Facile Metal-Mediated Synthesis of Macrocyclic Diselenoethers

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Keywords: Platinum / Selenium / Alkylation / Metallacycles / Synthesis design

Nucleophilic attack of $[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]$ on dihaloalkanes gives stable diselenolato complexes, which release macrocyclic diselenoethers upon treatment with dihaloalkanes. The overhead-bridged diplatinum intermediates have been isolated and structurally characterized by single-crystal X-ray crystallography.

Introduction

Organoselenium compounds are particularly valuable in electronic,[1] magnetic,[2] catalytic[3] as well as numerous chemotherapeutic[4] and biomedical[5] applications. However, the synthesis of many of these reagents is often tedious and cumbersome.[6] For example, the multi-step preparation of 1,2-bis[(3-chloro-1-propyl)selenio]benzene requires purification by column chromatography and gives a low yield of 31%.[6a] We are therefore interested in the use of organometallic selenido complexes as a source of new organoselenium compounds or an alternative convenient means to prepare known substrates. The complex $[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]$[7] (**1**) is particularly attractive because it can be prepared easily in good yields, is stable with a good shelf-life, and, most importantly, has two nucleophilic selenide centres where functionalization and transformation can take place. We hereby demonstrate a number of possibilities to activate selenide using common organic halides. In doing so, we prepared a range of new organoselenide ligands[8] that could have a significant bearing towards our ultimate goal in metal-assisted syntheses of new organoselenium materials.

Results and Discussion

Treatment of **1** in MeOH with an almost twofold excess of 1,4-dibromobutane at room temperature resulted in a solution which gave a yellow precipitate upon reaction with NH_4PF_6. Positive-mode ESMS analysis (CH_2Cl_2/MeOH) suggested alkylation at both selenide centres to give a dicationic selenolato complex $[Pt_2(\mu,\eta\text{-}Se_2C_4H_8)(PPh_3)_4]^{2+}$ (**2**; m/z = 825). A single-crystal X-ray structural determination of its acetone solvate revealed a hinged $\{Pt_2Se_2\}$ core [θ Pt(1)-Se(1)···Se(1A)−Pt(1A) 140.2°] with a C_4 overhead bridge across the two selenide atoms, thus giving a C_2 symmetry at the molecular centre (Figure 1). The inner C_2 moiety is disordered with an occupancy of 0.7 for C(2) and 0.3 for C(2A). Its ^{31}P NMR spectrum at room temp. suggests that all phosphanes are equivalent (δ = 19.1 ppm).

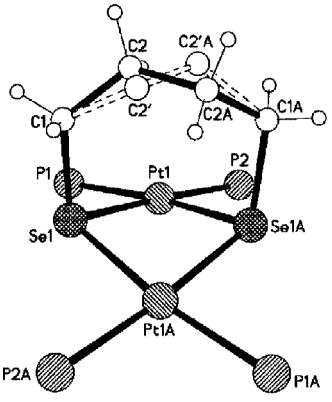

Figure 1. The cation of the molecular structure of $[Pt_2(\mu,\eta\text{-}Se_2C_4H_8)(PPh_3)_4][PF_6]_{1.5}[Cl]_{0.5}$ **2·2(CH$_3$)$_2$CO** with the phenyl rings omitted for clarity; selected bond lengths [A] and angles [°]: Pt(1)−P(1) 2.31(5), Pt(1)−P(2) 2.29(5), Pt(1)-Se(1) 2.48(2), Pt(1)−Se(1A) 2.46(2), Se(1)−C(1) 2.0(3), C(1)−C(2) 1.5(4), C(2)−C(2A) 1.540(19), C(1A)−C(2A) 1.4(3), Pt(1)−Se(1)−Pt(1A) 93.8(7), Se(1)−Pt(1)−Se(1A) 81.8(8), P(1)−Pt(1)−P(2) 99(2), P(1)−Pt(1)−Se(1) 87.1(15), P(2)−Pt(1)−Se(1) 174.0(15), P(1)−Pt(1)−Se(1A) 168.8(15), C(2)−C(1)−Se(1) 116(10), C(1)−C(2)−C(2A) 116(10)

