Oxaplatinacycles

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Cleavage of C–S and O–H Bonds by Platinum(0) Complexes To Give Five-Membered 1,2-Oxaplatinacycles**

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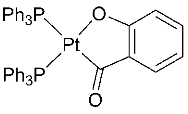
C–S bonds are known to be efficiently activated by transition metals and lead, through cleavage of C–S bonds, to novel sulfur compounds or sulfide complexes. This transformation allows insight into the related processes that may occur during heterogeneous catalytic processes.[1] The platinum(0)-mediated C–S bond cleavage reactions have been well studied and are established for the C(sp^2)–S bonds of thiophene,[2] thioester,[3] and vinyl sulfide.[4] However, to the best of our knowledge, a simple C(sp^3)–S bond activation with platinum(0) complexes has never been explored. Meanwhile, oxametallacycles are of great interest because of their unique structure and catalytic activity. Although there are several reports on the preparation and application of oxametallacycles containing nickel[5,6] or palladium,[7] the chemistry of oxaplatinacycle is limited. Pregosin and co-workers have reported the synthesis of five-membered acyl(oxa)platinacycle **1** by the reaction of salicylaldehyde with K_2PtCl_4 in the presence of PPh_3.[8] Also, Sweigart and co-workers have described that the platinum(0)-mediated C–O bond cleavage reaction of benzofuran afforded the six-membered oxaplatinacycle **2**.[9] As a four-membered analogue, Sharp and co-workers have reported the formation and unique reactivity of platinaoxetane **3** (cod = 1,5-cyclooctadiene).[10] Herein, we report the cleavage of C(sp^3)–S and O–H bonds of 2-hydroxybenzyl sulfide derivatives **4** mediated by platinum(0). This process led to an unusual formation of novel five-membered 1,2-oxaplatinacycles (**5a**, **5b**; see Scheme 2 for structures). We also describe the thermal reaction of **5a** involving the unexpected P–C/Pt–O metathesis.



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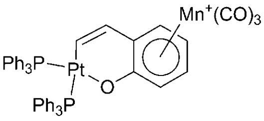

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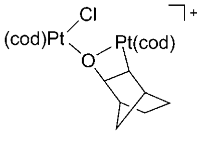

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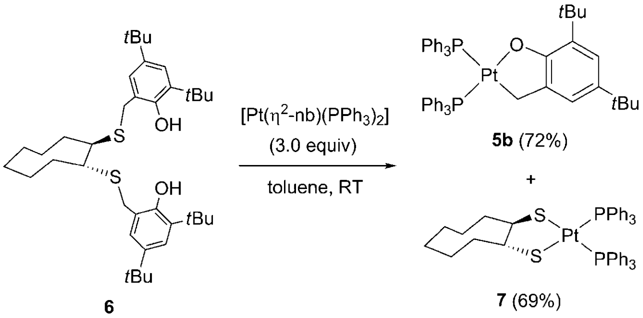
We have examined the coordination ability of [OSSO]-type diphenolate **6**[11] as a chelate ligand toward transition-metal complexes. When **6** was treated with 3 equivalents of $[Pt(\eta^2\text{-nb})(PPh_3)_2]$ in toluene,[12] the activation of both benzylic C–S and O–H bonds[13] in **6** occurred unexpectedly and gave novel 1,2-oxaplatinacycle **5b** and *cis*-(dithiolato)Pt^{II} complex **7**[14] in 72% and 69% yields, respectively (Scheme 1). On monitoring this reaction that was carried out in a sealed NMR tube, the generation of H_2 was observed by ^1H NMR spectroscopy ($\delta = 4.21$ ppm in C_6D_6).



Scheme 1. Reaction of [OSSO]-type diphenolate **6** with $[Pt(\eta^2\text{-nb})(PPh_3)_2]$. nb = norbornene.

