# Cationic thiolate and selenolate complexes of platinum(IV)

**Michael C. Janzen, Michael C. Jennings, and Richard J. Puddephatt**

**Abstract**: The reaction of the adamantanoid compounds $[Hg_4(EPh)_6(L)_4][ClO_4]_2$ (E = S or Se, L = $PEt_3$ or $PPh_3$) with $[PtMe_2(bu_2bpy)]$ ($bu_2bpy$ = 4,4′-di-*tert*-butyl-2,2′-bipyridine) occurs easily to give the first examples of cationic thiolate or selenolate derivatives of platinum(IV), $[PtMe_2(EPh)L(bu_2bpy)][ClO_4]$, and the addition is shown to occur with *trans* stereochemistry. The new complexes are characterized by NMR spectroscopy and when L = $PEt_3$ by X-ray structure determinations. When L = $PPh_3$, a competitive reaction leads to methyl group transfer from platinum to mercury to give MeHgEPh (E = S or Se).

*Key words*: oxidative-addition, platinum, thiolate, selenolate, mercury.

**Résumé** : La réaction de composés adamantanoïdes $[Hg_4(EPh)_6(L)_4][ClO_4]_2$ (E= S ou Se, L = $PEt_3$ ou $PPh_3$) avec $[PtMe_2(bu_2bpy)]$ ($bu_2bpy$ = 4,4′-di-*tert*-butyl-2,2′-bipyridine) se produit facilement pour fournier les premiers exemples de dérivés thiolates ou sélénolates cationiques du platine(IV), $[PtMe_2(EPh)L(bu_2bpy)][ClO_4]$ et on a observé que l'addition se produit avec une stéréochimie *trans*. Les nouveaux complexes ont été caractérisés par spectroscopie RMN et, lorsque L = $PEt_3$, par diffraction des rayons X. Lorsque L = $PPh_3$, une réaction parallèle conduit à un transfert de groupe méthyle à partir du platine vers le mercure pour donner le MeHgEPh (E = S ou Se).

*Mots clés* : addition oxydante, platine, thiolate, sélénolate, mercure.

[Traduit par la Rédaction]

## Introduction

There is a rich chemistry resulting from reactions of Hg—X bonds from mercury(II) compounds to the organoplatinum(II) centres in complexes $[PtMe_2L_2]$ and related compounds (1, 2). For example, oxidative addition of $HgX_2$ to $[PtMe_2(bu_2bpy)]$ ($bu_2bpy$ = 4,4′-di-*tert*-butyl-2,2′-bipyridine) (**1**) gives $[PtMe_2(HgX)(X)(bu_2bpy)]$ (X = Cl, Br, $O_2CCF_3$) (1). However, if the platinum(II) centre is less electron rich or the mercury centre is less electrophilic, the reaction may occur to give a platinum–mercury donor–acceptor bond. This form of reactivity is observed with $[Pt\{CH_2C_6H_4P(o\text{-tolyl})_2\}(S_2CNMe_2)]$ and $HgX_2$ (X = Br, I) and for the reaction of **1** with $[PtMe_2(HgX)(X)(bu_2bpy)]$ (X = Cl, Br, $O_2CCF_3$) (2). Further reactions of these products can occur to give overall alkyl–halide exchange reactions, with the formation of $[PtXMeL_2]$ and MeHgX (1*g*). No reactions involving Hg(II)—E (E = S, Se) bonds with organoplatinum(II) complexes have yet been reported. It is known that oxidative addition of the Sn(IV)—E bonds in the ring compounds $[(R_2SnE)_3]$ (R = Me, Ph) to complex **1** occurs easily, giving interesting platinum(IV) complexes containing PtESnESn rings (3). By analogy, it was considered possible that oxidative addition of the Hg(II)—E bonds of the adamantanoid compounds $[Hg_4(EPh)_6(L)_4][ClO_4]_2$ (**2a**–**d**) (Chart 1), might give novel cage complexes containing platinum(IV) centres (4, 5).

