

Oxidative Addition of Phenylselenenyl Halides to Platinum(0) Complexes: Characterisation and Reactivity of the Products [PtX(SePh)-(N,N-chelate)(olefin)] (X = Cl, Br, I)

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The oxidative addition of PhSeX (X = Cl, Br, I) to Pt⁰ complexes of formula [Pt(N,N-chelate)(olefin)] is described. The reaction quantitatively affords the trigonal-bipyramidal products [PtX(SePh)(N,N-chelate)(olefin)] with the X and SePh fragments in the axial positions. NMR spectroscopic data have allowed us to gain insights into the geometrical isomer-

ism of some of these complexes. The reactivity of the axial ligands towards electrophilic reagents is also investigated, and the molecular structures of [PtX(SePh)(dmphen)(dimethyl fumarate)] (X = Br, I) are compared.

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Introduction

Five-coordinate [M(X)(Y)(N,N-chelate)(olefin)] (**1**; M = Pd or Pt) complexes have proved to be particularly suitable for studying the coordination properties of several ions and molecules (Figure 1).^[1] Due to their stability and inertness, metal adducts of a series of ligand fragments have been isolated,^[1,2] including some containing ligands with poor stability in the “free” state.^[3] For example, a variety of organometallic fragments can sturdily occupy an axial position in a series of compounds containing the same {MX(N,N-chelate)(olefin)} moiety, thus offering the possibility to assess trends.^[2] Alternatively, unstable vinyl alcohol can be coordinated and its fairly rich chemical behaviour at the metal centre can be compared with that of a variety of olefins in the same environment.^[3]

Recently,^[4] we have focused our attention on five-coordinate complexes bearing organochalcogenide ligands ER (E = O, S, Se, Te) in the axial position. This study was started because coordinatively saturated Pt^{II} compounds

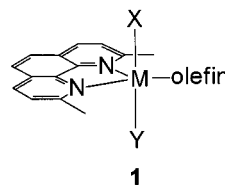


Figure 1. General formula for complexes **1**; M = Pd, Pt; X = Cl, Br, I, OR, SeR, TeR; Y = H, R, Ar, GeR_nCl_{3-n}, SnR_nCl_{3-n}, PbR_nCl_{3-n}, HgR, SeR, TeR

with chalcogenide ligands were not known^[5] and very limited information on the reactivity of these coordinated fragments was available.^[6]

Our previous work^[4a,4b] dealt with the characterisation of complexes of type **1** (M = Pt)^[7] containing two organochalcogenide ligands obtained by oxidative addition of RE–ER molecules to suitable Pt⁰ precursors **2** [Reaction (1) in Scheme 1]. During these studies we also found that, when E = Se, the reaction is a rare example of an equilibrium. This offered the uncommon opportunity to analyse the subtle effects of the ligand properties on the equilibrium.

In this paper we report on the addition of phenylselenenyl halides to the same Pt⁰ precursors [Reaction (2) in Scheme 1]. This has led to new five-coordinate compounds containing SePh and X in the apical sites. Analysis of the NMR spectroscopic and structural data of the new species revealed new information on the coordination properties of both organochalcogenides and halides. Furthermore, relevant aspects of the reactivity of the new compounds have been examined.

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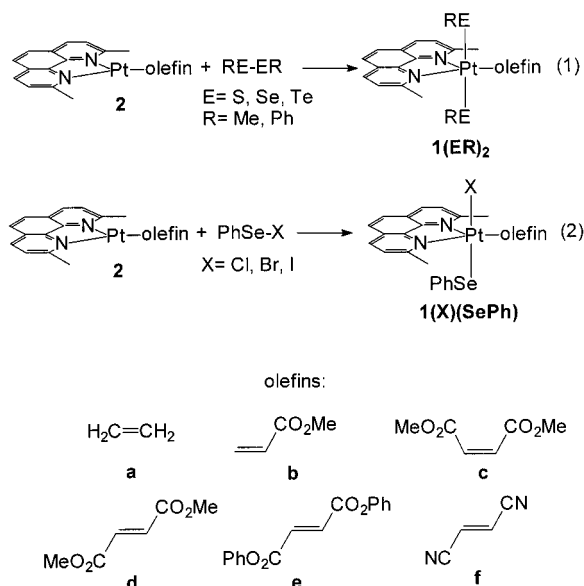
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Scheme 1

Results and Discussion

Synthesis of the Complexes

Oxidative addition of the phenylselenenyl halides was carried out with the three-coordinate precursors **2** shown in Scheme 1. The chelating ligand 2,9-dimethyl-1,10-phenanthroline (dmphen) was used due to its well-known ability to stabilise trigonal bipyramidal complexes of d^8 ions.^[1] Olefins with increasing electron-acceptor properties were used: ethylene (**a**), methyl acrylate (**b**), dimethyl maleate (**c**), dimethyl fumarate (**d**), diphenyl fumarate (**e**) and fumaronitrile (**f**). As a consequence the metal–olefin bond in the Pt^0 complexes containing **c**, **d**, **e** or **f** is characterised by a substantial π -backdonation contribution, thus enhancing the stability of the five-coordinate complexes by removing electronic density from the metal. These compounds are stable in solution and can be stored at room temperature for several days without appreciable decomposition. The ethylene or methylacrylate precursors are more sensitive to moisture, oxidising agents or heat, and were therefore freshly prepared before use.

