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Oxidative addition of Se–X bonds and reductive elimination of Se–C bonds in platinum compounds containing hydrocarbyl ligands

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Abstract

The oxidative addition of PhSe–X molecules (X = Cl or Br) to Pt(II) complexes of formula [PtR(R′)(*N*,*N*-chelate)] [R, R′ = Me, $CH(CO_2Me)_2$, $CH(CO_2Me)(CN)$; *N*,*N*-chelate = 4,4′-(*tert*-butyl)$_2$-2,2′-bipyridine] is described. The reaction quantitatively affords octahedral products [PtR(R′)(SePh)(X)(*N*,*N*-chelate)], and is highly selective, since only the isomers with -X and -SePh in *trans* position are obtained. When R = R′ = $CH(CO_2Me)_2$ or R = R′ = $CH(CO_2Me)_2(CN)$ an irreversible reductive elimination takes place in solution, giving rise to Pt(II) compounds [PtR(X)(*N*,*N*-chelate)] and organoselenium molecules PhSeR′.

Keywords: Platinum; Selenium; Oxidative addition; Reductive elimination; Octahedral complexes

1. Introduction

In the last few years, coordination chemistry of Group 16 ligands has attracted increasing attention [1,2]. Within this growing area, we explored the oxidative addition of Se–Se bonds to platinum(0) [3] and platinum(II) [4] complexes, respectively, of formula [Pt(*N*,*N*-chelate)(olefin)] (**1**) and [PtR(R′)(*N*,*N*-chelate)] (**2**), where *N*,*N*-chelate is a diimine, and R, R′ hydrocarbyl groups. New five-coordinate Pt(II) (**3**) and octahedral Pt(IV) (**4**) products could be isolated, according to the Eqs. (1) and (2)

$$[\mathrm{Pt}(N,N\text{-chelate})(\text{olefin})](\mathbf{1}) + \mathrm{R''Se{-}SeR''} = [\mathrm{Pt}(\mathrm{SeR''})_2(N,N\text{-chelate})(\text{olefin})](\mathbf{3}) \qquad (1)$$

$$[\mathrm{PtR(R')}(N,N\text{-chelate})](\mathbf{2}) + \mathrm{R''Se{-}SeR''} = [\mathrm{PtR(R')(SeR'')_2}(N,N\text{-chelate})](\mathbf{4}) \qquad (2)$$

$R'' = \mathrm{Me}$ or Ph

We also discovered that in some cases the addition is a "tuneable" equilibrium [3b,4]. This rare event offered the opportunity to gain useful insight into the thermodynamics of the reaction.

Stimulated by these results, we addressed our interest to the addition of Se–X bonds (X = halide) to Pt compounds, which, as far as we know, has not yet been investigated [5]. Within this communication we wish to present preliminary results obtained by using platinum(II) compounds of type **2** as precursors and phenylselenyl halides PhSeX (X = Cl, Br) as oxidants. Isolable octahedral products (**5**) were obtained and characterised through NMR spectroscopy

$$[\mathrm{PtR(R')}(N,N\text{-chelate})](\mathbf{2}) + \mathrm{PhSe{-}X} = [\mathrm{PtR(R')(SePh)(X)}(N,N\text{-chelate})](\mathbf{5}) \qquad (3)$$

Depending on the nature of the hydrocarbyl ligands, in solution the complexes may undergo reductive elimination of a Se–C bond with formation of new Pt(II) complexes and organoselenium compounds.

2. Experimental

^{1}H NMR and ^{13}C NMR spectra were recorded on Varian XL-200 or Varian Gemini spectrometers. ^{1}H and ^{13}C NMR chemical shifts are reported in δ(ppm) relative

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to the solvent ($CHCl_3$, $\delta = 7.26$; $^{13}CDCl_3$, $\delta = 77.0$). The following abbreviations are used in describing NMR multiplicities: s, singlet; d, doublet; t, triplet; m, multiplet. Phenylselenenyl chloride and phenylselenenyl bromide were commercially available. The platinum(II) precursors [$PtCl_2$(Bu_2-bipy)] [6] and [Pt{$CH(CO_2Me)_2$}(Me)(Bu_2-bipy)] [4] (Bu_2-bipy = 4,4′-(*tert*-butyl)$_2$-2,2′-bipyridine) were obtained according to described procedures. Solvents and reagents were of AnalaR grade and used without further purification.

