Alcohol Complexes of Platinum(II). Syntheses and Crystal Structures of [S-(R*,R*)]-(+)589-[Pt(OSO2CF3)2{1,2-C6H4(PMePh)2}] and [S-(R*,R*)]-(+)589-[Pt(HOCH2CH2OH){1,2-C6H4(PMePh)2}](CF3SO3)2

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Abstract: Ethane-1,2-diol reacts with [S-(R*,R*)]-(+)589-[Pt(OSO2CF3)2{1,2-C6H4(PMePh)2}] to give [S-(R*,R*)]-(+)589-[Pt(HOCH2CH2OH){1,2-C6H4(PMePh)2}](CF3SO3)2, the first simple alcohol complex of platinum(II) to be isolated. The X-ray crystal structures of the two complexes are reported.

Alcohols, among the most common of organic substances in the plant and animal kingdoms, are weak ligands for metal ions, especially bivalent palladium and platinum for which a simple alcohol complex has not been characterized in the solid state hitherto. In solution, however, there is clear evidence of coordination of monohydric alcohols to bivalent palladium and platinum perchlorates,[1] and to certain platinum metal trifluoromethane sulfonates (triflates),[2] and to platinum(II) chlorides when the alcohol is stabilized by chelation in a ring containing a tertiary phosphino group.[3] In the light of the interesting reactivity of platinum metal alkoxides,[4,5] and of the potential relevance of such compounds to catalysis,[5] and to asymmetric synthesis,[6] we have characterized [S-(R*,R*)]-(+)589-[Pt(OSO2CF3)2{1,2-C6H4(PMePh)2}], (S,S)-1,[7] a potent source of an optically active bis(tertiary phosphine)platinum(II) auxiliary, and its ethane-1,2-diol derivative [S-(R*,R*)]-(+)589-[Pt(HOCH2CH2OH){1,2-C6H4(PMePh)2}](CF3SO3)2, (S,S)-2, the parent of a new family of readily prepared platinum-diol complexes of potential application to organic synthesis.

The complex [S-(R*,R*)]-(+)589-[PtMe2{1,2-C6H4(PMePh)2}], [α]589 +108.5° (CH2Cl2),[8] reacts with 2 equiv. of trifluoromethane sulfonic acid (triflic acid) in dichloromethane at -78 °C with evolution of methane to give, in almost quantitative yield, [S-(R*,R*)]-(+)589-[Pt(OSO2CF3)2{1,2-C6H4(PMePh)2}], (S,S)-1, which crystallizes from dichloromethane - diethyl ether as colourless needles, [α]589 +6.7° (CH2Cl2). This method of preparation of a triflate complex is milder than the one described for [Pt(OSO2CF3)2(Ph2PCH2CH2PPh2)], which involves heating the corresponding dichloroplatinum(II) complex in triflic acid.[11] The structure of (S,S)-1 determined by X-ray analysis is shown in Figure 1.[12] There are two similar molecules in the unit cell of (S,S)-1; the distances and angles given in Figure 1 are for one of the

independent molecules. The bis(triflato) complex is a null-valent electrolyte in dichloromethane. When treated with ethane-1,2-diol in dichloromethane (S,S)-1 reacts to give, after dilution of the reaction mixture with diethyl ether, colourless prisms of $[S-(R^*,R^*)]$-(+)$_{589}$-[Pt(HOCH$_2$ CH$_2$OH){1,2-C$_6$H$_4$(PMePh)$_2$}](CF$_3$SO$_3$)$_2$, (S,S)-2, [α]$_{589}$ +40.9° (CH$_2$Cl$_2$). The structure of (S,S)-2 is shown in Figure 2.[12] The glycol complex is also a null-valent electrolyte in dichloromethane, but, whereas the bis(triflato) complex has $^2J_{PtP}$ = 4034 Hz in this solvent, glycol complex (S,S)-2 has $^2J_{PtP}$ = 3863 Hz, which implies coordination of the alcohol in the latter compound. In methanol, both (S,S)-1 and (S,S)-2 function as di-univalent electrolytes[13] and both compounds have the same $^2J_{PtP}$ value in this solvent (3890 Hz) consistent with complete dissociation of (S,S)-1 and alcohol exchange in (S,S)-2.
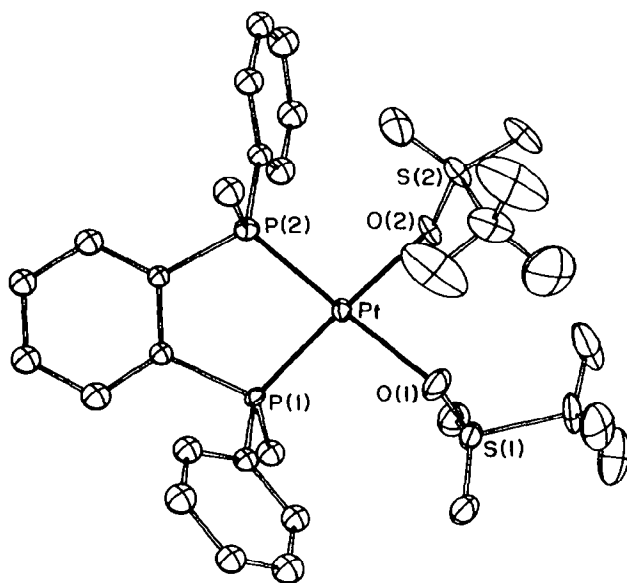

Figure 1. Molecular structure of (S,S)-1. Selected bond distances and angles for the independent molecule shown are as follows: Pt-P(1) 2.207(3), Pt-P(2) 2.204(3), Pt-O(1) 2.142(9), Pt-O(2) 2.091(8) Å, P(1)-Pt-P(2) 87.23(13), P(1)-Pt-O(1) 94.9(3) P(2)-Pt-O(2) 96.0(3), O(1)-Pt-O(2) 82.6(4), Pt-O(1)-S(1) 131.1(6), Pt-O(2)-S(2) 136.1(5) °.

