

# Preparation of bis(phosphine)bis(selenocarboxylato)-nickel(II), -palladium(II) and -platinum(II) complexes and their crystal structure analysis

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A series of bis(triorganophosphine)bis(selenocarboxylato)-nickel(II) **3**, -palladium(II) **4** and -platinum(II) **5** complexes have been synthesised from the reaction of sodium selenocarboxylates **1** or *O*-silyl selenocarboxylates **2** with the corresponding bis(phosphine)metal dichloride in good to high yields and have been characterized by <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P and <sup>77</sup>Se NMR spectroscopy and elemental analysis. Additionally [M(4-MeC<sub>6</sub>H<sub>4</sub>COSe)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] (M = Ni **3d**, Pd **4d** or Pt **5b**) have been crystallographically characterized and reveal four-co-ordinate planar structures with each of the two selenocarboxylate and phosphine ligands lying *trans*. The carbon–oxygen bond lengths [1.209(6), 1.203(8) and 1.212(6) Å] of the selenocarboxylate ligand of **3d**, **4d** and **5d** show values typical of a carbon–oxygen double bond; co-ordination of the carbonyl oxygen to the metal is not observed.

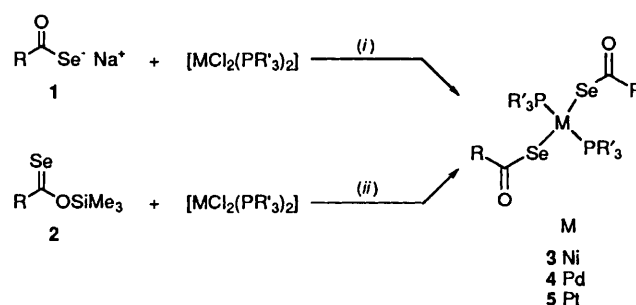
A number of carboxylic<sup>1</sup> and dithiocarboxylic acid transition-metal complexes<sup>2</sup> have been synthesised, and their structures and properties have been revealed. In contrast, there have been relatively few investigations concerning thiocarboxylic acid transition-metal complexes, especially their structures.<sup>3</sup> Selenocarboxylic acid transition-metal complexes have not been synthesised. The reason for this seemed to be the difficulty of the synthesis of the starting compounds such as selenocarboxylic acids and their alkali- and alkaline-earth-metal salts, *etc.* Previously, we have established a convenient synthesis of selenocarboxylic acid sodium salts (**1**)<sup>4</sup> which readily react with organo Group 14 and 15 element halides to give the corresponding esters [RCOSeER'<sub>3</sub> (E = Ge or Pb) and RCOSeAsR'<sub>2</sub> (R, R' = alkyl or aryl)].<sup>5</sup> In addition, the reaction of **1** with triorganosilyl halides has been found to give *O*-triorganosilyl selenocarboxylates **2**<sup>6</sup> (hereafter called *O*-silyl selenoesters) which act in aprotic solvents as effective selenocarboxylating agents.<sup>7</sup> These findings have prompted us to study the first synthesis of the transition-metal complexes bearing selenocarboxylate ligands. Here we describe the synthesis and structural analysis of bis(phosphine)bis(selenocarboxylato)-nickel(II) (**3**), -palladium(II) (**4**) and -platinum(II) (**5**) complexes by X-ray diffraction.

## Results and Discussion

### Synthesis of [Ni<sup>II</sup>(RCOSe)<sub>2</sub>(PR'<sub>3</sub>)<sub>2</sub>] **3**, [Pd<sup>II</sup>(RCOSe)<sub>2</sub>(PR'<sub>3</sub>)<sub>2</sub>] **4** and [Pt<sup>II</sup>(RCOSe)<sub>2</sub>(PR'<sub>3</sub>)<sub>2</sub>] **5**

Preliminarily, the synthetic procedure to form the palladium complexes **4** were examined by using dichlorobis(triethylphosphine)palladium(II) and sodium 4-methylbenzenecarboxylate **1d** (method A) or *O*-trimethylsilyl ester **2d** (method B). The reaction conditions shown in Scheme 1 appeared to be preferable.

When half an equivalent of dichlorobis(triethylphosphine)palladium(II) was added to a suspension of the sodium salt **1d** in methanol at 20 °C under an argon atmosphere (method A), a yellow solid gradually precipitated. After stirring for 1 h, the yellow precipitate, was filtered off, and after washing with water, bis(4-methylbenzenecarboxylato)bis-



**Scheme 1** R = Me, Ph, 2-MeC<sub>6</sub>H<sub>4</sub> or 4-MeC<sub>6</sub>H<sub>4</sub>; R' = Et or Ph. (i) Method A, Et<sub>2</sub>O, 1 h, 20 °C; (ii) method B, Et<sub>2</sub>O, 2 h, 20 °C

(triethylphosphine)palladium(II) **4d** was obtained in 85% yield. On the other hand, addition of a solution of *O*-trimethylsilyl selenoester **2d** in diethyl ether (method B) led to a change from purple to pale yellow with precipitation of a yellow solid. After stirring for 2 h, the precipitate was filtered off affording 95% of **4d** as a crude yellow solid. Recrystallization from dichloromethane–diethyl ether led to a 67% yield of **4d** as yellow columnar crystals. The reaction with dichlorobis(triphenylphosphine)palladium(II) under the same conditions gave the corresponding triphenylphosphine complex **4e** in quantitative yield. The yields of a variety of substituted selenobenzoate palladium complexes **4** are summarized in Table 1.

Method B has several advantages compared with method A: (i) the completion of the reaction can be readily determined by the colour of the reaction mixture, (ii) common aprotic solvents can be used and (iii) removal of the by-product, trimethylsilyl chloride, is easy.

Method B using *O*-silyl selenoester **2** was applicable to the synthesis of the platinum complexes **5**. When dichlorobis(phosphine)platinum(II) was added to a diethyl ether solution of **2**, the reaction mixture quickly changed from purple to pale yellow with precipitation of a yellow solid. Filtration of the yellow solid yielded the expected selenocarboxylate complexes **5** in almost quantitative yields. Under the same conditions, the reaction with dichlorobis(phosphine)nickel(II) afforded bis-(triethylphosphine)- and bis(triphenylphosphine)-bis(selenocarboxylato)nickel(II) **3** in good yields. It should be noted, however, that the synthesis of **3** via method B led to lower yields compared with method A.