To elucidate the general validity of this platinum(0)-mediated benzylic C–S and phenolic O–H bond activation, we examined the reactions of alkyl or aryl 2-hydroxybenzyl sulfides **4a–d**, which have only half the framework of **6** (i.e. $[Pt(\eta^2\text{-nb})(PPh_3)_2]$). The reactions readily proceeded in toluene at room temperature and gave the corresponding 1,2-oxaplatinacycles **5a** or **5b** in 55–84% yields, together with polymeric thiolato Pt^{II} complexes $[Pt(SR)_2]_n$ as insoluble materials (Scheme 2). When **4b** was allowed to react with $[Pt(\eta^2\text{-nb})(PPh_3)_2]$ in the presence of an excess amount of PPh_3 in toluene at room temperature, **5a** and the bis(thiolato) Pt^{II} complex *cis*-$[Pt(SPh)_2(PPh_3)_2]$ **8**,[15] instead of polymeric thiolato Pt complexes, were formed in 16% and 38% yields, respectively. These results show that substrates having a set of phenolic O–H and the *ortho* benzylic C–S bonds react with a platinum(0) complex to yield five-membered oxaplatinacycles and thiolato Pt^{II} complexes, where 1.5 equivalents of the platinum(0) complex are required for the stoichiometric reaction. In the ^1H NMR spectra, the characteristic benzylic protons resonate at $\delta = 2.75$ ppm (^3J(P,H) = 9, 3 Hz) for **5a** and 2.77 ppm (^3J(P,H) = 9, 3 Hz) for **5b** as a doublet of doublets. The $^{31}P\{^1H\}$ NMR spectra showed two doublet

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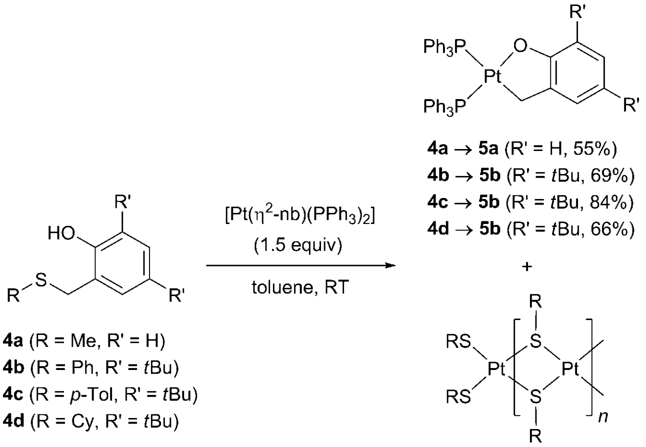


Scheme 2. Reactions of alkyl or aryl 2-hydroxybenzyl sulfides **4a–d** with $[Pt(\eta^2\text{-nb})(PPh_3)_2]$. Cy = cyclohexyl, Tol = tolyl.

signals with the ^{195}Pt satellites at $\delta = 16.3$ (^1J(Pt,P) = 3972 Hz) and 27.8 ppm (^1J(Pt,P) = 1788 Hz) for **5a** and $\delta = 17.4$ (^1J(Pt,P) = 3947 Hz) and 28.1 ppm (^1J(Pt,P) = 1743 Hz) for **5b** (see the Supporting Information). These resonances were assigned to the signals resulting from the phosphorus atoms lying *trans* with respect to the oxygen and benzylic carbon atoms, respectively. The molecular structure of **5a** was confirmed by X-ray crystallography (Figure 1).[16] In the crystalline state, the platinum core lies at the centre of a slightly distorted square-planar coordination sphere consisting of two PPh_3 ligands as well as oxygen and carbon atoms. The P1-Pt1-P2 angle of 98.33(10)° deviates considerably from the ideal 90° of a square-planar geometry. The Pt1–O1 bond length was 2.082(7) Å, which is similar to those of related oxaplatinacycles **1** (2.07(1) Å)[8] and **2** (2.067(1) Å).[9] The Pt1–P1 bond length (2.329(3) Å) was slightly longer than that of Pt1–P2 (2.232(2) Å), thus suggesting the higher *trans* influence of the benzylic carbon atom compared to the oxo ligand.