All the additions were performed in chloroform, in which the complexes generally display reasonable solubility. The reactions were complete within a few seconds, as revealed by the change of the solution colour from yellow (red for ethylene derivative) to pink. The products were crystallised in high yield by dropwise addition of diethyl ether to the reaction mixture. The ethylene complex could be isolated in pure form only with Cl-SePh , while in the case of the other haloselenenides it was always accompanied by significant impurities, which could not be removed even by careful crystallisation. The compounds are soluble in chloroform or dichloromethane with the exception of $[\mathbf{1f}(\text{Br})(\text{SePh})]$ ($M = \text{Pt}$), which displays a fair solubility only in tetrachloroethane.

Characterisation of the Products

The characterisation of the products was carried out by ^1H and ^{13}C NMR spectroscopy (Table 1) and elemental analysis. In two cases, namely $[\mathbf{1d}(\text{Br})(\text{SePh})]$ and $[\mathbf{1d}(\text{I})(\text{SePh})]$, the X-ray molecular structure was also determined.

Analysis of the ^1H NMR spectra confirmed that the additions proceed by activation of the selenium–halogen bond and unequivocally confirmed the trigonal bipyramidal geometry of the products. The most relevant features are the high-field shift of the olefin protons signals by at least 2 ppm with respect to the free alkene, as typically found in complexes of type **1**,^[1] and the significant high-field shift of the PhSe- protons, which is attributable to the presence of a specific interaction between the phenyl ring of the selenide ligand and the rings of dmphen. This interaction is also present in the solid state, and has already been discussed for $[\mathbf{1}(\text{EPh})_2]$ complexes.^[4a]

As for the stereochemical aspects, the number of possible isomers depends on the symmetry of the alkene. Of course, ethylene (D_{2h}) affords only one isomer and the alkene protons resonate as an AB quadruplet. In the presence of dimethyl maleate (C_{2v}), two isomers^[8] may exist according to the orientation of the olefin substituents. The NMR spectra of freshly dissolved $[\mathbf{1c}(\text{Cl})(\text{SePh})]$ and $[\mathbf{1c}(\text{Br})(\text{SePh})]$ suggest the presence of only one rotamer whose olefin protons resonate at $\delta = 4.31$ and $\delta = 4.28$ ppm, respectively. In both cases, on standing in solution, slow conversion (days to completion) to the thermodynamically stable isomers was observed. The chemical shifts of the olefin protons for the latter species are $\delta = 4.60$ and $\delta = 4.74$, respectively.

The correct geometry of the two isomers can be reasonably assigned by considering the NMR spectroscopic data of the known complexes $[\text{Pt}(\text{SePh})_2(\text{dmphen})(\text{dimethyl maleate})]$ ^[4b] and $[\text{PtCl}_2(\text{dmphen})(\text{dimethyl maleate})]$.^[9] In the former species the olefin protons are necessarily oriented towards the SePh ligand, and resonate at $\delta = 4.34$ ppm. This value is very close to that found for the first, kinetically formed isomer of $[\mathbf{1c}(\text{Cl})(\text{SePh})]$. In the dichloro species the maleate protons face the halide and their signal appears at $\delta = 4.79$ ppm, a value close to that found for the thermodynamically stable rotamer of $[\mathbf{1c}(\text{Cl})(\text{SePh})]$. Hence, it is inferred that the olefin protons are likely to face the selenide ligand in the initially formed isomer, while they are oriented towards the chloride in the thermodynamically stable rotamer. This correlation can be reasonably extended to the bromo species $[\mathbf{1c}(\text{Br})(\text{SePh})]$. It should be noted that an analogous relationship holds true for complexes of **1** bearing a halide and a hydrocarbyl group^[7] in the axial positions. In all cases, the chemical shift of the maleate protons is higher in the isomer in which these nuclei are oriented towards the halogen.