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**Table 1** Yields of bis(selenocarboxylato)bis(triorganophosphine)-nickel(II) **3**, -palladium(II) **4** and -platinum(II) **5**,  $[M(RCOSe)_2(PR'_3)_2]$ 

Compound	M	R	R'	Method	Yield <sup>a</sup> (%)	M.p. <sup>b</sup> /°C
<b>3b</b>	Ni	Ph	Et	A	61	92–99
<b>3c</b>		2-MeC <sub>6</sub> H <sub>4</sub>	Et	A	75	93–98
<b>3d</b>		4-MeC <sub>6</sub> H <sub>4</sub>	Et	B	65	
				A	91	108–113
<b>3e</b>		4-MeC <sub>6</sub> H <sub>4</sub>	Ph	B	49	
				A	71	120–129
<b>4a</b>	Pd	Me	Et	B	90	96–98
<b>4b</b>		Ph	Et	B	73	151–154
<b>4c</b>		2-MeC <sub>6</sub> H <sub>4</sub>	Et	B	75	173–179
<b>4d</b>		4-MeC <sub>6</sub> H <sub>4</sub>	Et	B	67	187–193
<b>4e</b>		4-MeC <sub>6</sub> H <sub>4</sub>	Ph	A	85	
				B	71	204–206
<b>5a</b>	Pt	Me	Et	A	82	
				B	74	108–112
<b>5b</b>		Ph	Et	B	79	142–148
<b>5c</b>		2-MeC <sub>6</sub> H <sub>4</sub>	Et	B	86	188–192
<b>5d</b>		4-MeC <sub>6</sub> H <sub>4</sub>	Et	B	78	225–228
<b>5e</b>		4-MeC <sub>6</sub> H <sub>4</sub>	Ph	B	71	249–251

<sup>a</sup> Isolated yield. <sup>b</sup> With decomposition.**Table 2** Spectral data of bis(selenocarboxylato)bis(triorganophosphine)-nickel(II) **3**, -palladium(II) **4** and -platinum(II) **5**,  $[M(RCOSe)_2(PR'_3)_2]$ 

Compound	M	R	R'	$\nu(C=O)^a/cm^{-1}$	$\delta_c^b$	$\delta_{se}^c$
<b>3b</b>	Ni	Ph	Et	1611	—	—
<b>3c</b>		2-MeC <sub>6</sub> H <sub>4</sub>	Et	1615	205.1	476.6
<b>3d</b>		4-MeC <sub>6</sub> H <sub>4</sub>	Et	1612	201.7	420.1
<b>3e</b>		4-MeC <sub>6</sub> H <sub>4</sub>	Ph	1611	—	—
<b>4a</b>	Pd	Me	Et	1638	204.4	387.1
<b>4b</b>		Ph	Et	1617	201.3	368.4
<b>4c</b>		2-MeC <sub>6</sub> H <sub>4</sub>	Et	1618	204.5	432.8
<b>4d</b>		4-MeC <sub>6</sub> H <sub>4</sub>	Et	1616	200.9	361.2
<b>4e</b>		4-MeC <sub>6</sub> H <sub>4</sub>	Ph	1613	—	—
<b>5a</b>			Pt	Me	Et	1643
<b>5b</b>		Ph	Et	1621	200.0	353.8
<b>5c</b>		2-MeC <sub>6</sub> H <sub>4</sub>	Et	1622	203.5	414.2
<b>5d</b>		4-MeC <sub>6</sub> H <sub>4</sub>	Et	1619	199.6	347.3
<b>5e</b>		4-MeC <sub>6</sub> H <sub>4</sub>	Ph	1616	—	—

<sup>a</sup> As KBr disc. <sup>b</sup> In CDCl<sub>3</sub>. <sup>c</sup> In CDCl<sub>3</sub>, standard Me<sub>2</sub>Se.**Table 3** Comparison of spectral data for  $[Pd(PhCOE)_2(PR'_3)_2]$  (E = O, S or Se)

E	R'	$\nu(C=O)/cm^{-1}$	$\delta_c^b$	Ref.
O	Ph	1623	—	8(g)
S	Ph	1570	—	3(i)
Se	Et	1617	201.3	

<sup>a</sup> As Nujol mull. <sup>b</sup> In CDCl<sub>3</sub>.

The selenocarboxylic acid palladium and platinum complexes **4** and **5** occur as yellow columnar crystals. They are thermally stable and are insensitive to oxygen and moisture; no appreciable change was observed for the complexes when allowed to stand in air at room temperature for a week. However, the acetyl derivatives (**4a**, **5a**) seem to be less stable than the aromatic derivatives and gradually decomposed with liberation of red selenium upon extended exposure to air. The nickel complexes **3** are yellowish brown to red columnar crystals and are less stable than the corresponding palladium and platinum complexes. For example, the aromatic derivatives **3b–3e**, turned black over 24 h upon exposure to air at room temperature, with formation of bis(4-methylbenzoyl) selenide.

All the triethylphosphine complexes dissolved in common solvents such as dichloromethane and diethyl ether and could be recrystallized, whereas the triphenylphosphine complexes **3e**, **4e** and **5e** showed poor solubility towards a variety of protic and aprotic solvents preventing acquisition of NMR data.

### Spectra

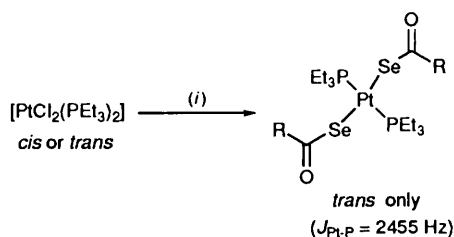
The ligands, RCO<sub>2</sub>, RCOS and RCS<sub>2</sub> in complexes  $[M(RCO_2)_2]_n$ ,<sup>1,8a,b</sup>  $[M(RCOS)_2]_n$ ,<sup>3i,8c</sup> and  $[M(RCS_2)_2]_n$ <sup>8d-f</sup> (M = Ni, Pd, Pt etc.) are bidentate, and chelate two metals, while the RCO<sub>2</sub> and RCOS ligands in monomeric *trans*- $[M(RCO_2)_2L_2]$  (L = NR'<sub>3</sub> or PR'<sub>3</sub>, M = Pd or Pt)<sup>8g</sup> and *trans*- $[M(RCOS)_2L_2]$  (L = NR'<sub>3</sub> or PR'<sub>3</sub>, M = Ni<sup>3a</sup> or Ru<sup>3b</sup>) complexes are unidentate. The carbonyl stretching frequencies of complexes **3–5** (Table 2) appear in the region 1610–1645 cm<sup>-1</sup>, showing higher wavenumber shifts than those of the corresponding alkali-metal salts (1500–1560 cm<sup>-1</sup>)<sup>4,9</sup> but are lower than the corresponding *Se*-alkyl and aryl esters (1660–1720 cm<sup>-1</sup>).<sup>10</sup> The  $\nu(C=O)$  band of the selenobenzoate palladium complex **4b** lies between that of the corresponding carboxylate (1623 cm<sup>-1</sup>) and thiocarboxylate complexes (1570 cm<sup>-1</sup>), which contains unidentate RCO<sub>2</sub> or RCOS ligands (Table 3). Carbon-13 NMR spectra of triethylphosphine complexes show <sup>13</sup>C=O resonances in the region  $\delta$  200–205, *i.e.* almost invariant of the metals. The <sup>77</sup>Se NMR signals occur at  $\delta$  350–480, showing an upfield shift in going from Ni to Pt. These results suggest that the selenocarboxylate ligands of **3–5** are unidentate, in which the carbonyl oxygen does not co-ordinate to the central metal.

