

# Ligand Functionalization, Reactivity, and Transformation at the Selenide Centers of $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4]$ with Organic Halides

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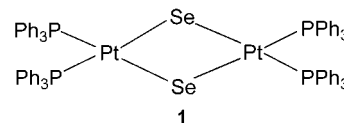
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The selenium centers of  $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4]$  are subject to electrophilic attack from various organic halides. Reactions with MeI, *n*-BuCl,  $\alpha,\alpha'$ -dichloro-*p*-xylene, and  $\alpha,\alpha'$ -dichloro-*o*-xylene give  $[\text{Pt}_2(\mu\text{-Se})(\mu\text{-SeMe})(\text{PPh}_3)_4]^+$ ,  $[\text{Pt}_2(\mu\text{-Se})(\mu\text{-SeBu})(\text{PPh}_3)_4]^+$ ,  $[\text{Pt}_2(\mu\text{-Se})(\mu\text{-SeCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-Cl})(\text{PPh}_3)_4]^+$ , and  $[\text{Pt}_2(\mu\text{-SeCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{Se})(\text{PPh}_3)_4]^{2+}$ , respectively, preserving the dinuclear core and giving rise to new selenium-derivatized ligand complexes. Reaction with oxalyl chloride gives  $[\text{Pt}(\eta^2\text{-Se}_2\text{C}_2\text{O}_2\text{-Se,Se})(\text{PPh}_3)_2]$ , leading to the disintegration of the core to a mononuclear complex supported by a new chelating selenium donor ligand. Reactions with malonyl chloride and succinyl chloride give  $[(\text{COCH}_2\text{COCl})\text{Se}]_2$  and  $[(\text{COCH}_2\text{CH}_2\text{COCl})\text{Se}]_2$  respectively, leading to complex disintegration and liberation of new selenium materials. The crystal structures of the aggregates  $[\text{Pt}_2(\mu\text{-Se})(\mu\text{-SeMe})(\text{PPh}_3)_4][\text{PF}_6]$ ,  $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4\text{-(CH}_2\text{C}_6\text{H}_4\text{CH}_2)] [\text{PF}_6]_{1.25}[\text{Cl}]_{0.75}$ , and  $[\text{Pt}(\eta^2\text{-Se}_2\text{C}_2\text{O}_2\text{-Se,Se})(\text{PPh}_3)_2]$  are described. The potential of using  $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4]$  as a source for metal-assisted synthesis of new and unusual organoselenium compounds is discussed.

## Introduction

Organoselenide chemistry has attracted considerable attention, primarily because of the biomedical,<sup>1</sup> catalytic,<sup>2</sup> and conducting<sup>3</sup> properties of the compounds. These applications provide a platform for the syntheses of various organoselenium and inorganic selenide substances. Relatively little, however, is known about the behavior of coordinated selenide. This is hardly surprising, since most of the selenides are in a  $\mu_3$  capping state, which is not particularly nucleophilic or electrophilic, acidic or basic, or oxidizing or reducing; hence, they are stable and inert. Although ligand functionalization and transformation remains a fascinating prospect for coordinated selenides, in terms of understanding their chemical and electronic behavior as well as a potentially new source of organoselenides, there is a serious lack of suitable models for such study. This work attempts to address this problem. Using  $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4]$ <sup>4</sup> (**1**) as a model substrate, and taking advantage of the



nucleophilic and basic nature of a  $\mu_2$  bridging selenide, we hereby demonstrate a number of possibilities to activate selenide using common organic halides. In doing so, we assembled a range of new organoselenide ligands that could have a significant bearing on our ultimate goal of metal-assisted syntheses of new organoselenium materials.<sup>5</sup>

## Results and Discussion

**(I) Reactivity of  $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4]$  with Organohalides.** We, together with other groups, have discussed the complicated nature of a seemingly straightforward alkylation of the sulfide analogue of **1**: viz.,  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$ .<sup>6</sup> Notably, alkylation by  $\text{CH}_3\text{I}$ , giving  $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SMe})(\text{PPh}_3)_4]\text{I}$ ,<sup>7</sup> was initially misidentified as the doubly alkylated, dicationic  $[\text{Pt}_2(\mu\text{-SMe})_2(\text{PPh}_3)_4]\text{-I}_2$ .<sup>8</sup> The latter complex thus far has eluded isolation, although it remains the most likely intermediate en

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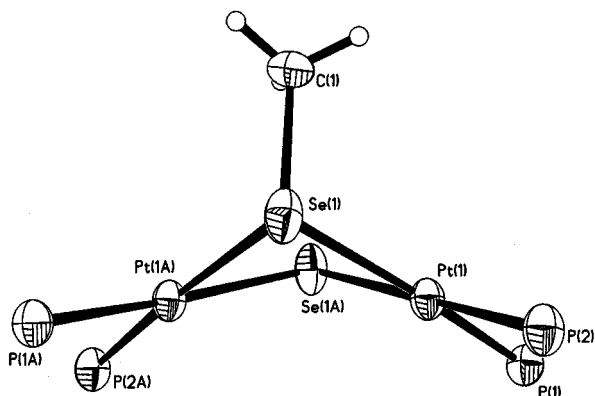
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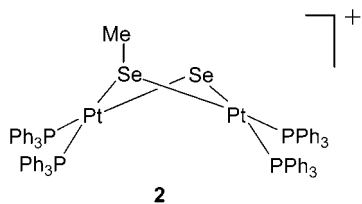
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**Figure 1.** ORTEP plot of the cation of the molecular structure of  $[\text{Pt}_2(\mu\text{-Se})(\mu\text{-SeMe})(\text{PPh}_3)_4][\text{PF}_6]$  (**2**) with 50% probability thermal ellipsoids. The phenyl rings are omitted for clarity.