2.1. Synthesis of type 2 complexes [PtR(R′)(Bu$_2$-bipy)] R = R′ = CH(CO$_2$Me)$_2$ (**2b**), CH(CO$_2$Me)(CN)(**2c**)

A stirred solution of [$PtCl_2$(Bu_2-bipy)] (0.20 g, 0.39 mmol) and KI (0.19 g, 1.2 mmol) in dimethylformamide (2.5 mL) was heated at 373 K for 5 min. After the orange solution was cooled at 313 K, the appropriate malonic ester (0.97 mmol) and anhydrous K_2CO_3 (0.11 g, 0.78 mmol) were added, and the mixture was stirred for 24 h at 313 K. The solvent and excess malonate were then removed in vacuo, and the resulting solid was extracted with chloroform. The yellow product was purified on a silica gel column, eluting first with dichloromethane and then with dichloromethane/methanol (methanol 5% v/v, yield: 60–70%). Selected ^1H [^{13}C]NMR data (δ, 295 K): **2b** 10.00 (d, 2H, NCH,$^3J_{Pt–H} = 32$ Hz), 4.66 (s, 2H, Pt–CH, $^2J_{Pt–H} = 128$ Hz, [19.1 ($^1J_{Pt–C} = 452$ Hz)]), 3.61 (s, 12H, OMe) ppm; **2c** (major diastereomer) 9.71 (d, 2H, NCH, $^3J_{Pt–H} = 23$ Hz), 4.04 (s, 2H, Pt–CH, $^2J_{Pt–H} = 123$ Hz, [11.0 ($^1J_{Pt–C} = 302$ Hz)]), 3.70 (s, 6H, OMe) ppm; **2c** (minor diastereomer) 9.50 (d, 2H, NCH, $^3J_{Pt–H} = 20$ Hz), 4.00 (s, 2H, Pt–CH, $^2J_{Pt–H} = 97$ Hz, [12.0]), 3.45 (s, 6H, OMe) ppm. Anal. Calcd for $C_{28}H_{38}N_2O_8Pt$ (**2b**) C, 46.35; H, 5.28; N, 3.86. Found: C, 46.51; H, 5.19; N, 3.77; $C_{26}H_{32}N_4O_4Pt$ (**2c**) C, 47.35; H, 4.89; N, 8.49. Found: C, 47.34; H, 4.86; N, 8.88.

2.2. Synthesis of type 5 complexes [Pt{CH(CO$_2$Me)$_2$}(Me)(SePh)(X)(Bu$_2$-bipy)] (X = Cl, **5aCl**; X = Br, **5aBr**)

The phenylselenyl halide (0.11 mmol) was added to a solution of the precursor **2a** (0.070 g, 0.11 mmol) in dichloromethane (1.5 ml). After stirring for 5 min at room temperature, addition of diethyl ether afforded the deep rose-violet product, which was washed with hexane and dried (yield: 80%). Selected ^1H [^{13}C]NMR data (δ, 295 K): **5aCl** 10.58 (d, 1H, NCH, $^3J_{Pt–H} = 13$ Hz), 8.84 (d, 1H, NCH, $^3J_{Pt–H} = 26$ Hz), 6.94 (t, 1H, 4H-Ph), 6.68 (d, 2H, 2,6-H-Ph), 6.48 (t, 2H, 3,5-H-Ph), 4.18 (s, 1H, Pt–CH, $^2J_{Pt–H} = 75$ Hz, [19.5 ($^1J_{Pt–C} = 600$ Hz)]), 3.82 (s, 3H, OMe), 3.78 (s, 3H, OMe), 2.18 (s, 3H, Pt–Me, $^2J_{Pt–H} = 62$ Hz [2.9 ($^1J_{Pt–C} = 540$ Hz)]) ppm; **5aBr** 10.48 (d, 1H, NCH, $^3J_{Pt–H} = 14$ Hz), 8.80 (d, 1H, NCH, $^3J_{Pt–H} = 17$ Hz), 6.94 (t, 1H, 4H-Ph), 6.62 (d, 2H, 2,6-H-Ph), 6.48 (t, 2H, 3,5-H-Ph), 4.07 (s, 1H, Pt–CH, $^2J_{Pt–H} = 89$ Hz, [18.6 ($^1J_{Pt–C} = 590$ Hz)]), 3.78 (s, 3H, OMe), 3.72 (s, 3H, OMe), 2.15 (s, 3H, Pt–Me, $^2J_{Pt–H} = 66$ Hz [1.3 ($^1J_{Pt–C} = 524$ Hz)]) ppm. Anal. Calcd for $C_{30}H_{39}ClN_2O_4PtSe$ (**5aCl**): C, 44.98; H, 4.91; N, 3.50. Found: C, 45.26; H, 4.82; N, 3.63. Calcd for $C_{30}H_{39}BrN_2O_4PtSe$ (**5aBr**): C, 42.62; H, 4.65; N, 3.31. Found: C, 42.57; H, 4.70; N, 3.44.

