# METAL COMPLEXES IN THE CATALYTIC REACTIONS OF OLEFINS.

## 1. COMPARISON OF THE CATALYTIC PROPERTIES OF TRIPHENYLPHOSPHINE NICKEL COMPLEXES BOTH INDIVIDUALLY AND HETEROGENIZED ON $Al_2O_3$ IN THE DIMERIZATION OF ETHYLENE

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The reaction of $Ni(CO)_4$ with $PPh_3$ in an adsorption bed leads to the formation of at least three types of heterogenized complexes on the surface of $Al_2O_3$: $NiPPh_3(CO)_2L/Al_2O_3$ (Cat-1; L = $PPh_3$, CO, $Al_2O_3$) [1]. In the presence of the system Cat-1—$Et_3Al_2Cl_3$ the dimerization of ethylene takes place with high activity and selectivity [2].

In this investigation a comparative study has been conducted of the reaction selectivity and the activity of Ziegler—Natta catalytic systems based on Cat-1 and a number of individual complexes simulating the possible active intermediates in the dimerization of ethylene in the presence of Cat-1—$Et_3Al_2Cl_3$. We used the complexes $Ni(PPh_3)_2(CO)_2$ (Cat-2), $Ni(PPh_3)_2(\eta^2\text{-}C_2H_4)$(Cat-3), $Ni[P(C_6H_{11})_3]_2(H)Cl$(Cat-4) and $Ni(PPh_3)_2(Et)Cl$(Cat-5).

## EXPERIMENTAL

The Cat-1 catalyst was prepared as in [1]; the complexes $Ni(PPh_3)_2(CO)_2$, $Ni(PPh_3)_2(\eta^2\text{-}C_2H_4)$, $Ni[P(C_6H_{11})_3]_2(H)Cl$, $Ni[P(C_6H_{11})_3]_2(Et)Cl$ were prepared as in [3-6].

Ethylene was dimerized and the reaction products analyzed as in [2], using absolute benzene, redistilled in Ar, as solvent.

## DISCUSSION

In the absence of organoaluminum activators the complexes studied do not lead to the dimerization of ethylene. Consequently, the presence of a previously formed Ni hydride (Cat-4) or Ni alkyl (Cat-5) bond as well as the π-bond of ethylene with Ni (Cat-3) is not a sufficient condition for a high activity of Ni complexes in the reaction being studied. Thus, within the bounds of the present investigation, hypotheses [7] that the process takes place as a result of the olefin penetrating along the inactive Ni—H and Ni—C bonds has not been confirmed, at least at its early stages.

In the dimerization of ethylene on the system Cat-1—$Et_3Al_2Cl_3$ an induction period has been found (Fig. 1), the most probable reason for which is the formation of active sites [8]. The similarity in the course of the dimerization of ethylene on the systems Cat-1—$Et_3Al_2Cl_3$ and Cat-2—$Et_3Al_2Cl_3$ is noteworthy: similar reaction selectivity and activity of the catalysts and the existence of induction periods (Table 1, Fig. 1).

In EPR studies of the reaction of Cat-1 with $Et_3Al_2Cl_3$ we found a conversion of an appreciable fraction of Ni (0) to Ni (I) (signals having $g_{\|} = 2.169 \pm 0.001$ and $g_{\perp} = 2.036 \pm 0.01$). The results obtained agree with those in [9] where $EtAlCl_3$ was used as the activator. The reaction of Cat-2 with $Et_3Al_2Cl_3$ takes place similarly: the signals have $g_{\|} = 2.175 \pm 0.001$ and $g_{\perp} = 2.038 \pm 0.001$.

Thus, the heterogenization of $Ni(PPh_3)_2(CO)_2$ on the surface of $Al_2O_3$ at the stage of the reaction of the Ni complex with the organoaluminum activator does not seem to bring about marked changes in the formation of an active site.

