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Preliminary communication

COMPLEX CATALYSIS

XXVI*. CATALYSIS OF THE OLIGOMERIZATION OF ETHYLENE BY CATIONIC ALLYLBIS-LIGAND-NICKEL(II) HEXAFLUOROPHOSPHATE COMPLEXES

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Summary

The cationic allylnickel(II) complexes, $[C_3H_5NiL_2]PF_6$ with L = $P(OPh)_3$, $P(OThym)_3$, $SbPh_3$, 1/2 COD, were found to be efficient catalysts for the oligomerization of ethylene. The main products are the dimers and trimers.

The ligand-stabilized allylnickel(II) halides, $[C_3H_5Ni(L)X]$ (X = Cl, Br, I; L = PR_3, $P(OR)_3$), in the presence of a suitable Lewis acid, act as catalyst for oligomerization of olefins. These reactions were extensively investigated by Wilke et al. The reactivity and the selectivity of the catalytic system can be influenced by chosing the most suitable ligand L, anion X^-, and Lewis acid [1—3]. Tkatchenko et al. showed also that the cationic allylnickel(II) complexes, $[2\text{-}RC_3H_4NiL_2]PF_6$ (R = Me, Ph; L = PPh_3, $(COD)_{1/2}$. THF), catalyze oligomerization of ethylene [4].

Recently we prepared a series of new complexes of this type with L = $P(OR)_3$, $P(OAr)_3$, $AsPh_3$, $SbPh_3$, CH_3CN, $(CH_3)_3CNC$, $(COD)_{1/2}$, and we investigated their catalytic potential for stereospecific 1,4-polymerization of butadiene. We have found, that it is possible to modify and influence the activity and selectivity of the catalyst through the electronic and steric influences of the ligand L [5—9]. In this respect we were interest to know

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*For part XXV see ref. 9.

whether the complexes $[C_3H_5NiL_2]PF_6$ (L = $P(OPh)_3$, $P(OThym)_3$, 1/2 COD, $SbPh_3$) also would catalyze the oligomerization of ethylene.

The results of the catalytic tests and the reaction conditions are compiled in Table 1. All the complexes are catalytically active under comparable reaction conditions with the activity sharply increasing in the following order: $P(OPh)_3 < P(OThym)_3 < SbPh_3 \sim$ COD. In the same order, the stability of the catalyst decreases significantly. In the case of the complexes with L = $SbPh_3$ and COD, decomposition started already after 4—5 minutes. The red colour of the solution turned black which was accompanied by a considerable drop in catalytic activity. With complex $[C_3H_5Ni(P(OThym)_3)_2]PF_6$ high activity could be detected after ca. 20 min which, later on, gradually diminished due to decomposition. Only the triphenylphosphite complex was found to catalyze oligomerization of ethylene during several hours without any sign of deactivation. The decay of the triarylphosphite complexes is indicated by the decolourization of the yellow reaction solutions. However, even after completion of the visible decomposition process of the catalyst, a low but significant catalytic activity is maintained. Releasing the pressure in the autoclave immediately after decomposition of the catalyst monitored by the characteristic colour change and analyzing the reaction products showed that butenes were formed in 80 to 90% yields besides 10 to 20% C_6 hydrocarbons.

TABLE 1

REACTION TIME *t*, TURNOVER NUMBER *U* IN mol ETHYLENE PER mmol Ni AND h, PRODUCT COMPOSITION IN % (Catalyst: 1 mmol; solvent: CH_2Cl_2 150 ml; $P(C_2H_4$ 10 atm)

L	t_{min}	*U*	C_4	C_6	C_8	C_{10}	But-1-en	But-2-en	
								trans	*cis*
$P(OPh)_3$	135	1.4	80.0	19.6	0.4	—	1.9	77.4	20.7
$P(OThym)_3$	14	18.1	77.7	19.8	2.5	—	2.2	74.9	22.9
	20 [a]	14.5	56.1	39.3	4.6	—	1.9	73.6	23.9
$SbPh_3$	4	24.4	91.1	8.2	0.5	0.2	1.9	75.6	22.6
COD	6	18.0	78.2	20.1	0.7	—	7.5	71.4	22.1
	28 [a]	10.5	53.3	40.3	6.4	—	2.3	76.1	21.5

[a] A sample of the reaction mixture at reaction time $t + 1$ h with no further ethylene addition after *t*.

Actually, all catalysts exhibit nearly the same selectivity. Increased formation of the C_6 formation in the products up to ca. 40% was achieved by continuation of the reaction for another hour without further addition of ethylene. Interestingly, the composition of the butene fraction remains constant during this time. The C_6 products consist mainly of *E*- and *Z*-3-methylpent-2-ene, 3-methylpent-1-ene, and minor amounts of hex-1-ene.

Our results make clear that the cationic allylnickel(II) complexes, $[C_3H_5NiL_2]PF_6$, do indeed catalyze oligomerization of olefins. Both, the catalytic activity and selectivity can be influenced by variation of the ligand L and the reaction conditions (e.g. the concentration of the monomer). The investigations will be continued.

Experimental

The catalytic tests were performed in a 500 ml-glass autoclave equipped with fittings for argon and ethylene pressure supply. Gases were purified as described elsewhere [10]. All experiments were carried out under strict anaerobic conditions [10]. The catalyst complexes were prepared by treating $(C_3H_5NiBr)_2$ with 2 equivalents of the appropriate ligand followed by precipitation with an aqueous solution of NH_4PF_6 or, alternatively, by protolysis of $Ni(C_3H_5)_2$ with 75% aqueous HPF_6 in the presence of 2 equivalents of the ligand L [7,8].

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