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The Reactions of Tetrakis(triphenylphosphine)platinum and -palladium with Selenium: X-Ray Crystal Structure of $[Pt(Se_2CH_2)(PPh_3)_2]$

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ABSTRACT

Treatment of tetrakis(triphenylphosphine)platinum with elemental selenium (red or vitreous) in toluene solution under reflux yields an insoluble solid. This dissolves in dichloromethane with reaction, eventually to form a 1 : 1 mixture of $[PtCl_2(PPh_3)_2]$ and the new compound $[Pt(Se_2CH_2)(PPh_3)_2]$, which has been characterized by multinuclear NMR spectroscopy and X-ray crystallography. Under the same conditions, tetrakis(triphenylphosphine)-palladium yields only decomposition products.

INTRODUCTION

The reactions of low-valent transition metal compounds with elemental selenium or tellurium (or their precursors) have attracted the attention of a number of research groups in recent years [1]. We are interested in the use of such reactions for the preparation of metal polychalcogenides, and in the reactivity of the products toward activated alkynes to yield dithiolenes, diselenolenes, etc. [2]. Chatt and Mingos [3] showed in 1970 that, on treatment with sulfur, zerovalent palladium and platinum complexes yield tetrasulfides $[MS_4L_2]$ (M = Pd, Pt; L = PPh_3 or L_2 = $Ph_2PCH_2CH_2PPh_2$). The crystal structures of two of the products were subsequently determined [4]. Further examination showed that the dimer $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ may also be isolated from the reaction of $[Pt(PPh_3)_4]$ with elemental sulfur [5]. The behavior of selenium in this system was investigated at around the same time by Ugo *et al.* [6], but they obtained only a low yield of an unidentified product. We were therefore prompted to re-examine the reactions of $[M(PPh_3)_4]$ (M = Pd, Pt) with red or vitreous selenium.

RESULTS AND DISCUSSION

No change was observed after a toluene solution of $[Pd(PPh_3)_4]$ had been stirred with six equivalents of selenium for several days at room temperature.

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When the mixture was heated to reflux, however, the solution rapidly decolorized, and a dark brown-black solid was precipitated. This insoluble material appeared to be a complex mixture, and was not characterized.

Although similar behavior at room temperature was exhibited by $[Pt(PPh_3)_4]$, after 4 hours at reflux the selenium was seen to dissolve, and a yellow-brown precipitate was produced. This was collected by filtration, washed with petroleum ether, and dried. Removal of the solvent from the filtrate yielded virtually pure triphenylphosphine selenide. The precipitate was soluble only in chlorinated solvents. After dissolution in dichloromethane, filtration to remove traces of unreacted selenium, and removal of the solvent by evaporation, a yellow-orange solid was obtained. Fast Atom Bombardment (FAB) mass spectroscopy (see Figure 1) and microanalysis indicate that this has the stoichiometry $Pt_2Se_2(PPh_3)_4 \cdot CH_2Cl_2$.

A sample was dissolved in $CDCl_3$ and examined by multinuclear NMR spectroscopy. The data obtained are summarized in Tables 1 and 2. These reveal that two compounds (1 and 2) are present in solution, in approximately equal proportions. Compound 2 may be identified as $[PtCl_2(PPh_3)_2]$ by comparison of the data with those for an authentic sample. The first component (1) may be isolated in a pure form by passing a dichloromethane solution of the mixture through a short alumina column and allowing the solvent to evaporate from the eluate. It is air- and water-stable and has been identified by spectroscopic and analytical methods as $[Pt(Se_2CH_2)(PPh_3)_2]$. The structure of this compound has been determined by X-ray crystallography and

TABLE 1 NMR Chemical Shifts for **1** and **2**

	1	2
$\delta(^1H)^a$	4.98	—
$\delta(^{13}C)^b$	3.9	—
$\delta(^{31}P)$	20.6	13.0
$\delta(^{77}Se)$	1320.3	—
$\delta(^{195}Pt)$	82.4	63.4

[a] C_6H_5: 7.50–7.45 (*o*-), 7.33–7.24 (*p*-), 7.18–7.13 (*m*-).
[b] C_6H_5: 134.7 (*o*-), 130.2 (*p*-), 129.6 (*ipso*-), 127.4 (*m*-).