2.3. Synthesis of type 5 complexes [Pt{CH(CO$_2$Me)$_2$}$_2$(SePh)(X)(Bu$_2$-bipy)] (X = Cl, **5bCl**; X = Br, **5bBr**) and [Pt{CH(CO$_2$Me)$_2$(CN)}(SePh)(X)(Bu$_2$-bipy)] (X = Cl, **5cCl**; X = Br, **5cBr**)

To a magnetically stirred solution of the type **2** precursor (0.15 mmol) in toluene (1.5 ml) the phenylselenyl halide compound (0.15 mmol) was added. The dark red solution was stirred for 5 min at room temperature. The addition of hexane afforded the product, which was washed with hexane and dried (yield: 70–80%). Selected ^1H NMR data (δ, 295 K): **5bCl** 10.50 (d, 2H, NCH, $^3J_{Pt–H} = 22$ Hz), 6.97 (t, 1H, 4H-Ph), 6.58 (d, 2H, 2,6-H-Ph), 6.40 (t, 2H, 3,5-H-Ph), 4.80 (s, 2H, Pt–CH, $^2J_{Pt–H} = 91$ Hz), 3.80 (s, 6H, OMe), 3.70 (s, 6H, OMe) ppm; **5bBr** 10.52 (d, 2H, NCH, $^3J_{Pt–H} = 29$ Hz), 6.92 (t, 1H, 4H-Ph), 6.58 (d, 2H, 2,6-H-Ph), 6.42 (t, 2H, 3,5-H-Ph), 4.80 (s, 2H, Pt–CH, $^2J_{Pt–H} = 92$ Hz), 3.80 (s, 6H, OMe), 3.72 (s, 6H, OMe) ppm; **5cCl** 9.70 (d, 2H, NCH, $^3J_{Pt–H} = 26$ Hz), 7.00 (t, 1H, 4H-Ph), 6.74 (d, 2H, 2,6-H-Ph), 6.47 (t, 2H, 3,5-H-Ph), 4.76 (s, 1H, Pt–CH, $^2J_{Pt–H} = 104$ Hz), 4.69 (s, 1H, Pt–CH, $^2J_{Pt–H} = 96$ Hz), 3.97 (s, 3H, OMe), 3.84 (s, 3H, OMe) ppm; **5cBr** 9.67 (d, 2H, NCH, $^3J_{Pt–H} = 25$ Hz), 7.07 (t, 1H, 4H-Ph), 6.72 (d, 2H, 2,6-H-Ph), 6.45 (t, 2H, 3,5-H-Ph), 4.80 (s, 1H, Pt–CH, $^2J_{Pt–H} = 108$ Hz), 4.70 (s, 1H, Pt–CH, $^2J_{Pt–H} = 100$ Hz), 3.98 (s, 3H, OMe), 3.88 (s, 3H, OMe) ppm. Anal. Calcd for $C_{34}H_{43}ClN_2O_8PtSe$ (**5bCl**): C, 44.53; H, 4.73; N, 3.05. Found: C, 44.79; H, 4.75; N, 2.99. Calcd for $C_{34}H_{43}BrN_2O_8PtSe$ (**5bBr**): C, 42.47; H, 4.51; N, 2.91. Found: C, 42.12; H, 4.38; N, 3.01. Calcd for $C_{32}H_{37}ClN_4O_4PtSe$ (**5cCl**): C, 45.16; H, 4.38; N, 6.58. Found: C, 45.30; H, 4.47; N, 6.89. Calcd for $C_{32}H_{37}BrN_4O_4PtSe$ (**5cBr**): C, 42.92; H, 4.16; N, 6.26. Found: C, 43.11; H, 4.25; N, 6.27.