route to other thiolato-type decomposition products. Similar decomposition in  $\text{CH}_2\text{Cl}_2$  has been reported for **1**, giving  $[\text{Pt}(\eta^2\text{-Se}_2\text{CH}_2)(\text{PPh}_3)_2]$  and  $[\text{PtCl}_2(\text{PPh}_3)_2]$ .<sup>9</sup> To date, almost all double-alkylated derivatives of both sulfide and selenide products have eluded isolation. The reason for their instability remains a mystery. We therefore decided to use organic dihalides to functionalize the two selenide centers and, in doing so, stabilize the dication product. We also continue our use of ESMS<sup>10</sup> to study species formed in situ in solution.

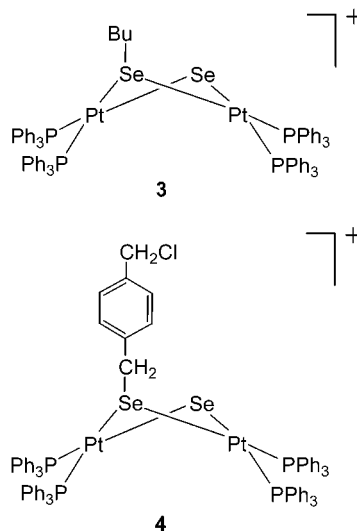
Excess MeI on **1** in  $\text{Et}_2\text{O}$  gave a yellow precipitate that can be metathesized with  $\text{NH}_4\text{PF}_6$ . Positive ion ESMS analysis of the isolated product in  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  showed a peak at  $m/z$  1612 corresponding to the expected  $[\text{Pt}_2(\mu\text{-Se})(\mu\text{-SeMe})(\text{PPh}_3)_4][\text{PF}_6]$  (**2**). Its  $^{31}\text{P}\{^1\text{H}\}$  NMR spec-



trum is in agreement with  $\text{AA}'\text{BB}'\text{X}$  and  $\text{AA}'\text{BB}'\text{XX}'$  spin systems that can be approximated to an ABX first-order pattern, because the long-range Pt–P and P–P coupling constants are similar to the line widths of the main resonances. The derivation of such spectra has been described.<sup>7,11</sup> A single-crystal X-ray structural analysis of **2** revealed a diplatinum structure bridged by selenido and methylselenato ligands (Figure 1, Tables 1 and 2). The  $\{\text{Pt}_2\text{Se}_2\}$  core is slightly bent with a dihedral angle ( $133.6^\circ$ ) significantly larger than that in  $[\text{Pt}_2(\mu\text{-SeH})_2(\text{PPh}_3)_4][\text{PF}_6]_2$  ( $71.9^\circ$ ).<sup>12</sup> These are in contrast with the planar structure found in  $[\text{Pt}_2\text{Cl}_2(\mu\text{-SeEt})_2(\text{PET}_3)_2]$ .<sup>13</sup>

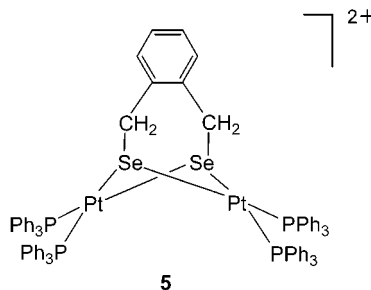
The use of bulkier or difunctional halides, viz. 1-chlorobutane and  $\alpha,\alpha'$ -dichloro-*p*-xylene, also afforded the

monocationic products  $[\text{Pt}_2(\mu\text{-Se})(\mu\text{-SeBu})(\text{PPh}_3)_4][\text{PF}_6]$  (**3**) and  $[\text{Pt}_2(\mu\text{-Se})(\mu\text{-SeCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{Cl})(\text{PPh}_3)_4][\text{PF}_6]$  (**4**), whose NMR spectral features are similar.



Interestingly, when the reaction between **1** and MeI was carried out in MeOH, it gave rise to a yellow solution from which a yellow precipitate could be isolated upon metathesis with  $\text{NH}_4\text{PF}_6$ . ESMS analysis of this product in  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  showed a peak at  $m/z$  814 corresponding to  $[\text{Pt}_2(\mu\text{-SeMe})_2(\text{PPh}_3)_4]^{2+}$ , along with a few unidentified peaks. This was the first evidence for dialkylation of this series of compounds. Its  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum gives a singlet at 18.4 ppm with the associated satellites ( $^1J(\text{P-Pt}) = 2979$  Hz), consistent with the equivalent phosphines expected in  $[\text{Pt}_2(\mu\text{-SeMe})_2(\text{PPh}_3)_4][\text{PF}_6]_2$ , and a few other signals similar to those of the decomposition products of  $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4]$  in  $\text{CDCl}_3$ . There is, however, no evidence for **2**. Attempts to obtain suitable crystals of the salts of  $[\text{Pt}_2(\mu\text{-SeMe})_2(\text{PPh}_3)_4]^{2+}$  for structural analysis were unsuccessful due to rapid loss of solvate.