The Pt-O bond lengths in square planar (S,S)-2 are only slightly shorter (av. 2.107 Å) than those in (S,S)-1 (av. 2.117 Å), which corroborates the solution data inferring competitive nucleophilicites of triflate and alcohol; indeed, (S,S)-1 can be recovered from methanol solution. The O*H* atoms in (S,S)-2 were not observed in the structure determination, but a consideration of hydrogen-bonding interactions in the structure indicated pseudo-axial and pseudo-equatorial positions for them.[14] The puckered glycol ring in (S,S)-2 has the λ configuration. Deprotonation of the hydroxyl groups in (S,S)-2 gives the stable glycolato-1*O*,2*O* derivative [S-(R^*,R^*)]-(+)$_{589}$-[Pt(OCH$_2$CH$_2$CH$_2$O){1,2-C$_6$H$_4$(PMePh)$_2$}], [α]$_{589}$ +181.5 (CH$_2$Cl$_2$); the structure of the related glycerolato-1*O*,2*O* compound has been reported previously.[6]

We are presently investigating the use of (S,S)-1 as a resolving agent for diols, and for the regioselective chelation and derivatisation of polyols. For example, (S,S)-1 forms crystalline derivatives with glycerol and 2-deoxy-D-ribose suitable for X-ray crystallography.
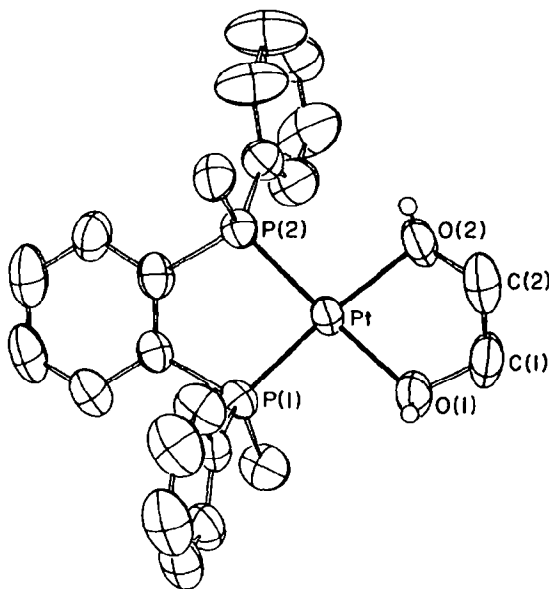

Figure 2. Molecular structure of cation in (S,S)-2. Selected bond distances and angles are as follows: Pt-P(1) 2.200(2), Pt-P(2) 2.210(2), Pt-O(1) 2.105(6), Pt-O(2) 2.109(5), O(1)-C(1) 1.443(11), O(2)-C(2) 1.449(20), C(1)-C(2) 1.54(3) Å, P(1)-Pt-P(2) 87.22(7), P(1)-Pt-O(1) 94.6(2), P(2)-Pt-O(2) 98.4(2), O(1)-Pt-O(2) 79.8(2), O(1)-C(1)-C(2) 107.6(9), O(2)-C(2)-C(1) 106.7(9)° .

References and Notes

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7. The stereochemical descriptors used here are consistent with recent Chemical Abstracts Service indexing practice; the compound numbers are preceded by simplified descriptors.

8. This compound was prepared from $[PtMe_2(1,5-C_8H_{12})]$[9] by reaction with $[R-(R^*,R^*)]-1,2-C_6H_4(PMePh)_2$.[10]

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12. Crystal data: (S,S)-1, $C_{22}H_{20}F_6O_6P_2PtS_2$, $M = 815.33$, orthorhombic; space group $P2_12_12_1$, $a = 15.517$ (4), $b = 16.281$ (5), $c = 21.595$ (4) Å, $U = 5456$ (3) Å^3, $D_c = 1.985$ g cm^{-3} for $Z = 8$, $F(000) = 3152$, $\mu(Mo\,K_\alpha) = 55.3$ cm^{-1}. Of 5906 measured intensities (Nicolet XRD P3; -135 °C), 4701 were considered observed $[I > 3\sigma(I)]$. After Lorentz, polarization, and absorption corrections, the structure was solved by the heavy atom method. Subsequent refinement (full matrix least-squares) afforded R and R_w values of 0.037 and 0.039, respectively; (S,S)-2, $C_{24}H_{26}F_6O_8P_2PtS_2$, $M = 877.60$, monoclinic, $P2_1$, $a = 8.816$ (1), $b = 18.775$ (2), $c = 9.517$ (1) Å, $\beta = 99.04$ (1)°, $U = 1555.7$ Å^3; $D_c = 1.873$ for $Z = 2$, $F(000) = 856$, $\mu(Mo\,K_\alpha) = 48.6$ cm^{-1}. Of 4703 measured reflections (Phillips PW 1100/20, 20 °C), 3781 were considered observed $[I > 3\sigma(I)]$. After Lorentz, polarization, and absorption corrections, the structure was solved by the heavy atom method. Subsequent refinement (full matrix least-squares) afforded R and R_w values of 0.029 and 0.032, respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Data Centre.

13. For (S,S)-1, $\Lambda_M = 198$ cm^2 Ω^{-1} mol^{-1} for a 10^{-3} M solution at 20 °C; for (S,S)-2, $\Lambda_M = 201$ cm^2 Ω^{-1} mol^{-1} under similar conditions.

14. Details of hydrogen bonding interactions are given in the Supplementary Material.