It was found that the reactions of **1** with compounds **2a**–**d** occurred easily but with fragmentation of the adamantanoid units to give the first cationic thiolato or selenelato complexes of platinum(IV), as described below. The $SE^-$ ligand (E = S or Se) is reducing in nature and tends to form stable complexes with platinum(II) rather than platinum(IV) (6). Since cationic platinum(IV) complexes are more easily reduced than neutral ones, it is not surprising that the known thiolate or selenolate derivatives of platinum(IV) are all neutral (7). However, it will be seen that cationic REPt(IV) complexes can be prepared and that they may have good thermal stability.

## Results

The reaction of complex **1** with $[Hg_4(EPh)_6(L)_4][ClO_4]_2$ (**2**) appeared to occur mostly according to eq. [1].

[1] $$[PtMe_2(bu_2bpy)]\ (\mathbf{1}) + 0.5[Hg_4(EPh)_6L_4][ClO_4]_2\ (\mathbf{2}) \rightarrow [PtMe_2(EPh)L(bu_2bpy)][ClO_4]\ (\mathbf{3}) + Hg(EPh)_2L + Hg(0)$$

For example, when L = $PEt_3$, a mixture of products was formed from which the corresponding complex $[PtMe_2(EPh)(PEt_3)(bu_2bpy)][ClO_4]$ (E = S (**3a**) or Se (**3b**)) could be crystallized as an air-stable yellow solid. The other products from the reaction were not isolated in pure form and the identity of the proposed product $Hg(EPh)_2L$ (eq. [1]) remains uncertain, as discussed below.

Received 10 August 2001. Published on the NRC Research Press Web site at http://canjchem.nrc.ca on 10 January 2002.

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 DOI: 10.1139/V01-187 

**Fig. 1.** A view of the molecular structure of complex **3a** roughly down the S—Pt bond, showing the orientation of the phenyl group with respect to the $bu_2bpy$ ligand. Only one component of each of the disordered ethylphosphorus groups is shown for clarity.

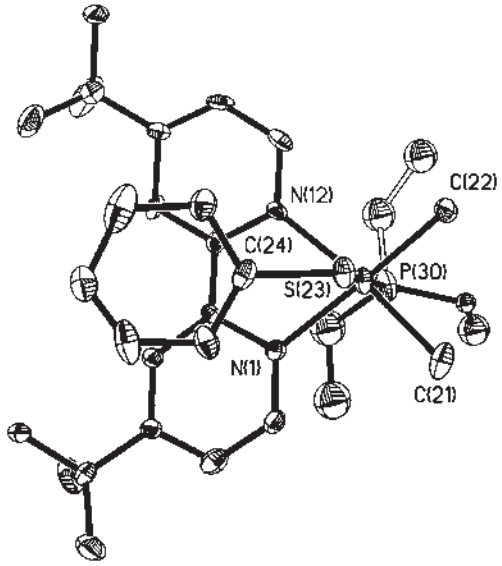
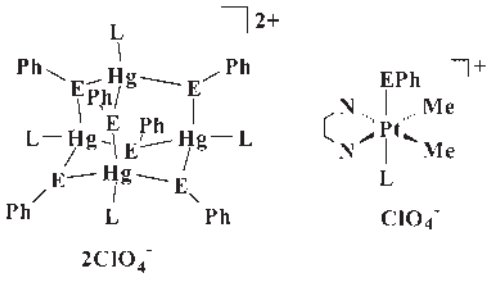


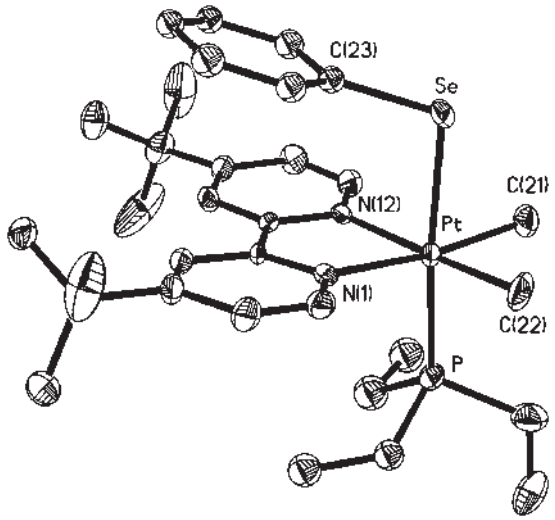

**Chart 1.** NN = $bu_2bpy$.




**2a**, E=S, L=$PEt_3$ **3a**, E=S, L=$PEt_3$
**2b**, E=Se, L=$PEt_3$ **3b**, E=Se, L=$PEt_3$
**2c**, E=S, L=$PPh_3$ **3c**, E=S, L=$PPh_3$
**2d**, E=Se, L=$PPh_3$ **3d**, E=Se, L=$PPh_3$