2.4. Behaviour in solution of type **5b** and **5c** complexes

Compound **5bCl** (0.10 g, 0.11 mmol) was dissolved in toluene (2 ml), and change of the colour of solution from orange to yellow was observed. After 3 h, the products of the reductive elimination [PtCl{CH(CO$_2$Me)$_2$}(Bu$_2$-bipy)] and PhSeCH(CO$_2$Me)$_2$ were isolated through filtration on a silica gel column, eluting first with dichloromethane and then with dichloromethane/methanol (methanol 5% v/v, yield: 70%). An analogous behaviour was observed by aging NMR samples of **5bBr** and **5cCl**. Selected ^{1}H NMR [^{13}C] data (δ, 295 K): [PtCl$\{CH(CO_2Me)_2\}$(Bu$_2$-bipy)]: 10.18 (d, 1H, NCH, $^3J_{Pt\text{–}H} = 39$ Hz), 9.60 (d, 1H, NCH, $^3J_{Pt\text{–}H} = 26$ Hz), 5.18 (s, 1H, Pt–CH, $^2J_{Pt\text{–}H} = 122$ Hz, [13.7 ($^1J_{Pt\text{–}C} = 574$ Hz)]), 3.59 (s, 6H, OMe) ppm; [PtBr$\{CH(CO_2Me)_2\}$(Bu$_2$-bipy)]: 10.18 (d, 1H, NCH, $^3J_{Pt\text{–}H} = 42$ Hz), 9.86 (d, 1H, NCH), 5.52 (s, 1H, Pt–CH, $^2J_{Pt\text{–}H} = 126$ Hz), 3.72 (s, 6H, OMe) ppm; [PtCl$\{CH(CO_2Me)(CN)\}$(Bu$_2$-bipy)]: 9.57 (d, 1H, NCH, $^3J_{Pt\text{–}H} = 42$ Hz), 9.38 (d, 1H, NCH, $^3J_{Pt\text{–}H} = 31$ Hz), 4.57 (s, 1H, Pt–CH, $^2J_{Pt\text{–}H} = 125$ Hz, [−1.8 ($^1J_{Pt\text{–}C} = 627$ Hz)]), 3.62 (s, 6H, OMe) ppm. Anal. Calcd for $C_{23}H_{31}ClN_2O_4Pt$ ([PtCl$\{CH(CO_2Me)_2\}$(Bu$_2$-bipy)]): C, 43.85; H, 4.96; N, 4.45. Found: C, 43.68; H, 4.92; N, 4.57.