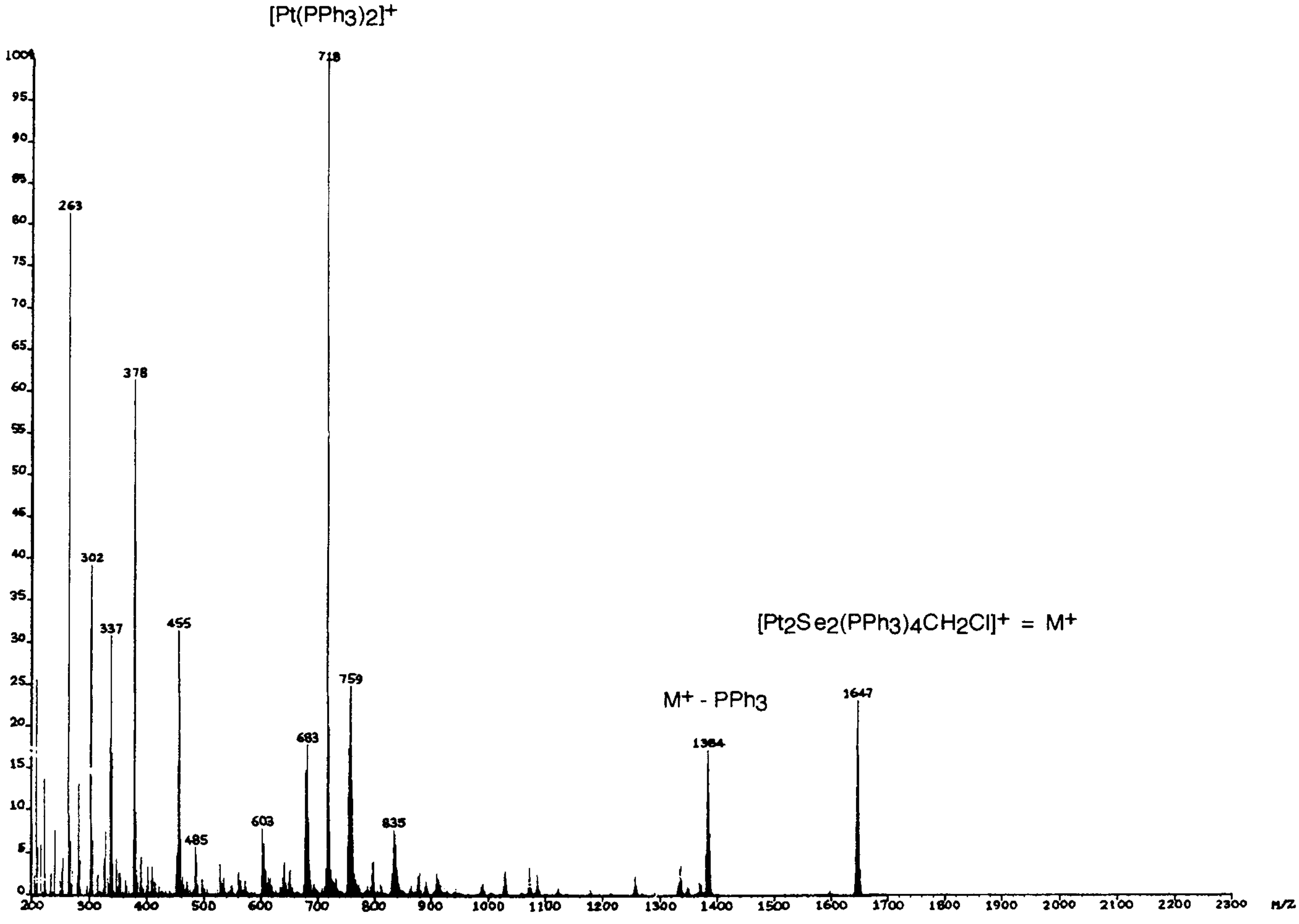


FIGURE 1 FAB mass spectrum of the product from the reaction of $[Pt(PPh_3)_4]$ with selenium, after dissolution in CH_2Cl_2.

