for 1 h. Removal of the solvent under reduced pressure (20 °C, 0.3 Torr) gave a yellow solid (0.195 g). Dichloromethane (0.5 cm³) and hexane (6 cm³) was added and the mixture stirred at room temperature for 15 min. Filtration of the insoluble parts gave 0.061 g (41%) of *trans*-bis(2-methoxybenzenecarbotelluroato)bis(triethylphosphine)platinum(II) **2d** as yellow microfine crystals. The IR and NMR spectra were consistent with *trans*-**2d**.

trans-[Pt(2-MeOC₆H₄COTe)₂(PPh₃)₂] 2'd. *Method A.* To a suspension of sodium 2-methoxybenzenecarbotelluroate (0.294 g, 1.03 mmol) in dichloromethane (7 cm³), *cis*-dichlorobis(triphenylphosphine)platinum(II) (0.285 g, 0.361 mmol) was added in a 20 cm³ two necked round bottom flask at 0 °C under an argon atmosphere. The mixture was stirred at the same temperature for 1 h. It gradually changed to reddish brown with precipitation of a yellow solid. Filtration of the insoluble parts and washing with water gave *trans*-bis(2-methoxybenzenecarbotelluroato)bis(triphenylphosphine)platinum(II) **2'd** as yellow microfine crystals (0.166 g, 37%), mp 175–178 °C (decomp.); IR/cm⁻¹ 3044, 2835, 1654 (C=O), 1636, 1591, 1480, 1433, 1279, 1170, 1095, 1029, 864, 776, 754, 746, 703, 692, 652, 604, 523, 512 and 500 (KBr).

Method C. To a solution of tetrakis(triphenylphosphine)platinum(0) (0.079 g, 0.063 mmol) in benzene (3 cm³), a benzene (9 cm³) solution of bis(2-methoxybenzoyl) ditelluride (0.033 g, 0.063 mmol) was added in a 20 cm³ two necked round bottom flask at 0 °C under an argon atmosphere. The mixture was stirred at room temperature for 1 h. A yellow solid was gradually deposited. Filtration of the insoluble parts and washing with benzene, dichloromethane and ether gave *trans*-bis(2-methoxybenzenecarbotelluroato)bis(triphenylphosphine)platinum(II) **2'd** as yellow microfine crystals (0.055 g, 70%). The IR spectrum was consistent with that of an authentic sample prepared from sodium 2-methoxybenzenecarbotelluroate with [PtCl₂(PPh₃)₂] (Method A).

trans-[Pt(4-MeOC₆H₄COTe)₂(PEt₃)₂] 2e. *Method A.* Similarly to complex **2b**, reaction of 4-MeOC₆H₄COTeNa and *trans*-[PtCl₂(PEt₃)₂] gave **2e** as yellow microfine crystals (66%). The solid (0.200 g) was dissolved in dichloromethane (1.5 cm³) and the dark reddish brown solution allowed to stand at -20°C for 16 h. Filtration of the resulting precipitates yielded chemically pure **2e** as yellow prisms (0.018 g, 6%), mp 104–106 °C (decomp.) (Found: C, 35.29; H, 4.7. C₂₈H₄₄O₄P₂PtTe₂ requires C, 35.15; H, 4.6%); $\lambda_{\text{max}}/\text{nm}$ (CH₂Cl₂) 226, 229, 233, 236, 275 and 373; IR/cm⁻¹ 2970, 2872, 1646, 1616 (C=O), 1596, 1572, 1500, 1458, 1416, 1378, 1263, 1200, 1183, 1157, 1112, 1025, 867, 837, 763, 722, 643, 612 and 592 (KBr); $\delta_{\text{H}}(399.7 \text{ MHz, CDCl}_3)$ 1.08 [18 H, td, $J(\text{HH})$ 8.2, $J(\text{HP})$ 15.9, 6 PCH₂CH₃], 2.34–2.42 (12 H, m, 6 PCH₂CH₃), 3.84 (6 H, s, CH₃O), 6.86 [4 H, d, $J(\text{HH})$ 8.9, aryl] and 7.97 [4 H, d, $J(\text{HH})$ 8.9 Hz, aryl]; $\delta_{\text{C}}(100.4 \text{ MHz, CDCl}_3)$ 9.2 [satellite $^3J(\text{CPt})$ 21.5, PCH₂CH₃], 20.6 [dd, $^1J(\text{CP}) + ^3J(\text{CP})$ 37.1, satellite $^2J(\text{CPt})$ 31.2, PCH₂CH₃], 55.5 (CH₃O), 113.3, 129.8 [satellite $^3J(\text{CPt})$ 13.2, aryl], 139.0, 163.0 (aryl) and 195.2 [satellite $^2J(\text{CPt})$ 24.8 Hz, C=O]; $\delta_{\text{p}}(161.7 \text{ MHz, CDCl}_3)$ -0.8 [satellite $^1J(\text{PPt})$ 2406 Hz]; $\delta_{\text{Te}}(126.0 \text{ MHz, CDCl}_3)$ 373.2 [satellite $^1J(\text{TePt})$ 711 Hz].

