Brief Communications

Ring opening in epichlorohydrin and β-methylepichlorohydrin under the action of the $[PtCl_4]^{2-}$ anion in aqueous solutions

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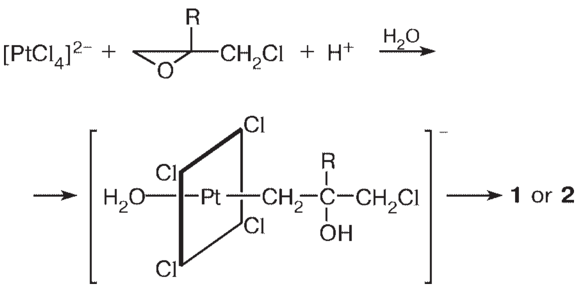
Oxidative addition of epoxides to $[PtCl_4]^{2-}$ in aqueous acids affords the platinum(IV) derivatives $[PtCl_5(CH_2CR(OH)CH_2Cl)]^{2-}$ (R = H (**1**) and Me (**2**)). Complex **1** was isolated as a cesium salt and characterized by IR spectroscopy. The complex is stable in acidic media; under basic conditions, the original epoxide and platinum(II) are recovered. The formation of complex **2** was detected by ^1H NMR spectroscopy.

Key words: platinum(II) acidocomplexes, epoxides, oxidative addition.

It is known that a β-hydroxyethyl complex of platinum(IV), $[PtCl_5(CH_2CH_2OH)]^{2-}$, is obtained by oxidation of the Zeise salt anion $[PtCl_3(C_2H_4)]^-$ with either molecular chlorine,[1] or the $[PtCl_6]^{2-}$ anion, or other oxidants.[2,3] Attempts to synthesize, in these ways, analogs with longer carbon chains have failed. For example, the oxidation of the $[PtCl_3(CH_3CH{=}CH_2)]^-$ anion with molecular chlorine gives[1] acetone and unidentified platinum compound rather than the expected β-hydroxypropyl complex $[PtCl_5(CH_2CH(OH)CH_3)]^{2-}$.

We found that Pt^{IV} derivatives $[PtCl_5(CH_2CR(OH)CH_2Cl)]^{2-}$ (R = H (**1**) and Me (**2**)) can be obtained by oxidative addition of the corresponding epoxides, namely, 1-chloro-2,3-epoxypropane (epichlorohydrin, ECH) and 1-chloro-2-methyl-2,3-epoxypropane (methylepichlorohydrin, MECH), to the $[PtCl_4]^{2-}$ anion (Scheme 1).

Scheme 1



When an excess of ECH was added to an aqueous solution of K_2PtCl_4 acidified with HCl or $HClO_4$, the original crimson-red solution of Pt^{II} turned straw-yellow in 20—30 min. The UV spectrum of the solution contains an intense band (λ = 262 nm) characteristic[4] of Pt^{IV}

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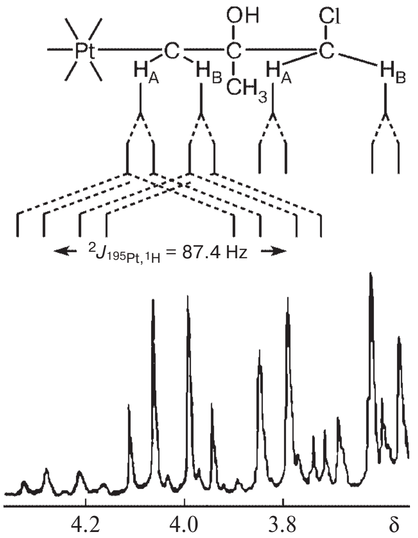