3. Results and discussion

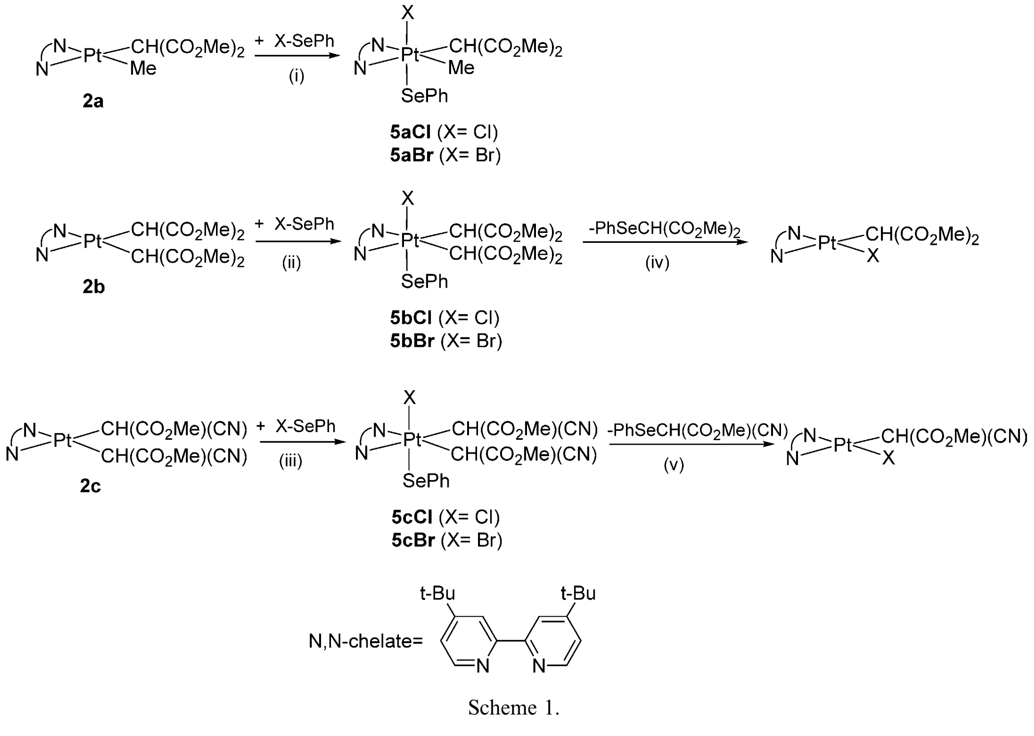
The three platinum(II) complexes used as substrates (**2a–c**) are shown in Scheme 1. The *N*,*N*-chelate is 4,4′-(*tert*-butyl)$_2$-2,2′-bipyridine (Bu$_2$-bipy). Complex **2a** is a mixed bis-hydrocarbyl compound containing a Me and a $–CH(CO_2Me)_2$ group. Instead, **2b** and **2c** display, respectively, two $–CH(CO_2Me)_2$ and two $–CH(CO_2Me)(CN)$ groups. The compounds can be obtained by treating the parent halo-precursors with the appropriate malonic derivative under basic conditions [7], as previously reported for **2a** [4]. E.g.

$$[PtCl_2(Bu_2\text{-bipy})] + 2KCH(CO_2Me)(CN) = [Pt\{CH(CO_2Me)(CN)\}_2(Bu_2\text{-bipy})](\mathbf{2c}) + 2KCl \tag{4}$$

The yellow complexes fairly dissolve in chlorinated solvents, also thanks to the presence of Bu$_2$-bipy as chelate, which is known [6] to improve the solubility of the complexes in the common organic solvents.

The NMR spectral features in $CDCl_3$ are in full agreement with the proposed structures. It should be noted that two stereogenic carbon atoms are directly bound to platinum in **2c**. This means that the compound can exist as racemate (RR/SS) and as meso molecule (RS). Remarkably, the NMR spectrum clearly shows the prevalence of one isomer (5:1 ratio), thus indicating that formation of **2c** according to Eq. (4) occurs with a significant degree of stereoselectivity. It is likely that the configuration of the first entered hydrocarbyl group directs the geometry of the second incoming carbanion. However, (at least at this stage, see below) the NMR features are not sufficient for identifying the geometry of the more abundant isomer. In fact, due to the symmetry (C_2 for the racemate and $C_s$for the meso), in both isomers the two hydrocarbyl groups are NMR equivalent, as well as the two halves of the chelate.

Precursors of type **2** readily react with phenylselenium halides PhSe–X (X = Cl, Br) in chloroform or toluene (Scheme 1), as revealed by the rapid change of



Scheme 1.

colour of the reaction mixture from yellow to orange. Addition of hexane affords the products (**5**) as orange powders.

According to the relative position of the substituents in the coordination sphere, type **5** products may give rise to several isomers (up to six in the case of **5aCl** and **5aBr**). However, high stereoselectivity is observed: if the equatorial plane is defined by the *N*,*N*-chelate, only the isomers showing –X and –SePh in axial position are detectable in solution. This geometry can be formulated on the grounds of the NMR features. We note:

(i) In all cases, the phenyl protons of the –SePh ligand undergo high-field shift with respect to the parent X–SePh molecule (ca. 1 ppm), which has been typically observed when this group occupies one axial position [1j,1r,3,4].