TABLE 2 NMR Coupling Constants for **1** (in Hz)

	$^{1}H^{a}$	$^{13}C^{a}$	^{31}P	^{77}Se	^{195}Pt
^{1}H^{a}	—	157	1.8	~12	38.4
^{13}C^{a}	157	—	<1.0	52.3	67.9
^{31}P	1.8	<1.0	21.8^{b}	31.0, 11.0^{c}	2964^{b}
^{77}Se	~12	52.3	31.0, 11.0^{c}	*	*
^{195}Pt	38.4	67.9	2964^{b}	*	—

*Not determined.
^{a}CH$_2$ group only.
^{b}Data for **2**: $J(^{31}P–^{31}P)$ = 15.7 Hz; $J(^{31}P–^{195}Pt)$ = 3674 Hz.
$^{c}J(^{31}P_{cis}–^{77}Se)$ and $J(^{31}P_{trans}–^{77}Se)$ have the same sign.

is shown in Figure 2. Selected bond lengths and angles are listed in Table 3.

No difference in reactivity between freshly prepared red selenium (Se$_8$) and the commercial vitreous form was observed. Similarly, samples of [Pt(PPh$_3$)$_4$] obtained either commercially or by a literature procedure [7] yielded the same result.

Several groups of workers have observed that sulfide groups bridging between two electron-rich metal centers are powerful nucleophiles. It has recently been demonstrated that [Pt$_2$(μ-S)$_2$(dppy)$_4$] (dppy = 2-diphenylphosphinopyridine) reacts with dichloromethane as shown in Equation 1 [8]. The reaction almost certainly proceeds via a cationic intermediate, analogous to that isolated by Gukathasan *et al.* (Equation 2) [5].

$$[Pt_2(\mu\text{-}S)_2(dppy)_4] + CH_2Cl_2 \longrightarrow [Pt(S_2CH_2)(dppy)_2] + [PtCl_2(dppy)_2] \qquad (1)$$

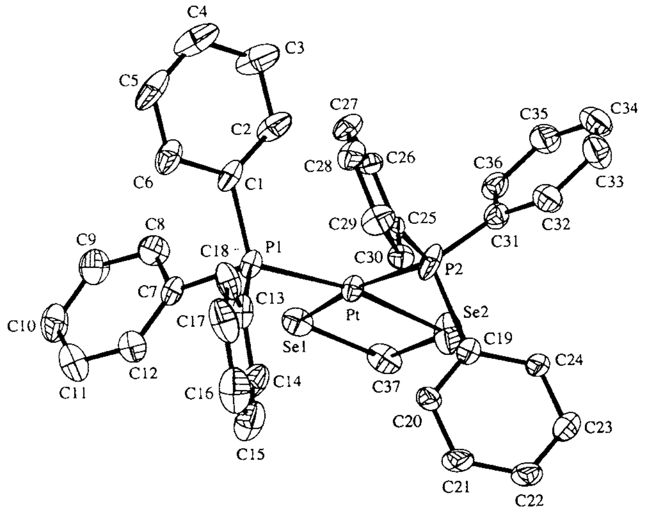
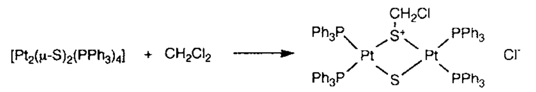
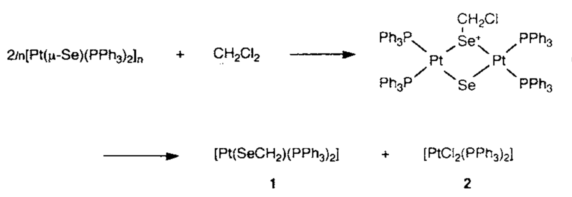


FIGURE 2 Structure of **1**, showing one orientation each of the three disordered phenyl rings on P(2). Hydrogen atoms and the other orientation of the disordered phenyl groups are omitted for clarity.