Repeating the preparation with a 100-fold excess of 1,4-dibromobutane (DBB) gave an orange oil which was characterized by ESMS to contain 1,6-diselenacyclodecane **P1** {[**P1** + MeCN + H]$^+$: m/z = 312; [**P1** + MeCN + Na]$^+$: m/z = 335} (Figure 2). Extraction with C_6H_6 followed by careful evaporation of the solvents in vacuo afforded pure **P1** as a white powder (71%); its composition was verified by ^1H and ^{13}C NMR spectroscopy.[9] Fujihara et al. reported the synthesis[9] of **P1** in low yields (3%) by the

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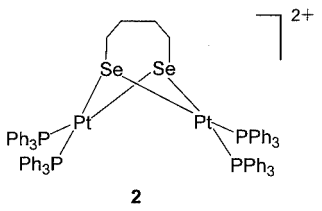
method given in Equation (1). **P1** can also be obtained by reacting **2** with a large excess of 1,4-dibromobutane.



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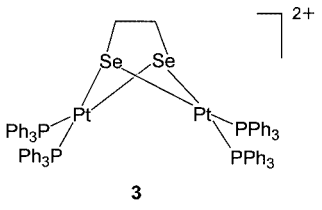

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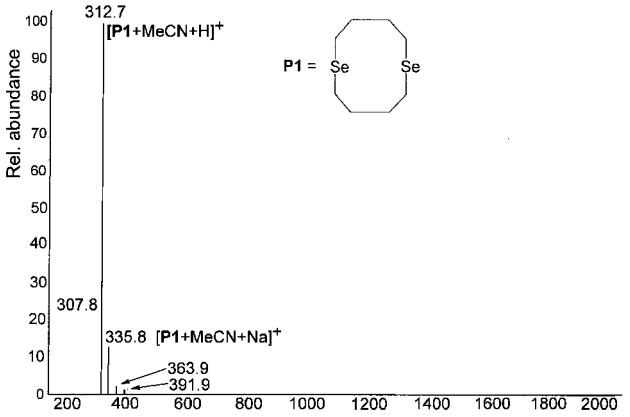
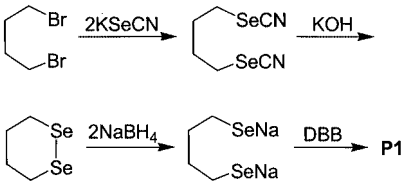


Figure 2. Positive-ion ESMS spectrum of 1,6-diselenacyclodecane (**P1**) in MeCN/H_2O (50:50) solution



(1)

Reaction of **1** with 1,2-dichloroethane gave another stable selenolato-bridged compound $[Pt_2(\mu,\eta\text{-}Se_2C_2H_4)(PPh_3)_4]^{2+}$ (**3**; Figure 3). The shorter alkyl chain does not appear to affect the stability of the $\{Pt_2Se_2\}$ core or the bridging or chelating ability of the diselenolate ligand. We are currently studying the synthesis of other $[Pt_2(\mu,\eta\text{-}Se_2R)_2(PPh_3)_4]^{2+}$ (R = $CH_2C{=}CCH_2$ and $CH_2C_6H_4CH_2$) and their synthetic utility.

The formation and/or isolation of these organoselenium products illustrates the potential use of a selenide complex such as **1** as a stoichiometric reagent for the synthesis of selenium-containing macrocycles. A likely formation pathway is illustrated in Scheme 1.

A key to this function is the nucleophilic nature of the μ_2-selenide. The stability of similar chalcogenolato complexes has been reported elsewhere.[10] The second alkylation would considerably weaken the metal-ligand bonds which facilitate the liberation of the organoselenium moiety. Re-entry of the chloride to the coordination sphere regenerates $[PtCl_2(PPh_3)_2]$, which is the precursor of **1**, and turns this from a stoichiometric to a potentially catalytic synthesis. The value of this cycle lies in its simplicity in terms of principle and experimental procedures, the use of simple reagents and ambient conditions, and the ease of isolation through extraction. The major advantages are the ability to choose a wide range of alkyl and aryl halides and the flexibility of the $\{Pt_2Se_2\}$ core in accommodating different organic residues as its overhead bridge. These collectively determine the molecular skeleton of the desirable products and make this a potentially powerful entry to selenium macrocycles.