Complexes **3a** and **3b** were characterized spectroscopically and crystallographically. The $^1$H NMR spectrum of **3a** contained a single methylplatinum resonance, with the coupling constant ($^2J_{Pt,Me}$ = 66 Hz) in the range expected for methylplatinum(IV) complexes with methyl *trans* to nitrogen (8). The presence of a single methylplatinum resonance indicates that the product is formed by *trans* oxidative addition and so supports the structure shown in Chart 1. The mirror symmetry ($C_s$) of **3a** is also shown by the presence of only three aromatic $bu_2bpy$ peaks and one *tert*-butyl peak in the $^1$H NMR spectrum. The presence of the triethylphosphine ligand is shown in the $^{31}$P NMR spectrum of **3a** by the presence of a singlet resonance at $\delta$ = 0.29, with satellites due to the coupling ($^1J_{Pt,P}$ = 1895 Hz) and in the $^1$H NMR spectrum by the observation of coupling to the methylplatinum protons with $^3J_{P,Pt,Me}$ = 5 Hz. The magnitude of the coupling constant ($^1J_{Pt,P}$ = 1895 Hz) is consistent with the phosphine being *trans* to EPh, but is too high for a phosphine *trans* to a methyl group (9, 10). The resonances in the

**Fig. 2.** A view of the molecular structure of complex **3b**. Only one component of each of the disordered ethyl and phenyl groups is shown for clarity.



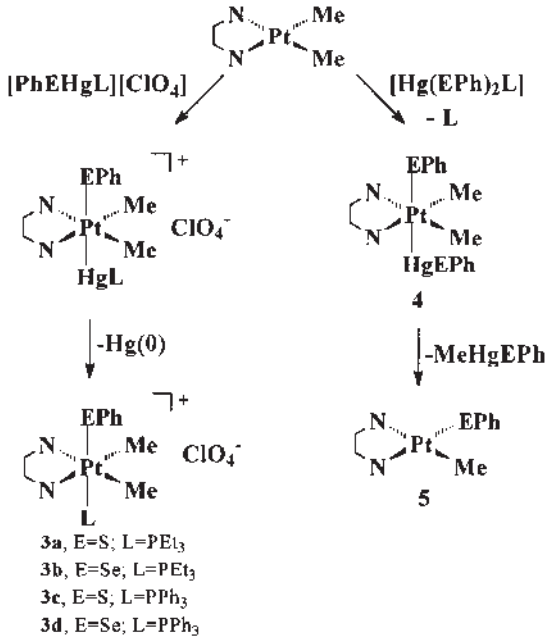

$^1$H NMR spectrum due to the EPh protons appear over the range $\delta$ = 6.25–6.52 and are lower in chemical shift than is normal for aryl protons, probably because they lie in the shielding region of the aromatic $bu_2bipy$ ligand (7). The NMR data has thus defined a structure with the phosphine ligand *trans* to the EPh group at platinum(IV). The spectra for complex **3b** are similar and are listed in the *Experimental* section.