(ii) For **5aCl** and **5aBr**, the chemical shift of Pt–Me (δ 2.18 and 2.15, respectively) clearly identifies its position in the equatorial plane defined by an aromatic *N*,*N*-chelate [8]. Furthermore, the $-CH(CO_2Me)_2$ resonances (δ 4.12 and 4.07, respectively) are very close to that observed in the related type **4** compound $[Pt\{CH(CO_2Me)_2\}(Me)(SePh)_2(Bu_2\text{-bipy})]$ [4], where this substituent is in the equatorial plane.

(iii) Also complexes **5bCl** and **5bBr** clearly display the hydrocarbyl groups in the equatorial plane, as indicated by the NMR equivalence of the two halves of Bu_2-bipy.

(iv) Due to the geometrical isomerism in the parent complex **2c** (see above), **5cCl** should exist as diastereomers as well. Anyway, the NMR spectrum reveals that only the more abundant one crystallises from the reaction mixture. Both the two halves of the chelating ligand and the two hydrocarbyl $-CH(CO_2Me)(CN)$ groups are not NMR equivalent. The methinic signals are very close (δ 4.76 and 4.69), which suggests that they lie in the equatorial plane (since one axial position is already assigned to –SePh, see point (i). The just mentioned lack of equivalence indicates that the stereogenic carbon atoms must display the same configuration. In fact, if the configuration had been RS, the complex would have shown a mirror plane bisecting the chelating ligand. This means that the major isomer in **2c** (see above) is the racemic molecule.

(v) Analogous considerations hold true for **5cBr**, although the signals of the major reaction product are accompanied by those of a minor species (<10%), conceivably the diastereomer arising from the meso form of **2c**.

Complexes of type **5a** are stable in solution and do not appreciably decompose after several hours. On the other hand, species **5b** undergo a slow and clean transformation, as depicted by paths (iv) and (v) in Scheme 1. Within a couple of hours an irreversible reductive elimination is complete, with formation of the new square-planar Pt(II) compounds $[Pt\{CH(CO_2Me)_2\}(X)(Bu_2\text{-bipy})]$ [9] and the organo-selenium species $PhSeCH(CO_2Me)_2$ [10]. When X = Cl, both compounds have been isolated by filtration on a short column of Silica gel. An analogous reaction involving **5cCl** has been monitored by NMR spectroscopy, although no efforts have been made to separate the products of the elimination.

The just described solution behaviour can be interpreted by assuming that the presence of two electron-poor hydrocarbyl groups destabilises the oxidation state IV in **5b** and **5c** species, and favours the reduction of the metal centre to a lower oxidation state. We are not aware of a similar coupling prompted by Pt(IV) species, while C–Se bond formation has been previously observed in the chemistry of octahedral Pd(IV) compounds [1i,1j]. On the other hand, the co-presence of a donor methyl group and an electron poor $-CH(CO_2Me)_2$ ligand apparently allows a stable electronic balance within **5aCl** and **5aBr**.

4. Conclusion

This preliminary communication reports the synthesis of new bis-hydrocarbyl square-planar Pt(II) compounds [PtR(R′)(*N*,*N*-chelate)] and their reaction with phenylselenyl halides, PhSe–X. The addition is in all cases quantitative, by contrast with the behaviour of related diselenides, e.g., MeSe–SeMe or PhSe–SePh [4], which react with the analogous precursors establishing an equilibrium in solution.

High stereoselectivity has been observed, and six octahedral Pt(IV) products bearing –X and –SePh ligands in *trans* position have been obtained. The stability of the compounds seems related to the electronic properties of the hydrocarbyl ligands. When both are electron-poor, the Pt(IV) species undergo an irreversible reductive elimination of a Se–C bond, which affords organoselenim molecules and Pt(II) compounds.

The synthesis and the study of the properties of several Pt(IV) compounds of type **5** will be pursued in the next future by using different R and R′ substituents.

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