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Preliminary communication

Reaction of (dichloro)(1,5-cyclooctadiene)platinum(II) with dimethyl diazomethylphosphonate. Crystal structure analysis of a bis-insertion product, (*R*,*R*)-bis[chloro(dimethoxyphosphonyl)methyl]-(1,5-cyclooctadiene)platinum(II)

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Abstract

The reaction of dichloro(1,5-cyclooctadiene)platinum(II), **1**, with dimethyl diazomethylphosphonate, **2**, results in the formation of products of insertion of the carbene moiety into one or both Pt–Cl bonds. An X-ray diffraction study of a crystal obtained from the major bis-insertion product of this reaction shows it to be (*R*,*R*)-bis[chloro(dimethoxyphosphonyl)methyl](1,5-cyclooctadiene)platinum(II), **5**. The space group is polar indicating that spontaneous resolution has occurred upon crystallization.

We have reported [1a–c] that reaction of diazomethane with a range of dihaloplatinum(II) complexes results in the formation of mono- and/or bis-halomethyl derivatives. For example, dichloro(1,5-cyclooctadiene)platinum(II), **1**, undergoes clean conversion into bis(chloromethyl)(1,5-cyclooctadiene)platinum(II), **3**, when exposed to an excess of diazomethane, as depicted in Scheme 1. We have since examined the reaction of **1** with some simple diazo compounds possessing a variety of steric and electronic attributes. While a recent paper [2] reports the isolation of only mono-insertion products from the reaction of ethyl diazoacetate with a number of dihaloplatinum(II) complexes (including **1**), we have found [1d] that with dimethyl diazomethylphosphonate and methyl diazoacetate both mono- and bis-insertion products are formed; however with trimethylsilyldiazomethane

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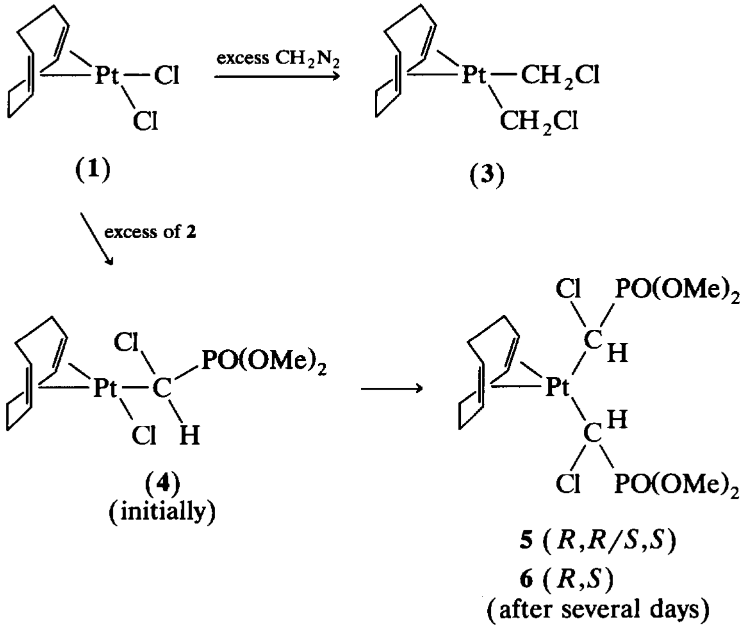

Scheme 1.

we too have been able to isolate only the mono-insertion product. The present communication focuses on the reaction with dimethyl diazomethylphosphonate, **2**.

Treatment of **1** with an excess of **2** (6 mol equiv.) in dichloromethane at room temperature results in rapid formation of the mono-insertion product, **4**. Upon further standing (a few days) this product is converted largely into a major, **5**, and a minor, **6**, bis-insertion product. All three, upon purification by preparative TLC (relative polarities, **4** < **5** < **6**) and crystallization, were obtained as colourless, air-stable, solids which have been characterized by elemental analysis, ^1H, ^{13}C, and ^{31}P NMR spectroscopy. For example, the PtCHP moieties showed the following: **4** δ_H 4.75 ppm [^2J(PtH) 83.3 Hz, ^2J(PH) 6.6 Hz], δ_C 40.4 ppm [^1J(PtC) 791.9 Hz, ^1J(PC) 136 Hz] and δ_P 27.8 ppm; **5** δ_H 4.29 ppm [^2J(PtH) 84.9 Hz, ^2J(PH) 11.3 Hz], δ_C 45.5 ppm [^1J(PtC) 891.5 Hz, ^1J(PC) 129 Hz] and δ_P 29.4 ppm [^2J(PtP) 31.7 Hz]; **6** δ_H 4.26 ppm [^2J(PtH) 92.2 Hz, ^2J(PH) 10.5 Hz], δ_C 39.9 ppm [^1J(PtC) 933.7 Hz, ^1J(PC) 133 Hz] and δ_P 30.5 ppm. The results of the following X-ray study establish that **5** is the (*R*,*R*/*S*,*S*) enantiomeric pair and thus **6** must be the (*R*,*S*) isomer.

The structure of $(COD)Pt\{HC(Cl)PO(OCH_3)_2\}_2$, **5**, was determined by X-ray diffraction methods [3*]. The data crystal is polar and the absolute configuration of the molecule studied was established unequivocally by the refinement to be the (*R*,*R*) isomer. Thus during the crystallization procedure a spontaneous resolution of the *R*,*R* and *S*,*S* isomers has occurred. The platinum atom lies on a two-fold axis and coordinates to the cyclooctadiene and the α-carbons of the phosphonate

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* Reference number with asterisk indicates a note in the list of references.