Coordination of dimethyl fumarate or fumaronitrile (C_{2h}) results in the formation of an enantiomeric couple, which, of course, is not distinguishable by NMR spectroscopy in the absence of a shift reagent. The olefin protons here are not equivalent, and resonate as doublets. It is interesting to note that the chemical-shift difference ($\Delta\delta$)

Table 1. Selected $^1\text{H}^{\text{a}}$ and $^{13}\text{C}^{\text{b}}$ NMR spectroscopic data for complexes $[\text{Pt}(\text{X})(\text{SePh})(\text{dmphen})(\text{olefin})]$

Compound	Olefin ^[c]	Me(dmphen)	Other selected signals
X = Cl, olefin = ethylene 1a(Cl)(SePh)	3.36 (app d, 2 H) 3.16 [app d, 2 H (70)] [32.8 (325)]	3.36 (s, 6 H)	6.68 (t, 1 H), 6.46 (d, 2 H), 6.30 (t, 2 H)
X = Cl, olefin = methyl acrylate 1b(Cl)(SePh)	Diast. ^[d] : 4.43 (dd, 1 H) 3.90 (d, 1 H), 3.17 (d, 1 H) Diast. ^[e] : 4.60 (dd, 1 H), 3.65 (d, 1 H), 3.41 (d, 1 H) 4.31 [s, 2 H (75)] ^[d] 4.60 [s, 2 H (79)] ^[e] [32.6 (376)] ^[e]	Diast. ^[d] : 3.49 (s, 3 H) 3.28 (s, 3 H) Diast. ^[e] : 3.60 (s, 3 H) 3.46 (s, 3 H) 3.42 (s, 6 H) ^[d] 3.50 (s, 6 H) ^[e]	Diast. ^[d] : 6.74 (t, 1 H), 6.49 (d, 2 H) 6.35 (t, 2 H), 3.75 (s, 3 H, OMe) Diast. ^[e] : 6.49 (t, 1 H), 6.26 (d, 2 H) 6.03 (t, 3 H), 3.82 (s, 3 H, OMe) Diast. ^[d] : 6.74 (t, 1 H), 6.49 (d, 2 H) 6.33 (t, 2 H), 3.78 (s, 6 H, OMe) Diast. ^[e] : 6.58 (t, 1 H), 6.33 (d, 2 H) 6.13 (t, 2 H), 3.83 (s, 6 H, OMe) 6.47 (t, 1 H), 6.27 (d, 2 H), 6.03 (t, 2 H) 3.82 (s, 3 H, OMe), 3.72 (s, 3 H, OMe)
X = Cl, olefin = dimethyl fumarate 1d(Cl)(SePh)	5.16 [d, 1 H (82)] 4.98 [d, 1 H (76)] [32.7 (332), 31.4 (346)]	3.70 (s, 3 H) 3.62 (s, 3 H)	6.47 (t, 1 H), 6.27 (d, 2 H), 6.03 (t, 2 H) 3.82 (s, 3 H, OMe), 3.72 (s, 3 H, OMe)
X = Cl, olefin = diphenyl fumarate 1e(Cl)(SePh)	5.54 [d, 1 H (82)] 5.29 [d, 1 H (77)] [33.3 (340), 32.0 (341)]	3.74 (s, 3 H) 3.72 (s, 3 H)	7.45–7.10 (m, 10 H), 6.51 (t, 1 H) 6.32 (d, 2 H), 6.08 (t, 2 H)
X = Cl, olefin = fumarodinitrile 1f(Cl)(SePh)	4.25 [d, 1 H (75)] 4.03 [d, 1 H (63)] [14.4 (374), 13.5 (354)] ^[f]	3.40 (s, 3 H) 3.26 (s, 3 H)	6.82 (t, 1 H), 6.49 (d, 2 H), 6.35 (t, 2 H)
X = Br, olefin = methyl acrylate 1b(Br)(SePh)	Diast. ^[d] : 4.52 (dd, 1 H) 4.12 (d, 1 H), 3.28 (d, 1 H) Diast. ^[e] : 4.85 (dd, 1 H), 3.88 (d, 1 H), 3.61 (d, 1 H) 4.28 [s, 2 H (75)] ^[d] 4.74 [s, 2 H (83)] ^[e] [34.2 (364)] ^[e]	Diast. ^[d] : 3.58 (s, 3 H) 3.38 (s, 3 H) Diast. ^[e] : 3.68 (s, 3 H) 3.54 (s, 3 H) 3.38 (s, 6 H) ^[d] 3.48 (s, 6 H) ^[e]	Diast. ^[d] : 6.74 (t, 1 H), 6.46 (d, 2 H) 6.34 (t, 2 H), 3.86 (s, 3 H, OMe) Diast. ^[e] : 6.46 (t, 1 H), 6.23 (d, 2 H) 6.02 (t, 2 H), 3.92 (s, 3 H, OMe) Diast. ^[d] : 6.73 (t, 1 H), 6.48 (d, 2 H) 6.33 (t, 2 H), 3.80 (s, 6 H, OMe) Diast. ^[e] : 6.62 (t, 1 H), 6.34 (d, 2 H) 6.18 (t, 2 H), 3.83 (s, 6 H, OMe) 6.50 (t, 1 H), 6.25 (d, 2 H) 6.06 (t, 2 H), 3.82 (s, 3 H, OMe) 3.72 (s, 3 H, OMe)