Similarly, the reaction of 4-MeOC₆H₄COTeNa and *cis*-[PtCl₂(PEt₃)₂] gave complex **2e** as yellow microfine crystals (42%). The IR and NMR spectra were consistent with *trans*-**2e**.

trans-[Pt(4-ClC₆H₄COTe)₂(PEt₃)₂] 2f. *Method A.* Similarly to complex **2b**, reaction of 4-ClC₆H₄COTeNa and *trans*-[PtCl₂(PEt₃)₂] gave **2f** as orange microfine crystals (48%). The

solid (0.214 g) was dissolved in dichloromethane (7 cm³) and the insoluble parts were filtered off by the use of a glass filter (G4). The dark red filtrate was allowed to stand at -20 °C for 16 h. Filtration of the resulting precipitates yielded chemically pure **2f** as orange needles and prisms (0.116 g, 26%), mp 115–117 °C (decomp.) (Found: C, 32.15; H, 3.8. C₂₆H₃₈Cl₂O₂P₂PtTe₂ requires C, 32.34; H, 4.0%); IR/cm⁻¹ 2924, 1619 (C=O), 1567, 1456, 1186, 1154, 1082, 1034, 1008, 859, 830, 765, 721, 631, 585, 547 and 460 (KBr); δ_H(399.7 MHz, CDCl₃) 1.08 [18 H, td, *J*(HH) 8.2, *J*(HP) 16.0, 6 PCH₂CH₃], 2.32–2.41 (12 H, m, 6 PCH₂CH₃), 7.34 [4 H, d, *J*(HH) 8.4, aryl] and 7.90 [4 H, d, *J*(HH) 8.4 Hz, aryl]; δ_C(100.4 MHz, CDCl₃) 9.2 [satellite ³*J*(CPT) 21.5, PCH₂CH₃], 19.1 [dd, ¹*J*(CP) + ³*J*(CP) 37.1, satellite ²*J*(CPT) 31.2, PCH₂CH₃], 128.4, 128.6 [satellite ³*J*(CPT) 12.7, aryl], 138.5, 144.3 (aryl) and 195.9 [satellite ²*J*(CPT) 27.3 Hz, C=O]; δ_p(161.7 MHz, CDCl₃) -0.3 [satellite ¹*J*(PPt) 2385 Hz]; δ_{Te}(126.0 MHz, CDCl₃) 410.3 [satellite ¹*J*(TePt) 696 Hz].

Similarly, the reaction of 4-ClC₆H₄COTeNa and *cis*-[PtCl₂(PEt₃)₂] gave complex **2f** as yellow microfine crystals (40%). The IR and NMR spectra were consistent with *trans*-**2f**.

Syntheses of the thio- and seleno-carboxylatoplatinum(II) complexes **4** and **5**

trans-[Pt(4-MeC₆H₄COS)₂(PEt₃)₂] **4**. *Method A*. To a suspension of sodium 4-methylbenzenecarbothioate (0.047 g, 0.272 mmol) in dichloromethane (5 cm³), *trans*-dichlorobis(triethylphosphine)platinum(II) (0.068 g, 0.136 mmol) was added in a 20 cm³ two necked round bottom flask under an argon atmosphere. The mixture was stirred at room temperature for 20 h. The precipitates were filtered off by a glass filter (G4). Removal of the solvent from the filtrate under reduced pressure (24 °C, 0.3 Torr) gave a pale yellow solid. Ether (5 cm³) was added and the mixture stirred at room temperature for 5 min (ether washing). Filtration of the insoluble parts gave *trans*-bis(4-methylbenzenecarbothioato)bis(triethylphosphine)platinum(II) **4** as colorless microfine crystals (0.065 g, 65%).