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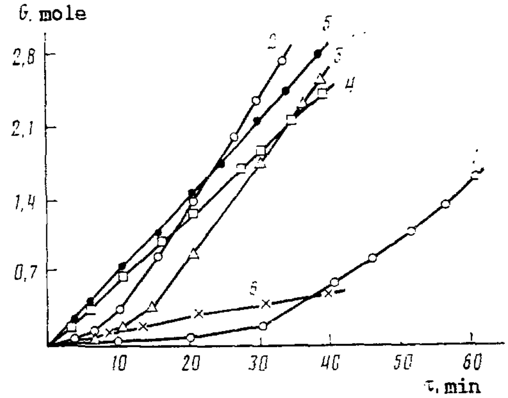

Fig. 1. Kinetic curves for the dimerization of ethylene in the presence of complexes heterogenized on $Al_2O_3$ and model complexes: 1, 2) $Ni(PPh_3)(CO)_2L/Al_2O_3$ (L = $PPh_3$, CO, $Al_2O_3$); 3) $Ni(PPh_3)_2(CO)_2$; 4) $Ni(PPh_3)_2(C_2H_4)$; 5) $Ni[P(C_6H_{11})_3]_2(H)Cl$; 6) $Ni(PPh_3)_2(Et)Cl$. Activator $Et_3Al_2Cl_3$; solvent, heptane; $[Ni]_0 = 2 \cdot 10^{-3}$ g·atom/liter; Al/Ni = 34; $[C_2H_4]_0$ = 0.45 for 1 and 0.65 M for 2-6; T = 20°C. G represents the amount of reacted ethylene.

TABLE 1. Composition of Products from Ethylene Dimerization in the Presence of Complexes of Ni and $Et_3Al_2Cl_3$* (20°C, $[Ni]_0 = 0.6 \cdot 10^{-2}$ g·atom/liter. [Al] : [Ni] = 25, $[C_2H_4]$ = 0.65 M)

| Complex | $C_4$ | $C_6$ | Butenes (B) | | | Hexenes (H), % | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | B-1 | trans-B-2 | cis-B-2 | 3MP-1 | G-1 | G-3 | trans-H-2, 2-EB-1 | cis-H-2, trans-3-MP-2 | cis-3-MP-2 |
| $NiPPh_3(CO)_2L$ | 91 | 9 | 4 | 67 | 29 | 4 | – | 5 | 27 | 27 | 37 |
| $Ni(PPh_3)_2(CO)_2$ | 89 | 11 | 5 | 67 | 28 | 5 | – | 8 | 33 | 22 | 32 |
| $Ni(PPh_3)_2(\eta^2\text{-}C_2H_4)$ | 88 | 12 | 4 | 66 | 30 | 5 | – | 6 | 27 | 29 | 33 |
| $Ni[P(C_6H_{11})_3]_2(H)Cl$ | 83 | 17 | 9 | 62 | 29 | 6 | 1 | 4 | 35 | 22 | 32 |
| $Ni(PPh_3)_2(Et)Cl$ | 94 | 6 | 30 | 48 | 22 | 7 | 6 | 6 | 48 | 16 | 17 |

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*L = $PPh_3$, CO, $Al_2O_3$; MP represents methylpentene.

According to IR spectra the gas-phase treatment of Cat-1 with ethylene causes the disappearance of the intense bands from the CO groups, which indicates that ligand exchange with the olefin molecules takes place [1]. The participation of ethylene in the formation of active intermediates is exhibited directly during the catalytic reaction. As may be seen from Fig. 1, an increase in the initial concentration reduces the length of the induction period markedly (curves 1, 2). One of such intermediates should most probably be taken to be a univalent $\eta^2$-ethylenephosphine nickel complex combined with the organoaluminum activator. Such an intermediate from Cat-1 or Cat-2 may be formed with the penetration of the first molecule of ethylene into the coordination sphere of Ni by the substitution or preliminary elimination of the CO ligand. In fact, in contrast to Cat-1 and Cat-2, which contain CO groups as ligands, the kinetic curve for the dimerization of ethylene on the system Cat-3—$Et_3Al_2Cl_3$ does not contain a section corresponding to an induction period. However, the selectivity of the reaction with respect to butenes (88-91%) and the distribution of isomers in the $C_4$ and $C_6$ fractions formed from ethylene on comparable catalytic systems are virtually identical (Table 1). It should also be noted that, according to the data in [7], mono- or diolefin complexes of Ni in combination with Lewis acids approach the most active systems of the Ziegler type in activity and in the dimerization of ethylene and propylene.