In an attempt to alkylate both selenido centers of **1** and to give stable/isolable products, we use a substrate that is structurally conducive to crossing both selenium atoms: viz.,  $\alpha,\alpha'$ -dichloro-*o*-xylene. Single-crystal X-ray analysis of the product confirmed the overhead-bridged diplatinum selenolato dication  $[\text{Pt}_2(\mu\text{-SeCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-Se})(\text{PPh}_3)_4]^{2+}$  (**5**) (Figure 2), with 1.25  $\text{PF}_6^-$  and 0.75  $\text{Cl}^-$



counteranions resulting from incomplete metathesis. As a result, the two selenido ligands have been transformed into a new  $\alpha,\alpha'$ -diselenato-*o*-xylene. This is the first structural representation of a  $[\text{Pt}_2(\text{SeR})_2\text{P}_4]$  framework in this series. It also marks a potentially simple metal-assisted process to synthesize  $(\text{HSeCH}_2)_2\text{C}_6\text{H}_4$ , thus

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**Table 1. Crystallographic Data for Compounds 2, 5, and 6**

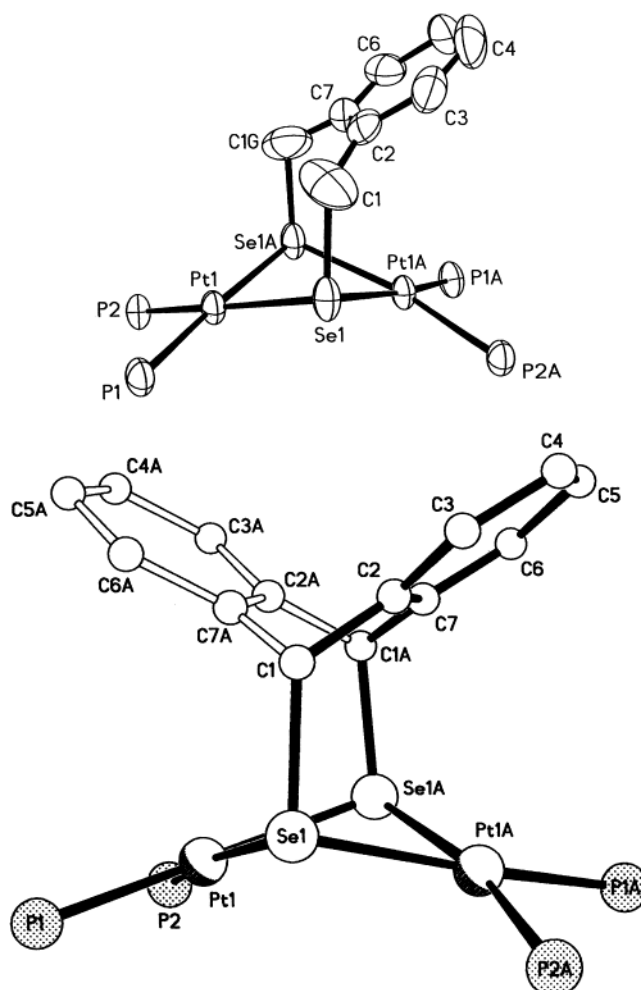
	<b>2</b>	<b>5·2H<sub>2</sub>O</b>	<b>6</b>
formula	C <sub>73</sub> H <sub>63</sub> F <sub>6</sub> Se <sub>2</sub> P <sub>5</sub> Pt <sub>2</sub>	C <sub>80</sub> H <sub>72</sub> Cl <sub>0.75</sub> F <sub>7.5</sub> O <sub>2</sub> Se <sub>2</sub> P <sub>5.25</sub> Pt <sub>2</sub>	C <sub>38</sub> H <sub>30</sub> O <sub>2</sub> Se <sub>2</sub> P <sub>2</sub> Pt
fw	1757.18	1945.31	933.57
cryst size (mm)	0.34 × 0.22 × 0.04	0.20 × 0.18 × 0.14	0.20 × 0.16 × 0.06
cryst syst	monoclinic	monoclinic	triclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>C</i> 2/ <i>m</i>	<i>P</i> 1
<i>a</i> /Å	18.1509(17)	26.45(8)	10.1941(6)
<i>b</i> /Å	10.3548(10)	23.71(6)	11.6717(6)
<i>c</i> /Å	18.3932(16)	16.78(4)	15.6797(8)
α/deg	90	90	69.693(1)
β/deg	107.029(2)	127.86(7)	85.515(1)
γ/deg	90	90	74.588(1)
<i>V</i> /Å <sup>3</sup>	3305.4(5)	8304(38)	1686.53(16)
<i>Z</i>	2	4	2
μ/mm <sup>-1</sup>	5.510	4.429	6.446
<i>T</i> /K	223(2)	223(2)	223(2)
θ range (deg)	1.97–30.01	1.30–25.00	1.95–30.01
index ranges	–25 < <i>h</i> < 24 –14 < <i>k</i> < 14 –13 < <i>l</i> < 24	–31 < <i>h</i> < 31 –28 < <i>k</i> < 28 –19 < <i>l</i> < 19	–14 < <i>h</i> < 14 –16 < <i>k</i> < 16 –22 < <i>l</i> < 22
no. of rflns collected	25 772	34 436	26 263
no. of unique rflns	5769	5438	8400
no. of obsd rflns ( <i>I</i> > 2σ( <i>I</i> ))	9255	7512	9793
<i>R</i> 1 ( <i>I</i> > 2σ( <i>I</i> ))	0.0499	0.0515	0.0348
<i>wR</i> 2 (all data)	0.0803	0.1388	0.0631

**Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compounds 2, 5, and 6**

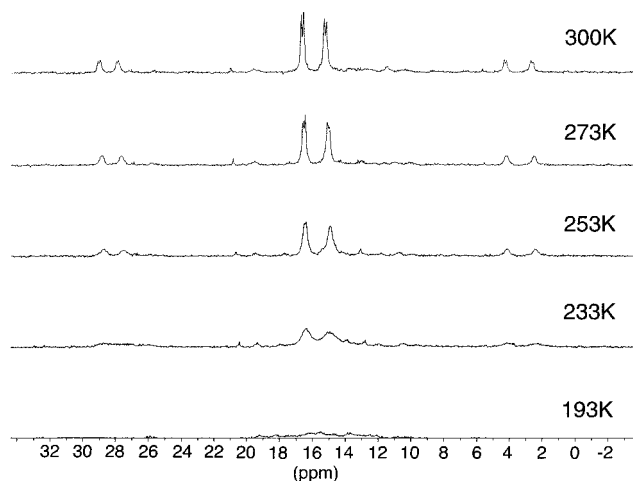
	<b>2</b>	<b>5·2H<sub>2</sub>O</b>	<b>6</b>
Pt(1)–P(1)	2.3011(18)	2.291(6)	2.2877(8)
Pt(1)–P(2)	2.2890(17)	2.307(7)	2.3030(9)
Pt(1)–Se(1)	2.4623(7)	2.465(6)	2.4458(4)
Pt(1)–Se(1A)	2.4827(7)	2.473(6)	2.4611(4)
Pt(1A)–Se(1)	2.4827(7)	2.473(6)	
Pt(1A)–Se(1A)	2.4623(7)		
Se(1)–C(1)	2.033(14)	2.012(13)	1.905(4)
Se(1A)–C(2)			1.865(4)
O(1)–C(1)			1.214(4)
O(2)–C(2)			1.214(4)
C(1)–C(2)			1.535(5)
Pt(1)–Se(1)–Pt(1A)	88.26(2)	91.30(19)	
Se(1)–Pt(1)–Se(1A)	81.47(3)	81.2(2)	88.329(13)
P(1)–Pt(1)–P(2)	97.42(6)	99.87(19)	97.24(3)
P(1)–Pt(1)–Se(1)	169.51(5)	91.5(2)	91.66(2)
P(1)–Pt(1)–Se(1A)	88.06(3)	172.60(6)	174.06(2)
P(2)–Pt(1)–Se(1)	93.02(5)	167.53(7)	170.78(2)
P(2)–Pt(1)–Se(1A)	174.31(5)	87.53(17)	83.06(2)
C(1)–Se(1)–Pt(1)	100.3(5)	104.3(4)	105.10(12)
C(1)–Se(1)–Pt(1A)	100.1(4)	100.7(3)	

avoiding a process involving the noxious H<sub>2</sub>Se and (ClCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> in a cumbersome multistep synthesis. The structure of **5** shows an interesting disorder of the xylyl ring at the methylene groups across the {Se<sub>2</sub>C<sub>2</sub>} plane (Figure 2b, Tables 1 and 2). This generates a 2-fold symmetry with the C<sub>6</sub> ring flipping from one end of the molecule to the other divided by the {Se<sub>2</sub>C<sub>2</sub>} plane. Accordingly, the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum also shows two discrete resonances, corresponding to the phosphines at the proximal and distal ends of the C<sub>6</sub> ring. A low-temperature study in CD<sub>2</sub>Cl<sub>2</sub> (Figure 3) gave peak broadening, beginning at ca. 253 K and resulting in a featureless spectrum at 193 K. It possibly points to a low-energy rocking process of the {Pt(1 (or Pt1A))–Se1–Se1A–C1–C1G–C2–C7} bicyclic ring. Apart from differentiating the two proximal phosphines (P1A and P2A) from the distal phosphines (P1 and P2), the slow rocking motion would destroy the σ symmetry along the Pt1Pt1A axis. These motions would collectively generate four inequivalent phosphorus nuclei. This static state, however, is not reached at the limit of the experiments (193 K).