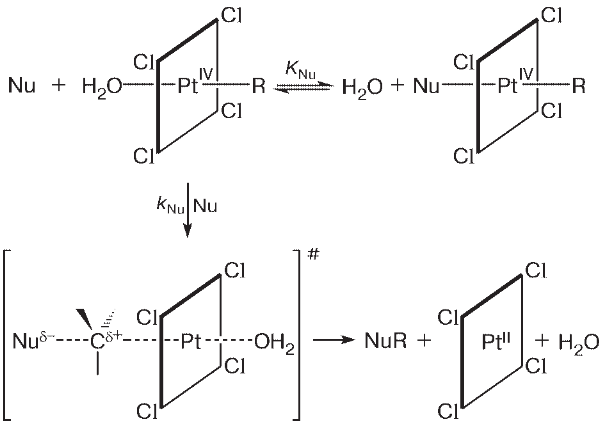
Fig. 1. A fragment of the ^1H NMR spectrum of the reaction mixture containing MECH (0.045 mol L^{-1}), K_2PtCl_4 (0.05 mol L^{-1}), DCl (0.3 mol L^{-1}), and D_2O one hour after the reagents were mixed.

monoalkyl chloride complexes. The addition of CsCl yields $Cs_2PtCl_5[CH_2CH(OH)CH_2Cl] \cdot H_2O$ (**1**). The IR spectrum of this complex shows a low-intensity band at 545 cm^{-1}, which can be assigned**[4]** to the Pt—C stretching vibrations. The ^1H NMR data revealed no epoxide ring in complex **1**; however, the lines in the strongly coupled spectrum (three groups of ill-resolved lines at δ 3.50—3.65, 3.65—3.85, and 3.85—4.00) are difficult to assign because of a high multiplicity of signals for the assumed chlorohydrin fragment.

The low-field region of the ^1H NMR spectrum of complex **2**, which is the product of oxidative addition of MECH (an ECH homolog) to the $[PtCl_4]^{2-}$ anion, can be interpreted more easily (Fig. 1). A singlet for the Me group appears at δ 1.27, and signals for the CH_2Cl protons form an AB system (δ_{H_A} 3.59 and δ_{H_B} 3.81, $^2J_{AB}$ = 11.32 Hz). Signals for the protons of the $—CH_2—Pt—$ fragment are a superposition of an AB system and the AB part of an ABX system (X is the ^{195}Pt nucleus*) with a relative intensity ratio of ~2 : 1 (δ_{H_A} 4.08 and δ_{H_B} = 3.97, $^2J_{AB}$ = 9.7 Hz). This spectrum suggests that the $[PtCl_4]^{2-}$ anion attacks the least substituted C atom in the epoxide ring (see Scheme 1).

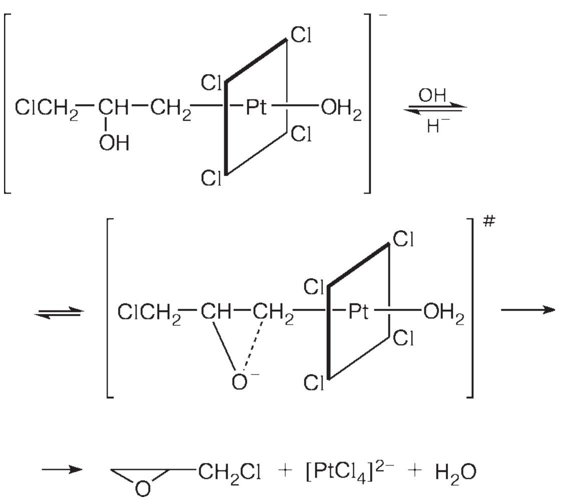
Decomposition of most of the known Pt^{IV} alkyl chloride complexes in aqueous solutions follows the S_N2 mechanism, *i.e.*, a nucleophile Nu (Nu = Cl^-, Br^-, I^-, $S_2O_3^{2-}$, H_2O, *etc.*) attacks the α-carbon atom of the alkyl group**[5,6]** (Scheme 2). The reductive elimination rate characterized by a constant *k* is virtually independent of the pH of a medium; this rate increases with the concentration of Nu in accordance with the equation $k = k_{Nu}[Nu]/(1 + K_{Nu}[Nu])$, where k_{Nu} and K_{Nu} are the rate and equilibrium constants, respectively (see Scheme 2).