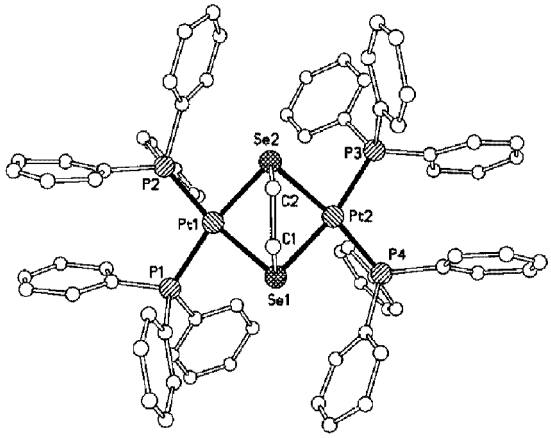
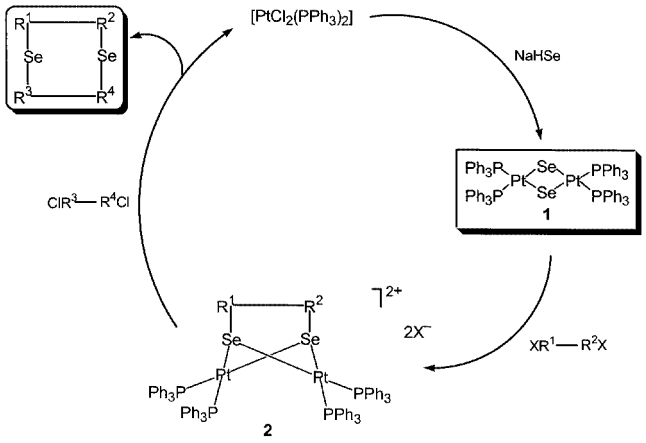


Figure 3. The cation of the molecular structure of $[Pt_2(\mu,\eta\text{-}Se_2C_2H_4)(PPh_3)_4][PF_6]_2$, **3·0.33$CH_2Cl_2$·0.17MeCN·2.83$H_2O$**; selected bond lengths [Å] and angles [°]: Pt(1)−P(1) 2.300(15), Pt(1)−P(2) 2.293(14), Pt(1)−Se(1) 2.478(6), Pt(1)−Se(2) 2.476(6), Se(1)−C(1) 2.00(6), Se(2)−C(2) 1.98(5), C(1)−C(2) 1.50(7), Pt(1)−Se(1)−Pt(2) 86.34(18), Se(1)−Pt(1)−Se(2) 77.78(19), P(1)−Pt(1)−P(2) 97.6(5), P(2)−Pt(1)−Se(1) 172.2(4), P(1)−Pt(1)−Se(2) 167.4(4), C(1)−C(2)−Se(2) 112(4)



Scheme 1. A stoichiometric pathway with a catalytic-like cycle showing the roles played by **1** and a general representation of **2** and **3** in the preparation of organoselenium compounds

Conclusion

The high nucleophilicity of bridging selenide towards various organic halides makes **1** a potentially rich source of organoselenium substrates. This could lead to many new materials since **1** is reactive to many forms of organic halides. The question is the delicate control of the disintegration of the dinuclear core, stabilization of the mononuclear complex, and its subsequent breakdown to liberate the organoselenium residue. Our next target is to understand the subtle balance of these sequential, yet competing, processes. Such understanding is a prerequisite for us to harness a complex disintegration process whereby we can develop synthetically viable methods for laboratory-scale preparation of materials that are otherwise difficult to obtain.

Experimental Section

General Procedures and Chemicals: All substrates used for analysis were commercially available from Aldrich. We followed a modified preparation of $[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]$ (**1**).[11] All reactions were performed under a positive pressure of purified Ar unless otherwise stated. Solvents were distilled and degassed before use.