X = Br, olefin = dimethyl fumarate 1d(Br)(SePh)	5.24 [d, 1 H (84)] 4.93 [d, 1 H (78)] [32.6 (322), 32.0 (353)]	3.68 (s, 3 H) 3.61 (s, 3 H)	6.06 (t, 2 H), 3.82 (s, 3 H, OMe) 3.72 (s, 3 H, OMe)
X = Br, olefin = diphenyl fumarate 1e(Br)(SePh)	5.65 [d, 1 H (74)] 5.33 [d, 1 H (83)]	3.68 (s, 3 H) 3.63 (s, 3 H)	7.40–7.20 (m, 10 H), 6.64 (br, 1 H) 6.36 (br, 2 H), 6.20 (br, 2 H)
X = Br, olefin = fumarodinitrile 1f(Br)(SePh)	4.38 [d, 1 H (76)] 4.02 [d, 1 H (67)] [12.1 (388), 11.8 (362)] ^[f]	3.41 (s, 3 H) 3.26 (s, 3 H)	6.83 (t, 1 H), 6.48 (d, 2 H), 6.40 (t, 2 H)
X = I, olefin = dimethyl fumarate 1d(I)(SePh)	5.34 [d, 1 H (83)] 4.84 [d, 1 H (76)] [31.0 (356), 30.7 (346)]	3.62 (s, 3 H) 3.59 (s, 3 H)	6.55 (t, 1 H), 6.22 (d, 2 H), 6.06 (t, 2 H) 3.80 (s, 3 H, OMe), 3.75 (s, 3 H, OMe)
$[\text{PtCl}(\text{dmphen})\{\text{Se}(\text{Ph})\text{Me}\}(\text{ethylene})]\text{BF}_4$ 1a(Cl)(SePhMe)	3.62 (app d, 2 H) 3.41 (app d, 2 H)	3.46 (s, 3 H) 3.24 (s, 3 H)	7.17 (t, 1 H), 6.84 (t, 2 H), 6.51 (d, 2 H) 2.35 (s, 3 H, SeMe, $^3J_{\text{Pt,H}} = 35$, $^2J_{\text{Se,H}} = 9$ Hz)
$[\text{PtCl}(\text{dmphen})\{\text{Se}(\text{Ph})\text{Me}\}-(\text{dimethyl maleate})]\text{BF}_4$ 1c(Cl)(SePhMe)	Diast. ^[d] : 4.56 [ABq, 2 H (71)] Diast. ^[e] : 4.99 [d, 1 H (77)], 4.62 [d, 1 H (76)]	Diast. ^[d] : 3.58 (s, 3 H) 3.36 (s, 3 H) Diast. ^[e] : 3.42 (s, 3 H) 3.21 (s, 3 H)	Diast. ^[d] : 3.78 (s, 6 H, OMe) 2.51 (s, 3 H, SeMe, $^3J_{\text{Pt,H}} = 33$, $^2J_{\text{Se,H}} = 6$ Hz) Diast. ^[e] : 3.88 (s, 3 H, OMe), 3.86 (s, 3 H, OMe) 1.84 (s, 3 H, SeMe, $^3J_{\text{Pt,H}} = 36$, $^2J_{\text{Se,H}} = 6$ Hz)
$[\text{PtCl}(\text{dmphen})\{\text{Se}(\text{Ph})\text{Me}\}-(\text{dimethyl fumarate})]\text{BF}_4$ 1d(Cl)(SePhMe)	5.00 [ABq, 2 H (72)] ^[g]	3.69 (s, 3 H) 3.42 (s, 3 H)	6.81 (t, 1 H), 6.49 (t, 2 H), 6.28 (d, 2 H) 3.98 (s, 3 H, OMe), 3.78 (s, 3 H, OMe) 3.01 (s, 3 H, SeMe, $^3J_{\text{Pt,H}} = 30$, $^2J_{\text{Se,H}} = 7$ Hz)
$[\text{Pt}(\text{SePh})(\text{dmphen})(\text{MeCN})(\text{ethylene})]\text{BF}_4$ 1a(SePh)(MeCN)	3.78 (app d, 2 H, 69) 3.41 (app d, 2 H, 61)	3.18 (s, 6 H)	6.99 (m, 1 H), 6.57 (m, 4 H)