This form of ligand modification through dialkylation of **1** by an organic dihalide can be extended to other systems. For example, ESMS analysis of the reaction



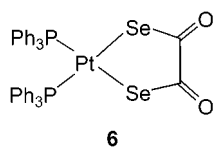
**Figure 2.** (a, top) ORTEP plot of the cation of the molecular structure of [Pt<sub>2</sub>(μ<sub>3</sub>-Se)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)]-[PF<sub>6</sub>]<sub>1.25</sub>[Cl]<sub>0.75</sub> (**5**) with 50% probability thermal ellipsoids. Phenyl rings are omitted for clarity. (b, bottom) Structure of compound **5**, showing the disorder in the ring attached to the {Pt<sub>2</sub>Se<sub>2</sub>} framework.



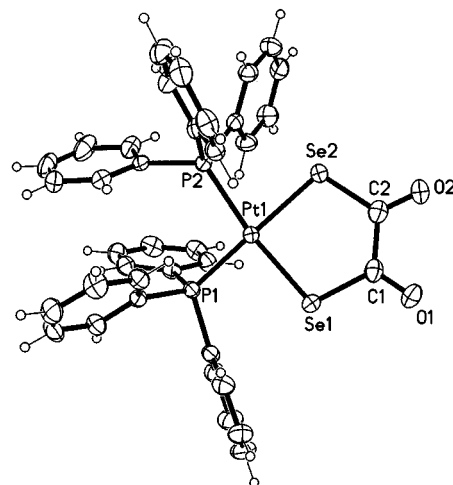
**Figure 3.** VT  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of compound **5** in  $\text{CD}_2\text{Cl}_2$ .

mixtures of **1** and 1,3-dichloroacetone or 1,8-bis(bromomethyl)naphthalene also gave the analogous dicationic products. We have described earlier that this use of ESMS can help us screen for positive reactions and products and that, in many cases, successful hits can be synthesized and isolated.<sup>14</sup> We chose not to pursue these substrates further, since the derivatives are expected to behave similarly.

**(II) Reactivity of  $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4]$  with Acid Chlorides.** We were interested in testing the reactivity of selenide toward an  $\text{sp}^2$  carbon source. The use of a non-hydrocarbon substrate was appealing, as we could develop a new entry to other inorganic selenide materials. Addition of oxalyl chloride to **1** in dry  $\text{CH}_3\text{CN}$  resulted in an instantaneous formation of an orange suspension, which subsequently led to the isolation of the new complex  $[\text{Pt}(\eta^2\text{-Se}_2\text{C}_2\text{O}_2\text{-Se,Se}')(\text{PPh}_3)_2]$  (**6**). A

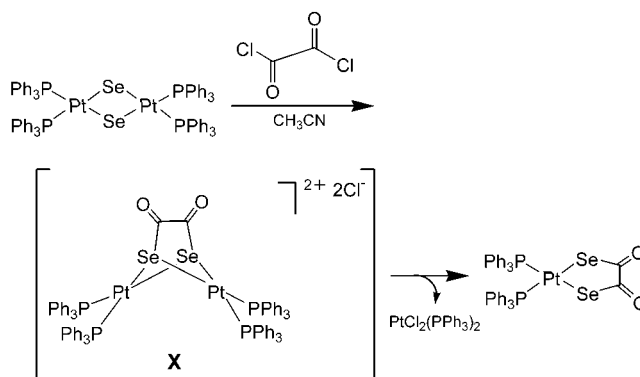


single-crystal X-ray crystallographic study revealed a mononuclear square-planar Pt(II) complex with another new ligand—diselenooxalate serving as a chelate through the selenium centers (Figure 4, Tables 1 and 2). This breakup of the dinuclear structure (from **1** to **6**) (Scheme 1) epitomizes the difficulty of dialkylation of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  without destroying the  $\{\text{Pt}_2\text{S}_2\}$  core, as described earlier. It, however, turns a destructive process to one that is potentially useful—ligand transformation and metal-assisted assembly of a new selenium material. This represents a facile entry to the rare 1,2-diselenooxalate complexes,<sup>15</sup> as compared to the relatively common dithiooxalate complexes.<sup>16</sup> To the best of our knowledge, this is also the only entry through ligand modification from selenide. This is significant, since it avoids the laborious synthesis of potassium



**Figure 4.** ORTEP plot of the molecular structure of  $[\text{Pt}(\eta^2\text{-Se}_2\text{C}_2\text{O}_2\text{-Se,Se}')(\text{PPh}_3)_2]$  (**6**) with 50% probability thermal ellipsoids.

**Scheme 1. Formation of  $[\text{Pt}(\eta^2\text{-Se}_2\text{C}_2\text{O}_2\text{-Se,Se}')(\text{PPh}_3)_2]$  (**6**) from **1** and Oxalyl Chloride Possibly through a Double-Alkylation Process**



diselenooxalate.<sup>17</sup> The proposed intermediate **X** could not be detected or trapped, but liberation of  $\text{PtCl}_2(\text{PPh}_3)_2$  was easily verified by spectroscopic or chemical means. Formation of **6** from **1** is driven by Se–C bond formation, which is related to S–C bond formation as in the formation of  $\text{Pt}[\text{S}_2(\text{CR})_2](\text{PPh}_3)_2$  from  $\text{PtS}_4(\text{PPh}_3)_2$  and RCCR.<sup>18</sup> These are in contrast to the literature approach to related  $[\text{OC}(\text{R})=\text{C}(\text{R}')\text{Se}]^{2-}$  complexes through Se–C bond cleavage, for example, of acyl-substituted diselenetanes.<sup>19</sup> The other method that can be used is a metal exchange, for example, between titanium maleate and  $\text{PtCl}_2(\text{PPh}_3)_2$ .<sup>20</sup>