Method B. To a suspension of potassium 4-methylbenzenecarbothioate (1.00 g, 5.28 mmol) in ether (12 cm³), trimethylsilyl chloride (3 cm³, 24 mmol) was added at room temperature followed by stirring at the same temperature for 5 h. The solution changed from pale yellow to yellow. Filtration of the precipitates (potassium chloride) and removal of the solvent from the filtrate under reduced pressure (27 °C, 0.3 Torr) gave 1.15 g (5.14 mmol, 97%) of *O*-trimethylsilyl 4-methylbenzenecarbothioate as a yellow liquid. *trans*-Dichlorobis(triethylphosphine)platinum(II) (0.398 g, 0.792 mmol) was added to a solution of the silyl ester (1.15 g, 5.14 mmol) in ether (15 cm³) at room temperature (27 °C). A mixture was stirred at the same temperature for 20 h. (No change was observed for 4 h.) A white solid was gradually deposited. Filtration of the insoluble parts (removal of the solvent, excess of silyl ester and by-product, trimethylsilyl chloride) and washing by ether (1 cm³ × 3) gave *trans*-bis(4-methylbenzenecarbothioato)bis(triethylphosphine)platinum(II) **4** as a colorless microfine solid (0.548 g, 94%).

Method C. To a solution of tetrakis(triethylphosphine)platinum(0) (0.126 g, 0.189 mmol) in benzene (1 cm³), a benzene (4 cm³) solution of bis(4-methylbenzoyl) disulfide (0.057 g, 0.188 mmol) was added in a 20 cm³ two necked round bottom flask under an argon atmosphere. The mixture was stirred at room temperature for 2 h. Removal of the solvent under reduced pressure (20 °C, 0.3 Torr) gave a pale yellow solid. Ether (2 cm³) and hexane (4 cm³) were added and the mixture was stirred at room temperature for 5 min. Filtration of the insoluble parts gave *trans*-bis(4-methylbenzenecarbothioato)bis(triethylphosphine)platinum(II) **4** as colorless microfine crystals (0.101 g, 73%), mp 250–255 °C (decomp.) (Found: C, 45.6; H, 5.95. C₂₈H₄₄O₂P₂PtS₂ requires C, 45.8; H, 6.04%); IR/cm⁻¹ 2965, 1609 (C=O), 1570, 1449, 1413, 1376, 1292, 1252, 1216, 1201,

1170, 1112, 1036, 915, 828, 791, 765, 729, 651, 640, 631, 530 and 475 (KBr); δ_H(399.7 MHz, CDCl₃) 1.15 [18 H, td, *J*(HH) 7.9, *J*(HP) 15.9, 6 PCH₂CH₃], 1.96–2.03 (12 H, m, 6 PCH₂CH₃), 2.38 (6 H, s, 2 CH₃C₆H₄), 7.18 [4 H, d, *J*(HH) 8.2, aryl] and 7.99 [4 H, d, *J*(HH) 8.2 Hz, aryl]; δ_C(100.4 MHz, CDCl₃) 8.1 [satellite ³*J*(CPT) 19.5, PCH₂CH₃], 13.6 [dd, ¹*J*(CP) + ³*J*(CP) 34.1, satellite ²*J*(CPT) 28.3, PCH₂CH₃], 21.5 (CH₃C₆H₄), 127.9, 128.6, 139.3 [satellite ³*J*(CPT) 19.5, aryl], 141.5 (aryl), 197.8 [satellite ²*J*(CPT) 26.3 Hz, C=O]; δ_p(161.7 MHz, CDCl₃) 12.0 [satellite ¹*J*(PPt) 2465 Hz].