^[a] At 200 or 300 MHz and 298 K. ^[b] At 50.2 or 75.4 MHz and 298 K; values given in square brackets. ^[c] $^2J_{\text{Pt,H}}$ and $^1J_{\text{Pt,C}}$ [Hz] in parentheses (when measurable). ^[d] Kinetically formed isomer. ^[e] Thermodynamically stable isomer. ^[f] Spectra recorded in $\text{C}_2\text{D}_2\text{Cl}_4$ ($^{13}\text{C}_2\text{D}_2\text{Cl}_4$: $\delta = 74.15$ ppm as internal standard). ^[g] More abundant isomer.

between the CH= signals in the dimethyl fumarate complexes is close to that for the corresponding maleate rotamers. This is in agreement with the fact that one fumarate proton is oriented towards the halide, while the other faces the selenide ligand.

Finally, two enantiomeric couples are formed with methyl acrylate. Actually, two patterns are present in the NMR spectra of both **[1b(Cl)(SePh)]** and **[1b(Br)(SePh)]**. The spectrum of a freshly prepared solution of the latter compound shows the two isomers in a 2:1 ratio. After three

hours the species are present in equimolar amounts, and within six days the conversion to the stable isomer is complete. In a similar fashion the isomeric ratio for the chloro derivative is initially 1:1 and after five days one isomer becomes by far the more abundant. The correlation mentioned above for the dimethyl maleate complexes (see Table 1) indicates that the carboxymethyl groups are oriented towards the halide in the thermodynamically stable isomer.

The X-ray Molecular Structures of [1d(Br)(SePh)] and [1d(I)(SePh)]

The crystals of the title species are isomorphous (see Exp. Sect.), therefore the molecules are strictly isostructural in the solid state and experience equal force fields. This situation allows close comparisons of the bond values so that even minor differences can be discussed. Figure 2 shows a perspective drawing of the molecules; an axial view is shown in Figure 3. Table 2 contains a comparison of the most significant bond parameters of the two species.

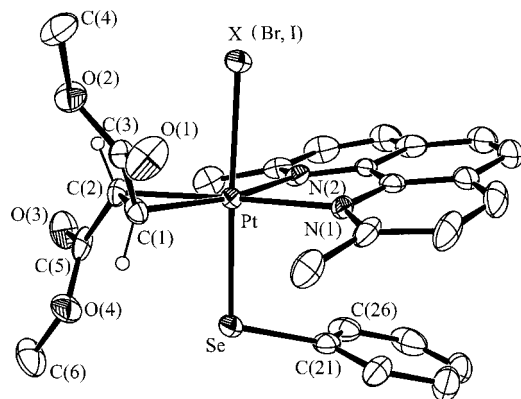


Figure 2. ORTEP drawing (30% probability thermal ellipsoids) of [PtX(SePh)(dmphen)(dimethyl fumarate)] [1d(X)(SePh)] (X = Br, I); only the olefinic hydrogens are shown for the sake of clarity

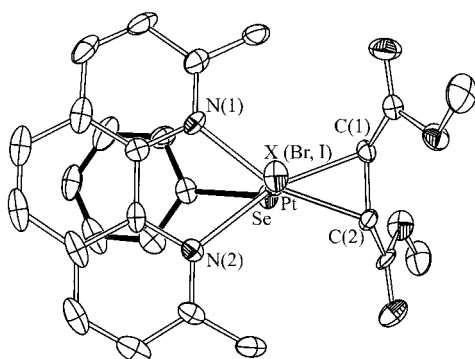


Figure 3. View down the X-Se-Pt axis (X = Br, I) of [PtX(SePh)(dmphen)(dimethyl fumarate)] [1d(X)(SePh)]; hydrogen atoms are omitted for clarity

The molecular geometry is as expected. The phenanthroline nitrogen atoms and fumarate double bond define the equatorial coordination plane, and the halide and selenide atoms occupy the axial positions. The molecules exhibit an

Table 2. Selected bond lengths [Å] and angles [°] for [1d(Br)(SePh)] and [1d(I)(SePh)]

	[1d(Br)(SePh)]	[1d(I)(SePh)]
Pt-Br	2.5195(9)	
Pt-I	—	2.6855(9)
Pt-Se	2.4537(9)	2.472(1)
Pt-N(1)	2.160(7)	2.190(8)
Pt-N(2)	2.201(7)	2.180(9)
Pt-C(1)	2.087(9)	2.09(1)
Pt-C(2)	2.101(8)	2.11(1)
C(1)-C(2)	1.44(1)	1.43(2)
Se-C(21)	1.930(5)	1.922(6)
N(1)-Pt-N(2)	76.2(3)	75.9(3)
Se-Pt-Br	177.12(3)	—
Se-Pt-I	—	176.81(4)
Pt-Se-C(21)	103.6(2)	104.0(2)
I-Pt-C(1)	—	91.9(3)
I-Pt-C(2)	—	91.0(3)
I-Pt-N(1)	—	87.0(2)
I-Pt-N(2)	—	86.1(2)
Br-Pt-C(1)	91.7(3)	—
Br-Pt-C(2)	90.6(3)	—
Br-Pt-N(1)	87.5(2)	—
Br-Pt-N(2)	85.7(2)	—

asymmetric configuration because the C_2 symmetry of dimethyl fumarate does not match the idealised C_s symmetry of the remaining moiety. It should be noted that the phenyl ring of the SePh ligand is approximately placed above the central ring of the phenanthroline (Figure 2), while in the bis(phenylselenide) derivative [Pt(SePh)₂(dimethyl fumarate)(dmphen)] the phenyl rings match both pyridine rings from opposite sides.^[4a] In that case we assumed the presence of preferential interactions between the ring dipoles. It is likely that the C_s geometry found in the present case allows an efficient crystal packing rather than a conformation that would optimise the intramolecular interactions. The non-equivalence of the axial ligands causes a tilting of the phenanthroline on the side of the less bulky halide ligand [angle between coordination and phenanthroline planes of 10.6(3)° and 10.5(4)° for bromide and iodide, respectively].