We also examined other acid chloride substrates to determine if the dinuclear disintegration and ligand functionalization process can lead to any isolable organoselenium residues. Reactions of **1** with malonyl or succinyl chloride did not give the expected products  $[\text{Pt}(\eta^2\text{-Se}_2\text{C}_2\text{O}_2(\text{CH}_2)_n\text{-Se,Se}')(\text{PPh}_3)_2]$ , where  $n = 1$  (**I**), 2 (**II**). Instead, they gave rise to an almost instantaneous

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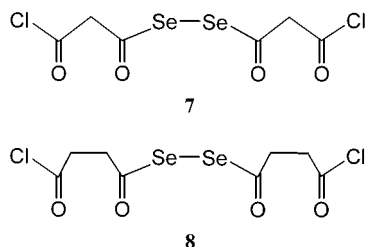
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formation (at room temperature or  $-78\text{ }^{\circ}\text{C}$ ) of an orange-brown solution in  $\text{CH}_3\text{CN}$ . ESMS analysis of the malonate solution gave the dication  $\{[(\text{COCH}_2\text{COCI})\text{Se}]_2 + 2\text{Na}\}^{2+}$  ( $m/z$  207). The most likely source of  $\text{Na}^+$  is from the solvent, as traces are often present in even HPLC-grade solvents.<sup>21</sup> The parent diselenium ligand,  $[(\text{COCH}_2\text{COCI})\text{Se}]_2$  (**7**), could be isolated in analytically pure



form. Similarly, the succinyl ion  $\{[(\text{COCH}_2\text{CH}_2\text{COCI})\text{Se}]_2 + \text{Na}\}^+$  ( $m/z$  419) was detected, which led to the isolation of analytically and spectroscopically pure  $[(\text{COCH}_2\text{CH}_2\text{COCI})\text{Se}]_2$  (**8**). To our best of our knowledge, these are hitherto unknown organoselenium materials.

### Conclusion

The high nucleophilicity of bridging selenide toward various organic halides makes **1** a rare and valuable precursor for complexes with unusual selenium-containing ligands and a potentially rich source of organoselenium substrates. There is virtually no limit on the number of new materials that we can produce, since **1** is reactive essentially with all forms of haloorganics. The question is the delicate control of the disintegration of the dinuclear core, the 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 an 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

**Instrumentation.** 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– $\text{H}_2\text{O}$  (50:50) mobile phase driven at  $0.03\text{ mL min}^{-1}$  using a Thermo Separation Products SpectraSystem TSP4000 LC pump. Samples were injected via a Rheodyne valve fitted with a  $5\text{ }\mu\text{L}$  sample loop. The source temperature was  $200\text{ }^{\circ}\text{C}$ . The capillary potential tip was 4500 V, with nitrogen used as both 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.<sup>22</sup> The  $m/z$  values given are for the most intense peak in the envelope in each case.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded at  $25\text{ }^{\circ}\text{C}$  on a Bruker ACF 300 spectrometer (at 300 and 75.47 MHz, respectively) with  $\text{Me}_4\text{Si}$  as internal standard. The  $^{31}\text{P}$  NMR spectra were recorded at 121.39 MHz with 85%  $\text{H}_3\text{PO}_4$  as external reference. Infrared spectra were recorded in the range  $4000\text{--}400\text{ cm}^{-1}$ , on a Perkin-Elmer FTIR spectrometer. Elemental analyses were performed by the microanalytical laboratory of the Department of Chemistry at the National University of Singapore.

**Materials.** All substrates used for analysis were commercially available from Aldrich. We have followed a modified preparation of  $\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4$  (**1**), which has been repeated.<sup>14</sup> All reactions were performed under a positive pressure of purified Ar, unless otherwise stated. Solvents were distilled and degassed before use.

**Syntheses.**  $[\text{Pt}_2(\mu\text{-Se})(\mu\text{-SeMe})(\text{PPh}_3)_4][\text{PF}_6]$  (**2**). An excess of MeI (9.3 mg,  $4.10\text{ }\mu\text{L}$ , 0.0656 mmol) was added to a brown suspension of **1** (53.5 mg, 0.0335 mmol) in diethyl ether (20 mL), and the mixture was stirred for 3 h. The resultant yellow precipitate was filtered and redissolved in MeOH (15 mL). Excess  $\text{NH}_4\text{PF}_6$  (10.0 mg, 0.0614 mol) was added. After this mixture was stirred for 1 h, deionized water (50 mL) was added to induce precipitation. The suspension was filtered and the solid washed successively with 100 mL portions of deionized water and  $\text{Et}_2\text{O}$  and dried under vacuum, yielding a yellow powder of **2** (0.0270 g, 46%). Anal. Found: C, 49.0; H, 3.4; P, 8.1. Calcd for  $\text{C}_{73}\text{H}_{63}\text{F}_6\text{Se}_2\text{P}_5\text{Pt}_2$ : C, 49.9; H, 3.6; P, 8.8.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{P}}$  20.9 (m,  $^1J(\text{P-Pt}) = 2686\text{ Hz}$ ), 23.1 ppm (m,  $^1J(\text{P-Pt}) = 3241\text{ Hz}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  1.21 (t, 3H,  $\text{SeCH}_3$ ), 6.92–7.41 ppm (m, 60H,  $12\text{C}_6\text{H}_5$ ). ESMS ( $\text{MeCN-H}_2\text{O}$ ):  $m/z$  1612  $[\text{M}]^+$ .