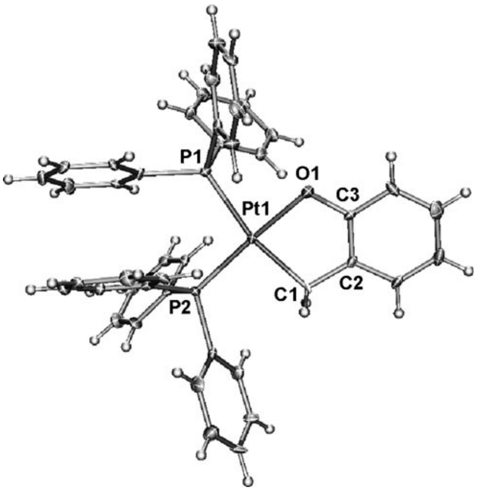
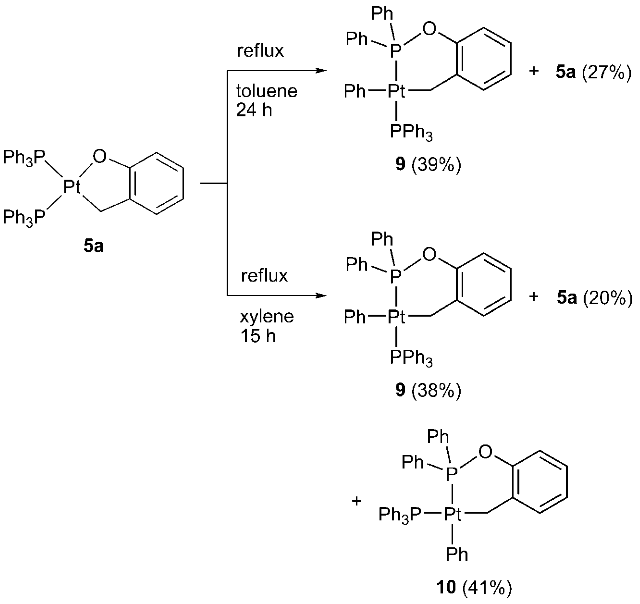


Figure 1. ORTEP drawing of oxaplatinacycle **5a** with thermal ellipsoids drawn at the 30% probability level. Selected bond lengths [Å] and bond angles [°]: Pt1–O1 2.082(7), Pt1–C1 2.096(9), Pt1–P1 2.329(3), Pt1–P2 2.232(2); O1-Pt1-C1 82.9(3), O1-Pt1-P1 85.1(2), C1-Pt1-P2 94.5(2), P1-Pt1-P2 98.33(10), Pt1-C1-C2 107.3(6), C1-C2-C3 117.5(10), C2-C3-O1 121.9(11).

We next investigated the thermal reaction of oxaplatinacycle **5a**.[17] A solution of **5a** in toluene at reflux for 24 hours gave the novel six-membered 1,2,3-oxaphosphaplatinacycle **9** in 39% yield after column chromatography on silica gel (Scheme 3). The thermal reaction of **5a** in xylene at reflux produced **9** and its *cis* isomer **10** in 38% and 41% yield, respectively (Scheme 3). A small amount of the starting material, **5a**, was recovered from these thermal reactions (27% and 20% yield, respectively). It is interesting to compare this ring expansion by the insertion of a ligated phosphorus atom into the Pt–O bond. Van Leeuwen and Roobeek reported the insertion of a ligated phosphorus atom accompanied by a 1,2-shift of a phenyl group on the phosphorus atom with the thermal ring contraction of 1,3,2-oxaphosphaplatinacycle **11** that gave platinum(II) complex **12**, which has a 3H-2,1-benzoxaphosphole ligand.[18,19] They proposed a mechanism involving nucleophilic attack of the oxygen atom bound at the platinum center at the phosphorus atom in the ring and a 1,2-shift of a phenyl group on the phosphorus atom (Scheme 4).[18b,19]



Scheme 3. Thermal reactions of oxaplatinacycle **5a**.

The molecular structures of **9** and **10** were characterized by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy, and finally verified by X-ray crystallography. The ^{31}P{^{1}H} NMR spectrum of **9** displays two nonequivalent doublet signals with ^{195}Pt satellites and ^{31}P coupling at $\delta = 29.9$ (^2J(P,P) = 475, ^1J(Pt,P) = 2948 Hz) and 142.3 ppm (^2J(P,P) = 475, ^1J(Pt,P) = 3899 Hz). In sharp contrast, the ^{31}P{^{1}H} NMR spectrum of **10** exhibits two nonequivalent singlet signals at $\delta = 22.8$ and 137.3 ppm with the ^{195}Pt satellites of 2080 and 2300 Hz, respectively. The lower-field signals of complexes **9** ($\delta = 142.3$ ppm) and **10** ($\delta = 137.3$ ppm) are assigned to the phosphorus atoms of the phosphinite ligands, and these chemical shift values are