The structures of **3a** and **3b** were determined crystallographically and are shown in Figs. 1 and 2, respectively, with relevant bond parameters listed in Table 1. The two compounds are isomorphous and have similar structures, with the EPh and $PEt_3$ ligands mutually *trans* at platinum(IV). In each complex, the phenyl substituent of the EPh ligand is oriented above the bipyridyl ligand. This leads to $\pi$-stacking (11) with intercentroid distances between the phenyl and N(1) pyridyl ring of 3.81 Å for **3a** and 3.64 Å for **3b** and between the phenyl and N(12) pyridyl ring of 4.04 Å for **3a** and 4.45 Å for **3b**. The Pt—P bond lengths are 2.315(5) and 2.291(4) Å for complexes **3a** and **3b**, respectively; comparison with other phosphine complexes of platinum(IV) (12) suggests that these distances are relatively short and, therefore, the EPh ligand has only a moderate *trans* influence. The slightly longer Pt—P bond in **3a** as compared to **3b** may indicate that the SPh ligand has a marginally higher *trans*-influence than SePh. In **3a**, the Pt—S bond distance of 2.398(5) Å and the Pt-S-C angle of 108.9(8)° are unexceptional. The only other structurally characterized arylthiolate complex of platinum(IV) with a two-coordinate sulfur atom is [($\eta^5$-$C_5Me_5$)$PtMe_2$(S-*p*-$C_6H_4Me$)], which has Pt—S = 2.344(1) Å and Pt-S-C = 108.4(2)° (13), very similar to the corresponding values in **3a**. The cubane complex [{$PtMe_3(\mu_3$-SPh)}$_4$], which contains four-coordinate sulfur atoms with sulfur *trans* to methyl, has a longer Pt—S = 2.506(5) Å and a more open angle Pt-S-C = 118.1(7)° (14). Several arylthiolate complexes of platinum(II) with two-coordinate sulfur atoms have been structurally characterized, and the bond parameters for the Pt-S-C units are similar to those for complex **3a** (15). In complex

**Table 1.** Selected bond distances (Å) and angles (°) for complexes **3a** and **3b**.

| | **3a** (E = S) | **3b** (E = Se) |
|---|---|---|
| **Bond distances** (Å) | | |
| Pt—P | 2.315(5) | 2.291(4) |
| Pt—E | 2.398(5) | 2.512(2) |
| Pt—N(1) | 2.14(1) | 2.13(1) |
| Pt—N(12) | 2.16(1) | 2.12(1) |
| Pt—C(21) | 2.13(2) | 2.10(2) |
| Pt—C(22) | 2.05(2) | 2.10(1) |
| **Bond angles** (°) | | |
| P-Pt-E | 176.7(2) | 174.9(1) |
| C-E-Pt | 108.9(8) | 106.1(8) |

**Scheme 1.** NN = $bu_2bpy$.




**3b**, the distance Pt—Se = 2.512(2) Å and angle Pt-Se-C = 106.1(9)° are similar to those in the known neutral Pt(IV)–SePh complexes. For example, corresponding parameters are $[PtMe_2(SePh)_2(phen)]$ (2.4896(9) Å, 103.7(2)°) (7) and $[PtMe_2(SePh)_2(bpy)]$ (2.478(1) Å, 2.498(1) Å, 103.4(4)°, 103.1(3)°) (7).

The reaction of complex **1** with $[Hg_4(SPh)_6(PEt_3)_4][ClO_4]_2$ (**2a**) was monitored by $^1H$ and $^{31}P$ NMR spectroscopy in an attempt to identify the other products of eq. [1]. Complex **3a** was readily identified as a major product (ca. 75% based on **1**), and it was shown that one equivalent of **2a** consumed at least 2 equivalents of **1** as required by eq. [1]. A second major product was identified by a resonance in the $^{31}P$ NMR spectrum at $\delta$ = 16.7, with satellites due to the coupling ($^1J_{P,Hg}$ = 2817 Hz). It is tentatively suggested that this complex is $Hg(SPh)_2(PEt_3)$ (eq. [1]), but it was not possible to isolate it in pure form to carry out further characterization. If the formulation is correct, it is likely to form a dimer or oligomer by forming $Hg_2(\mu\text{-SR})$ bridges (4, 16). The formation of trace amounts of metallic mercury was visually evident. In a similar reaction of **1** with **2b**, complex **3b** was identified as the major product, but several mercury(II) phosphine complexes appeared to be formed as indicated by several singlet resonances in the range $\delta$ = 5–24 in the $^{31}P$ NMR spectrum.

