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SYNTHESIS OF Pt(II) π-OLEFIN COMPLEXES BY REACTION OF Na_2PtCl_6 OR Na_2PtCl_4 WITH OLEFINS IN ACETONE USING LIGHT IRRADIATION

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It is known that Pt(IV) complexes are reduced by methanol when irradiated with light (at λ = 365 nm) [1], while Pt(II) derivatives are oxidized by chloroform (280 nm < λ < 300 nm) [2], in which connection Pt(III) compounds are formed as intermediates in both cases. The photolysis (λ 320-350 nm) of the $(CH_2{=}CH_2)PtCl_3^-$ ion in aqueous HCl solution leads to replacing the ethylene by H_2O [3].

We found that Pt(II) π-olefin complexes are formed quickly and in good yield (up to 98%) when an acetone solution of the olefin and $Na_2PtCl_6 \cdot 6H_2O$ is irradiated with the light of a KGM 9-70 quartz incandescent lamp with an iodine cycle ($\lambda \geqslant 300$ nm). The reaction also goes when irradiated with a DRSh-1000 high-pressure mercury lamp, an incandescent lamp, or direct sunlight. The complexes were isolated either as the dimers or as the adducts with pyridine (Py).

$$Na_2PtCl_6 + RCH{=}CH_2 \xrightarrow[CH_3COCH_3]{h\nu} [(RCH{=}CH_2)PtCl_2]_2 \xrightarrow{Py} \rightarrow (RCH{=}CH_2)PtCl_2Py$$

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Some of the kinetic traits of the reaction were studied on the example of the reaction with styrene, which proves to be first order in Pt(IV) and zero order in olefin. Within experimental error, the reaction rate is independent of the temperature in the range from −20 to 25°C. The addition of water or the bubbling of air inhibits the reaction. Styrene is converted to a mixture of several oxidation products, with the addition of Cl atoms to the double bond and dimerization (based on the PMR and IR spectral data). Irradiation of the mixture at 77°K leads to the appearance of signals in the EPR spectrum that could be assigned [1] to the Pt(III) complex. At 58° the reaction also goes in the dark, but lowering the temperature to 38° leads to a four- to sixfold retardation of the reaction, and at 10° the rate of the photochemical process is greater than the rate of the thermal reaction by 10^3-10^4 times.

We also found that Pt(II) π-olefin complexes are quickly formed in 40-90% yield when an aqueous acetone solution of the olefin and Na_2PtCl_4 is irradiated with visible light.

$$Na_2PtCl_4 + RCH{=}CH_2 \xrightarrow[CH_3COCH_3-H_2O]{h\nu} [(RCH{=}CH_2)PtCl_2]_2$$

As a result, the photoinduced reaction of olefins with either Na_2PtCl_6 or Na_2PtCl_4 can be recommended for the rapid and convenient preparation of platinum(II) π-olefin complexes.

EXPERIMENTAL

All of the reactions were run by irradiating the solutions in a glass vessel, contained in a water-cooled jacket, with the unfiltered light of a KGM 9-70 lamp (lamp at a distance of 2.5 cm and area of window = 9.5 cm^2). The initial reaction rates were determined by the drop in the intensity of the absorption band of the Na_2PtCl_6 solution in the visible region of the spectrum. The synthesized compounds were characterized by comparing (R_f, PMR, melting point) with specimens that had been prepared by conventional methods [4].

Reaction of Na_2PtCl_6 with Styrene. A solution of 0.2 g of $Na_2PtCl_6 \cdot 6H_2O$ and 1 ml of $PhCH{=}CH_2$ in 20 ml of acetone was irradiated at 10° for 50 min. The solvent was evaporated in vacuo and the residue was chromatographed on silica gel (eluant = 1:1 acetone–hexane) to give 0.13 g (98%) of the complex $[(PhCH{=}CH_2)PtCl_2]_2$. In another experiment aqueous Py solution was added to a $CHCl_3$ solution of this complex, the solvent was evaporated in vacuo, and the residue was chromatographed on silica gel (eluant - $CHCl_3$) to give 0.06 g (50%) of the complex $(PhCH{=}CH_2)PtCl_2(C_5H_5N)$.

Reaction of Na_2PtCl_6 with 1-Hexene. The complex (1-hexene) $PtCl_2(C_5H_5N)$ (0.06 g, 39%) was obtained in a similar manner by irradiating for 1 h a solution of 0.2 g of $Na_2PtCl_6 \cdot 6H_2O$ and 1 ml of 1-hexene in 25 ml of acetone and subsequently adding Py.

Reaction of Na_2PtCl_4 with Styrene. The irradiation of a solution of 0.2 g of $Na_2PtCl_4 \cdot 4H_2O$, 0.4 ml of H_2O, and 1 ml of $PhCH{=}CH_2$ in 18 ml of acetone for 1 h gave 0.12 g (91%) of the complex $[(PhCH{=}CH_2)PtCl_2]_2$, which was isolated as described above.

Reaction of Na_2PtCl_4 with Vinylferrocene. In a similar manner, the irradiation of 0.23 g of $Na_2PtCl_4 \cdot 4H_2O$ and 0.1 g of $FcCH{=}CH_2$ (Fc = ferrocenyl) in 10 ml of aqueous acetone for 1 h gave 0.165 g (77%) of the complex $[(FcCH{=}CH_2)PtCl_2]_2$.

Reaction of Na_2PtCl_4 with 1-Hexene. The complex (1-hexene) $PtCl_2(C_5H_5N)$ (0.06 g, 39%) was obtained by irradiating for 1 h a solution of 0.2 g of $Na_2PtCl_4 \cdot 4H_2O$, 1 ml of 1-hexene, and 0.4 ml of H_2O in 10 ml of acetone, and was isolated after treatment with pyridine as described above.

CONCLUSIONS

The reaction of olefins with either Pt(IV) or Pt(II) salts, with irradiation by visible light, is a convenient method for the synthesis of Pt(II) π-olefin complexes.

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