

ROLE OF  $\text{AgClO}_4$  IN ACTIVATING SIGMA-ARYLNICKEL HALIDE COMPLEX  
FOR ETHYLENE DIMERIZATIONYoshimasa ISHIMURA, Ken-ichi MARUYA, Yoshiyuki NAKAMURA,  
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$\text{C}_6\text{F}_5\text{Ni}(\text{PPh}_3)_2\text{Br}$  gives a maximum activity for ethylene dimerization when mole ratio of added  $\text{AgClO}_4$  to the complex reaches two.  $^{31}\text{P}$ -NMR study of the reaction between  $\text{AgClO}_4$  and the complex reveals that the variation in dimerization activity runs parallel with concentration of  $\text{C}_6\text{F}_5\text{Ni}(\text{PPh}_3)\text{ClO}_4$  formed by the reaction with  $\text{AgClO}_4$ , thus disclosing a catalytically active species.

It has been shown that  $\sigma$ -arylnickel complexes such as  $\text{PhNi}(\text{PPh}_3)_2\text{X}$  acquire catalytic activity for ethylene dimerization on addition of  $\text{BF}_3\text{OEt}_2$ <sup>1)</sup>. One of the roles of  $\text{BF}_3\text{OEt}_2$  has been claimed to be a complex formation with halide ion<sup>2)</sup>, while no definite proof has been given. In this respect  $\text{AgClO}_4$ , instead of  $\text{BF}_3\text{OEt}_2$ , was used successfully to activate  $\text{C}_6\text{Cl}_5\text{Ni}(\text{PPh}_3)_2\text{Cl}$  for the same reaction<sup>3)</sup>. Since  $\text{AgClO}_4$  is expected to abstract halide ion from the complex, the role of  $\text{AgClO}_4$  would be more readily clarified than that of  $\text{BF}_3\text{OEt}_2$ . The present communication deals with stoichiometry of the reaction between  $\text{C}_6\text{F}_5\text{Ni}(\text{PPh}_3)_2\text{Br}$  and  $\text{AgClO}_4$ , giving reference to the catalytic activity of the system. The fluoro compound was chosen because of its higher solubility in solvents.

$\text{C}_6\text{F}_5\text{Ni}(\text{PPh}_3)_2\text{Br}$  (C-1) was synthesized after a method given in literature<sup>4)</sup>. Since  $\text{AgClO}_4$  is deliquescent, it was dissolved into toluene after vacuum drying at 60°C for 5 hr so that desired amount of  $\text{AgClO}_4$  could be obtained precisely. Fixed amount of C-1 (0.02 or 0.05 mmol) was dissolved into solvent (o-dichlorobenzene or dichloromethane, 5 cm<sup>3</sup>) in nitrogen atmosphere and the toluene solution of  $\text{AgClO}_4$  was added dropwise up to varied mole ratio,  $m(=\text{AgClO}_4/\text{C-1})$ . The mixture was kept stirring for 1 hr at room temperature prior to the activity measurement for the ethylene dimerization which was carried out in a flask at ice temperature following the pressure change. The reaction between C-1 and  $\text{AgClO}_4$  was monitored by  $^{31}\text{P}$ -NMR measurement at -30°C or -80°C.

Figure 1 summarizes the rate of ethylene absorption by o-dichlorobenzene solution of C-1 at ice temperature as a function of  $m$ . It was confirmed that the absorption of ethylene was caused by dimerization (selectivity >97%) so that the rate of absorption represented the dimerization rate or the catalytic activity. As is seen from Fig. 1, the activity increases with increase in  $m$  above 0.5 and passes a maximum at  $m=2$  irrespective of catalyst concentration 0.004 or 0.01 mol cat.dm<sup>-3</sup>,

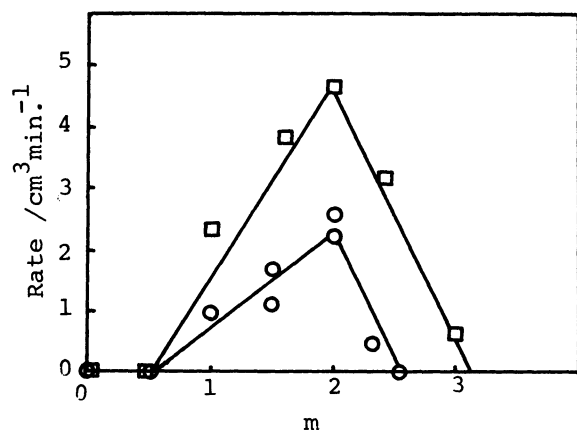


Fig. 1. Ethylene dimerization activity as a function of  $m$  in *o*-dichlorobenzene.

