Letters to the Editor

Iodoplatination of a triple bond by platinum(IV) complexes: formation of a σ-vinyl derivative

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It has been shown previously[1] that hydroiodination of acetylene in aqueous iodide-containing solutions is catalyzed by platinum(IV), presumably *via* intermediate formation of Pt^{IV}—CH=CHI σ-vinyl complexes. Using propargyl alcohol as a model compound and in the presence of I_2 added to suppress the possible reduction of Pt^{IV} (see Ref. 2), we obtained direct evidence for the occurrence of iodoplatination.

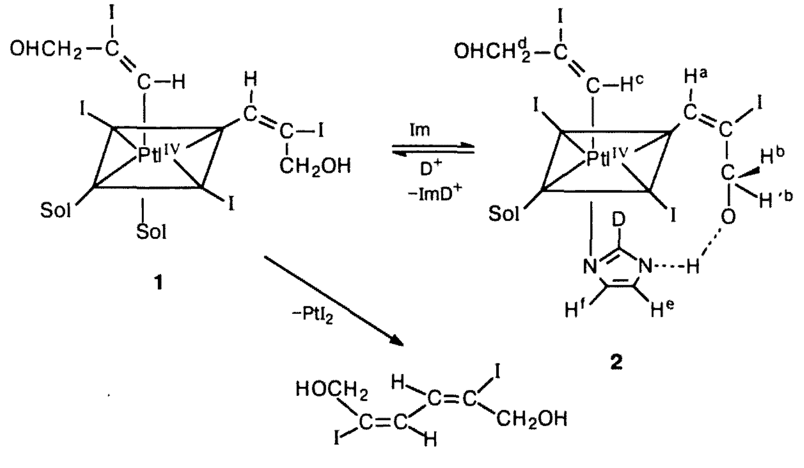
The addition of $HC{\equiv}CCH_2OH$ (78 mg) to the K_2PtI_6 (426 mg)—KI (125 mg)—I_2 (38 mg)—H_2O (10 mL) system at 10—15 °C leads to the accumulation of a precipitate over a period of 6 h. Methanol extraction of this precipitate, preliminarily washed with aqueous solution of KI and water, after concentration affords a dark-brown compound (95 g). Found (%): C, 9.8; H, 1.4; I, 61.3; Pt, 23.0. $Pt(CH{=}CI{-}CH_2OH)_2I_2(CH_3OH)$. Calculated (%): C, 9.92; H, 1.42; I, 59.98; Pt, 23.02.

Spectroscopic data confirm the formation of the σ-vinyl derivative: ^1H NMR (CD_3OD), δ: 6.44 (t, 2 H, $J_{H,H} = 2.0$ Hz, $J_{Pt,H} = 31.1$ Hz); 4.50 (d, 4 H, $J_{H,H} = 2.0$ Hz, $J_{Pt,H} = 2.5$ Hz); $^{13}C\{^1H\}$ NMR (CD_3OD), δ: 100.9 (—CH=, $J_{C,Pt} = 801.4$ Hz); 82.3 (—CI=, $J_{C,Pt} = 24.4$ Hz); 72.6 (—CH_2—, $J_{C,Pt} = 30.2$ Hz). IR (pellets with KBr), ν/cm^{-1}: 3030 vw ν(H—C=), 2920, 2860 w ν(CH_2), 1630 m ν(C=O), 1430 w ν(CH_2—C=), 1000, 940 m σ(H—C=).

To elucidate the mutual orientation of the vinyl ligands, 2-deuteroimidazole (Im) was added to a solution of complex **1** obtained in CD_3OD. Addition of one Im molecule, according to the ^1H NMR data, yields complex **2**, in which the protons of the vinyl ligands are no longer equivalent. As this takes place, three groups of signals appear, δ: 7.40 (s, H(a), $J_{Pt,H(a)} = 80.5$ Hz); 6.82 (t, H(c), $J_{cd} = 2$ Hz, $J_{Pt,H(c)} = 18.2$ Hz); 4.62 (d, 2 H(d), $J_{cd} = 2$ Hz); 4.02 (dd, H(b) H′(b), $J_{av,bb'} = 3.2$ Hz); 7.64 (d, H(f), $J_{ef} = 1.7$ Hz, $J_{Pt,H(f)} = 9.0$ Hz); 7.24 (d, H(e), $J_{ef} = 1.7$ Hz, $J_{Pt,H(e)} = 2.6$ Hz) with an H(a) : H(c) : H(f) intensity ratio of 1 : 1 : 1, which corresponds to a *trans*-coordination of Im with respect to one of the vinyl ligands. Taking into account the strong *trans*-effect of vinyl ligands (*cf.* Ref. 3), structure **1** may be attributed to the initial complex, and the nonequivalence of the b and b′ protons could be due to the formation of the cyclic structure of complex **2**. The addition of $DClO_4$ to a solution of complex **2** results in regeneration of the starting compound **1**.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 500—501, February, 1996.

1066-5285/96/4502-0480$15.00



Heating a solution of complex **1** in CD_3COOD for 3 h at 80 °C affords products of inner-sphere reductive elimination, *viz.*, *E,E*-2,5-diiodohexa-2,4-diene-1,6-diol and PtI_2. The *E,E* structure of the diene points to the *trans*-addition of platinum(IV) and I^- to the alkyne in the steps of iodoplatination.

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Received August 2, 1995
in revised form November 27, 1995