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LETTERS TO THE EDITOR

Catalytic Activity of Pt(II) Complexes in Addition of Tetrachloromethane to Alkenes

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The use of catalytic systems based on Cu(I) and Co(II) complexes for addition of tetrachloromethane to alkenes was reported previously [1, 2]; CCl_4, as a rule, was taken in a 5–10-fold molar excess. In this work we discovered that platinum(II) phosphine complexes also exhibit a catalytic activity in this reaction, and with these complexes the reaction can be performed with only a slight excess of $CCl_4 : CCl_4 :$ 1-hexene = 1.3 : 1.0. For example, when a 1 : 1 : 1 (by volume, at 25°C) mixture of CCl_4, 1-hexene, and acetonitrile is heated to 67–140°C in the presence of Pt(II) complexes (10^{-3}–10^{-2} M), an addition product, 1,1,1,3-tetrachloroheptane, is formed in a yield of up to 35% (all the experiments were performed in sealed degassed evacuated ampules). As catalysts we used dichlorobis(triphenylphosphine)platinum(II), dichlorobis[tri(*m*-tolyl)phosphine] platinum(II), dimethylbis(triphenylphosphine)platinum(II), diiodobis(triphenylphosphine)platinum(II), and other compounds. The reaction can also be performed with other alkenes (1-heptene, cyclohexene). The results of these experiments will be reported in the subsequent papers.

The major product of the reaction of CCl_4 with 1-hexene is 1,1,1,3-tetrachloroheptane. 3-Chloro-1-hexene, idenitified by gas chromatography–mass spectrometry, is formed as by-product in a yield of up to 0.5% (based on 1-hexene). It is known [3] that Pt(II) complexes catalyze metathesis of C–H bonds in alkanes and C–Cl bonds in CCl_4. In our case, 3-chloro-1-hexene is formed by radical substitution of chlorine for hydrogen at the C^3 atom of 1-hexene, catalyzed by the Pt(II) complexes. Preliminary experiments showed that metathesis is slower by three orders of magnitude than addition. Furthermore, in contrast to the previously described [4] addition of polyhaloalkanes to olefins in the presence of organic peroxides, we have not identified in our system appreciable amounts of telomers among reaction products.

1,1,1,3-Tetrachloroheptane. n_D^{23} 1.477. IR spectrum, ν, cm^{-1}: 2980, 2950, 2880, 1470, 1420, 1380, 785, 710. ^{1}H NMR spectrum (C_6D_6), δ, ppm: 4.14 m, 3.04 q, 2.73 q, 1.49 m, 1.21 m, 0.85 t. ^{13}C NMR spectrum (C_6D_6), δ_C, ppm: 98.1, 63.3, 58.3, 39.6, 29.0, 23.0, 14.8. Mass spectrum, *m/z* (I_{rel}, %): 201 (0.5), 165 (19), 145 (2), 131 (12), 117 (7), 96 (12), 83 (51), 69 (79), 55 (100), 51 (20). Found, %: C 33.21; H 3.49; Cl 55.70. $C_7H_{12}Cl_4$. Calculated, %: C 35.33; H 5.08; Cl 59.58.

Mass-spectrometric analysis was performed with a Perkin–Elmer Turbo Mass Gold spectrometer [30 000 × 0.32-mm capillary column, stationary phase XLB-5, carrier gas He, flow rate 1.2 ml min^{-1}, mass-spectrometric detector (total ion current), linear heating from 50 to 280°C (7.5 deg min^{-1}) followed by keeping at 280°C (3 min), internal reference *n*-tetradecane].

The IR spectra were recorded on a Bruker Vektor-22 spectrophotometer (thin liquid film, KBr, 3600–400 cm^{-1}).

The NMR spectra were recorded on a Varian Unity-300 spectrometer at 25°C (working frequency 300 MHz for ^{1}H and 75 MHz for ^{13}C). The chemical shifts in the ^{1}H NMR spectra were determined relative to residual proton signals of $CDCl_3$, and those in the ^{13}C NMR spectra, relative to the ^{13}C signals of C_6D_6.

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