In Table 4, the <sup>31</sup>P chemical shifts and <sup>195</sup>Pt–<sup>31</sup>P coupling constants of platinum complexes **5a–5d** are given together with those of *cis*- and *trans*- $[PtCl_2(PEt_3)_2]$  and *trans*- $[Pt(PhCOS)_2(PMe_2Ph)_2]$ . Comparison with the *trans* isomer of  $[PtCl_2(PEt_3)_2]$  suggests that complexes **5** are *trans* isomers. With either *cis*- or *trans*- $[PtCl_2(PEt_3)_2]$  used as the starting

**Table 4** Phosphorus-31 NMR spectra of bis(selenocarboxylato)bis-(triethylphosphine)platinum(II) complexes **5**, [Pt(RCOSe)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>], and related compounds

Compound	R	<i>J</i> <sub>PtP</sub> /Hz	δ <sub>P</sub> <sup>a</sup>
<b>5a</b>	Me	2454	7.6
<b>5b</b>	Ph	2451	7.6
<b>5c</b>	2-MeC <sub>6</sub> H <sub>4</sub>	2461	7.5
<b>5d</b>	4-Me <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	2455	7.6
<i>cis</i> -[PtCl <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub> ]		3520	9.6 <sup>b</sup>
<i>trans</i> -[PtCl <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub> ]		2400	12.3 <sup>b</sup>
<i>trans</i> -[Pt(PhCOS) <sub>2</sub> (PMe <sub>2</sub> Ph) <sub>2</sub> ]		2546	6.2 <sup>c</sup>

<sup>a</sup> In CDCl<sub>3</sub>, standard H<sub>3</sub>PO<sub>4</sub>. <sup>b</sup> Ref. 11. <sup>c</sup> Ref. 3(i).



**Scheme 2** (i) RC(Se)OSiMe<sub>3</sub>

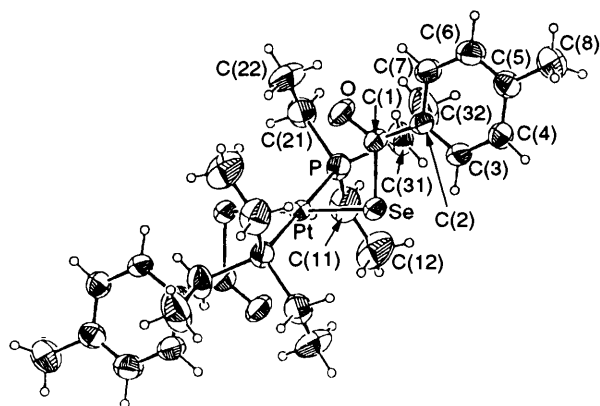
material, only the *trans* isomer was obtained (Scheme 2). Presumably, nickel(II) **3** and palladium(II) complexes **4** have similar *trans* configuration.

### X-Ray structural analysis

Although the synthesis of transition-metal complexes with thiocarboxylate ligands has been extensively studied, X-ray structural analysis has been limited to only one example, *viz.* (4-amino-2-imino-4-methylpentane)bis(benzenecarbothioato)bis(dimethylphenylphosphine)ruthenium(II).<sup>3b</sup> No X-ray structural analysis of [M(RCO<sub>2</sub>)<sub>2</sub>L<sub>2</sub>] or [M(RCOS)<sub>2</sub>L<sub>2</sub>] (L = NR'<sub>3</sub> or PR'<sub>3</sub>, M = Pd or Pt) has been reported. As mentioned above, the selenocarboxylate ligands in **3–5** were considered to be unidentate and to adopt a *trans* conformation on the basis of IR and <sup>31</sup>P NMR spectroscopy. In order to confirm this structure, the X-ray single-crystal structural analyses of the 4-methylbenzenecarboxylate derivatives **3d**, **4d** and **5d** was performed. They are all isostructural, and an ORTEP<sup>12</sup> drawing of **5d** is shown in Fig. 1. Crystal data and data collection parameters are given in Table 5 and bond lengths and angles in Table 6. In each complex the metal is four-co-ordinate and adopts a planar geometry with the two selenocarboxylate and phosphine ligands in *trans* positions. The C=O bond lengths of the selenocarboxyl group are in the range 1.203(8)–1.212(6) Å, similar to those of common carboxylic acid esters (1.23 ± 0.01 Å)<sup>13</sup> and that in a caesium 2-methoxybenzenecarboxylate [1.226(5) Å].<sup>14</sup> The C–Se bond lengths are 1.906–1.913 Å which are close to that of the caesium salt [1.868(5) Å]. No interaction between the carbonyl oxygen and the central metal is observed, the distances between each carbonyl oxygen and the central metal being much longer than the sum of the ionic radius of the central metal and the van der Waals radius of oxygen. These results demonstrate that the selenocarboxylate ligands of **3d**, **4d** and **5d** are unidentate, similar to carboxylate and thiocarboxylate complexes. The torsion angles [O–C(1)–C(2)–C(3)] between the benzene ring and selenocarboxyl group are in the range 167.7–169.1°, smaller than that found for the caesium salt [57.7(6)°].

### Conclusion

The first synthesis and characterization of selenocarboxylic acid transition-metal complexes, bis(phosphine)bis(seleno-



**Fig. 1** ORTEP drawing of bis(4-methylbenzenecarboxylato)bis-(triethylphosphine)platinum(II) **5d**

carboxylato)-nickel(II) **3**, -palladium(II) **4** and -platinum(II) complexes **5** are described. The complexes are obtained in good to high yields from the reaction of sodium selenocarboxylates or *O*-silyl selenoesters with [MCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] (M = Ni, Pd or Pt). The selenocarboxylate complexes are yellow to red crystals, and the nickel complexes **3** are much more labile thermally and air-sensitive in comparison with the palladium **4** and platinum complexes **5**. X-Ray crystal structure analysis of three selenocarboxylate complexes establishes four-co-ordinate planar structures, with selenocarboxylate and phosphine ligands in a *trans* configuration; no co-ordination of selenocarboxyl oxygen to the metal is observed.