(2)

$$n[Pt(PPh_3)_4] + 3n/xSe_x \xrightarrow[\Delta]{\text{Toluene}} [Pt(\mu\text{-}Se)(PPh_3)_2]_n + 2nPh_3PSe \qquad (3)$$


(4)

Bridging selenide groups may be expected to display similar reactivity. We therefore conclude that the first-formed product in the reaction of [Pt(PPh$_3$)$_4$] with selenium is dimeric or oligomeric, e.g., [Pt(μ-Se)(PPh$_3$)$_2$]$_n$ (Equation 3). There is no evidence to suggest that a mononuclear polyselenide analogous to [PtS$_4$(PPh$_3$)$_2$] is produced. Reaction of the oligomer with dichloromethane then yields a 1 : 1 mixture of **1** and **2** quantitatively, presumably via a cationic intermediate (Equation 4).

Compound **1** is a derivative of the unknown methanediselenol and contains a novel planar Pt-Se$_2$C four-membered ring. The only previously reported example of a selenium-containing ligand of this type is found in the cyclopentadienylcobalt complex [C$_5$H$_5$Co(Se$_2$CMe$_2$)PMe$_3$], where the CoSe$_2$C ring was assumed to be folded on the basis of NMR data [9]. The four-membered ring in **1** is substantially distorted by the different bonding preferences of the atoms involved, and the angle subtended at platinum (77.05°) shows considerable deviation from the ideal value (90°). Analogous geometries have been observed in platinum methanedithiolate complexes, as summarized in Table 4 [8,10]. The bond lengths in **1** are normal, and similar to those in the phenylselenolate complex [Pt(SePh)$_2$(dppm)] (Pt–Se = 2.434, 2.461 Å) [11].

The NMR parameters for **1** may be compared with those obtained previously for platinum selenolate and methanedithiolate complexes (see Tables 5 and 6). The CH$_2$ group exhibits a relatively large $^{1}J(^{1}H–^{13}C)$ for an sp^3-hybridized carbon atom, as a consequence of the compressed Se–C–Se angle. The $^{13}C–^{31}P$ coupling for this group is, however, undetectably small. We also have not been able to observe $^{77}Se–^{77}Se$ or $^{77}Se–^{195}Pt$ coupling.

Figure 3 shows the central satellite structure of the ^{31}P resonances for **1** and **2**, resulting from coupling to the ^{13}C nuclei at the *ipso*- and *ortho*-positions in the phenyl rings, and, in the case of **1**, one of the two possible ^{77}Se nuclei. The coupling constants $J(^{13}C–^{31}P)$ are similar for the two compounds (see Table 7), and the satellites are effectively the superposition of two (for **2**) or three (for **1**) AA′X subspectra.

