ORGANOMETALLIC COMPLEXES AS CATALYST PRECURSORS: ADVANTAGES AND DISADVANTAGES

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Introduction

Homogeneous catalysis has been an active area of research for a number of years, and a great variety of industrial processes is the result of many fruitful investigations [1 - 3]. It is generally assumed and accepted that the true catalyst consists of one or more metals surrounded by ligands. The function of the ligands modifying the steric or electronic environment of the active catalytic species is not too well understood. In most cases the catalysts are prepared by one of the three routes outlined in Fig. 1a.

In principle, reaction conditions should exist for all three pathways, generating identical catalytic species and reflecting the impact and importance of the ligand field. All three routes have been disclosed, but there have been very few systematic comparisons within one system.

The reduction route is most frequently used, and its beginnings go back to the work of Karl Ziegler, who found that combinations of metal alkyls (or hydrides) of Group I - III metals and a transition metal salt of Group IV - VIII metals, such as $AlEt_3$ plus $TiCl_4$, yield active catalysts for olefin polymerization. Ziegler catalysts can also be prepared in the presence of ligands, thus providing the reduction route with a high degree of applicability and versatility. Two examples are shown in eqns. (1) and (2) demonstrating this principle:

 $Ni^{2+} + AlEt_3 \xrightarrow{butadiene}$ cyclododecatriene (1)

$$Ni^{2+} + AlEt_3 + phosphite \xrightarrow{butadiene} cyclooctadiene$$
 (2)

If nickel(II)acetylacetonate is reduced with aluminum alkyls in the presence of butadiene a nickel (0)butadiene complex is formed via reduction, which cyclotrimerizes butadiene to cyclododecatriene. However, addition of a phosphite ligand to the trimerization catalyst produces a system capable of selectively yielding 1,5-cyclooctadiene [4].

Whenever possible, industry will use the reduction route, due to its lower cost and ease of catalyst preparation. Multiple reducing agents can be



(COD)2NI + W2PCH2COOH

Fig. 1. Preparation of a homogeneous catalyst.

applied, thus giving a high degree of flexibility to this method. The number of papers and patents in this field in nearly unlimited.

Less common is the catalyst preparation by oxidizing a low-valent metal complex to a catalytically active higher oxidation state. This route should be also very general and can also be conducted in the presence of ligands.

Very often, isolated and well characterized organometallic complexes are applied in homogeneous catalysis. However, one must be aware, that the active catalytic species is not necessarily the same compound that is put into the reaction mixture as a catalyst. Many transformations of the nominal catalyst often occur prior to generating the true catalyst. Here reference to the organometallic starting complex as catalyst is misleading.

The use of organometallic complexes as catalyst precursors offers many advantages, especially regarding understanding of the reaction mechanism.

The individual steps of homogeneous catalytic reactions are usually reactions that are well known from organometallic coordination chemistry. Thus starting from an organometallic complex as a catalyst precursor, the use of *in situ* spectroscopy is possible providing some insight into the single reaction steps occurring.

In this paper two systems with a specific ligand field have been chosen to demonstrate that the use of organometallic complexes is not always free of perils and one must be aware of many traps. A detailed knowledge of the chemical behaviour of the precursor complex chosen often is mandatory.

Dimerization of butene

The predominantly linear dimerization of 1-butene can be carried out using the three catalyst routes described in Fig. 1b.

The redution of nickel(II)hexafluoroacetylacetonate with AlEt₃ yields a system which dimerises 1-butene in 84% selectivity to a mixture of noctenes [5, 6]. Similar results were obtained by oxidizing bis(1,5-cyclooctadiene)nickel(0) [(COD)₂Ni] with hexafluoroacetylacetone. We also succeeded in isolating complex 1, which can be used as a catalyst precursor showing identical catalytic behaviour in 1-butene dimerization. The hydride mechanism shown in Fig. 2 was proposed by us to account for this dimeri-



Fig. 2. Hydride mechanism of oligomerization.

zation. The nickel hydride 2 is formed via elimination of bicyclo[3.3.0]oct-2-ene which could be isolated quantitatively. Coordination of 1-butene followed by insertion yields the dimers n-octene. Indeed, in situ NMR spectroscopy revealed the presence of a nickel hydride at -16.3 ppm. Further support for the proposed hydride mechanism is provided with the isolation of the complex (CF₃COCHCOCF₃)Ni[P(iPr)₃]₂H, which is active in the olefin dimerization [7]. During our catalytic investigations we observed that the presence of butadiene inactivated the catalyst system. We assumed that the hydride 2 reacts with butadiene, yielding an inactive η^3 -allylic complex. To prove this assumption, complexes 3 and 4 were synthesized (eqns. (3) and (4)).



Indeed, when applying the reaction conditions used for 1, both complexes 3 and 4 are inactive. An obvious explanation is that 3 and 4 cannot yield the nickel hydride assumed as the catalytically active species because the equilibria in eqns. (3) and (4) lie on the left side. Therefore, if we had started our catalytic experiments with the precursor complexes 3 and 4, the linear 1-butene dimerization would not have been detected. These results clearly indicate that the use of organometallic complexes as catalyst precursors bears substantial dangers, and one must always consider potential organometallic pathways leading to assumed and possible catalytically active species.

Oligomerization of ethene

In analogy to Fig. 1a and b, ethylene oligomerization catalysts can be prepared by the three routes elucidated in Fig. 1c.

