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A Novel Synthesis of Platinum(II)-Olefin Complexes*

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A novel synthesis of platinum(II)-olefin complexes is described in which normal alcohols containing between two and four carbon atoms are treated with sodium tetrachloroplatinate(II) at room temperature. The branched alcohols i–propanol, i–butanol, t–butanol or 3–methylbutan–1–ol all react with sodium tetrachloroplatinate(II) to deposit platinum metal, but do not form olefin complexes.

Introduction

Although ethanol is one of the best organic solvents for sodium tetrachloroplatinate(II) (in terms of the weight that can be dissolved in a given volume of solvent) it suffers from the disadvantage that slow decomposition occurs with deposition of metallic platinum. Until the present work no detailed investigations of the products of this reaction have been reported. The closely related reaction of alcohols and platinum(IV) salts has been known since 1830 to give platinum(II)-olefin complexes.[1-3]

Experimental Section

A solution of sodium tetrachloroplatinate(II) in the alcohol (analytical reagent grade except for ethanol where absolute alcohol was used) was shaken at room temperature for four days. A considerable amount of platinum metal was deposited. After filtering this off with the aid of animal charcoal, the initial red colour of the solution was seen to have lightened to an orange colour. The orange residue obtained after evaporating this solution to dryness was dissolved in dilute hydrochloric acid and after adding animal charcoal the solution was filtered to remove the traces of platinum metal formed during evaporation of the alcohol. The filtrate was treated with a solution of tetra–*n*–butylammonium chloride and with the normal alcohols this yielded a pale yellow precipitate which was recrystallised from methanol to give long yellow needles. The solutions obtained from the branched alcohols did not yield precipitates with tetra–*n*–butylammonium chloride; however, pale pink precipitates were obtained with tetraphenylarsonium chloride.

Ethanol. When ethanol was treated by the method described above yellow needles of $^{n}Bu_4N^+[Pt(CH_2{=}CH_2)Cl_3]^-$ were obtained in 20% yield. Melting point 143-144°C. Found: C, 37.73; H, 6.98; N,2.38%. $C_{18}H_{40}Cl_3NPt$ requires C, 37.82; H, 7.05; N, 2.45%.

n–*Propanol.* When *n*–propanol was treated by the method described above yellow needles of $^{n}Bu_4N^+[Pt(CH_3{-}CH{=}CH_2)Cl_3]^-$ were obtained in 32% yield. Melting point 97-98°C. Found: C, 38.88; H, 7.31; N, 2.32%. $C_{19}H_{42}Cl_3NPt$ requires C, 39.00; H, 7.20; N, 2.39%.

n–*Butanol.* When *n*–butanol was treated by the method described above yellow needles of $^{n}Bu_4N^+[Pt(CH_3CH_2CH{=}CH_2)Cl_3]^-$ were obtained in 40% yield. Melting point 54-55°C. Found: C, 40.60; H, 7.30; N, 2.27%. $C_{20}H_{44}Cl_3NPt$ requires C, 40.00; H, 7.39; N, 2.34%.

i–*Propanol.* When *i*–propanol was treated by the method described above all the platinum(II) present in solution was reduced to platinum metal.

i–*Butanol.* When *i*–butanol was treated by the method described above no precipitate was obtained on adding tetra–*n*–butylammonium chloride. On adding tetraphenylarsonium chloride a pale pink precipitate of $[(C_6H_5)_4As^+]_2[PtCl_4^{2-}]$ was obtained. Found: C, 51.94; H, 3.91%. $C_{48}H_{40}As_2Cl_4Pt$ requires C, 52.30; H, 3.65%.

t–*Butanol.* t–Butanol reacted in an identical manner to *i*–butanol to give $[(C_6H_{54}As^+]_2[PtCl_4^{2-}]$. Found: C, 51.72; H, 3.69%. $C_{48}H_{40}As_2Cl_4Pt$ requires C, 52.30; H, 3.65%.

3-Methylbutan-1-ol. 3-Methylbutan-1-ol reacted in an identical manner to *i*–butanol to give $[(C_6H_5)_4As^+]_2[PtCl_4^{2-}]$. Found: C, 52.48; H, 3.92%. $C_{48}H_{40}As_2Cl_4Pt$ requires C, 52.30; H, 3.65%.

Preparation of $^{n}Bu_4N^+[Pt(CH_2{=}CH_2)Cl_3]^-$. A sample of $^{n}Bu_4N^+[Pt(CH_2{=}CH_2)Cl_3]^-$ for comparison purposes was prepared from Zeise's salt, which was prepared by bubbling ethylene into a solution of potassium tetrachloroplatinate(II) containing stannous chloride using the method described recently by the present author.[4] Melting point 143-144°C. Found: 37.97; H, 7.54; N, 2.41%. $C_{18}H_{40}Cl_3NPt$ requires C, 37.82; H, 7.05; N, 2.45%.

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Results

The olefin complexes were characterised by their elemental analyses and also by their melting points, infrared and N.M.R. spectra. In the case of the ethylene complex all these results were compared with an authentic sample prepared from gaseous ethylene.

The reaction of alcohols with sodium tetrachloroplatinate(II) to give olefin-platinum(II) complexes appears to be limited to the straight chain alcohols since all the branched alcohols investigated, which included *i*–propanol, *i*–butanol, *t*–butanol and 3-methylbutan-1-ol, did not react except to give platinum metal. This is consistent with the first stage of the reaction involving coordination of the alcohol to platinum(II), since it has been established from kinetic studies that whilst the straight chain normal alcohols methanol,[6] ethanol[7] and *n*–propanol[7] give a significant amount of the $[(\text{alcohol})PtCl_3]^-$ complex, the branched alcohol *t*–butanol gives an insignificant amount of the $[(\text{alcohol})PtCl_3]^-$ complex.[7] The initial reversible formation of an $[(\text{alcohol})PtCl_3]^-$ species is also consistent with the observation that when sodium tetrachloroplatinate(II) was treated with ethanol in dilute hydrochloric acid, no reaction occurred even efter four months at room temperature and no decomposition to platinum metal was observed. It is too early to speculate on a detailed mechanism for the reaction but further studies of the reaction are currently in progress.

The present reaction between normal alcohols and platinum(II) salts is very similar to the reaction reported previously by the present author[8] in which a solution of potassium tetrachloroplatinate(II) was found to react with 3–buten–1–ol to give butadiene. Although at the time it was suggested that the formation of the conjugated diolefin butadiene provided the driving force for the dehydration of the alcohol the present work with *n*–butanol appears to refute this.

The reaction between sodium tetrachloroplatinate(II) and terminal alcohols provides a useful synthetic route for preparing terminal olefin complexes without the need to purchase expensive cylinders of olefins. The yields, though modest and varying between 20% for the ethylene and 40% for the but-1-ene complex (based on platinum), are higher than those obtained from the well-established synthesis of platinum(II)-olefin complexes by treatment of platinum(IV) salts with alcohols.[1-3]

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