### Experimental

Melting points were determined with a Yanagimoto micromelting point apparatus, and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer FT-IR 1640 spectrophotometer and a JASCO grating IR spectrophotometer IR-G. The <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P and <sup>77</sup>Se NMR spectra were recorded on a JEOL JNM-GX-270 instrument at 270, 67.9, 109.4 and 51.5 MHz, respectively. Deuteriochloroform was employed as solvent with tetramethylsilane (<sup>1</sup>H) and CDCl<sub>3</sub> (<sup>13</sup>C) as internal standards; H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P) and SeMe<sub>2</sub> (<sup>77</sup>Se NMR) were used as external standards. Elemental analyses were performed by the Elemental Analyses Centre of Kyoto University. The X-ray crystal structural analyses were carried out at the Research Laboratory of Resources Utilization, Tokyo Institute of Technology.

### Materials

Sodium selenocarboxylates,<sup>4</sup> *O*-trimethylsilyl selenocarboxylates,<sup>6</sup> dichlorobis(triethylphosphine)-<sup>15a</sup> and bis(triphenylphosphine)-nickel(II),<sup>15b</sup> dichlorobis(triethylphosphine)-<sup>16a</sup> and bis(triphenylphosphine)-palladium(II),<sup>16b</sup> and dichlorobis(triethylphosphine)-<sup>17a</sup> and bis(triphenylphosphine)-platinum(II)<sup>17b</sup> were prepared as described in the literature. The following solvents were purified under argon and dried as indicated: diethyl ether and hexane (refluxing with sodium metal using benzophenone as indicator and distilling before use); dichloromethane (distillation over phosphorus pentoxide, after refluxing for 5 h). Solvents were degassed before use and all manipulations were performed under argon.

### X-Ray structure analysis

All intensity data measurements were carried out on a Rigaku AFC5R four-circle diffractometer with graphite-monochromated Mo-K<sub>α</sub> radiation (λ = 0.710 69 Å). All structures were solved and refined using the TEXSAN software package<sup>18</sup> on a MicroVAX II computer. Crystals of **3d**, **4d** and **5d** suitable for X-ray diffraction were obtained by recrystallization from dichloromethane at –20 °C. The crystals were sealed in a glass

**Table 5** Crystal data, and data collection and refinement parameters for **3d**, **4d** and **5d** \*

Compound	<b>3d</b>	<b>4d</b>	<b>5d</b>
Empirical formula	C <sub>28</sub> H <sub>44</sub> NiO <sub>2</sub> P <sub>2</sub> Se <sub>2</sub>	C <sub>28</sub> H <sub>44</sub> O <sub>2</sub> P <sub>2</sub> PdSe <sub>2</sub>	C <sub>28</sub> H <sub>44</sub> O <sub>2</sub> P <sub>2</sub> PtSe <sub>2</sub>
<i>M</i>	691.22	738.92	827.62
<i>a</i> /Å	9.161(2)	9.313(3)	9.373(4)
<i>b</i> /Å	11.978(2)	11.958(2)	11.959(4)
<i>c</i> /Å	14.958(2)	14.908(2)	14.821(4)
β/°	103.22(1)	102.08(2)	101.96(3)
<i>U</i> /Å <sup>3</sup>	1597.9(4)	1623.4(6)	1625.3(10)
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.436	1.512	1.691
Crystal size/mm	0.10 × 0.25 × 0.30	0.20 × 0.20 × 0.30	0.15 × 0.35 × 0.35
μ(Mo-Kα)/cm <sup>-1</sup>	29.8	29.0	67.0
Transmission factor for absorption correction	0.88–1.00	0.87–1.00	0.59–1.00
2θ <sub>max</sub> /°	50.5	54	54
No. of measured reflections	3234	3943	3941
No. of unique reflections	3036	3720	3716
<i>R</i> <sub>int</sub>	0.017	0.028	0.016
No. of observations [ <i>I</i> > 3σ( <i>I</i> )]	1820	1911	2377
No. of variables	226	160	160
Residuals: <i>R</i> ( <i>F</i> ), <i>R</i> '( <i>F</i> )	0.038, 0.046	0.050, 0.056	0.030, 0.034
Max. and min. residual electron density/e Å <sup>-3</sup>	0.4, -0.4	0.8, -0.8	0.7, -0.7
Goodness of fit	1.63	1.92	1.30

\* Details in common: monoclinic, space group *P*2<sub>1</sub>/*c*; *Z* = 2; 296 K.**Table 6** Selected bond lengths (Å), bond angles (°) and torsion angles (°) for **3d**, **4d** and **5d**

	<b>3d</b> (M = Ni)	<b>4d</b> (M = Pd)	<b>5d</b> (M = Pt)
M–Se	2.3426(7)	2.456(1)	2.452(1)
M–P	2.238(2)	2.323(2)	2.304(2)
Se–C(1)	1.910(6)	1.906(8)	1.913(6)
P–C(11)	1.861(9)	1.781(13)	1.797(10)
P–C(21)	1.848(8)	1.841(11)	1.840(7)
P–C(31)	1.816(10)	1.854(10)	1.848(7)
O–C(1)	1.209(6)	1.203(8)	1.212(6)
C(1)–C(2)	1.502(8)	1.51(1)	1.480(9)
C(2)–C(3)	1.385(8)	1.38(1)	1.380(7)
C(2)–C(7)	1.381(8)	1.39(1)	1.394(8)
C(3)–C(4)	1.373(9)	1.37(1)	1.385(8)
C(4)–C(5)	1.378(9)	1.38(1)	1.375(9)
C(5)–C(6)	1.386(10)	1.39(1)	1.366(10)
C(5)–C(8)	1.521(11)	1.50(1)	1.512(10)
C(6)–C(7)	1.378(10)	1.38(1)	1.384(9)
O...M	3.177(5)	3.270(7)	3.362(5)
Se–M–Se	180.00	180.00	180.00
Se–M–P	87.33(5)	86.90(6)	86.96(5)
Se–M–P	92.67(5)	93.10(6)	93.04(5)
P–M–P	180.00	180.00	180.00
M–Se–C(1)	98.3(2)	99.0(3)	101.7(2)
M–P–C(11)	115.1(3)	110.7(4)	111.5(3)
M–P–C(21)	119.5(3)	114.1(4)	113.5(3)
M–P–C(31)	110.0(3)	117.8(3)	117.8(3)
C(11)–P–C(21)	100.7(4)	103.3(6)	103.2(4)
C(11)–P–C(31)	104.4(5)	107.1(6)	106.4(4)
C(21)–P–C(31)	105.7(4)	102.6(5)	103.1(4)
Se–C(1)–O	122.0(5)	122.6(7)	122.3(5)
Se–C(1)–C(2)	117.1(4)	116.2(6)	116.4(4)
O–C(1)–C(2)	121.0(6)	121.2(8)	121.3(6)
M–Se–C(1)–O	11.0(5)	9.0(8)	9.4(6)
M–Se–C(1)–C(2)	168.2(4)	170.0(5)	169.8(4)
O–C(1)–C(2)–C(3)	167.7(6)	169.1(8)	168.8(6)
O–C(1)–C(2)–C(7)	13.3(9)	12.6(13)	12.3(10)