$[\text{Pt}_2(\mu\text{-Se})(\mu\text{-SeBu})(\text{PPh}_3)_4][\text{PF}_6]$  (**3**). Excess  $n\text{-BuCl}$  (7.1 mg,  $9.0\text{ }\mu\text{L}$ , 0.0573 mmol) was added to a brown suspension of **1** (44.1 mg, 0.0276 mmol) in MeOH (20 mL). The resulting yellow solution was stirred for 3 h, after which excess  $\text{NH}_4\text{PF}_6$  (10.0 mg, 0.0614 mol) was added to give a yellow suspension. After this mixture was stirred for 1 h, deionized water (50 mL) was added to induce precipitation. The suspension was filtered and the solid washed successively with 100 mL portions of deionized water and  $\text{Et}_2\text{O}$  and dried under vacuum, yielding a yellow powder of **3** (0.0323 g, 65%). Anal. Found: C, 50.0; H, 3.7; P, 8.1. Calcd for  $\text{C}_{76}\text{H}_{69}\text{F}_6\text{Se}_2\text{P}_5\text{Pt}_2$ : C, 50.7; H, 3.9; P, 8.6.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{P}}$  20.0 (m,  $^1J(\text{P-Pt}) = 2699\text{ Hz}$ ), 22.4 ppm (m,  $^1J(\text{P-Pt}) = 3277\text{ Hz}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  0.67 (t, 3H,  $\text{CH}_3$ ), 0.84–0.89 (m, 4H,  $2\text{CH}_2$ ), 1.20 (t, 2H,  $\text{CH}_2$ ), 7.08–7.41 ppm (m, 60H,  $12\text{C}_6\text{H}_5$ ). ESMS ( $\text{MeCN-H}_2\text{O}$ ):  $m/z$  1654  $[\text{M}]^+$ .

$[\text{Pt}_2(\mu\text{-Se})(\mu\text{-SeCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{Cl})(\text{PPh}_3)_4][\text{PF}_6]$  (**4**). By a procedure similar to that described for **3**,  $\alpha,\alpha'$ -dichloro-*p*-xylene (5.0 mg, 0.0286 mmol) and **1** (45.7 mg, 0.0286 mmol) gave a yellow powder of **4** (0.0306 g, 57%). Anal. Found: C, 51.0; H, 3.5; P, 8.0. Calcd for  $\text{C}_{80}\text{H}_{68}\text{F}_6\text{Cl}_2\text{Se}_2\text{P}_5\text{Pt}_2$ : C, 51.1; H, 3.6; P, 8.2.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{P}}$  19.3 (m,  $^1J(\text{P-Pt}) = 2663\text{ Hz}$ ), 22.1 ppm (m,  $^1J(\text{P-Pt}) = 3254\text{ Hz}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  4.57 (m, 4H,  $2\text{CH}_2$ ), 6.67–7.11 (m, 4H,  $\text{C}_6\text{H}_4$ ), 7.31–7.77 (m, 60H,  $12\text{C}_6\text{H}_5$ ). ESMS ( $\text{MeCN-H}_2\text{O}$ ):  $m/z$  1737  $[\text{M}]^+$ .

$[\text{Pt}_2(\mu\text{-SeCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{Se})(\text{PPh}_3)_4][\text{PF}_6]_{1.25}[\text{Cl}]_{0.75}$  (**5**). By a procedure similar to that described for **3**,  $\alpha,\alpha'$ -dichloro-*o*-xylene (17.9 mg, 0.1023 mmol) and **1** (161.4 mg, 0.1010 mmol) gave an orange powder of **5** (0.1731 g, 90%). Anal. Found: C, 50.0; H, 3.6; P, 8.3. Calcd for  $\text{C}_{80}\text{H}_{68}\text{Cl}_{0.75}\text{F}_{7.5}\text{Se}_2\text{P}_{5.25}\text{Pt}_2$ : C, 50.3; H, 3.6; P, 8.5.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{P}}$  15.1 (dt,  $^1J(\text{P-Pt}) = 3056$ ,  $^2J(\text{P-P}) = 19\text{ Hz}$ ), 16.4 ppm (dt,  $^1J(\text{P-Pt}) = 3016$ ,  $^2J(\text{P-P}) = 15\text{ Hz}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  4.11 (m, 4H,  $2\text{CH}_2$ ), 6.70–7.03 (m, 4H,  $\text{C}_6\text{H}_4$ ), 7.18–7.53 (m, 60H,  $12\text{C}_6\text{H}_5$ ). ESMS ( $\text{MeCN-H}_2\text{O}$ ):  $m/z$  851  $[\text{M}]^{2+}$ .