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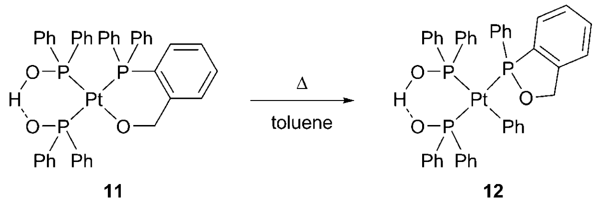


Scheme 4. Thermal reaction of 1,3,2-oxaphosphaplatinacycle **11**.

similar to that reported by van Leeuwen and Roobeek for complex **11** ($\delta = 125.9$ ppm ($^1J(\text{Pt,P}) = 2730$ Hz)).[18] In the X-ray structures (Figure 2 and 3),[16] the platinum atoms in each oxaphosphaplatinacycle **9** and **10** formed a distorted square-planar coordination sphere with phenyl, PPh_3, phosphinite, and benzylic carbon ligands. In both complexes **9** and **10**, the Pt1–P1 bond lengths (**9**: 2.2240(16), **10**: 2.2618(10) Å) were somewhat shorter than those of the Pt1–P2 (**9**: 2.2968(15), **10**: 2.2920(10) Å), thus indicating weaker coordination of the PPh_3 ligand to the central platinum atom than that of the cyclic phosphinite ligand , and results from the lower σ-donor ability of PPh_3. The Pt1–C1 bond lengths were 2.153(6) Å for **9** and 2.119(4) Å for **10**, which are longer than those of five-membered oxaplatinacycles **5a** (2.066(9) Å) and **1** (1.96(2) Å).[8]

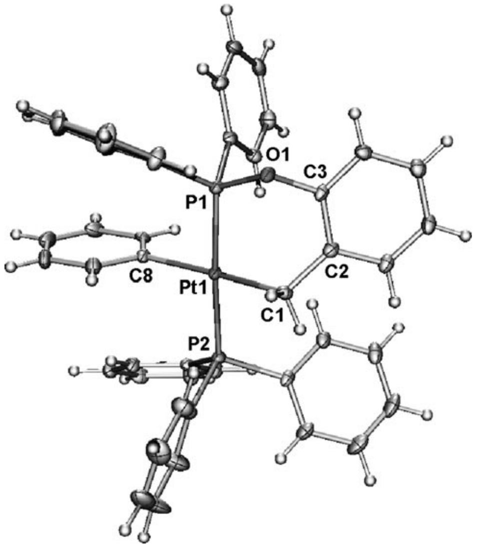


Figure 2. ORTEP drawing of 1,2,3-oxaphosphaplatinacycle **9** with thermal ellipsoids drawn at the 30% probability level (the solvated CH_2Cl_2 molecules were omitted for clarity). Selected bond lengths (Å) and bond angles [°]: Pt1–C1 2.153(6), Pt1–C8 2.088(6), Pt1–P1 2.2240(16), Pt1–P2 2.2968(15), P1–O1 1.635(4); C1-Pt1-P1 87.55(17), C1-Pt1-P2 91.96(18), C8-Pt1-P1 89.92(17), C8-Pt1-P2 91.25(17), Pt1-P1-O1 113.81(17), P1-O1-C3 117.2(4), O1-C3-C2 121.6(6), C2-C1-Pt1 114.4(4).

To gain insight into the mechanism of formation for oxaphosphaplatinacycles **9** and **10**, we studied the thermolyses of **9** and **10**. Heating of *trans* complex **9** in xylene at reflux for 15 hours resulted in the formation of a mixture of *cis* complex **10**, **5a**, and the starting material **9** in the ratio of 13:24:63 based on the integral ratio of the $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture. In addition, the conversion of **10** into **9** and/or **5a** was also observed when **10** was heated under the same reaction conditions (the ratio of **9**/**5a**/**10** was 35:20:45 based on the integral ratio of the $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture). These results indicate that the rearrangement is governed by the thermal equilibrium among five-membered oxaplatinacycle **5a** and six-membered oxaphosphaplatinacycles **9** and **10**. As shown in Scheme 5, the rearrangement of **5a** into **9** and **10** can be explained by the initial nucleophilic attack of the phenoxido ligand in **5a** at the coordinated *cis* phosphorus center to give a betaine intermediate **13**, and subsequent migration of a