capillary. The unit-cell dimensions were determined from a least-squares fit of the setting angles of 25 reflections in the range  $25 \leq 2\theta \leq 30^\circ$ . Three standard reflections were measured every 150 reflections and showed no significant intensity variations during the data collection. The data were corrected for Lorentz and polarization effects, and empirical absorption corrections based on azimuthal scans of several reflections were applied. The structures were solved by the direct method. Full-matrix least-squares refinement was employed with anisotropic

thermal parameters for non-hydrogen atoms. The function minimized was  $\sum w(|F_o| - |F_c|)^2$ , and the weighting scheme employed was  $w = 4|F_o|^2/\sigma^2(F_o)$ . Hydrogen atoms placed at calculated positions were isotropically refined (with fixed thermal parameters) for **3d** and included in the structure-factor calculations for **4d** and **5d**. Scattering factors were taken from ref. 19. Crystal data and parameters for data collection and refinement are summarised in Table 5.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

### Syntheses of complexes

#### From *O*-trimethylsilyl selenocarboxylate **2** (Method B).

*trans*-Bis(selenoacetato)bis(triethylphosphine)palladium(II) **4a**. Dichlorobis(triethylphosphine)palladium(II) (0.207 g, 0.50 mmol) was added to a solution of *O*-trimethylsilyl selenoacetate **2a** (0.205 g, 1.05 mmol) in diethyl ether (10 cm<sup>3</sup>) at 20 °C under an argon atmosphere. On stirring for 1 h the solution changed from orange to pale yellow. Removal of the solvent under reduced pressure gave 0.264 g (90%) of bis(selenoacetato)bis(triethylphosphine)palladium(II) **4a** as a yellow solid. Recrystallization from diethyl ether–hexane (1:1, 10 cm<sup>3</sup>) at –20 °C for 24 h yielded chemically pure **4a** as yellow columnar crystals (0.248 g, 85%), m.p. 96–98 °C (decomp.) (Found: C, 32.70; H, 6.4. Calc. for C<sub>16</sub>H<sub>36</sub>O<sub>2</sub>P<sub>2</sub>PdSe<sub>2</sub>: C, 32.75; H, 6.2%;  $\nu_{\max}$ (KBr)/cm<sup>-1</sup> 2968, 1638 (C=O), 1446, 1096, 1032, 924, 764, 722 and 587;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 1.09 (18 H, m, PCH<sub>2</sub>CH<sub>3</sub>), 2.04 (12 H, m, PCH<sub>2</sub>CH<sub>3</sub>) and 2.41 (6 H, s, CH<sub>3</sub>CO);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>) 8.6 (PCH<sub>2</sub>CH<sub>3</sub>), 16.0 (PCH<sub>2</sub>CH<sub>3</sub>), 39.0 (CH<sub>3</sub>CO) and 204.4 (C=O);  $\delta_{\text{P}}$ (CDCl<sub>3</sub>) 12.5;  $\delta_{\text{Se}}$ (CDCl<sub>3</sub>) 387.1.

*trans*-Bis(benzenecarboxylato)bis(triethylphosphine)palladium(II) **4b**. Similarly to **4a**, *O*-trimethylsilyl benzenecarboxylate **2b** (0.201 g, 0.78 mmol) and dichlorobis(triethylphosphine)palladium(II) (0.161 g, 0.39 mmol) were stirred in diethyl ether (10 cm<sup>3</sup>) at 20 °C under an argon atmosphere for 1 h. The solution changed from purple to pale yellow with precipitation of a yellow solid. Filtration of the precipitate, followed by washing with diethyl ether (1 cm<sup>3</sup>) and recrystallization from dichloromethane–hexane (1:2, 3.6 cm<sup>3</sup>) yielded bis(benzenecarboxylato)bis(triethylphosphine)palladium(II) **4b** as yellow columnar crystals (0.201 g, 73%; m.p. 151–154 °C (decomp.);  $\nu_{\max}$ (KBr)/cm<sup>-1</sup> 2961, 1617 (C=O),