**Table 2.** Crystal data and experimental details.

| Complex | **3a**·$CH_2Cl_2$ | **3b**·$CH_2Cl_2$ |
|---|---|---|
| Empirical formula | $C_{33}H_{52}Cl_3N_2O_4PSPt$ | $C_{33}H_{52}Cl_3N_2O_4SePt$ |
| FW | 890.12 | 952.14 |
| $T$ (K) | 200 | 200 |
| $\lambda$ (Å) | 0.71073 | 0.71073 |
| Space group | $P2_1$ | $P2_1$ |
| $a$ (Å) | 13.4447(6) | 13.3754(4) |
| $b$ (Å) | 8.0461(4) | 8.1982(3) |
| $c$ (Å) | 18.9052(9) | 18.9704(6) |
| $\beta$ (°) | 109.443(3) | 109.970(1) |
| $V$ (Å$^3$) | 1928.5(2) | 1955.1(1) |
| $Z$ | 2 | 2 |
| $D_{calcd.}$ (g cm$^{-3}$) | 1.533 | 1.617 |
| $\mu$ (mm$^{-1}$) | 3.977 | 4.801 |
| $F(000)$ | 882 | 948 |
| $R_1$ [$I > 2\sigma(I)$][a] | 0.1054 | 0.0442 |
| $wR_2$ [$I > 2\sigma(I)$][a] | 0.2691 | 0.1125 |

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_o^2)^2/\Sigma wF_o 4]^{1/2}$.

The reaction of **1** and the triphenylphosphine derivatives $[Hg_4(EPh)_6L_4][ClO_4]_2$ (L = $PPh_3$; E = S (**2c**) or Se (**2d**)) were somewhat more complex. Again, the complexes $[PtMe_2(EPh)L(bu_2bpy)][ClO_4]$ (E = S (**3c**) or Se (**3d**)) were isolated as yellow solids. They were readily characterized by comparison of their $^1H$ and $^{31}P$ NMR spectra with those of the structurally characterized complexes **3a** and **3b**. When the reaction of **1** with **2c** was monitored by NMR spectroscopy, complex **3c** was identified as one major product. In addition, the $^{31}P$ spectrum contained a resonance at $\delta$ = 26.2 ($^1J_{P,Hg}$ = 3215 Hz) tentatively assigned to $Hg(SPh)_2(PPh_3)$. In the $^1H$ NMR spectrum, the known methylmercury(II) compound MeHgSPh was readily identified (17), present at about half the concentration of **3c**. A similar reaction of **1** with **2d** gave complex **3d** and a compound having $\delta(^{31}P)$ = 29.2 ($^1J_{P,Hg}$ = 3177 Hz), tentatively identified as $Hg(SePh)_2(PPh_3)$, while MeHgSePh was identified by its $^1H$ NMR spectrum (18).

The stoichiometry of these reactions can be understood by considering that the adamantanoid mercury(II) complexes (**2**) react as if they were comprised of two components: $[Hg_4(EPh)_6L_4][ClO_4]_2$ = 2[PhEHgL][$ClO_4$] + 2[$Hg(EPh)_2$L] (Scheme 1). The major product **3** is formed by oxidative addition of the fragment [PhEHgL][$ClO_4$] to **1** with loss of mercury metal. It is not known at which stage the mercury atom is extruded, or even at what stage the adamantane derivative fragments, but Scheme 1 shows one possible route. The oxidative addition probably occurs by a polar mechanism initiated by nucleophilic attack of the electron-rich platinum(II) centre of complex **1** to the electrophilic mercury(II), leading to the observed *trans* addition in the product complex **3**. There are several precedent-setting examples for the loss of mercury(0) from Pt–Hg bonded compounds, such as the reaction of *trans*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pt]$ with $Hg(O_2CMe)_2$ to yield $[(2\text{-}Me_2NCH_2C_6H_4)_2Pt(O_2CMe)_2]$ and Hg(0) (19).

The minor product MeHgEPh formed in the reactions of **1** with **2c** and **2d** is likely to be formed by the competing oxidative-addition reaction of complex **1** with the fragment $[Hg(EPh)_2L]$ to give intermediate **4** (Scheme 1), which can undergo reductive elimination to yield MeHgEPh and [PtMe(EPh)($bu_2$bpy)] (**5**). Complex **5** would then react with more **2** to give additional MeHgEPh. The formed complexes (**3**) are thermally stable, and therefore, cannot be the source of formation of MeHgEPh.

Clearly these reactions are more complex than was envisaged and they did not yield the anticipated platinum–mercury-bonded cage complexes. Nevertheless, they do give a simple route to the first cationic thiolate and selenolate complexes of platinum(IV), and it is shown that these compounds are both air-stable and thermally stable.