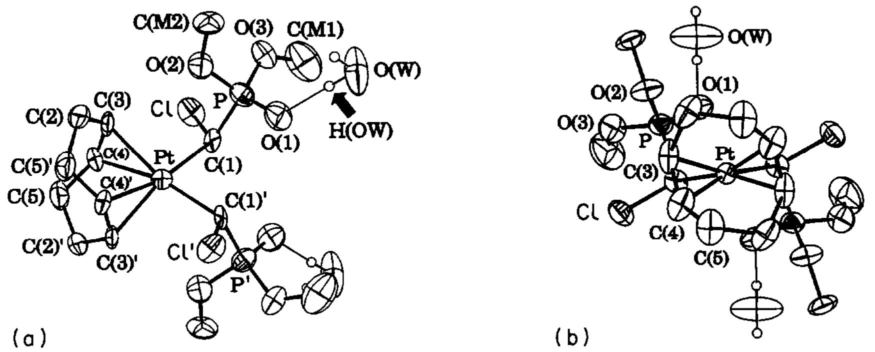

Fig. 1. (a) A side view of the (*R*,*R*)-(COD)Pt{HC(Cl)PO(OCH$_3$)$_2$}$_2$ molecule showing our numbering scheme and (b) a view down the crystallographic two-fold axis. All non-hydrogen atoms are thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) are: Pt–C(1) 2.088(11), Pt–C(3) 2.195(17), Pt–C(4) 2.306(22), C(3)=C(4) 1.37(3), P–O(1) 1.448(15), P–O(2) 1.553(13), P–O(3) 1.571(13), P–C(1) 1.805(21), Cl–C(1) 1.818(16), O(1) ··· O(W) 2.81(2). Selected angles (°): C(1)–Pt–C(1)′ 86.5(6), C(1)–Pt–C(3) 91.1(6), C(1)–Pt–C(3)′ 161.3(8), C(1)–Pt–C(4) 98.7(7), C(1)–Pt–C(4)′ 163.1(7), C(3)–Pt–C(3)′ 96.9(6), C(3)–Pt–C(4) 35.4(8), C(3)–Pt–C(4)′ 78.8(7), C(4)–Pt–C(4)′ 80.8(8), O(1) ··· O(W) ··· O(1)′ 93.4(7).

moieties in a square planar fashion as depicted in Fig. 1(a) with Pt–C(1) 2.088(11), Pt–C(3) 2.195(17), Pt–C(4) 2.306(22) Å. A water of crystallization on a two-fold axis is hydrogen bonded to the phosphonate P=O oxygen (O(1)) of adjacent molecules, (O(1) ··· O(W) 2.81(2) Å, O(1) ··· O(W) ··· O(1)′ 93.4(7)°), forming a polymeric hydrogen bonded chain. The cyclooctadiene ligand adopts the same distorted tub conformation (torsion angles C(5)′–C(2)–C(3)–C(4) 40(1) and C(3)–C(4)–C(5)–C(2)′ −92(2)°) as was found [7] in **1** itself.

Supplementary material available. The tables of crystallographic data (atomic coordinates, bond lengths and angles, anisotropic thermal parameters, hydrogen atom parameters, selected torsion angles, structure factor listing) for this work are available from the authors; crystallographic parameters have been deposited with the Cambridge Crystallographic Data Centre and are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK. Any request should be accompanied by the full literature citation for this communication.

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3 *Crystal data:* $C_{14}H_{28}O_7P_2Cl_2Pt$ (**5**), $M = 636.3$, orthorhombic, space group $P2_122_1$ (from the systematic absences $h00$: $h = 2n + 1$ and $00l$: $l = 2n + 1$, an alternative setting of $P2_12_12$, No. 18),

$a = 7.992(6)$, $b = 9.964(4)$, $c = 13.705(9)$ Å, $V = 1091(1)$ Å^3, $Z = 2$, $D_{\text{calc}} = 1.94$ g cm^{-3}, $\lambda(\text{Mo-}K_\alpha) = 0.71073$ Å, $\mu = 69.2$ cm^{-1}, $F(000) = 620$, $T = 293$ K. The crystals were not of very good quality, but eventually a possible crystal was obtained. The selected crystal had dimensions $0.45 \times 0.55 \times 0.60$ and data were collected on an Enraf–Nonius CAD4 diffractometer (in the range $4 < 2\theta < 54°$, 1359 measured reflections, of which 1269 had intensities $I > 3\sigma(I)$). The structure was solved by the Patterson heavy atom method. Data were corrected for Lorentz, polarization and (ψ-scan) absorption. All non-hydrogen atoms were refined anisotropically, hydrogens were positioned geometrically and included as riding atoms in the structure factor calculations. $R = 0.067$, $R_w = 0.095$ and *GoF* of 1.35 for the (R,R) configuration and 0.076, 0.106 and 1.50 for the (S,S) configuration. A final difference map had no chemically significant features. All atoms were treated for the effects of anomalous dispersion; scattering factors were from *International Tables for Crystallography* [4], and all calculations were performed on a Silicon Graphics 4D-35TG computer using the NRCVAX [5] programs. Figures 1(a) and 1(b) are views of the molecule prepared using ORTEP-II [6] (Johnson, 1976).

4 International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham, 1974 (Present distributor Kluwer Academic Publishers, Dordrecht).

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