TABLE 3 Selected Bond Lengths (Å) and Angles (°) for **1**

Pt–P(1)	2.274(2)	Pt–P(2)	2.290(2)
Pt–Se(1)	2.4177(8)	Pt–Se(2)	2.4352(11)
Se(1)–C(37)	1.967(8)	Se(2)–C(37)	1.949(8)
P(1)–C(1)	1.806(4)	P(1)–C(7)	1.840(4)
P(1)–C(13)	1.836(4)	P(2)–C(19)	2.020(6)
P(2)–C(19′)	1.599(7)	P(2)–C(25)	1.907(7)
P(2)–C(25′)	1.937(7)	P(2)–C(31)	1.608(7)
P(2)–C(31′)	2.050(8)		
P(1)–Pt–P(2)	101.46(7)	P(1)–Pt–Se(1)	93.08(5)
P(2)–Pt–Se(1)	165.44(6)	P(1)–Pt–Se(2)	167.81(6)
P(2)–Pt–Se(2)	88.59(6)	Se(1)–Pt–Se(2)	77.05(3)
C(37)–Se(1)-Pt	90.9(2)	C(37)–Se(2)–Pt	90.8(2)
C(1)–P(1)–Pt	117.6(2)	C(7)–P(1)–P(t)	115.1(2)
C(13)–P(1)–Pt	111.0(2)	C(1)–P(1)–C(7)	100.0(2)
C(1)–P(1)–C(13)	108.9(2)	C(13)–P(1)–C(7)	102.9(2)
C(19)–P(2)–Pt	107.4(3)	C(25)–P(2)–Pt	119.3(3)
C(31)–P(2)–Pt	117.3(4)	C(25)–P(2)–C(19)	96.2(4)
C(31)–P(2)–C(19)	106.6(4)	C(31)–P(2)–C(25)	107.3(5)
C(19′)–P(2)–Pt	121.4(4)	C(25′)–P(2)–Pt	120.5(3)
C(31′)–P(2)–Pt	105.2(3)	C(19′)–P(2)–C(25′)	105.9(5)
C(19′)–P(2)–C(31′)	105.9(5)	C(25′)–P(2)–C(31′)	93.1(4)
C(2)–C(1)–P(1)	118.7(3)	C(6)–C(1)–P(1)	121.1(3)
C(8)–C(7)–P(1)	116.7(3)	C(12)–C(7)–P(1)	123.3(3)
C(14)–C(13)–P(1)	115.8(3)	C(18)–C(13)–P(1)	124.2(3)
C(20)–C(19)–P(2)	123.8(5)	C(24)–C(19)–P(2)	116.1(5)
C(20′)–C(19′)–P(2)	115.3(7)	C(24′)–C(19′)–P(2)	124.4(7)
C(26)–C(25)–P(2)	109.6(5)	C(30)–C(25)–P(2)	130.2(5)
C(26′)–C(25′)–P(2)	108.3(5)	C(30′)–C(25′)–P(2)	131.6(5)
C(32)–C(31)–P(2)	122.2(6)	C(36)–C(31)–P(2)	117.2(6)
C(32′)–C(31′)–P(2)	116.6(6)	C(36′)–C(31′)–P(2)	123.4(6)
Se(2)–C(37)–Se(1)	101.1(3)		

TABLE 4 Bond Lengths (Å) and Angles (°) for $[Pt(E_2CH_2)(PR_3)_2]$ Derivatives [8,10]

	1	$[Pt(S_2CH_2)(PMe_2Ph)_2]$	$[Pt(S_2CH_2)(dppy)_2]$
Pt–E	2.4177, 2.4352	2.301, 2.309	2.314, 2.310
Pt–P	2.274, 2.290	2.244, 2.257	2.279, 2.277
E–C	1.967, 1.949	1.82, 1.84	1.814, 1.831
E–Pt–E	77.05	76.1	76.23
E–Pt–P_{cis}	88.59, 93.08	94.6, 95.0	90.72, 92.38
P–Pt–P	101.46	94.3	100.65
Pt–E–C	90.9, 90.8	91.3, 90.4	90.3, 90.0
E–C–E	101.1	102.1	103.0

TABLE 5 NMR Parameters for Platinum Selenolate Complexes [11,12][a]

	1	$[PtX_2(dppm)]$	$[PtX_2(dppe)]$	$[PtX_2(dppp)]$	cis-$[PtX_2(PPh_3)_2]$
$\delta(^{31}P)$	20.6	−51.7	46.4	−5.8	27.2
$J(^{31}P–^{195}Pt)$	2964	2530	2957	2798	3007
$\delta(^{77}Se)$	1320.3	*	*	*	321
$J(^{31}P–^{77}Se)_{trans,cis}$	31.0, 11.0	32, ~9	*	45	45.3

*Not determined.

[a] X = SePh; dppm, dppe, dppp = $Ph_2P(CH_2)_nPPh_2$ (n = 1, 2, 3).