Significant variations are observed for the bonding interactions of the axial ligands. The difference in the Pt-halogen distances [Pt-Br 2.520(1) and Pt-I 2.685(1) Å] is consistent with the difference between their covalent radii (0.19 Å). The Pt-Se interaction is 0.02 Å shorter in the bromide derivative [2.453(1) and 2.472(1) Å, respectively]. This effect, if compared with the even longer value found in the bis(selenide) derivative [Pt(SePh)₂(dimethyl fumarate)(dmphen)] [average value 2.517(1) Å],^[4a] suggests a correlation of the Pt-Se distance with the electronegativity difference between the apical donor atoms. In other words, as the bonds in the linear Se-Pt-X unit (X = Br, I, Se) result from interactions with the same metal-atom orbitals, the ligand-to-metal donation is balanced between the competitors according to their donor properties, and the Pt-Se bond becomes stronger in the bromide and weaker in the bis(selenide) derivative.

The equatorial Pt–N and Pt–C interactions are affected much less by the changes in the axial ligands, and the differences are barely significant in terms of experimental errors. However, we note that, in agreement with the situation discussed for the axial ligands, the bonds in the bromide derivative are slightly, but systematically, shorter than in the iodide. The average values are as follows: Pt–N 2.180(7), 2.185(8) and Pt–C 2.086(8), 2.097(9) Å, respectively. Correspondingly, the olefin C=C distance is slightly longer in the bromide derivative [1.437(12) against 1.425(15) Å], and the C–C=C–C torsion angle is slightly higher in the bromide [46.1(9) against 44.5(9)°], indicating slightly more sp³ rehybridisation where more donation is allowed.

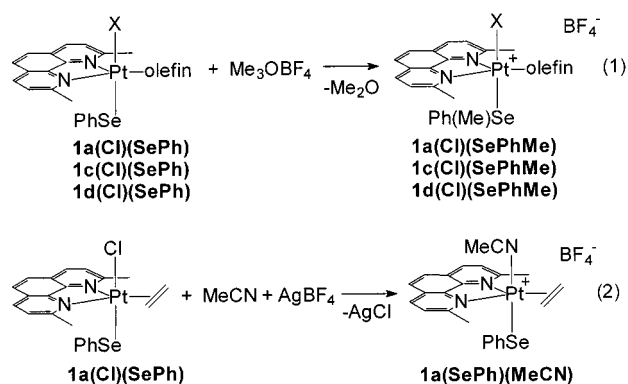
Reactivity

In no case was the oxidative addition of phenylselenenyl halides to the platinum(0) precursors found to be an equilibrium. The reaction was quantitative even with fumarodinitrile, which stabilises the low oxidation state of the metal through a very effective π -backdonation. These results parallel those obtained when PhSe–SePh^[4b] is allowed to react with the same complexes, while with MeSe–SeMe^[4a] the reactions were found to be an equilibrium. However, these findings are not surprising since the Pt–X bond strengths^[10] are relatively high compared to those of the other bonds that form or break in the reaction. Thus, the addition of the selenenyl halides is enthalpically driven towards the products. Furthermore, the above-mentioned intramolecular interaction between aromatic rings helps to stabilise the five-coordinate complexes.

Some relevant aspects of the reactivity of the new complexes have been explored. The ability of the coordinated SeR ligands to undergo electrophilic attack was confirmed by reacting [1a(Cl)(SePh)], [1c(Cl)(SePh)] (kinetic isomer) and [1d(Cl)(SePh)] with trimethyloxonium tetrafluoroborate (reaction 1 of Scheme 2). The corresponding products are formally monopositive cationic complexes bearing Se(Me)Ph as the axial ligand. Accordingly, the compounds are fairly soluble only in nitromethane. The presence of Me on selenium was confirmed by the presence of a singlet coupled to both ⁷⁷Se and ¹⁹⁵Pt in the ¹H NMR spectrum. Of course, upon addition of the methyl group, the selenium atom becomes stereogenic. In the presence of a prochiral olefin such as dimethyl fumarate, two diastereomeric couples form, and these were observed in solution for [1d(Cl)(SePhMe)] in an 8:3 ratio.