Scheme 2



A different mechanism operates for complex **1**. It is rather stable in acidic media (the ^1H NMR spectrum of the complex in 3.0 *M* HCl at ~20 °C remains unchanged for 3 days), but rapidly decomposes at pH 8.15 in 3.0 *M* $NaClO_4$ at 25 °C (the first-order rate constant k_1 = 0.0061 s^{-1}); in the presence of chloride ions, this reaction occurs more slowly (k_1 = 0.0025 s^{-1} in 3.0 *M* NaCl). According to the ^1H NMR data, alkalification of an aqueous solution of complex **1** with K_2CO_3 causes rapid (over two to three minutes) recovery of the original epoxide (ECH). Apparently, such a behavior is associated with the mechanism of reductive elimination that includes an intramolecular nucleophilic attack of the alkoxide anion formed at the equilibrium stage on the α-carbon atom (Scheme 3).

Scheme 3



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* The natural content of ^{195}Pt is ~35%, $^2J_{^{195}Pt,^1H} \approx 90$ Hz.

Earlier, an analogous way of decomposition was assumed for β-hydroxyethyl[7] and β-aminoethyl[8] complexes of Pt^{IV}.

In conclusion, note that the oxidative addition of epoxides to Pt^{II} acidocomplexes seems to be the most convenient method for the synthesis of a whole class of organometallic derivatives (platinumhydrins) of the general formula $[Cl_5Pt^{IV}CH_2CR(OH)\text{-}CH_2R']^{2-}$.

Experimental

The starting complex K_2PtCl_4 was prepared according to the known procedure.[9] Freshly distilled ECH and MECH were used. Acids (HCl and $HClO_4$), NaCl, and anhydrous K_2CO_3 (reagent grade) were used as purchased.

^{1}H NMR spectra were recorded on a Gemini-200 spectrometer with Bu^{t}OH as the internal standard. IR and UV spectra were recorded on Perkin—Elmer 180 and Specord UV-VIS spectrophotometers, respectively.

Cesium salt of complex 1. A saturated aqueous 0.3 *M* solution of K_2PtCl_4 was kept at ~20 °C for 20 min, and 0.3 *M* HCl or 0.3 *M* $HClO_4$ and an excess of epichlorohydrin to its concentration of 1.3 mol L^{-1} were added. The reaction mixture was stirred at ~20 °C for 20—30 min and cooled to 0 °C. The product was precipitated with a cold saturated solution of CsCl. The resulting fine crystalline yellow plates were filtered off, washed three times with small portions of ice water, and dried in air. The yield was 83%. Found (%): C, 4.52; H, 0.97. $C_3H_6O_2Cl_6Cs_2Pt$. Calculated (%): C, 4.81; H, 0.94. IR (Nujol), ν/cm^{-1}: 3453 (m), 2953 (w), 2913 (m), 1627 (s), 1413 (m), 1331 (w), 1293 (s), 1267 (w), 1105 (vs), 1080 (vs), 1013 (w), 852 (w), 793 (w), 752 (w), 626 (m), 600 (m), 545 (w).

The formation of complex **2** was monitored by ^{1}H NMR spectroscopy. An equimolar amount of MECH was added at ~20 °C to a solution of K_2PtCl_4 (0.05 mol L^{-1}) in D_2O containing DCl ([DCl] = 0.5 mol L^{-1}). As the reaction proceeded, the signals of MECH became less intense, and those of the product appeared.

The constants k_1 ($k_1 = -(1/[Pt^{IV}—R])(d[Pt^{IV}—R]/dt)$) were measured from the optical density decrease at λ = 262 nm for ~10^{-4} *M* solutions of complex **1**.

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