trans-[Pt(2-MeOC₆H₄COSe)₂(PEt₃)₂] **5b**. *Method C*. To a solution of tetrakis(triethylphosphine)platinum(0) (0.195 g, 0.292 mmol) in benzene (1 cm³), a benzene (5 cm³) solution of bis(2-methoxybenzoyl) diselenide (0.125 g, 0.292 mmol) was added in a 20 cm³ two necked round bottom flask at 0 °C under an argon atmosphere. After stirring at room temperature for 1 h, the mixture was concentrated to a quarter of the original volume under reduced pressure (20 °C, 0.3 Torr). Hexane (6 cm³) was added to the concentrate and the mixture stirred at room temperature for 15 min. Filtration of the insoluble parts and hexane washing gave *trans*-bis(2-methoxybenzenecarbo-selenoato)bis(triethylphosphine)platinum(II) **5b** as pale yellow microfine crystals (0.178 g, 71%), mp 198–210 °C (decomp.) (Found: C, 38.9; H, 4.95. C₂₈H₄₄O₄P₂PtSe₂ requires C, 39.1; H, 5.16%); IR/cm⁻¹ 2962, 1642 (C=O), 1592, 1484, 1458, 1278, 1243, 1189, 1117, 1037, 1022, 882, 854, 766, 726 and 656 (KBr); δ_H(399.7 MHz, CDCl₃) 1.17 [18 H, td, *J*(HH) 8.1, *J*(HP) 15.9, 6 PCH₂CH₃], 2.19–2.26 (12 H, m, 6 PCH₂CH₃), 3.82 (6 H, s, CH₃O), 6.87 [2 H, d, *J*(HH) 7.7, aryl], 6.93 [2 H, t, *J*(HH) 7.7, aryl], 7.31 [2 H, t, *J*(HH) 7.7, aryl] and 7.57 [2 H, d, *J*(HH) 7.7 Hz, aryl]; δ_C(100.4 MHz, CDCl₃) 8.6 [satellite ³*J*(CPT) 20.7, PCH₂CH₃], 15.0 [dd, ¹*J*(CP) + ³*J*(CP) 34.7, satellite ²*J*(CPT) 29.0, PCH₂CH₃], 55.8 (CH₃O), 111.7, 119.8, 127.9, 130.6, 135.5, 154.2 (aryl) and 200.2 [satellite ²*J*(CPT) 29.8 Hz, C=O]; δ_p(161.7 MHz, CDCl₃) 7.3 [satellite ¹*J*(PPt) 2453 Hz]; δ_{Se}(76.2 MHz, CDCl₃) 417.0 [satellite ¹*J*(SePt) 61.0 Hz].

Crystallography

The measurements were carried out on a Rigaku AFC7R four-circle diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å). A Rigaku XR-TCS-2-050 temperature controller was used for low temperature measurement. The crystals of complexes **2c** and **4** were cut from the grown needles and were mounted on glass fibers. Since the sample of **2c** was somewhat unstable in air, it was coated with an epoxy resin. The cell dimensions were determined from a least-squares refinement of the setting diffractometer angles for 25 automatically centered reflections. Three standard reflections were measured every 150 and showed no significant intensity variations during the data collection. The structures were solved and refined using the TEXSAN³⁸ crystallographic software package on an IRIS Indigo computer. Scattering factors for neutral atoms were from Cromer and Waber³⁹ and anomalous dispersion⁴⁰ was used. The structures were solved by direct methods using SHELXS 86⁴¹ and expanded using DIRDIF 94.⁴² Lorentz-polarization corrections were applied to the data, and empirical absorption corrections [DIFABS⁴³ (**2c**), ψ scans⁴⁴(**4**)] were also applied. A full-matrix least-squares refinement was executed with non-hydrogen atoms being anisotropic. The final least-squares cycle included fixed hydrogen atoms at calculated positions of which each isotropic thermal parameter was set to 1.2 times of that of the connecting atom. The crystal data and data collection parameters are summarized in Table 5.

CCDC reference number 186/1386.

See <http://www.rsc.org/suppdata/dt/1999/1677/> for crystallographic files in .cif format.

Table 5 Crystal data, data collection and refinement parameters for complexes **2c** and **4**

	2c	4
Chemical formula	C ₂₈ H ₄₄ O ₂ P ₂ PtTe ₂	C ₂₈ H ₄₄ O ₂ P ₂ PtS ₂
Formula weight	924.89	733.81
Color	Orange	Colorless
Crystal system	Monoclinic	Monoclinic
Space group	<i>P2₁/c</i>	<i>P2₁/c</i>
<i>a</i> /Å	9.216(6)	9.523(1)
<i>b</i> /Å	12.072(4)	11.902(1)
<i>c</i> /Å	14.533(3)	14.5038(8)
β /°	96.57(3)	102.347(5)
<i>U</i> /Å ³	1606.3(9)	1605.9(2)
<i>T</i> /°C	−80.0	23.0
<i>Z</i>	2	2
<i>D_c</i> /g cm ^{−3}	1.912	1.517
Crystal size/mm	0.09 × 0.09 × 0.11	0.34 × 0.31 × 0.20
μ (Mo-K α)/cm ^{−1}	62.52	46.03
Transmission factors	0.57–1.00	0.61–0.99
No. measured reflections	4114	4101
No. unique reflections	3882	3877
<i>R</i> _{int}	0.116	0.022
No. observations [<i>I</i> > 3 σ (<i>I</i>)]	1428	2235
No. variables	160	161
Residuals: <i>R</i> , <i>R</i> '	0.054, 0.051	0.031, 0.041
Max. and min. residual electron density/e Å ^{−3}	1.06, −1.17	0.66, −0.92
Goodness of fit	1.24	1.33

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