In the spectrum of [1c(Cl)(SePhMe)], which is obtained upon addition of trimethyloxonium tetrafluoroborate to the kinetic isomer of [1c(Cl)(SePh)], the CH= protons resonate as two doublets, while the methoxy groups are still equivalent. The lack of sensitivity of the methoxy protons towards the transformation of the selenide ligand suggests that the coordination stereochemistry of the olefin is retained. In solution, the compound slowly isomerises into the most stable isomer, as is the case for the parent compound.

Another aspect of this study has dealt with the reactivity of the other axial ligand — the halide. This can be replaced by a neutral ligand, for example acetonitrile, upon treat-



Scheme 2

ment with a silver salt (reaction 2 of Scheme 2). The reaction was performed with the ethylene compound [1a(Cl)(SePh)] and affords the corresponding monocationic cation of [1a(SePh)(MeCN)], which, again, is fairly soluble only in nitromethane.

Conclusions

The chemistry described in this paper confirms the peculiar aptitude of trigonal bipyramidal complexes of platinum(II), such as **1**, to function as effective models for comparing the behaviour of ligands. Thus, new five-coordinate Pt^{II} complexes with a halide and the SePh ligand in axial positions have been isolated and relevant aspects of their reactivity elucidated. The availability of the new compounds has allowed a comparison of the coordination and spectral properties of halides and organochalcogenides in identical environments. NMR spectroscopy has also been employed for this homogeneous class of compounds to analyse the geometrical isomerism displayed by some of the compounds.

Experimental Section

General: ¹H and ¹³C NMR spectra were recorded with Varian XL-200 or Varian Gemini spectrometers. The NMR spectroscopic data are reported in Table 1. ¹H and ¹³C NMR chemical shifts are reported in δ units (ppm) relative to the solvent (CHCl₃: δ = 7.26 ppm; CHD₂NO₂: δ = 4.33 ppm; ¹³CDCl₃: δ = 77.0 ppm; ¹³C₂D₂Cl₄: δ = 74.15 ppm). Phenylselenenyl chloride, phenylselenenyl bromide, the diphenyl diselenide compound with iodine (1:1) and the trimethyloxonium salt were commercially available. Platinum(0) precursors were obtained according to a described method.^[11] Solvents and reagents were of AnalaR grade and used without further purification.

Synthesis of Complexes 1 of Formula [PtX(SePh)(dmphen)(olefin)] (X = Cl, Br): A solution of the appropriate selenenyl compound PhSeX (0.15 mmol) in a minimum amount of chloroform (0.5 mL) was added to a suspension of the three-coordinate compound **2a–f** (0.15 mmol) in chloroform (0.5 mL). After stirring at room temperature for 5 min, addition of diethyl ether afforded the deep rose-

violet product, which was washed with diethyl ether and dried. **[1a(Cl)(SePh)]**: Yield: 75 mg (80%). $C_{22}H_{21}ClN_2PtSe$ (622.8) calcd. C 42.43, H 3.40, N 4.50; found C 42.12, H 3.22, N 4.37. **[1b(Cl)(SePh)]**: Yield: 85 mg (83%). **[1c(Cl)(SePh)]**: Yield: 100 mg (90%). $C_{26}H_{25}ClN_2O_4PtSe$ (738.8) calcd. C 42.27, H 3.41, N 3.79; found C 42.03, H 3.54, N 3.63. **[1d(Cl)(SePh)]**: Yield: 98 mg (88%). **[1e(Cl)(SePh)]**: Yield: 110 mg (85%). **[1f(Cl)(SePh)]**: Yield: 91 mg (90%). **[1b(Br)(SePh)]**: Yield: 87 mg (80%). **[1c(Br)(SePh)]**: Yield: 102 mg (87%). **[1d(Br)(SePh)]**: Yield: 96 mg (82%). $C_{26}H_{25}BrN_2O_4PtSe$ (783.3) calcd. C 39.87, H 3.22, N 3.58; found C 40.02, H 3.18, N 3.69. **[1e(Br)(SePh)]**: Yield: 112 mg (82%). **[1f(Br)(SePh)]**: Yield: 92 mg (86%). $C_{24}H_{19}BrN_4PtSe$ (717.2) calcd. C 40.19, H 2.67, N 7.81; found C 40.35, H 2.81, N 7.60.

Synthesis of [PtI(SePh)(dmphen)(dimethylfumarate)] [1d(I)(SePh)]: The 1:1 diphenyl diselenide compound with iodine (0.11 mmol) was added to a magnetically stirred suspension of **2d** (0.12 g, 0.22 mmol) in chloroform (1 mL). The dark-red solution was stirred at room temperature for 5 min. Subsequent addition of diethyl ether afforded the product, which was washed with diethyl ether and dried. Yield: 100 mg (80%).

