CHEMISTRY LETTERS, pp. 551-552, 1977. Published by the Chemical Society of Japan

DIMERIZATION OF ETHYLENE CATALYZED BY BIS(TRIPHENYLPHOSPHINE)-PENTACHLOROPHENYL(CHLORO)NICKEL(II) ACTIVATED WITH SILVER SALT

Takao KOIKE, Kiyoshi KAWAKAMI, Ken-ichi MARUYA,
Tsutomu MIZOROKI, and Atsumu OZAKI
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo 152

Bis(triphenylphosphine)pentachlorophenyl(chloro)nickel(II) activated with silver perchlorate effectively catalyzes ethylene dimerization in bromobenzene at 0°C under 76 cmHg. The catalytic activity was further enhanced by adding a catalytic amount of triphenylphosphine. An analogous phenyldimethylphosphine complex, however, was much less active for ethylene dimerization.

It is generally accepted that the activity of nickel complex catalyst for olefin dimerization is substantially enhanced by Lewis acid.$^{1)}$ Bis(triphenylphosphine)aryl(halo)nickel(II), for example, is so much activated in the presence of boron trifluoride etherate that the activity for ethylene dimerization attains 10^3 times as high as that in the absence of Lewis acid.$^{2)}$ The significant role of boron trifluoride etherate, however, has not been clarified yet, since no direct information on the interaction of the nickel complex with boron trifluoride etherate was available. During the course of our study on the activation of thermally stable bis(triphenylphosphine)pentachlorophenyl(chloro)nickel(II), $C_6Cl_5Ni(PPh_3)_2Cl$, for ethylene dimerization, we found that both silver perchlorate and silver tetrafluoroborate also act as excellent activators.

A mixture of $C_6Cl_5Ni(PPh_3)_2Cl$ prepared according to the literature,$^{3)}$ a dried $AgClO_4$,$^{4)}$ or $AgBF_4$,$^{4)}$ and a dried $C_6H_5Br^{4)}$ (5 ml) was vigorously stirring at room temperature under nitrogen atmosphere for about one hour, within which period the colour of solution gradually changed from pale yellow to reddish brown. The rate of ethylene absorption under 76 cmHg at 0°C was measured by means of gas burrette. The results are summarized in Table 1. Ethylene was absorbed almost linearly with respect to reaction time for about 20 min. to give 2-butenes predominantly, no induction period being observed. The rate of dimerization increases with increasing the added amount of $AgClO_4$(run 2-4). $AgBF_4$ seems more effective(run 5), while separate runs disclosed that $AgNO_3$, $NaClO_4$, and $NaBF_4$ give no activation. Another enhancement of the rate is observed when a catalytic amount of triphenylphosphine ($PPh_3/AgClO_4 \leqq 1$) is added to the bromobenzene solution of the catalyst mixture before introduction of ethylene(run 6, 8, and 9). An excess triphenylphosphine($PPh_3/AgClO_4 \geqq 2$), however, almost stops ethylene dimerization(run 7 and 10). On the other hand, analogous phenyldimethylphosphine complex, $C_6Cl_5Ni(PPhMe_2)_2Cl$,$^{3)}$ is much less active even at 15°C (run 11-13). Contrary to the triphenylphosphine complex, the phenyldimethylphosphine complex could not be activated even by enough pretreatment with $AgClO_4$ or $AgBF_4$ at room temperature more than 4 hr, or by addition of a catalytic amount of triphenylphosphine.

Table 1. Rate of Ethylene Absorption Catalyzed by Bis(tertiaryphosphine)-pentachlorophenyl(chloro)nickel(II) Activated with Silver Salt

Run	Catalyst(mmol)		Activater(mmol)		Rate(ml/min)
1	trans-$C_6Cl_5Ni(PPh_3)_2Cl$	(0.05)	$AgClO_4$	(0)	0
2	"	(")	"	(0.05)	8.1
3	"	(")	"	(0.10)	15
4	"	(")	"	(0.20)	21
5	"	(")	$AgBF_4$	(")	very fast
6	"	(")	$AgClO_4$	(0.10)+PPh_3 (0.05)	46
7	"	(")	"	(")+ " (0.20)	0
8	"	(")	"	(0.20)+ " (0.10)	49
9	"	(")	"	(")+ " (0.20)	35
10	"	(")	"	(")+ " (1.00)	0
11	trans-$C_6Cl_5Ni(PPhMe_2)_2Cl$	(1.00)	"	(0.10)	0.3
12	"	(")	"	(0.20)	1.1
13	"	(")	$AgBF_4$	(0.10)	0.6

C_6H_5Br 5 ml, 76 cmHg, 0°C(run 1-10), 15°C(run 11-13).

Wada et al.[5)] reported that trans-$C_6Cl_5Ni(PPhMe_2)_2X$ (X=Cl, Br) reacts with $AgClO_4$ in benzene to give $[C_6Cl_5Ni(PPhMe_2)_2L]^+ClO_4^-$ (L=phosphine ligand or solvent), while no corresponding ionic complex was isolated from trans-$C_6Cl_5Ni(PPh_3)_2X$. This is reasonable because $AgClO_4$ removes triphenylphosphine ($Ag(PPh_3)_nClO_4$, $n \leqq 4$[6)]), but not the phenyldimethylphosphine from the nickel complexes. The contrast between triphenylphosphine and phenyldimethylphosphine complexes seems to be realized in the ethylene dimerization shown in Table 1. Namely, $AgClO_4$ removes both the chloride ligand and the triphenylphosphine from trans-$C_6Cl_5Ni(PPh_3)_2Cl$ to give a coordinatively highly unsaturated nickel species, which would be active for ethylene dimerization. ^{31}P-NMR indicated that $AgClO_4$ really gives complexes with triphenylphosphine in bromobenzene, while no interaction is observed with phenyldimethylphosphine.

Enhancement of the activity of trans-$C_6Cl_5Ni(PPh_3)_2Cl$ by a catalytic amount of triphenylphosphine may be attributable to an increase in the solubility of $AgClO_4$. The present catalyst system is also active for propylene dimerization and codimerization of ethylene with styrene or butadiene, which will be reported in detail elsewhere.

References and Notes

1) P.W.Jolly and G.Wilke, The Organic Chemistry of Nickel, Academic Press, New York, San Francisco, London, 1975.

2) K.Maruya, T.Mizoroki, and A.Ozaki, Bull. Chem. Soc. Jpn., 43, 3630 (1970).

3) J.M.Coronas and J.Sales, J. Organometal. Chem., 94, 107 (1975).

4) $AgClO_4$ and $AgBF_4$ were dried by evacuation at 40-50 °C. C_6H_5Br was dried with P_2O_5 and distilled under vacuum.

5) M.Wada and K.Oguro, Inorg. Chem., 15, 2346 (1976).

6) F.A.Cotton and D.M.L.Goodgame, J. Chem. Soc., 1960, 5267.

(Received March 9, 1977)