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Research Note

Effect of phosphine–CS_2 adducts on the nickel-catalyzed butenes oligomerization in organochloroaluminate imidazolium ionic liquids

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Abstract

The PR_3–CS_2 adduct displays an unusual promoting effect on the activity of butene oligomerization catalyzed by nickel complexes in biphasic dialkylimidazolium organochloroaluminate ionic liquid (IL) systems. The promoting effect on the activity was studied and was found to be dependent on the nature of the anionic aluminum species present on the IL, making it observable only in acid ILs.

Keywords: Organochloroaluminate; Promoting effect; Phosphine–CS_2; Latent acidity

1. Introduction

The oligomerization of olefins catalyzed by soluble transition metal complexes has been thoroughly studied [1–4]. It gives good results in terms of activity and selectivity and allows selective access to higher olefins, yet has the drawback of separation of the catalyst from the reaction products. One of the most attractive proposed solutions for overcoming this drawback is to perform the oligomerization in biphasic media [5]. A considerable body of literature describing the advantages of ionic liquids (ILs) as media for the catalytic oligomerization of light olefins has appeared over the last 10 years [6–10]. 1,3-Dialkylimidazolium organochloroaluminate-based systems have become prominent ILs because of their favorable physical and chemical properties. The biphasic oligomerization procedure enables the separation of the products and catalyst by simple decantation, allowing easy and inexpensive recycling of the catalyst as an IL solution, immiscible with the reaction products.

The system comprising $[Ni(MeCN)_6][BF_4]_2$ **1** dissolved in 1-butyl-3-methylimidazolium organochloroaluminate IL produces significantly enhanced oligomerization activity on the addition of tricyclohexylphosphonio–carbon disulphide adduct **2** [11]. Until now, a more detailed study of the origin of this promotion effect was lacking, probably due to the complexity of the anionic moieties present in the IL and their interactions with charged organometallic catalysts. In this paper, we describe a systematic study of the effect of tricyclohexylphosphonio–carbon disulphide adduct **2** on the oligomerization of butenes in the presence of $[Ni(MeCN)_6][BF_4]_2$ **1** dissolved in 1-butyl-3-methylimidazolium organochloroaluminate systems of varying acidity. The elucidation of the factors contributing to the promoting effects of adducts like **2** could provide insight into the design of new technologically attractive oligomerization catalytic systems with improved performance.

2. Experimental

All experiments were performed using standard Schlenk tube techniques. All solvents were purified and dried by standard procedures and distilled under argon.

2.1. Precatalyst preparation

The precatalyst, $[Ni(MeCN)_6][BF_4]_2$, was prepared as described previously [12,13] by mixing 12 mmol of metallic nickel (Riedel) and 20 mmol of $NOBF_4$ (Acros), with acetonitrile as the solvent. The solution was kept under stirring for 24 h at 25 °C, at which point the unreacted nickel was removed with a magnetic bar and the acetonitrile was removed

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under reduced pressure. The complex was recrystallized from acetonitrile/ethyl acetate. After decantation, the excess solvent was removed and the complex dried under reduced pressure.

2.2. Tricyclohexylphosphonio–carbon disulphide adduct preparation

For the preparation of tricyclohexylphosphonio–carbon disulphide adduct **2**, 10 mmol of tricyclohexylphosphine (Aldrich) was placed in contact with 1 mL of carbon disulphide (Merck) and stirred at 25 °C. After 1 h under stirring, 10 mL of predried absolute ethanol was added, and the solution was cooled to −10 °C. The ethanol was removed, and the resulting red solid was dried under reduced pressure.

2.3. IL synthesis

For the synthesis of the ILs used in this study, 1-butyl-3-methylimidazolium chloride was slowly added over sublimed $AlCl_3$ in amounts required to achieve the desired composition. The temperature was controlled so as not to exceed 30 °C, avoiding decomposition of the IL thus formed. To complete the IL preparation, the desired quantity of $AlEtCl_2$ was added, and the IL was stirred overnight.