## Experimental

### General

NMR spectra were recorded by using a Varian 300 MHz spectrometer. Chemical shifts are reported with respect to TMS ($^1$H) or external $H_3PO_4$ ($^{31}$P) references. Solvents were dried and freshly distilled prior to use. Complexes **2** (4) and [$PtMe_2$($bu_2$bpy)] (20) were prepared according to the literature procedures. CAUTION: toxic methylmercury compounds are formed in some reactions; appropriate precautions should be taken.

#### *[($PtMe_2$(SPh)($PEt_3$)($bu_2$bpy)][$ClO_4$] (3a)*

A mixture of [$PtMe_2$($bu_2$bpy)] (80 mg, 0.162 mmol) and **2a** (133 mg, 0.162 mmol) was dissolved in $CH_2Cl_2$ (5 mL) and the mixture was stirred for 10 min. The yellow solution was filtered through dry Celite, and pentane (40 mL) was added to the filtrate to precipitate the product as a yellow microcrystalline solid, which was isolated by filtration, washed with pentane, and dried in vacuo. Yield: 58%. $^1$H NMR ($CD_2Cl_2$) δ: 8.56 (d, $^3J_{6,5}$ = 6 Hz, $^3J_{Pt,H6}$ = 14 Hz, 2H, H6), 7.95 (d, $^4J_{3,5}$ = 2 Hz, 2H, H3), 7.70 (dd, $^3J_{5,6}$ = 6 Hz, $^3J_{5,3}$ = 2 Hz, 2H, H5), 6.52–6.25 (m, 5H, $C_6H_5$), 1.42 (d, $^3J_{P,Me}$ = 5 Hz, $^2J_{Pt,H}$ = 66 Hz, 6H, Pt-Me), 1.46 (s, 18H, *t*-Bu), 1.38 (m, $J_{H,H}$ = 8 Hz, $J_{P,H}$ = 8 Hz, 6H, $CH_2$), 0.81 (m, $J_{H,H}$ = 8 Hz, $J_{P,H}$ = 8 Hz, 9H, $CH_3$). $^{31}$P NMR δ: –2.7 (s, $^1J_{Pt,P}$ = 1976 Hz, P-Pt). Anal. calcd. for $C_{32}H_{50}ClN_2O_4PSPt\cdot CH_2Cl_2$: C 43.78, H 5.79, N 3.09; found: C 43.88, H 5.83, N 2.99. Crystals suitable for X-ray crystallographic study were grown over a period of several days by slow diffusion of pentane into a $CH_2Cl_2$ solution at 22°C.

#### *[($PtMe_2$(SePh)($PEt_3$)($bu_2$bpy)][$ClO_4$] (3b)*

This complex was prepared similarly, except that **2b** was used instead of **2a**. Yield: 52%. $^1$H NMR ($CD_2Cl_2$) δ: 8.52 (d, $^3J_{6,5}$ = 6 Hz, $^3J_{Pt,H6}$ = 14 Hz, 2H, H6), 8.05 (d, $^4J_{3,5}$ = 2 Hz, 2H, H3), 7.59 (dd, $^3J_{5,6}$ = 6 Hz, $^3J_{5,3}$ = 2 Hz, 2H, H5), 6.85–6.42 (m, 5H, $C_6H_5$), 1.52 (d, $^3J_{P,Me}$ = 5 Hz, $^2J_{Pt,H}$ = 65 Hz, 6H, Pt-Me), 1.46 (s, 18H, *t*-Bu), 1.38 (m, $J_{H,H}$ = 7 Hz, $J_{P,H}$ = 7 Hz, 6H, -$CH_2$), 0.81 (m, $J_{H,H}$ = 7 Hz, $J_{P,H}$ = 8 Hz, 9H, -$CH_3$). $^{31}$P NMR δ: –5.83 (s, $^1J_{Pt,P}$ = 1966 Hz, P-Pt). Anal. calcd. for $C_{32}H_{50}ClN_2O_4PSePt\cdot CH_2Cl_2$: C 41.68, H 5.50, N 2.94; found: C 41.55, H 5.41, N 2.84. Crystals were grown as described for **3a**.