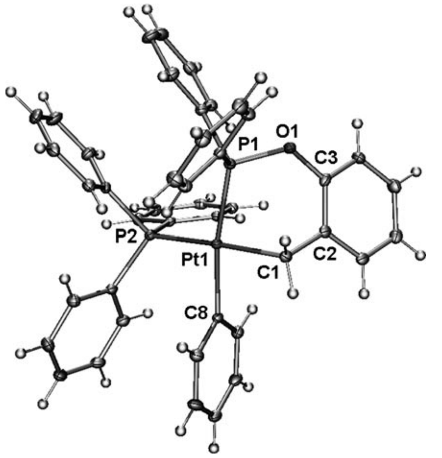
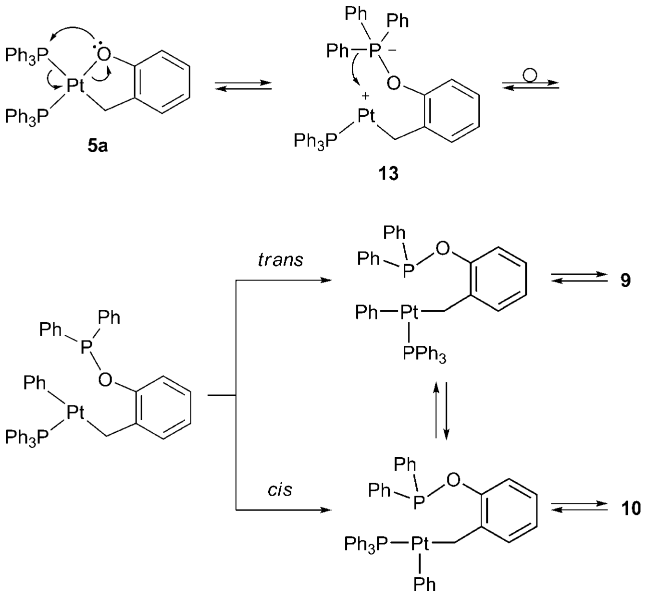


Figure 3. ORTEP drawing of 1,2,3-oxaphosphaplatinacycle **10** with thermal ellipsoids drawn at the 30% probability level (a solvated hexane molecule was omitted for clarity). Selected bond lengths (Å) and bond angles [°]: Pt1–C1 2.119(4), Pt1–C8 2.057(4), Pt1–P1 2.2618(10), Pt1–P2 2.2920(10), P1–O1 1.640(3); C1-Pt1-P1 81.44(12), C1-Pt1-C8 87.70(16), C8-Pt1-P2 88.45(11), P1-Pt1-P2 102.35(4), Pt1-P1-O1 111.21(11), P1-O1-C3 123.03, O1-C3-C2 120.5(4), C2-C1-Pt1 106.0(3).



Scheme 5. A plausible mechanism for the formation of oxaphosphaplatinacycles **9** and **10**.

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phenyl group from the anionic phosphorus atom to the cationic platinum center.[18b,19]

In summary, we have found unusual C(sp^3)–S and O–H bond cleavage in the reactions of a series of 2-hydroxybenzyl sulfide derivatives **4** or **6** with [Pt(η^2-nb)(PPh$_3$)$_2$] to form 1,2-oxaplatinacycles **5a** and **5b**. The thermal isomerization of **5a** afforded novel six-membered 1,2,3-oxaphosphaplatinacycles **9** and **10** as *trans* and *cis* isomers, respectively. In addition, **5a**, **9**, and **10** are in equilibrium under the experimental reaction conditions. Studies on the intrinsic reactivity of **5** are currently in progress.

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[16] CCDC 771775 (**5a**), 771776 (**5b**), 771777 (**9**), and 771778 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[17] We examined the thermal reaction of **5b** in xylene at reflux, but the reaction did not occur. This failure is probably a result of steric hindrance from the *t*Bu group *ortho* to the Pt–O group in the formation of the intermediate corresponding to **13**.

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