**Table 7** Fractional atomic coordinates of **3d**, **4d** and **5d**

Atom	x	y	z
<b>3d</b> (M = Ni)			
M	0	0	0
Se	0.176 65(7)	-0.100 29(5)	0.108 32(4)
P	0.113 5(2)	-0.065 5(1)	-0.106 8(1)
O	0.280 5(5)	0.115 5(4)	0.132 0(3)
C(1)	0.295 6(6)	0.022 7(5)	0.164 6(4)
C(2)	0.408 5(6)	-0.000 1(5)	0.252 7(4)
C(3)	0.450 2(7)	-0.106 8(5)	0.284 2(4)
C(4)	0.554 6(8)	-0.122 0(6)	0.365 2(5)
C(5)	0.619 9(7)	-0.032 3(7)	0.416 8(5)
C(6)	0.573 5(9)	0.073 9(7)	0.385 9(6)
C(7)	0.470 5(7)	0.090 9(6)	0.304 2(5)
C(8)	0.736 4(11)	-0.049 1(10)	0.506 2(6)
C(11)	0.152 1(10)	-0.218 2(8)	-0.100 7(6)
C(12)	0.018 8(16)	-0.286 5(9)	-0.099 0(12)
C(21)	0.021 1(10)	-0.050 1(7)	-0.229 6(5)
C(22)	0.108 2(16)	-0.091 2(11)	-0.297 2(6)
C(31)	0.296 9(10)	-0.001 5(11)	-0.093 3(6)
C(32)	0.292 4(13)	0.123 1(10)	-0.103 3(9)
<b>4d</b> (M = Pd)			
M	0	0	0
Se	0.184 3(1)	0.100 53(7)	0.113 40(6)
P	0.122 8(3)	0.065 2(2)	-0.110 1(2)
O	0.279 8(7)	-0.117 0(5)	0.137 1(4)
C(1)	0.298(1)	-0.023 9(7)	0.168 1(6)
C(2)	0.411 1(8)	0.000 2(7)	0.254 3(5)
C(3)	0.453(1)	0.106 8(7)	0.285 1(6)
C(4)	0.558(1)	0.121 0(7)	0.364 0(6)
C(5)	0.621(1)	0.033(1)	0.417 4(6)
C(6)	0.576(1)	-0.074(1)	0.387 0(7)
C(7)	0.473(1)	-0.090 4(7)	0.306 8(7)
C(8)	0.735(1)	0.050(1)	0.503 4(7)
C(11)	0.300(1)	0.003(1)	-0.095 5(8)
C(12)	0.298(1)	-0.122(1)	-0.103 0(10)
C(21)	0.163(1)	0.216(1)	-0.102 3(7)
C(22)	0.031(2)	0.285(1)	-0.099 7(10)
C(31)	0.032(1)	0.048(1)	-0.232 4(7)
C(32)	0.095(2)	0.092(1)	-0.300 7(9)
<b>5d</b> (M = Pt)			
M	0	0	0
Se	0.186 16(7)	0.095 30(5)	0.114 91(4)
P	0.120 3(2)	0.066 71(14)	-0.109 63(11)
O	0.285 8(5)	-0.121 7(3)	0.140 1(3)
C(1)	0.301 9(7)	-0.027 7(5)	0.171 1(4)
C(2)	0.411 8(7)	-0.002 5(4)	0.255 8(4)
C(3)	0.453 1(7)	0.103 9(5)	0.286 6(4)
C(4)	0.558 3(7)	0.120 8(6)	0.366 1(4)
C(5)	0.621 5(7)	0.032 1(6)	0.418 6(5)
C(6)	0.578 4(8)	-0.073 2(6)	0.389 0(5)
C(7)	0.476 1(7)	-0.092 5(5)	0.308 8(5)
C(8)	0.737 0(8)	0.050 6(8)	0.505 0(5)
C(11)	0.298 9(11)	0.006 2(8)	-0.096 8(7)
C(12)	0.296 8(11)	-0.118 1(9)	-0.105 6(7)
C(21)	0.157 8(10)	0.217 7(6)	-0.099 9(5)
C(22)	0.023 9(13)	0.286 0(6)	-0.098 5(7)
C(31)	0.030 9(10)	0.049 6(7)	-0.232 2(5)
C(32)	0.096 3(13)	0.095 3(9)	-0.301 0(5)

1578, 1451, 1410, 1188, 1165, 1030, 882, 764, 722, 671 and 621;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.12 (18 H, m,  $\text{PCH}_2\text{CH}_3$ ), 2.03 (12 H, m,  $\text{PCH}_2\text{CH}_3$ ) and 7.37–8.10 (10 H, m, Ph);  $\delta_{\text{C}}(\text{CDCl}_3)$  8.6 ( $\text{PCH}_2\text{CH}_3$ ), 16.0 ( $\text{PCH}_2\text{CH}_3$ ), 127.6, 127.8, 127.9, 128.1, 131.5, 143.2 (Ph) and 201.3 (C=O);  $\delta_{\text{P}}(\text{CDCl}_3)$  13.3;  $\delta_{\text{Se}}(\text{CDCl}_3)$  368.4.

*trans*-Bis(2-methylbenzenecarboselenoato)bis(triethylphosphine)palladium(II) **4c**. Yellow columnar crystals (75%); m.p. 173–179 °C (decomp.) (Found: C, 45.20; H, 6.0. Calc. for  $\text{C}_{28}\text{H}_{44}\text{O}_2\text{P}_2\text{PdSe}_2$ : C, 45.50; H, 6.0%;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2960, 1618 (C=O), 1455, 1415, 1385, 1205, 1190, 1121, 1030, 890, 870, 770, 730, 670 and 630;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.17 (18 H, m,  $\text{PCH}_2\text{CH}_3$ ),

2.14 (12 H, m,  $\text{PCH}_2\text{CH}_3$ ), 2.41 (6 H, s,  $\text{CH}_3\text{C}_6\text{H}_4$ ) and 7.12–7.91 (8 H, m, aryl H);  $\delta_{\text{C}}(\text{CDCl}_3)$  8.8 ( $\text{PCH}_2\text{CH}_3$ ), 16.2 ( $\text{PCH}_2\text{CH}_3$ ), 20.2 ( $\text{CH}_3\text{C}_6\text{H}_4$ ), 125.2, 128.8, 129.6, 131.0, 133.2, 144.8 (aryl C) and 204.5 (C=O);  $\delta_{\text{P}}(\text{CDCl}_3)$  13.1;  $\delta_{\text{Se}}(\text{CDCl}_3)$  432.8.

*trans*-Bis(4-methylbenzenecarboselenoato)bis(triethylphosphine)palladium(II) **4d**. Yellow columnar crystals (67%); m.p. 187–193 °C (decomp.) (Found: C, 45.55; H, 6.0. Calc. for  $\text{C}_{28}\text{H}_{44}\text{O}_2\text{P}_2\text{PdSe}_2$ : C, 45.50; H, 6.0%;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3000, 2900, 1616 (C=O), 1605, 1570, 1420, 1200, 1165, 1030, 885, 825, 790, 770, 730, 625 and 615;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.11 (18 H, m,  $\text{PCH}_2\text{CH}_3$ ), 2.04 (12 H, m,  $\text{PCH}_2\text{CH}_3$ ), 2.36 (6 H, s,  $\text{CH}_3\text{C}_6\text{H}_4$ ), 7.16 (4 H, d, aryl H) and 8.01 (4 H, d, aryl H);  $\delta_{\text{C}}(\text{CDCl}_3)$  8.7 ( $\text{PCH}_2\text{CH}_3$ ), 16.0 ( $\text{PCH}_2\text{CH}_3$ ), 21.6 ( $\text{CH}_3\text{C}_6\text{H}_4$ ), 127.9, 128.7, 140.8, 142.0 (aryl C) and 200.9 (C=O);  $\delta_{\text{P}}(\text{CDCl}_3)$  13.2;  $\delta_{\text{Se}}(\text{CDCl}_3)$  361.2.

*trans*-Bis(4-methylbenzenecarboselenoato)bis(triphenylphosphine)palladium(II) **4e**. Yellow microfine crystals (82%); m.p. 204–206 °C (decomp.);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3049, 1613 (C=O), 1432, 1198, 1165, 1094, 886, 820, 786, 747, 690, 615, 520, 511 and 497.