Instrumental: Samples for ESMS analysis were prepared in 1 mL MeCN solutions of the analytes. Electrospray mass spectra were obtained with a Finnigan/MAT TSQ 7000 mass spectrometer with the MeCN/H_2O (50:50) mobile phase driven at 0.03 mL min^{-1} using a Thermo Separation products SpectraSystem TSP4000 LC pump. Samples were injected through a Rheodyne valve fitted with a 5 μL sample loop. The source temperature was 200 °C. The capillary potential tip was 4500 V, with nitrogen used both as a drying and a nebulizing gas. Peaks were assigned from the *m*/*z* values and from the isotope distribution patterns that were simulated using the ISOTOPE program.[12] The *m*/*z* values given are for the most intense peak in the envelope in each case. ^1H NMR and ^{13}C NMR spectra were recorded at 25 °C on a Bruker ACF 300 spectrometer (at, 300 and 75.47 MHz respectively) with Me_4Si as internal standard. The ^{31}P NMR spectra were recorded at 121.39 MHz with 85% H_3PO_4 as external reference. Elemental analyses were performed by the microanalytical laboratory of the Department of Chemistry at the National University of Singapore.

$[Pt_2(\mu\text{-}Se_2C_4H_8)(PPh_3)_4][PF_6]_{1.5}[Cl]_{0.5}$ (2): Excess 1,4-dibromobutane (11.1 mg, 20.0 μL, 0.0512 mmol) was added to a brown suspension of **1** (44.1 mg, 0.0276 mmol) in methanol (20 mL). The resultant yellow solution was stirred for 3 h, after which excess NH_4PF_6 (10.0 mg, 0.0614 mol) was added to give a yellow suspension. After stirring for 1 h, deionized water (50 mL) was added to induce precipitation. The suspension was filtered, the solid washed successively with 100 mL portions of deionized water and diethyl ether, and dried under vacuum yielding a yellow powder of **2**. The solid was dissolved in dichloromethane/acetone and this solution layered with hexane. Pale yellow crystals suitable for X-ray analysis were obtained. Yield: 24.2 mg (46%). $C_{76}H_{68}Cl_{0.5}F_9P_{5.5}Pt_2Se_2$ (1888.6): calcd. C 48.3, H 3.6, P 9.0; found C 47.6, H 3.6, P 8.2. ^1H NMR ($CDCl_3$): δ = 1.18−1.26 (m, 8 H, $4CH_2$), 6.92−7.74 (m, 60 H, 12 C_6H_5) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 19.1 (t, $^1J_{P,Pt}$ = 2964 Hz) ppm.

$[Pt_2(\mu\text{-}SeC_2H_4)_2(PPh_3)_4][PF_6]_2$ (3): By using a similar procedure as for **2**, excess 1,2-dichloroethane (8.1 mg, 10.2 μL, 0.0821 mmol) and **1** (50.7 mg, 0.0317 mmol) gave an orange powder of **3**. The solid was dissolved in dichloromethane/acetonitrile and this solution layered with hexane. Orange crystals suitable for X-ray analysis were obtained. Yield: 26.4 mg (43%). $C_{74}H_{64}F_{12}P_6Pt_2Se_2$ (1915.3): calcd. C 46.4, H 3.4, P 9.7; found C 46.0, H 3.3, P 9.0. ^1H NMR ($CDCl_3$): δ = 1.18 (s, 4 H, $2CH_2$), 6.98−7.77 (m, 60 H, 12 C_6H_5) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 12.9 (t, $^1J_{P,Pt}$ = 3117 Hz) ppm.

X-ray Crystal Structure Determinations

$2\cdot 2(CH_3)_2CO$: $C_{82}H_{80}Cl_{0.5}F_9O_2P_{5.5}Pt_2Se_2$: M = 2004.62, crystal dimensions: 0.32 × 0.30 × 0.08 mm^3. Monoclinic, space group *I*2/*m*, a = 17.6277(16), b = 24.464(2), c = 20.905(3) Å, β = 91.887(2)°, V = 9010.2(18) $Å^3$, Z = 4, $d_{calcd.}$ = 1.478 $g\cdot cm^{-3}$, μ(Mo-K_α) = 4.081 mm^{-1}. 25888 Reflections measured, 8126 unique (R_{int} = 0.0812), final $R1$ and $wR2$ values 0.0639 and 0.1775 for 4807 independent reflections [$I \geq 2\sigma(I)$] and 424 parameters.