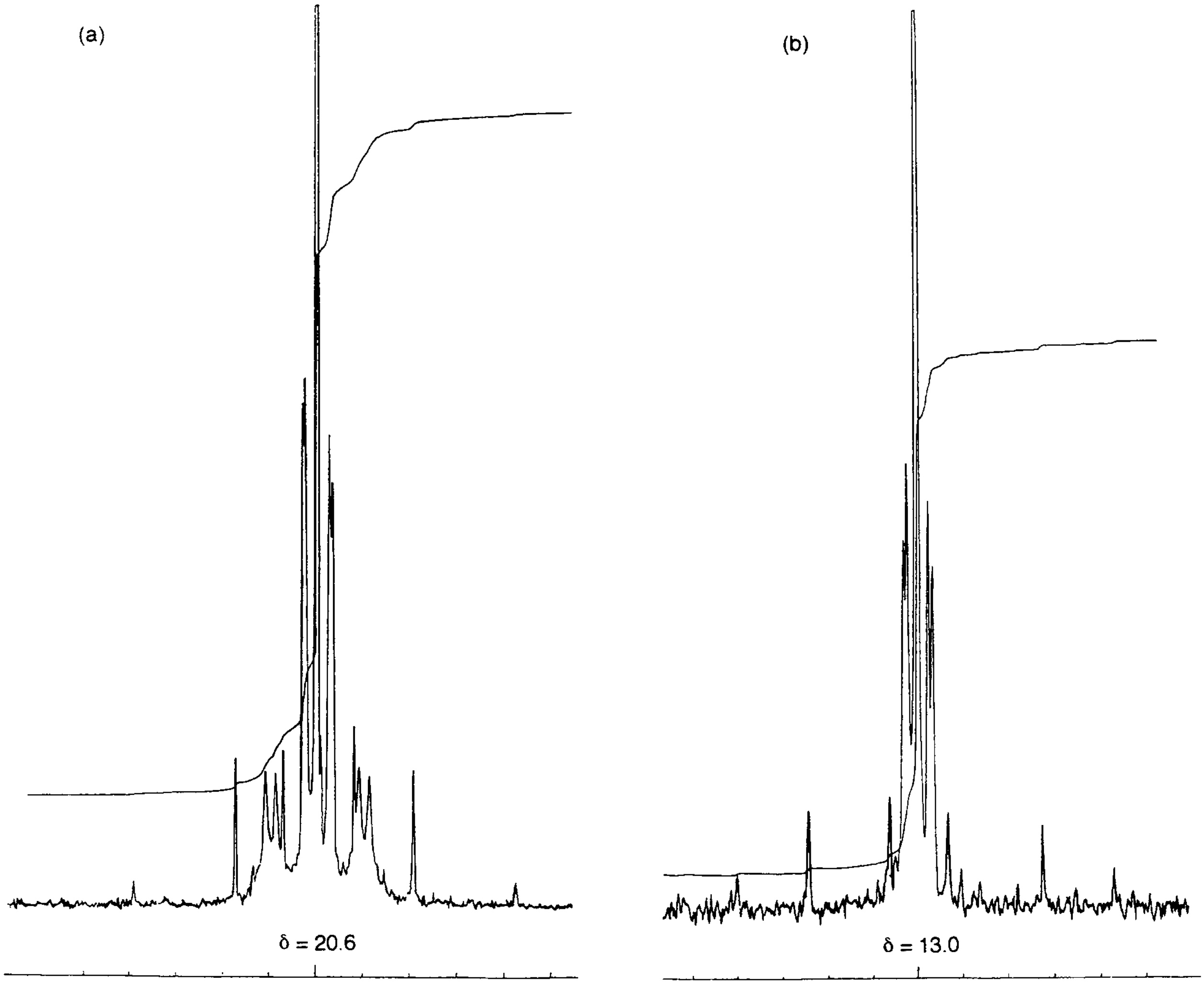


FIGURE 3 Details of ^{31}P NMR spectra of (a) **1** and (b) **2**, showing central satellite structure. Each scale division represents 10 Hz.