On using the hydride complex of Cat-4 in combination with $Et_3Al_2Cl_3$ a similar course of the reaction with Cat-3 is also observed. Such a similarity in the features of the course of dimerization would seem to indicate an analogy in the structures of the intermediates formed in the reactions of Cat-3 and Cat-4 with $Et_3Al_2Cl_3$ in the presence of ethylene.

The system based on the σ-ethyl complex (Cat-5) differs markedly in catalytic properties: the activity of this system is ~6-8 times less (Fig. 1) and the fraction of α-olefins is ~2-3 times higher than in the remaining cases studied (Table 1). Such features in the behavior of Cat-5 may be associated with its instability [10]: the decomposition of Cat-5 in solvents is accompanied by the liberation of ethylene and ethane (1:1). In addition [11], the primary product from the dimerization of ethylene in such systems is 1-butene, the rate of conversion of which to 2-butene increases with an increase in catalyst concentration.

Thus, the reaction of $Et_3Al_2Cl_3$ with Cat-1 in the presence of ethylene, besides causing the oxidation of Ni(0) to Ni(I) evidently also causes a weakening of the M—CO bond, which promotes the substitution of CO by an olefin molecule. Consequently, an ionic $\eta^2$-ethylenephosphine Ni complex is formed as an intermediate in the dimerization of ethylene, in which one of the coordination sites is either free or occupied by an ethylene molecule. The proposed structure for the intermediate agrees with current concepts on the model of an active oligomerization site on nickel complexes [12].

## CONCLUSIONS

By studying the liquid-phase dimerization of ethylene in the presence of $Cat—Et_3Al_2Cl_3$ catalytic systems based on a nickel complex heterogenized on $Al_2O_3$ and a number of model nickel complexes, a similar activity and selectivity of the process has been established (Cat = $NiPPh_3(CO)_2L$, where L = $PPh_3$, CO, $Al_2O_3$; $Ni(PPh_3)_2(CO)_2$; $Ni(PPh_3)_2(\eta^2\text{-}C_2H_4)$; $Ni[P(C_6H_{11})_3]_2(H)Cl$ and $Ni(PPh_3)(Et)Cl$).

The results of the investigation agree with the hypothesis that mono- and diolefinic nickel complexes are formed as the active intermediates in the reaction.

## LITERATURE CITED

1. N. V. Volchkov, D. B. Furman, L. I. Lafer, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 507 (1983).
2. D. B. Furman, L. A. Makhlis, N. V. Volchkov, et al., Inventor's Certificate 981,307 (USSR), Byull. Izobret., No. 16 (1982); D. B. Furman, N. V. Volchkov, L. A. Makhlis, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1962 (1981).
3. A. N. Nesmeyanov, L. S. Isaeva, and L. N. Morozova, Inorg. Chim. Acta, 29, 210 (1978).
4. P. W. Jolly and K. Jones, Inorg. Synth., 15, 29 (1974).
5. M. L. H. Green, T. Saito, and P. J. Tonfield, J. Chem. Soc. A, 152 (1971).
6. A. N. Nesmeyanov, L. S. Isaeva, and L. N. Morozova, Inorg. Chim. Acta, 33, 173 (1979).
7. V. Sh. Fel'dblyum, The Dimerization and Disproportionation of Olefins [in Russian], Khimiya, Moscow (1978).
8. D. B. Furman, N. V. Volchkov, L. A. Makhlis, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 573 (1983).
9. V. A. Shvets, L. A. Makhlis, V. É. Vasserberg, and V. B. Kazanskii, Kinet. Katal., 25, 1496 (1984).
10. A. N. Nesmeyanov, L. S. Isaeva, and L. N. Morozova, Inorg. Chim. Acta, 3, 1 (1980).
11. D. B. Furman, N. V. Volchkov, L. A. Makhlis, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1962 (1981).
12. V. Kaim, Abstract of Papers. Fifth International Symposium on the Connections Between Homogeneous and Heterogeneous Catalysis 1986, Vol. 2 [in Russian], p. 174.