*trans*-Bis(selenoacetato)bis(triethylphosphine)platinum(II) **5a**. Similarly to **4a**, *O*-trimethylsilyl selenoacetate **2a** (0.266 g, 1.36 mmol) and *cis*-dichlorobis(triethylphosphine)platinum(II) (0.342 g, 0.68 mmol) were stirred in diethyl ether (10 cm<sup>3</sup>) at 20 °C under an argon atmosphere for 1 h. The solution changed from orange to pale yellow with precipitation of a pale yellow solid. Filtration of the precipitate, followed by washing with diethyl ether (1 cm<sup>3</sup>) and recrystallization from dichloromethane–hexane (1:2, 4.5 cm<sup>3</sup>) yielded *trans*-bis(selenoacetato)bis(triethylphosphine)platinum(II) **5a** as pale yellow columnar crystals (0.342 g, 74%); m.p. 108–112 °C (Found: C, 28.20; H, 5.4. Calc. for  $\text{C}_{16}\text{H}_{36}\text{O}_2\text{P}_2\text{PtSe}_2$ : C, 28.45; H, 5.4%;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3000, 2950, 2900, 1643 (C=O), 1455, 1410, 1380, 1340, 1270, 1260, 1100, 1030, 940, 770, 760, 740, 700, 640, 580, 500 and 440;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.16 (18 H, m,  $\text{PCH}_2\text{CH}_3$ ), 2.10 (12 H, m,  $\text{PCH}_2\text{CH}_3$ ) and 2.39 (6 H, s,  $\text{CH}_3\text{CO}$ );  $\delta_{\text{C}}(\text{CDCl}_3)$  8.7 ( $\text{PCH}_2\text{CH}_3$ ), 17.7 ( $\text{PCH}_2\text{CH}_3$ ), 39.7 ( $\text{CH}_3\text{CO}$ ) and 205.0 (C=O);  $\delta_{\text{P}}(\text{CDCl}_3)$  6.8 [ $J(\text{Ppt}) = 2454 \text{ Hz}$ ];  $\delta_{\text{Se}}(\text{CDCl}_3)$  371.5.

*trans*-Bis(benzenecarboselenoato)bis(triethylphosphine)platinum(II) **5b**. Yellow columnar crystals (79%); m.p. 142–148 °C;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2961, 2871, 1621 (C=O), 1571, 1445, 1410, 1188, 1168, 1032, 881, 766, 726, 672 and 624;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.13 (18 H, m,  $\text{PCH}_2\text{CH}_3$ ), 2.10 (12 H, m,  $\text{PCH}_2\text{CH}_3$ ) and 7.34–8.08 (10 H, m, Ph);  $\delta_{\text{C}}(\text{CDCl}_3)$  8.3 ( $\text{PCH}_2\text{CH}_3$ ), 14.8 ( $\text{PCH}_2\text{CH}_3$ ), 127.4, 127.5, 127.9, 128.0, 131.4, 143.0 (Ph) and 200.0 (C=O);  $\delta_{\text{P}}(\text{CDCl}_3)$  7.6 [ $J(\text{Ppt}) = 2451 \text{ Hz}$ ];  $\delta_{\text{Se}}(\text{CDCl}_3)$  353.8.

*trans*-Bis(2-methylbenzenecarboselenoato)bis(triethylphosphine)platinum(II) **5c**. Pale yellow columnar crystals (86%); m.p. 188–192 °C (Found: C, 40.50; H, 5.5. Calc. for  $\text{C}_{28}\text{H}_{44}\text{O}_2\text{P}_2\text{PtSe}_2$ : C, 40.65; H, 5.4%;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2970, 2950, 1622 (C=O), 1450, 1410, 1380, 1205, 1190, 1120, 1030, 890, 870, 785, 730, 670 and 630;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.18 (18 H, m,  $\text{PCH}_2\text{CH}_3$ ), 2.19 (12 H, m,  $\text{PCH}_2\text{CH}_3$ ), 2.41 (6 H, s,  $\text{CH}_3\text{C}_6\text{H}_4$ ) and 7.13–7.86 (8 H, m, aryl H);  $\delta_{\text{C}}(\text{CDCl}_3)$  8.6 ( $\text{PCH}_2\text{CH}_3$ ), 15.1 ( $\text{PCH}_2\text{CH}_3$ ), 20.0 ( $\text{CH}_3\text{C}_6\text{H}_4$ ), 125.1, 128.4, 129.6, 131.0, 133.2, 144.7 (aryl C) and 203.5 (C=O);  $\delta_{\text{P}}(\text{CDCl}_3)$  7.5 [ $J(\text{Ppt}) = 2461 \text{ Hz}$ ];  $\delta_{\text{Se}}(\text{CDCl}_3)$  414.2.

*trans*-Bis(4-methylbenzenecarboselenoato)bis(triethylphosphine)platinum(II) **5d**. Pale yellow columnar crystals (78%); m.p. 225–228 °C (Found: C, 40.35; H, 5.1. Calc. for  $\text{C}_{28}\text{H}_{44}\text{O}_2\text{P}_2\text{PtSe}_2$ : C, 40.65; H, 5.4%;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3000, 2950, 2900, 1619 (C=O), 1600, 1450, 1415, 1200, 1160, 1030, 880, 820, 790, 770, 730, 620 and 615;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.12 (18 H, m,  $\text{PCH}_2\text{CH}_3$ ), 2.11 (12 H, m,  $\text{PCH}_2\text{CH}_3$ ), 2.36 (6 H, s,  $\text{CH}_3\text{C}_6\text{H}_4$ ), 7.16 (4 H, d, aryl H) and 7.99 (4 H, d, aryl H);  $\delta_{\text{C}}(\text{CDCl}_3)$  8.4 ( $\text{PCH}_2\text{CH}_3$ ), 14.9 ( $\text{PCH}_2\text{CH}_3$ ), 21.6 ( $\text{CH}_3\text{C}_6\text{H}_4$ ), 127.7, 128.7, 140.7, 142.0 (aryl C) and 199.6 (C=O);  $\delta_{\text{P}}(\text{CDCl}_3)$  7.6 [ $J(\text{Ppt}) = 2454 \text{ Hz}$ ];  $\delta_{\text{Se}}(\text{CDCl}_3)$  347.3.

trans-Bis(4-methylbenzenecarbosenoato)bis(triphenylphosphine)platinum(II) **5e**. Yellow microfine crystals (71%); m.p. 249–251 °C (decomp.);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3067, 1616 (C=O), 1480, 1432, 1199, 1165, 1094, 886, 818, 785, 748, 690, 614, 523, 514, 501 and 461.