TABLE 6 NMR Parameters for [Pt(E_2CH_2)(PR_3)$_2$] Derivatives [8,10]

	1	*[Pt(S_2CH_2)(PPh_3)$_2$]*	*[Pt(S_2CH_2)(dppy)$_2$]*
$\delta(^1H)$	4.98	5.67	5.54
$J(^1H–^{195}Pt)$	38.4	43	42.2
$J(^1H–^{31}P)$	1.8	1.8	1.8
$\delta(^{31}P)$	20.6	21.4	20.8
$J(^{31}P–^{195}Pt)$	2964	2979	2910

TABLE 7 $^{13}C–^{31}P$ Coupling Constants (Hz) for **1** and **2**[a]

	1	**2**
$^1J(C_{ipso}–P)$, $^3J(C_{ipso}–P')$	52.1, 1.6	65.6, 1.3
$^2J(C_{ortho}–P)$, $^4J(C_{ortho}–P')$	10.3, 0.6	11.7, 0.7

[a] The members of each pair have the same sign.

Coupling to ^{13}C nuclei in the *meta-* or *para*-positions is not resolved. The peaks corresponding to the AA'XX' system, which would result from the simultaneous presence of two ^{77}Se nuclei in **1**, are too weak to be observed.

CONCLUSION

It is evident that there are significant differences between the reactions of sulfur and selenium with tetrakis(triphenylphosphine)palladium and -platinum. In the latter case, a mononuclear polychalcogenide is not produced. The product obtained reacts with dichloromethane to yield a 1 : 1 mixture of the methanediselenolate [Pt(Se_2CH_2)(PPh_3)$_2$] (**1**) and [$PtCl_2$(PPh_3)$_2$] (**2**). It is therefore presumed to contain bridging selenide ligands, and may be formulated as [Pt(μ-Se)(PPh_3)$_2$]$_n$. We are currently investigating further the structure and reactivity of this material.

EXPERIMENTAL

All reactions were performed by use of standard Schlenk techniques and pre-dried solvents under nitrogen. Tetrakis(triphenylphosphine)platinum was either obtained commercially (Aldrich), or prepared according to the literature [10]. Tetrakis(triphenylphosphine)palladium was prepared by an analogous procedure. Selenium was used either in the commercially available vitreous form (Aldrich), or as the red form prepared by ferrous ion reduction of selenious acid.

NMR spectra: Bruker ACP400. Standards: internal Me_4Si(^1H, ^{13}C); 85% H_3PO_4 (^{31}P); Me_2Se in $CDCl_3$ (^{77}Se); Na_2PtCl_6 in D_2O (^{195}Pt). Mass spectra were recorded by the SERC Mass Spectrometry Centre using the Fast Atom Bombardment (FAB) technique.

Preparation of Methanediselenolatobis-(triphenylphosphine)platinum(II), 1

A mixture of $[Pt(PPh_3)_4]$ (0.87 g, 0.7 mmol) and selenium (0.33 g, 4.2 mmol) in toluene (50 mL) was heated for 4 hours under reflux. During this time, the selenium was seen to dissolve, and a yellow-brown precipitate was produced. The solid was collected by filtration, washed with petroleum ether (bp 40–60°C), and dried under reduced pressure. It was dissolved in dichloromethane, giving a yellow-orange solution. This was filtered to remove traces of residual selenium, and the solvent then removed by evaporation under reduced pressure to yield a yellow-orange solid. Yield: 0.55 g (93%). MS: see Figure 1. Anal. calcd. for $C_{73}H_{62}Cl_2P_4Pt_2Se_2$ (1682.8): C, 52.12; H, 3.72. Found: C, 52.09; H, 3.75.

Examination of a $CDCl_3$ solution of the product by NMR spectroscopy revealed it to be a mixture of 1 and 2. It was redissolved in dichloromethane and passed through a short alumina column to yield a single orange band. The eluate was diluted with toluene, and the solvent then slowly allowed to evaporate. Compound 1 crystallized as orange prisms, which were collected by decantation, washed with petroleum ether (bp 40–60°C), and dried in air at room temperature. Yield: 0.25 g (40%). NMR spectroscopic data for 1 are summarized in Tables 1 and 2. MS: $m/z = 892$ (M^+, with expected isotope distribution pattern).