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**$[Pt(\eta^2\text{-Se}_2\text{C}_2\text{O}_2\text{-Se,Se})(PPh_3)_2]$  (6).** An excess of oxalyl chloride (34.4 mg, 50.00  $\mu\text{L}$ , 0.2707 mmol) was added to a brown suspension of **1** (321.5 mg, 0.2013 mmol) in MeCN (40 mL), which resulted in an instantaneous formation of an orange suspension. The mixture was filtered and the orange solid collected and redissolved in  $\text{CH}_2\text{Cl}_2$  (15 mL). *n*-Hexane (40 mL) was added to induce precipitation. The suspension was filtered and the solid washed successively with 100 mL of  $\text{Et}_2\text{O}$  and dried under vacuum, yielding an orange powder of **6** (0.1743 g, 93%). Anal. Found: C, 48.7; H, 3.2; P, 6.3. Calcd for  $\text{C}_{38}\text{H}_{30}\text{O}_2\text{Se}_2\text{P}_2\text{Pt}$ : C, 48.9; H, 3.2; P, 6.6%.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{P}}$  16.1 ppm (s,  $^1J(\text{P-Pt}) = 3109$  Hz).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  6.91–7.42 ppm (m, 30H,  $6\text{C}_6\text{H}_5$ ). ESMS ( $\text{MeCN-H}_2\text{O}$ ):  $m/z$  957  $[\text{M}+\text{Na}]^+$ . IR ( $\nu(\text{CO})$ , in  $\text{CH}_2\text{Cl}_2$ ): 1632  $\text{cm}^{-1}$ .

**$[(\text{COCH}_2\text{COCl})\text{Se}]_2$  (7).** An excess of malonyl chloride (11.4 mg, 55.78  $\mu\text{L}$ , 0.0809 mmol) was added to a brown suspension of **1** (90.5 mg, 0.0567 mmol) in MeCN (40 mL). The resulting orange-brown solution was filtered and the filtrate reduced to dryness under vacuum. The orange oil obtained was extracted with benzene, and subsequent careful solvent removal of the extract under vacuum afforded a white solid. The solid was dried under vacuum, yielding a white powder of **7** (0.0069 g, 33%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  2.07 ppm (s, 4H,  $2\text{CH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  62.8 (2C,  $2\text{CH}_2$ ), 173.8 ppm (4C, 4CO). ESMS ( $\text{MeCN-H}_2\text{O}$ ):  $m/z$  207  $[\text{M}+2\text{Na}]^{2+}$ . IR ( $\nu(\text{CO})$ , in  $\text{CH}_2\text{Cl}_2$ ): 1601  $\text{cm}^{-1}$ .

**$[(\text{COCH}_2\text{CH}_2\text{COCl})\text{Se}]_2$  (8).** Following a procedure similar to that described for **7**, succinyl chloride (7.2 mg, 33.02  $\mu\text{L}$ , 0.0465 mmol) and **1** (46.6 mg, 0.0292 mmol) gave a white powder of **8** (0.0069 g, 60%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  1.93 ppm (s, 8H,  $4\text{CH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  40.5 (4C,  $4\text{CH}_2$ ), 173.5 ppm (4C, 4CO). ESMS ( $\text{MeCN-H}_2\text{O}$ ):  $m/z$  419  $[\text{M}+\text{Na}]^+$ . IR ( $\nu(\text{CO})$ , in  $\text{CH}_2\text{Cl}_2$ ): 1605  $\text{cm}^{-1}$ .

**Crystal Structure Determination and Refinement.** The data collection was performed on a Bruker AXS SMART

diffractometer, equipped with a CCD area detector using Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073$  Å). The software SMART<sup>23</sup> was used for collecting frames of data, indexing reflections, and determining lattice parameters, SAINT<sup>23</sup> for integration of intensity of reflections and scaling, SADABS<sup>24</sup> for empirical absorption correction, and SHELXTL<sup>25</sup> 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 ( $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ , and  $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$  (where  $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ ). A summary of parameters for the data collections and refinements is given in Table 1.

Suitable single crystals of  $[Pt_2(\mu\text{-Se})(\mu\text{-SeMe})(PPh_3)_4][PF_6]$  (**2**),  $[Pt_2(\mu\text{-SeCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{Se})(PPh_3)_4][PF_6]_{1.25}[Cl]_{0.75}$  (**5**), and  $[Pt(\eta^2\text{-Se}_2\text{C}_2\text{O}_2\text{-Se,Se})(PPh_3)_2]$  (**6**) for structure determination were obtained by layering a  $\text{CH}_2\text{Cl}_2$  solution of each compound with hexane. For compound **5**, the xylene ring attached to **1** is disordered. Only isotropic thermal parameters were refined for the C atoms of phenyl ring D. The positions of Cl and O of water were very severely disordered (Cl in four places and O in seven places). The C atoms of phenyl rings show highly anisotropic thermal parameters in general.

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**Supporting Information Available:** Data in CIF format, showing details of the crystal structure determinations, atom coordinates, equivalent isotropic displacement factors, bond lengths and angles, and hydrogen coordinates for compounds **2**, **5**, and **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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