trans-Bis(2-methylbenzenecarbosenoato)bis(triethylphosphine)nickel(II) **3c**. Similarly to **4a**, *O*-trimethylsilyl 2-methylbenzenecarbosenoate **2c** (0.228 g, 0.84 mmol) and dichlorobis(triethylphosphine)nickel(II) (0.154 g, 0.42 mmol) were stirred in diethyl ether (10 cm<sup>3</sup>) at 20 °C under an argon atmosphere for 2 h. The solution changed from purple to brown with precipitation of orange solids. Filtration of the precipitate, followed by washing with diethyl ether (3 cm<sup>3</sup>) and recrystallization from dichloromethane–hexane (1:2, 6 cm<sup>3</sup>) yielded bis(2-methylbenzenecarbosenoato)bis(triethylphosphine)nickel(II) **3c** as red columnar crystals (0.190 g, 65%); m.p. 93–98 °C (decomp.);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3000, 2950, 2900, 1615 (C=O), 1450, 1420, 1385, 1205, 1190, 1035, 890, 870, 770, 720, 675 and 635;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.24 (18 H, m, PCH<sub>2</sub>CH<sub>3</sub>), 1.95 (12 H, m, PCH<sub>2</sub>CH<sub>3</sub>), 2.43 (6 H, s, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>) and 7.11–7.95 (8 H, m, aryl H);  $\delta_{\text{C}}(\text{CDCl}_3)$  8.9 (PCH<sub>2</sub>CH<sub>3</sub>), 15.8 (PCH<sub>2</sub>CH<sub>3</sub>), 20.2 (CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 125.2, 129.1, 129.7, 131.0, 133.2, 144.5 (aryl C) and 205.1 (C=O).

trans-Bis(4-methylbenzenecarbosenoato)bis(triethylphosphine)nickel(II) **3d**. Orange solid (49%); m.p. 108–113 °C (decomp.);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3000, 2900, 1612 (C=O), 1600, 1570, 1450, 1200, 1165, 1110, 1085, 1000, 885, 825, 790, 770, 720, 620 and 615;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.19 (18 H, m, PCH<sub>2</sub>CH<sub>3</sub>), 1.85 (12 H, m, PCH<sub>2</sub>CH<sub>3</sub>), 2.36 (6 H, s, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 7.19 (4 H, d, aryl H) and 8.02 (4 H, d, aryl H);  $\delta_{\text{C}}(\text{CDCl}_3)$  8.8 (PCH<sub>2</sub>CH<sub>3</sub>), 15.7 (PCH<sub>2</sub>CH<sub>3</sub>), 21.5 (CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 127.8, 128.6, 140.6, 142.0 (aryl C) and 201.7 (C=O).

trans-Bis(4-methylbenzenecarbosenoato)bis(triphenylphosphine)nickel(II) **3e**. Yellowish brown microfine crystals (71%); m.p. 120–129 °C (decomp.);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3048, 1611 (C=O), 1603, 1477, 1432, 1202, 1165, 1088, 886, 819, 783, 747, 691, 615, 521, 508 and 497.

**From sodium selenocarboxylate 1 (Method A).** trans-Bis(benzenecarbosenoato)bis(triethylphosphine)nickel(II) **3b**. To a suspension of sodium benzenecarbosenoate **1b** (0.521 g, 2.00 mmol) in diethyl ether (10 cm<sup>3</sup>) was added trans-dichlorobis(triethylphosphine)nickel(II) (0.366 g, 1.00 mmol), at 20 °C under an argon atmosphere. The mixture was stirred at the same temperature for 1 h and immediately changed from pale yellow to dark reddish brown with precipitation of orange-brown solids. Filtration of the precipitate by the use of a Umkehr filter (G4) and washing with diethyl ether (1 cm<sup>3</sup>) gave orange-brown solids containing sodium chloride. The solids were dissolved in dichloromethane (1.4 cm<sup>3</sup>). Filtration of the insoluble parts (NaCl) and cooling of the filtrate at –20 °C for 1 h yielded **3b** as deep red columnar crystals (0.543 g, 61%); m.p. 92–99 °C (decomp.);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2967, 2922, 2867, 1611 (C=O), 1578, 1448, 1189, 1165, 1030, 883, 762, 691, 673 and 622.

trans-Bis(2-methylbenzenecarbosenoato)bis(triethylphosphine)nickel(II) **3c**. Deep red columnar crystals (75%); m.p. 93–98 °C (decomp.) (Found: C, 48.45; H, 6.5. Calc. for C<sub>28</sub>H<sub>44</sub>NiO<sub>2</sub>P<sub>2</sub>Se<sub>2</sub>: C, 48.65; H, 6.4%);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3000, 2950, 2900, 1615 (C=O), 1450, 1420, 1385, 1205, 1190, 1035, 890, 870, 770, 720, 675 and 635;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.24 (18 H, m, PCH<sub>2</sub>CH<sub>3</sub>), 1.95 (12 H, m, PCH<sub>2</sub>CH<sub>3</sub>), 2.43 (6 H, s, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>) and 7.11–7.95 (8 H, m, aryl H);  $\delta_{\text{C}}(\text{CDCl}_3)$  8.9 (PCH<sub>2</sub>CH<sub>3</sub>), 15.8 (PCH<sub>2</sub>CH<sub>3</sub>), 20.2 (CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 125.2, 129.1, 129.7, 131.0, 133.2, 144.5 (aryl C) and 205.1 (C=O);  $\delta_{\text{Se}}(\text{CDCl}_3)$  476.6.

trans-Bis(4-methylbenzenecarbosenoato)bis(triethylphosphine)nickel(II) **3d**. Deep red columnar crystals (91%); m.p. 108–113 °C (decomp.) (Found: C, 48.40; H, 6.4. Calc. for C<sub>28</sub>H<sub>44</sub>NiO<sub>2</sub>P<sub>2</sub>Se<sub>2</sub>: C, 48.65; H, 6.4%);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3000, 2900, 1612 (C=O), 1600, 1570, 1450, 1200, 1165, 1110, 1085,

1000, 885, 825, 790, 770, 720, 620 and 615;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.19 (18 H, m, PCH<sub>2</sub>CH<sub>3</sub>), 1.85 (12 H, m, PCH<sub>2</sub>CH<sub>3</sub>), 2.36 (6 H, s, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 7.19 (4 H, d, aryl H) and 8.02 (4 H, d, aryl H);  $\delta_{\text{C}}(\text{CDCl}_3)$  8.8 (PCH<sub>2</sub>CH<sub>3</sub>), 15.7 (PCH<sub>2</sub>CH<sub>3</sub>), 21.5 (CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 127.8, 128.6, 140.6, 142.0 (aryl C) and 201.7 (C=O);  $\delta_{\text{Se}}(\text{CDCl}_3)$  420.1.

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