Synthesis of Complexes 1 of Formula [PtCl(dmphen){Se(Ph)Me}-(olefin)]BF₄: A solution of trimethyloxonium tetrafluoroborate salt (0.019 g, 0.13 mmol) in nitromethane (0.5 mL) was added to the appropriate coordinatively saturated compound **[1a(Cl)(SePhMe)]**, **[1c(Cl)(SePhMe)]** or **[1d(Cl)(SePhMe)]** (0.13 mmol). After stirring at room temperature for 5 min, slow addition of diethyl ether to the resulting solution afforded the yellow product, which was washed with diethyl ether and dried. **[1a(Cl)(SePhMe)]**: Yield: 70 mg (74%). **[1c(Cl)(SePhMe)]**: Yield: 77 mg (70%). $C_{27}H_{28}BClF_4N_2O_4PtSe$ (840.7) calcd. C 38.58, H 3.36, N 3.33; found C 39.01, H 3.35, N 3.40. **[1d(Cl)(SePhMe)]**: Yield: 74 mg (68%).

Synthesis of [Pt(SePh)(dmphen)(MeCN)(ethylene)]BF₄ [1a(SePh)-(MeCN)]: A solution of silver tetrafluoroborate in acetonitrile

(0.13 mmol) was added to a solution of five-coordinate product **[1a(Cl)(SePh)]** (0.13 mmol) in nitromethane under nitrogen at 273 K. After stirring for 30 min, the residual solid was filtered through a small Celite pad. The addition of diethyl ether to the resulting solution afforded the light-yellow product, which was washed with diethyl ether and dried. Yield: 74 mg (80%).

X-ray Crystallography: Crystals of suitable quality were grown from a 1:1 mixture of chloroform and diethyl ether. The X-ray intensity data for **[1d(Br)(SePh)]** and **[1d(I)(SePh)]** were measured with a Bruker AXS SMART 2000 diffractometer, equipped with a CCD detector. Cell dimensions and the orientation matrix were initially determined from a least-squares refinement on reflections measured in three sets of 20 exposures, collected in three different ω regions, and eventually refined against all data. For all crystals, a full sphere of reciprocal space was scanned by $0.3^\circ \omega$ steps, with the detector kept at a distance of 5.0 cm from the sample. The software SMART^[12] was used for collecting frames of data, indexing the reflections and determining the lattice parameters. The collected frames were then processed for integration by the SAINT program,^[12] and an empirical absorption correction was applied using SADABS.^[13] The structures were solved by direct methods (SIR 97)^[14] and subsequent Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELXTL),^[15] using anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms except the olefinic hydrogen atoms, which were located in the Fourier map and refined isotropically, were added in calculated positions, included in the final stage of refinement with isotropic thermal parameters, $U(H)$, of $1.2 U_{eq}(C)$ [$U(H) = 1.5 U_{eq}(C-Me)$], and allowed to ride on their carrier carbon atoms. Crystal data and details of the data collection for all structures are reported in Table 3. CCDC-237837 and -237838 for **[1d(Br)(SePh)]** and **[1d(I)(SePh)]**, respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge

Table 3. Crystal data and experimental details for **[1d(Br)(SePh)]** and **[1d(I)(SePh)]**

	[1d(Br)(SePh)]	[1d(I)(SePh)]
Empirical formula	$C_{26}H_{25}BrN_2O_4PtSe$	$C_{26}H_{25}IN_2O_4PtSe$
Formula mass	783.44	830.43
T [K]	298(2)	298(2)
λ [Å]	0.71073	0.71073
Crystal symmetry	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a [Å]	11.3454(4)	11.4073(5)
b [Å]	16.1178(7)	16.1014(7)
c [Å]	14.0108(6)	14.1829(6)
β [°]	93.367(1)	93.194(1)
Cell volume [Å ³]	2557.6(2)	2601.0(2)
Z	4	4
D_c [Mg·m ⁻³]	2.035	2.121
μ (Mo- $K\alpha$) [mm ⁻¹]	8.507	8.016
$F(000)$	1496	1568
Crystal size [mm]	$0.14 \times 0.16 \times 0.25$	$0.12 \times 0.15 \times 0.15$
θ limits [°]	2.53–24.99	2.53–29.99
Reflections collected	20312 ($\pm h, \pm k, \pm l$)	21966 ($\pm h, \pm k, \pm l$)
Unique observed reflections	4355 [$R(\text{int}) = 0.055$]	7523 [$R(\text{int}) = 0.079$]
$[F_o > 4\sigma(F_o)]$		
Goodness-of-fit-on F^2	1.069	0.989
$R_1(F)$ $wR_2(F^2)^{[b]}$	0.0430, 0.0979	0.0542, 0.1375
Largest diff. peak and hole [$e \cdot \text{\AA}^{-3}$]	1.95 and -1.48	1.68 and -2.56

^[a] $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. ^[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = (F_o^2 + 2F_c^2)/3$.

Crystallographic Data, 12 Union Road, Cambridge, CB2 1EZ, UK;
Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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