$3\cdot 0.33CH_2Cl_2\cdot 0.17MeCN\cdot 2.83H_2O$:
$C_{74.67}H_{70.83}Cl_{0.67}F_{12}N_{0.17}O_{2.83}P_6Pt_2Se_2$: M = 2001.37, crystal dimensions: 0.20 × 0.10 × 0.08 mm^3. Monoclinic, space group $P2_1/c$, a = 32.6363(19), b = 18.0886(10), c = 43.093(3) Å, β = 100.262(2)°, V = 25033(3) $Å^3$, Z = 12, $d_{calcd.}$ = 1.593 $g\cdot cm^{-3}$, μ(Mo-K_α) = 4.427 mm^{-1}. 145023 Reflections measured, 44105 unique (R_{int} = 0.1330), final $R1$ and $wR2$ values 0.0678 and 0.1710 for 16422 independent reflections [$I \geq 2\sigma(I)$] and 942 parameters.

The data collection was performed on a Bruker AXS APEX diffractometer, equipped with a CCD area-detector using Mo-K_α radiation (λ = 0.71073 Å) at −50 °C. The SMART[13] software package was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT[13] for integration of intensity of reflections and scaling, SADABS[14] for empirical absorption correction, and SHELXTL[15] for space group and structure determination, refinements, graphics, and structure reporting. Hydrogen atoms were not located. The structures were refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for non-hydrogen atoms, unless otherwise indicated [$R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$, and $wR_2 = \{\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$ (where $w^{-1} = \sigma^2(F_0^2) + (aP)^2 + (bP)$].

For **$2\cdot 2(CH_3)_2CO$**, the original cell data in *C*2/*m* were transformed to the equivalent nonstandard space group *I*2/*m*. The cation has a crystallographic twofold symmetry and the C(2) carbon was found to be disordered. Two positions for this methylene carbon atom were resolved with occupancies of 0.7 and 0.3. Only isotropic thermal parameters were refined for these carbon atoms. The carbon atoms C(1F) to C(6F) of a phenyl ring were treated as a regular hexagon and only isotropic thermal parameters were refined. During the metathesis reaction with NH_4PF_6 half a molecule of chloride ions were retained in the compound which was found to be severely disordered. They were found in seven places in the asymmetric unit and each chloride was found on the mirror plane. In total two acetone molecules were disordered over three locations on the twofold crystallographic axis. All the hydrogen atoms were added in the calculated positions for the purpose of structure factor calculations only. In the final least-squares refinement based on F^2, the model converged at $R1$ = 0.0639 and $wR2$ = 0.1775 for 4807 reflections with $I \geq 2\sigma(I)$ and 424 variables. Despite the disorder of the methylene group and the chloride anions, the structural connectivity is proved beyond any doubt in the cation. We were unable to solve the structure in *C*2. In any case, between centrosymmetric and noncentrosymmetric space groups, the centrosymmetric description is recommended by Marsh.[16]

For **3·0.33CH_2Cl_2·0.17MeCN·2.83H_2O** all the carbon atoms of the phenyl rings were treated as regular hexagons and only isotropic thermal parameters were refined. Common isotropic thermal parameters were refined for the F atoms of each PF_6^- anion and soft constraints were imposed to maintain the octahedral geometry around the phosphorus atom. All the hydrogen atoms were added in their calculated positions for the purpose of structure factor calculations only. From the Fourier-difference routines a molecule of CH_2Cl_2 and half a molecule of MeCN were located. Hard geometrical constraints were imposed for these molecules in the least-squares refinement. Of the twelve sites of the asymmetric unit containing 8.5 H_2O molecules, seven were assigned to disordered O atoms with occupancies of 0.5. In the final least-squares refinement based on F^2, the model converged at $R1 = 0.0678$ and $wR2 = 0.1710$ for 16422 reflections with $I \geq 2\sigma(I)$ and 942 variables. Despite the weak data, the structural connectivity is proved beyond any doubt in the cation.

CCDC-175722 and CCDC-175723 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 Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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