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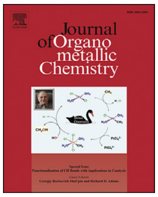

Review

Stable organoplatinum complexes as intermediates and models in hydrocarbon functionalization

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This historical review is dedicated to the Memory of Professor A.E. Shilov.

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ABSTRACT

This review narrates a story about the early stages of developing the alkane-platinum and aryl-platinum chemistry. Characterization and isolation of intermediate σ-organyl complexes is in the focus of the paper. The first works in this area have been carried out in Chernogolovka (Shilov), Donetsk (Rudakov) and Moscow (Shul'pin). The review concerns also a progress in this area. A comparison of alkane reactions with Pt(II) on the one hand and Pd(II) as well as other C—H-activating reagents on the other hand shows that Shilov's system is "a black swan" in this field and further detailed studies of its intimate mechanism seem to be required. At the same time, in alkane activation a striking similarity can be seen between behavior of Pt(II) complexes and hydroxyl radicals. An aqua-platinum(II) complex can be compared with a wasp which pricks C—H bonds using a sting (coordinated hydroxyl radical).

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Introduction

It is commonly accepted that saturated hydrocarbons (alkanes) are the most inert organic compounds and very “difficult” substrates for metal complex catalysis [1]. Only at temperatures higher than 300–500 °C and in the presence of heterogeneous catalysts alkanes can be easily transformed into valuable products in reactions of complete and partial oxidation, dehydrogenation, aromatization, creaking, isomerization, conversion with water vapor. These reactions constitute the basis of contemporary industrial usage of hydrocarbons of oil and natural gas. Nevertheless, under relatively mild conditions (temperature lower than 150 °C, in the absence of radiation) saturated hydrocarbons, and especially methane and ethane, are usually very unreactive. Development of new methods for alkane transformations under mild conditions is very important because low-temperature processes are less energy-demanding and more selective ones. Many practically important low-temperature reactions of alkanes are thermodynamically favorable.

It is worthy that Nature solved this problem and transforms hydrocarbons including methane in living cells at ambient temperature and pressure. Enzymes containing certain metal ions (mainly iron-based methanemonooxygenase, MMO, and cytochrome P450) catalyze conversions of alkanes and other C–H compounds. In the end of 1960s Aleksandr Shilov with his coworkers at the scientific center Chernogolovka (Moscow region, 59 km far from the Kremlin; see Fig. 1) inspired by the idea of his teacher Nobel laureate Nikolay Semenov (“to imitate Nature in chemical flasks”) decided to explore the possibility to model enzymes using metal complexes. The Chernogolovka group (Shilov, Shteinman, Gol'dshleger and newcomers Lavrushko, Shestakov, Moravskii, Geletii and others) discovered and then carefully studied the H/D exchange in alkanes, RH, under the action of a simple platinum(II) salt, Na_2PtCl_4 in solution of D-containing water or acetic acid (1969):

$$RH + D_2O \xrightarrow{Na_2PtCl_4} RD + HOD \quad (1)$$

In 1972, the same team described the oxidation of alkanes with H_2PtCl_6 in the presence of a catalytic amount of Na_2PtCl_4. In this case alkane was transformed into the corresponding alcohol and alkyl chloride:

$$RH + H_2PtCl_6 + H_2O \xrightarrow{Na_2PtCl_4} RCl + ROH + H_2PtCl_4 \quad (2)$$

It is astonishing that simple platinum salts in water or aqueous acetic acid under relatively mild conditions could carry out such challenging reactions. Indeed, these reactions (“Shilov system”, “Shilov chemistry” or “the Shilov reactions”; see an early review [2]) occurred in aqueous solution which is typical for processes in biological systems. However, temperature of both reactions was higher (around 100 °C) than ambient, the most efficient solvent is aggressive (acetic acid) and it is hard to say that this is a typical model of natural enzymes. Nevertheless, in discussions of the recent years Shilov began to draw a parallel between the alkane-platinum chemistry and methane oxidation in Nature under anaerobic conditions. On the other hand, the Shilov reactions presented the first examples of “genuine, organometallic” (that is occurring with the formation of carbon-metal bonds) activation of C–H bonds in alkanes by metal complexes. Many publications, including books and reviews, have been devoted to the description of peculiarities [3], mechanisms [4] and quantum chemical calculations [5] of these reactions. Careful studies showed that certain difference exists between behavior of Shilov reactions and alkane

Fig. 1. Surrounded by fantastic forests scientific town Chernogolovka in Moscow region.