OXIDATIVE AND REDUCTIVE PROCESSES UNDER CONDITIONS FOR THE PALLADATION OF 2,6-DIBENZYLIDENECYCLOHEXANONE IN METHANOL

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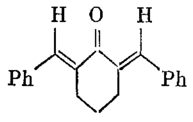
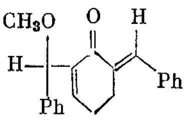
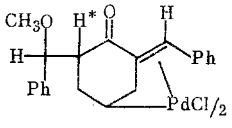
A broad range of oxidation, reduction, metallation, and isomerization reactions has been reported for the commonly used Pd^{2+}—CH_3OH—olefin system [1]. Methanol in these systems is capable of acting not only as a nucleophile but also as a hydride ion donor, which leads to the reductive decomposition of intermediate palladium π-allyl derivatives with the formation of olefins and Pd(0) [2]. We have discovered the first example of a regio- and stereoselective reaction, in which the transfer of a hydride ion from the CH_3OH molecule is accompanied by the metallation of the unsaturated substrate.



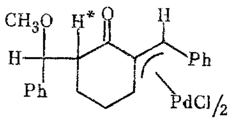
(I)



(II)



(IIIa)



(III b)

In a study of the heteroorganic transformations of isosemiquinone olefins (structural isomers of semiquinoid systems [3]), we showed that the reaction of 2,6-dibenzylidenecyclohexanone (I) with two equivalents of Na_2PdCl_4 in methanol (in the presence of $CuCl_2$ and Na_2CO_3 at 20°C over 20 h) in the first stage involves oxidation of the ligand and elimination of the hydride ion, 1,2-double bond shift, and the formation of intermediate methoxydienone (II),† which undergoes palladation in the second step with accompanying reduction of the endocyclic double bond and formation of the organometallic final product, $C_{20}H_{18}O\cdot PdCl\cdot OCH_3$, in 30% yield. Elemental analysis and PMR spectroscopy indicated that this product has structure (IIIa) or (IIIb). The methanol methyl group was found to be the source of the hydride ion thereby acquired (δH^* 2.98 ppm). This was proven by the formation of the strictly monodeuterated ($H^* = D$) organopalladium product (III) as the only regio- and stereoisomer upon carrying out the reaction of methoxydienone (II) with $Na_2PdCl_4/CuCl_2/Na_2CO_3$ in CD_3OH. The lack of dideuteration upon carrying out this reaction in CD_3OD shows that the source of the second hydrogen atom may be the second equivalent of the unsaturated substrate (I) or (II) [4], possibly with intramolecular shifts of the CH bonds of the central C_6 ring accompanying metallation.

This reaction may hold interest as a new model in the study of the homogeneous hydrogenation of olefins by the action of methanol, which is now considered one of the most promising hydrogen sources [5] in the reduction of organic substrates in the presence of transition metal complexes.

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†Upon carrying out the reaction with equimolar amounts of (I) and Na_2PdCl_4, this compound was isolated in 60% yield and its structure was established by elemental analysis and PMR spectroscopy.

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CHROMIUM AND MANGANESE ALLENYLPHOSPHONIUM COMPLEXES

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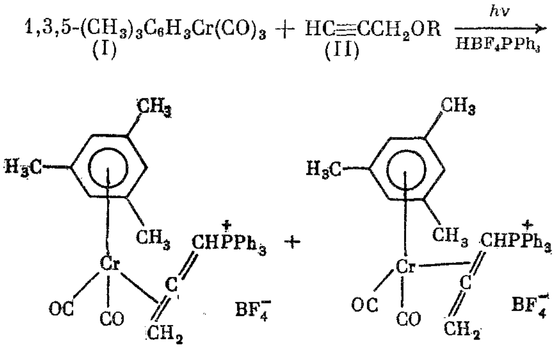
Allenic complexes of transition metals have not been studied intensively [1]. This is especially true of compounds containing functional substituents in the allene ligand. We have found that UV irradiation of a mixture of 1 mmole (I) and 4 mmoles (II) in the presence of 2 mmoles of 48% HBF_4 and 1 mmole PPh_3 in ether gives a 1:7 mixture of previously unreported (IIIa) and (IIIb) in 65% yield. Reprecipitation of (IIIb) from CH_2Cl_2 upon the addition of ether gave a pure sample of this compound. The irradiation of a mixture of 1 mmole (I) and 4 mmoles (II) at −30°C with the intermediate formation of $(CH_3)_3C_6H_3Cr(CO)_2(\eta^2\text{-}HC{\equiv}CCH_2OR)$ (monitored by IR spectroscopy) and subsequent treatment by 2 mmoles HBF_4 and 1 mmole PPh_3 leads to a 1:1 mixture of (IIIa) and (IIIb). Even at 20°C, (IIIa) in CH_2Cl_2 or acetone solution is slowly and irreversibly converted upon standing to (IIIb).



$$\underset{(I)}{1,3,5\text{-}(CH_3)_3C_6H_3Cr(CO)_3} + \underset{(II)}{HC{\equiv}CCH_2OR} \xrightarrow[HBF_4,PPh_3]{h\nu}$$

(IIIa) (IIIb)

R = H, CH_3.

This is the first example of the irreversible migration of a metal atom from one part of the allene ligand to the other part. IR spectrum in CH_2Cl_2 (ν CO, cm^{-1}): 1898, 1952 (IIIa) and (IIIb). PMR spectrum in $(CD_3)_2CO$ (δ, ppm, J, Hz): 1.15 d. d (CH_2, J_{HH} = 2.3, J_{PH} = 4.2), 2.12 s ($3CH_3$), 5.68 s (3HAr), 7.21 d. t (CH, J_{HH} = 2.5, J_{PH} = 30.0), 7.81 m (3 Ph) (IIIa); 2.81 m (CH, J_{HH} = 2.7, J_{PH} = 5.4), 2.26 s ($3CH_3$), 5.94 s (3HAr), 6.12 m ($\underline{H}HC$), 6.58 m ($H\underline{H}C$), 7.81 m (3Ph) (IIIb). Analogously, previously unreported $C_5H_5Mn(CO)_2\cdot$

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