2.4. Catalytic runs

The catalytic runs were performed in a double-walled glass reactor equipped with a magnetic stirrer and a thermocouple, with a continuous feed of 1-butene at 1.08 bar. The dimerization temperature was controlled by a thermostatic circulation bath. The amount of precatalyst used in each experiment was 0.10 mmol with or without the presence of 1 equivalent of **2**, with 7 mL of cyclohexane. The catalytic runs were performed at 10 °C. The system was purged with 1-butene, after which 3 mL of IL was added. After 60 min, the reaction was stopped, and the phases were allowed to separate. The organic phase was analyzed by gas chromatography. For selectivity determination of linear dimers (S_L), mono-branched dimers (S_{B1}) and di-branched dimers (S_{B2}), 1 mL of the organic phase was added to 5 mL of methyl alcohol and hydrogenated with a 5% Pd/carbon catalyst (Degussa). Chromatographic analyses were performed on a Varian 3400CX gas chromatograph, equipped with a Petrocol DH capillary column (methyl silicone, 100 m long, 0.25 mm i.d., and 0.5 µm film thickness). Analysis conditions were 50 °C for 30 min, followed by heating to 250 °C at a rate of 5 °C/min, with the temperature maintained at 250 °C for 5 min. The imprecision of the TOF values, defined as moles of converted butenes per mole of precatalyst and per reaction time (in h), was ±10%, as determined by two independent experiments in each case. The imprecision in terms of dimers selectivity reached ±3%, and the imprecision in terms of dimers composition was ±1%.

2.5. ^{31}P nuclear magnetic resonance analysis

Acquisition of ^{31}P nuclear magnetic resonance (NMR) spectra was performed at 121.42 MHz on an Inova 300 MHz instrument. Several ^{31}P-NMR spectra of adduct **2** were collected in four different ILs and dichloromethane. In addition, the ^{31}P-NMR spectra of tricyclohexylphosphine in several environments—namely tricyclohexylphosphine in toluene, tricyclohexylphosphine complexed by $AlCl_3$ in toluene, and tricyclohexylphosphine in a neutral IL-like reference—were measured.

Table 1
Promoting effect of **2**[a]

Entry	Ionic liquid (molar ratio)	**2**	TOF (h^{-1})	S_{C8} (%)	S_L (%)	S_{B1} (%)	S_{B2} (%)
1	$BMIC/AlCl_3/AlEtCl_2$ (0.45/0.50/0.05)	–	5663	95	8	58	34
2	$BMIC/AlCl_3/AlEtCl_2$ (0.45/0.50/0.05)	1 eq.	5868	95	7	59	34
3	$BMIC/AlCl_3/AlEtCl_2$ (0.40/0.55/0.05)	–	2772	96	9	58	33
4	$BMIC/AlCl_3/AlEtCl_2$ (0.40/0.55/0.05)	1 eq.	9072	93	7	58	35

[a] General conditions: 0.1 mmol of precatalyst, 0.1 mmol of **2**, 3 mL of ionic liquid, continuous feed of 1-butene (1.08 bar) for 1 h, at 10 °C.

3. Results and discussion

The catalytic runs carried out in different ILs produced results dependent on the IL composition. The catalytic activity decreased with increasing $AlCl_3$ content in the IL, as can be seen by comparing entries 1 and 3 of Table 1. This signifies that such species as $Al_2Cl_7^-$, well known to exist in acidic chloroaluminate IL, have a depleting effect on activity. A similar depleting action of these species was observed by Wasserscheid et al. [14] with the (cod)Ni(hfacat) system (in which cod means 1,5-cyclooctadiene and hfacat means 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) and was resolved by these researchers using buffered ILs.

From entries 2 and 4, it can be seen that the behavior of the system containing the tricyclohexylphosphonio–carbon disulphide adduct **2** added to the IL changed profoundly. The IL with an aluminum molar fraction of 0.50 (entry 2) exhibited no significant change in activity and selectivity on the addition of **2**. Alternatively, adding **2** to an IL with aluminum molar fraction 0.55 led to an increase in activity by a factor of ca. 3. This impressive increase in activity with no change in selectivity toward dimers suggests that the main component is probably a modification of the electronic properties of the catalytically active species. The observed change in activity with no loss of selectivity may be linked to the modified electronic properties of the aluminum species, which must be coordinated with the nickel, through the reaction with **2**. The coordination of aluminum species to nickel has been reported previously [15,16]. The ILs represented in entries 1 and 2 contain two anionic aluminum species ($AlCl_4^-$ and, in smaller amounts, $Al_2EtCl_6^-$), and the ILs represented in entries 3 and 4 contain three anionic aluminum species ($AlCl_4^-$, $Al_2Cl_7^-$, and $Al_2EtCl_6^-$).