#### *[($PtMe_2$(SPh)($PPh_3$)($bu_2$bpy)][$ClO_4$] (3c)*

This was prepared similarly except that **2c** was used instead of **2a**. Yield: 43%. $^1$H NMR ($CD_2Cl_2$) δ: 7.88 (d, $^4J_{3,5}$ = 2 Hz, 2H, H3), 7.85 (d, $^3J_{6,5}$ = 6 Hz, $^3J_{Pt,H6}$ = 15 Hz, 2H, H6), 7.46–7.00 (m, 15H, $C_6H_5$), 6.61–6.30 (m, 5H, $SC_6H_5$), 1.71 (d, $^3J_{P,Me}$ = 5 Hz, $^2J_{Pt,H}$ = 65 Hz, 6H, Pt-Me), 1.43 (s, 18H, *t*-Bu). $^{31}$P NMR δ: –0.2 (s, $^1J_{Pt,P}$ = 1802 Hz, P-Pt). Anal. calcd. for $C_{44}H_{50}ClN_2O_4PSPt$: C 54.80, H 5.23, N 2.90; found: C 54.71, H 5.19, N 2.80.

#### *[($PtMe_2$(SePh)($PPh_3$)($bu_2$bpy)][$ClO_4$] (3d)*

This was prepared similarly except that **2d** was used instead of **2a**. Yield: 39%. $^1$H NMR ($CD_2Cl_2$) δ: 7.93 (d, $^4J_{3,5}$ = 2 Hz, 2H, H3), 7.81 (d, $^3J_{6,5}$ = 6 Hz, $^3J_{Pt,H6}$ = 14 Hz, 2H, H6), 7.50–6.95 (m, 15H, $C_6H_5$), 6.53–6.20 (m, 5H, $SeC_6H_5$), 1.75 (d, $^3J_{P,Me}$ = 5 Hz, $^2J_{Pt,H}$ = 66 Hz, 6H, Pt-Me), 1.44 (s, 18H, *t*-Bu). $^{31}$P NMR δ: –3.6 (s, $^1J_{Pt,P}$ = 1860 Hz, P-Pt). Anal. calcd. for $C_{44}H_{50}ClN_2O_4PSePt$: C 52.25, H 4.98, N 2.77; found: C 52.07, H 4.79, N 2.69.

### X-ray structure determinations

Crystals of **3a** and **3b**, as perchlorate salts, were mounted on glass fibres. Data were collected using a Nonius Kappa-CCD diffractometer using COLLECT software (21*a*). Crystal cell refinement and data reduction were carried out using the Nonius DENZO package (21*a*). The data were scaled using SCALEPACK (21*a*) and no other absorption corrections were applied. The SHEXTL 5.1 program was used to solve the structure by direct methods, followed by successive difference Fouriers (21*b*). Crystallographic details are listed in Table 2.[2] The two compounds are isomorphous, each crystallizing in space group $P2_1$ with one molecule of $CH_2Cl_2$ of solvation. For complex **3a**, two of the ethyl groups on the phosphorus atom were modeled as isotropic, half occupancy moieties. Only one of each disordered ethyl group is shown in Fig. 1 for clarity. The third ethyl group was also kept isotropic. For complex **3b**, the phenyl ring attached to the selenium atom was modeled as two half-occupancy rings with isotropic carbon atoms. Two of the ethyl groups on the phosphorus atom were also modeled as isotropic, half-occupancy moieties. In Fig. 2 only one of each disordered group is shown for clarity. In both compounds, there was disorder of the $CH_2Cl_2$ molecule and of the $ClO_4^-$ anion, and they were modeled with geometrical constraints.

## Acknowledgments

We thank the NSERC (Canada) for financial support and for a scholarship to MCJ. RJP thanks the Government of Canada for a Canada Research Chair. Thanks are given to

[2] Supplementary material may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada. For information on obtaining material electronically go to http://www.nrc.ca/cisti/irm/unpub_e.shtml. Crystallographic information has also been deposited with the Cambridge Crystallographic Data Centre (CCDC Nos. 168359–168360). Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk)

Prof. P.A.W. Dean for a generous gift of samples of complexes **2** and for helpful discussions.

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