The reduction of a nickel(II) salt in the presence of (diphenylphosphino)acetic acid yields a catalyst which is highly active for the linear oligomerization of ethene to α -olefins. A nearly identical catalyst can be obtained upon oxidation of bis(cyclooctadiene)nickel(0) with (diphenylphosphino)acetic acid. Attempts to isolate a complex which could be used as catalyst precursor led to the isolation of complex 5 [8]. Indeed, starting from complex 5 as catalyst precursor, similar results were obtained. There are some differences in activity (turnover numbers), whereas the selectivities to linear products are nearly identical. In all three cases, the linearities amount to 99% and the α -olefin content ranges around 95%. To account for the α -olefins, a hydride mechanism similar to that shown in Fig. 2 is proposed. Again, a nickel hydride is assumed to be the catalytically active species. For instance, starting from complex 5 cyclooctadiene is freed, leading to a nickel hydride. A self-explanatory reaction sequence analogous to that of Fig. 2, involving coordination and insertion of ethene, accounts for the products obtained.

The hydride mechanism is supported by the isolation of the three PO—nickel hydrides 6 [7], 7 [7], 8 [9], all three of which oligomerize ethene to highly linear α -olefins. The structure of complex 8 could be confirmed by X-ray analysis.



Using in situ systems of $\phi_2 PCH_2(CF_3)_2 COH/(COD)_2 Ni$, NMR spectroscopy revealed that upon addition of ethene the hydride signal at -23.8 ppm disappeared and a new signal at 0.6 ppm arose, which can be attributed to a Ni-CH₂ species. By working at -20 °C, the corresponding ethyl complex $[\phi_2 PCH_2 C(CF_3)_2 O]Ni(PCy_3)C_2H_5$ could be isolated and characterized spectroscopically [10].

Again it was observed that addition of larger amounts of butadiene led to a catalyst deactivation, presumably via formation of η^3 -allylic nickel complexes. To investigate the catalytic behaviour of such η^3 -allylic complexes, the compounds 9, 10 and 11 were synthesized and reacted with ethene (Fig. 3). Complexes 9, 10 and 11 react with ethene, yielding comparable α -olefin distributions indicative of identical selectivity. However, different temperatures are needed to start the reaction, as is exhibited in Fig. 3. Upon heating of 11 for ~10 min at 40 °C and 70 bar ethene pressure, the oligomerization started. To initiate the reaction with complex 10, 70 °C is needed and for complex 9 even 130 °C is required. In addition, with complex 9 an initiation period of more than 30 min is needed.

This temperature effect can be easily understood by considering that 9, 10 and 11 are only the catalyst precursors leading to the true catalyst, the nickel hydride. To obtain a nickel hydride from complex 11, equilibria similar to those shown in eqns. (3) and (4) can be considered, which this time lie more to the right side. To convert 10 to a hydride requires an initiation period in which — as we could experimentally demonstrate — the reaction shown in eqn. (5) takes place. To generate a hydride from 9 takes higher temperatures and longer initiation periods, and the activity is low.



Fig. 3. Influence of temperature on catalysts preparation.

$$\begin{pmatrix} 0 \\ P \\ Ni \\ \phi \end{pmatrix}^{Ni} \begin{pmatrix} \phi_{3}P \\ \phi \end{pmatrix} \xrightarrow{H_{2}C=CH_{2}} \begin{pmatrix} 0 \\ P \\ Ni \\ CH_{2}-CH_{2}-\phi \end{pmatrix} \xrightarrow{-\phi-HC=CH_{2}} \begin{pmatrix} 0 \\ P \\ Ni \\ H \end{pmatrix}^{Ni} \begin{pmatrix} \phi_{3}P \\ H \end{pmatrix}$$
(5)

These data quite convincingly demonstrate the impact of using organometallic complexes as catalyst precursors. Apparently, the catalytic properties of the systems discussed stem from the chelate part \overrightarrow{OO} or \overrightarrow{PO} . As shown in Fig. 4 for the \overrightarrow{PO} system, the precursor complex can be broken down into a chelate part and an organyl part such as cyclooctenyl, cyclopentadienyl, phenyl or R_3P . The organyl part is only needed to stabilize the organometallic precursor complex from which the nickel hydride is generated. This implies that the chelate alone controls the reaction (chelate control) [11]. Bönnemann also reports the unique behaviour of a cyclopentadienyl cobalt system and elucidates the impact of temperatures when



Fig. 4. Breakdown of a precursor complex into chelate and organyl parts.

using various organometallic complexes as precursors [12]. The comparison of a parked car (catalyst precursor) and a moving car (catalyst) may be appropriate to describe this behaviour illustratively. The use of organometallic complexes as catalyst precursors may necessitate finding the right reaction conditions. Therefore, it is advisable to apply various temperatures when searching for catalytic activity starting from organometallic complexes. This certainly complicates the search for homogeneous catalysts.

On the other hand, the use of precursor complexes allows, via *in situ* spectroscopy, better pursuit of the chemistry involved leading to a catalyst and may provide a possible description or conclusion concerning the nature of the catalytically active species.

A comparison of the usefulness of the three catalyst preparation routes exhibited in Fig. 1 is quite difficult. All three ways can be applied and should be kept in mind when searching for catalytic reactions.

Finally, it should be mentioned that \hat{P} O ligands are active in the SHOP process [13], which was found by the author during his stay with Shell Development. This process, due to its ligand, possesses outstanding selectivity and activity. With almost one million tons of α -olefins in 1990 [14], the SHOP process is one of the most important applications of homogeneous catalysis.

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