Table 2
^{31}P Chemical shifts of phosphorous compounds[a]

Entry	System	δ (ppm)
5	**2** + CH_2Cl_2	19.9
6	**2** + BMIC/$AlCl_3$ (0.50/0.50)	31.3
7	**2** + BMIC/$AlCl_3$ (0.45/0.55)	41.5
8	**2** + BMIC/$AlCl_3$/$AlEtCl_2$ (0.45/0.50/0.05)	48.0
9	**2** + BMIC/$AlCl_3$/$AlEtCl_2$ (0.40/0.55/0.05)	48.1
10	$P(Cy)_3$ + toluene	9.7
11	$P(Cy)_3$ + toluene + $AlCl_3$	31.5
12	$P(Cy)_3$ + BMIC/$AlCl_3$ (0.50/0.50)	31.0

[a] H_3PO_4 as internal reference in D_2O.

To verify whether **2** reacts in the presence of anionic aluminum species, several ^{31}P-NMR spectra of adduct **2** were collected in four different ILs and dichloromethane. In addition, the ^{31}P-NMR spectra of tricyclohexylphosphine in several environments—tricyclohexylphosphine in toluene, tricyclohexylphosphine complexed by $AlCl_3$ in toluene, and tricyclohexylphosphine in a neutral IL-like reference—were measured.

The results, given in Table 2, show that **2** interacted with the ILs. Pure **2** displayed a chemical shift of 19.9 (entry 5), which was displaced to higher chemical shifts in the presence of different ILs (entries 6–9). It is noteworthy that there no free tricyclohexylphosphine exists in any IL; this would appear at 9.7 ppm (entry 10), in good agreement with the literature (10.5 ppm) [17].

When **2** was in presence of a neutral IL (entry 6), the chemical shift was displaced to 31.3 ppm. This chemical shift corresponds to that of tricyclohexylphosphine complexed by $AlCl_3$ (entry 11), indicating that when $AlCl_4^-$ is the main anionic species in the IL, the adduct **2** reacts with $AlCl_4^-$, forming $AlCl_3$–$P(Cy)_3$ and Cl^-, as can be seen by comparing entries 6, 11, and 12. The decomposition of **2** in the presence of an IL containing $AlCl_4^-$ anionic species suggests that basic aluminum species could lead to the decomposition of phosphine–CS_2 compounds. The reactivity of $AlCl_4^-$ with a basic compound was described by Osteryoung et al. as "latent acidity" [18].

A slightly increased aluminum molar ratio in the global composition of the IL (as in entry 7) gives the appearance of a new signal in the phosphorous NMR at 41.5 ppm, indicating that this IL had a different reactivity toward **2**. The IL of entry 7 contained anionic species, such as $Al_2Cl_7^-$, whereas the IL of entry 8 also contained $Al_2EtCl_6^-$. The substitution of a chloroaluminate species by an organochloroaluminate species increased the chemical shift from 41.5 ppm to ca. 48 ppm (see supplementary material). Such a change in chemical shift can be explained by the electron-withdrawing effect of aluminum species. It is known that changing the aluminum molar ratio in the IL changes the electronegativity of the ILs, due to the relative amounts of aluminum species present [19]. Polynuclear aluminum species have a greater electronegativity than their mononuclear counterparts, increasing the electron-withdrawing capacity. This implies that the species with a chemical shift of 41.5 ppm is probably of the $AlCl_3$–**2** type, while the species appearing at ca. 48 ppm is of the $Al_2EtCl_6^-$–**2** type. This latter species would be responsible for the increased activity observed after **2** is added to acidic systems. The main difference between entries 8 and 9 is that in the latter system, the $AlCl_3$–$P(Cy)_3$ species does not exist, consequently there is no free chlorine to coordinate to nickel, avoiding poisoning of the catalyst. Such an effect suggests that $Al_2EtCl_6^-$–**2** could coordinate to the nickel catalytic core with a significant increase in activity, due to the strong electron-withdrawing action on the metal.

These results demonstrate that the observed catalytic activity improvement is a consequence of the new anionic in IL species formed by the reaction of $Al_2EtCl_6^-$ with the zwitterionic species **2**. Formation of this species, coordinated to nickel through the chlorine atom, changed the electronic properties of the catalytically active species by the electron-withdrawing action of $Al_2EtCl_6^-$–**2**, increasing the dimerization activity.

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Supplementary material

The online version of this article contains additional supplementary material.

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