ELECTROCHEMICAL GENERATION OF CATALYSTS FOR ALKENE METATHESIS

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ABSTRACT. The electrochemical reduction of WCl₆ results in the formation of stable and active olefin metathesis catalysts. Reduction of this salt in chlorinated solvents under controlled potential at a platinum cathode with an aluminium anode gives in situ formation of the active species "([W]=CH₂)+(AlC₁₄)⁺". The initial rates of catalysis is very high with a substrate such as 2-pentene, with nearly 100% selectivity. Stability is defined by the fact that the "Pt/WCl₆/e⁻/CH₂Cl₂/Al" system maintains a good activity even after several charges of olefins have been metathesized. From an analysis of the initial by-products and labelling experiments conducted with CD₂Cl₂, it is shown that the metallacarbene initiator arises from a reaction between the transition metal salt and an organoaluminium compound generated in situ by an EC mechanism.

1. INTRODUCTION

Under suitable conditions, the association of transition metal complexes or salts with reducing reagents and Lewis acids such as organoaluminic compounds leads to the synthesis of neutral or ionic species having catalytic properties for the activation of unsaturated hydrocarbons such as mono and diolefins. However, in some cases, it is difficult to determine carefully the precise nature of the active species responsible for the catalysis or to know exactly the oxidation state of the central atom and the number of available coordination sites of these moieties. Moreover, the organoaluminic cocatalyst are in practice very dangerous to handle and very often give by-products arising from isomerization or polymerisation of the substrates.

For these reasons, electrochemistry seems to be a useful tool for the synthesis of catalytic moieties because the number of electrons transferred can be easily checked and consequently, by controlling the electrode potential one can often obtain specifically different oxidation states. Furthermore the absence of an excess of cocatalyst avoids the

side reactions occurring when chemical reducing agents are used. The following equation and cycle give the principle of this process using electroreduction:

1.1. Electrogeneration of catalytic species

\[ + \text{H}^+ \rightarrow L_nM^{x-p}Z^{+}H^+ + pX^- \]

\[ "L_nMX_xZ_z" + p e^- \rightarrow "L_nMX_x-pZ_z" \]  

(Eq 1)

1.2. Catalytic cycle when \( x = p \) in neutral medium

Thus, taking an organometallic complex of general formula \"ML_nX_xZ_z\" where M is the metal atom, L a two-electron donor ligand (phosphine, CO...), X a one-electron ligand (an halogen for instance) and Z a zero-electron ligand (a Lewis acid), one can generate organometallic unsaturated species by electroreduction according to the equation (1). After this electrochemical process, and as a vacant coordination site is now available, a catalytic cycle can occur in the presence of an organic substrate, through an organometallic intermediate which decomposes further into product and generates again the catalytic species. All the intermediates are in accordance with the 18 electrons Tolman's rule [1].