Crystal Structure Analysis

Crystal Data for 1. $C_{37}H_{32}P_2PtSe_2$; $M = 891.58$; monoclinic, space group $P2_1/c$, $a = 10.943(3)$, $b = 9.619(1)$, $c = 31.478(1)$ Å, $\beta = 97.240(6)°$, $V = 3287.0(9)$ Å^3; $Z = 4$; $D_c = 1.802$ Mgm^{-3}; $F(000) = 1720$; orange prism, $T = 293$ K; crystal size 0.35 × 0.20 × 0.15 mm; μ(Mo-K_α) = 6.606 mm^{-1}.

Data Collection and Processing. The intensity data were collected on a FAST TV area detector diffractometer with Mo-K_α radiation ($\lambda = 0.71069$ Å) following previously described procedures [13]. 11177 reflections were measured giving 5340 unique data. The structure was solved by Patterson methods (SHELX-S) [14] and refined by full-matrix least-squares on Fo^2 (SHELXL-93) [15] using all unique data corrected for absorption (DIFABS) [16]. Final wR_1 (on Fo^2) and R_1 (on F) were 0.0939 and 0.0482 for all data [0.0730 and 0.0302 for 3434 data with $I > 2\sigma(I)$]. The phenyl rings were idealized with C–C = 1.390 Å and C–C–C = 120.0°. All non-H atoms were refined anisotropically, the H atoms riding with U_{iso}'s set at 1.2 times the U_{eq} of the parent. The three phenyl rings on $P(2)$ were orientationally disordered: these were refined with fractional occupancies.

Atomic coordinates and thermal parameters are available on request from the Cambridge Crystallographic Data Centre.

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REFERENCES

[1] S. M. Stuczynski, Y. U. Kwon, M. L. Steigerwald, *J. Organomet. Chem., 449*, 1993, 167; S. J. Hibble, D. A. Rice, M. J. Almond, K. A. H. Mohammed, S. P. Pearse, J. R. Sagar, *J. Mater. Chem., 2*, 1992, 1237.

[2] C. M. Bollinger, T. B. Rauchfuss, *Inorg. Chem., 21*, 1982, 3947; D. S. Dudis, C. King, J. P. Fackler, Jr., *Inorg. Chim. Acta, 181*, 1991, 99.

[3] J. Chatt, D. M. P. Mingos, *J. Chem. Soc. (A)*, 1970, 1243.

[4] D. S. Dudis, J. P. Fackler, Jr., *Inorg. Chem., 21*, 1982, 3577; C. E. Briant, M. J. Calhorda, T. S. A. Hor, N. D. Howells, D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1983, 1325.

[5] R. R. Gukathasan, R. H. Morris, A. Walker, *Can. J. Chem., 61*, 1983, 2490.

[6] R. Ugo, G. La Monica, C. Cennini, A. Segre, F. Conti, *J. Chem. Soc. (A)*, 1971, 522.

[7] R. Ugo, F. Cariati, G. La Monica, *Inorg. Synth., 11*, 1968, 105.

[8] V. W-W. Yam, P. K.-Y. Yeung, K.-K. Cheung, *J. Chem. Soc., Chem. Comm.*, 1995, 267.

[9] L. Hofmann, H. Werner, *Chem. Ber., 118*, 1985, 4229.

[10] A. Shaver, R. D. Lai, P. H. Bird, W. Wickramasinghe, *Can. J. Chem., 63*, 1985, 2555.

[11] V. K. Jain, S. Kannan, R. J. Butcher, J. P. Jasinski, *J. Chem. Soc., Dalton Trans.*, 1993, 1509.

[12] V. W. Day, D. A. Lesch, T. B. Rauchfuss, *J. Am. Chem. Soc., 104*, 1982, 1290.

[13] J. A. Darr, S. R. Drake, M. B. Hursthouse, K. M. A. Malik, *Inorg. Chem., 32*, 1993, 5704.

[14] G. M. Sheldrick, *Acta Crystallogr., Sect. A, 46*, 1990, 467.

[15] G. M. Sheldrick: *SHELXL-93 Program for Crystal Structure Refinement*, University of Göttingen, Germany, 1993.

[16] N. P. C. Walker, D. Stuart, *Acta Crystallogr., Sect. A, 39*, 1983, 158.