□ 0.01 mol cat. dm<sup>-3</sup>  
○ 0.004 mol cat. dm<sup>-3</sup>

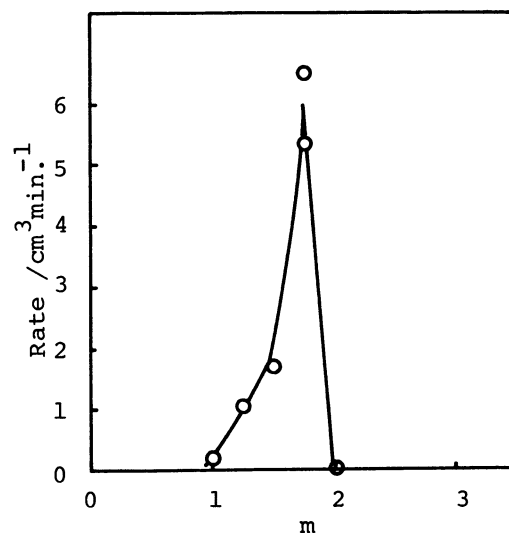
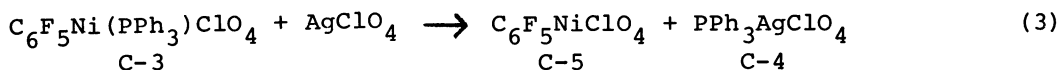
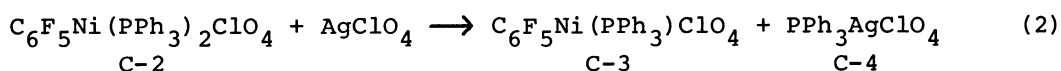
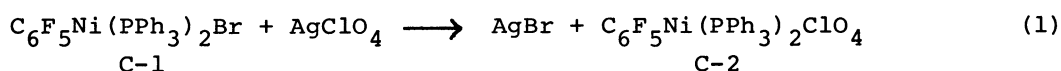


Fig. 2. Ethylene dimerization activity as a function of  $m$  in dichloromethane, 0.004 mol cat. dm<sup>-3</sup>.

while the  $m$  value at which the activity is lost depends on the amount of catalyst. Thus when  $m=2.5$ , the activity is very little for 0.004 mol cat. dm<sup>-3</sup>, while fairly large for 0.01 mol cat. dm<sup>-3</sup>. Similar measurement in dichloromethane gave analogous result as illustrated in Fig. 2, although the effective range of  $m$  ( $=1\sim 2$ ) as well as the optimum value of  $m$  ( $=1.75$ ) is somewhat different from the result in *o*-dichlorobenzene. At any rate it is clear that there is an optimum value of  $m$  at around 2.

The above results suggest a reaction between C-1 and AgClO<sub>4</sub> to give an active species. The probable reactions would be as follows:



The reaction (1) is known<sup>5)</sup> and it can be indicated by the formation of AgBr. In fact, AgBr was obtained, when  $m=1$ , with a yield of 85% based on C-1.

Further evidences for the reactions were studied by <sup>31</sup>P-NMR in dichloromethane which permitted low temperature measurements. As shown in Fig. 3, four different and sharp <sup>31</sup>P-NMR peaks were found at -30°C when  $m$  was increased from 0 to 3. The peak I is reasonably ascribed to C-1 because it was observed only when  $m=0$  (Fig. 3-a). The peak II is ascribed to C-2 because it was observed predominantly when  $m=1$  (Fig. 3-b). Figure 4 illustrates the variation of relative peak intensity (% of

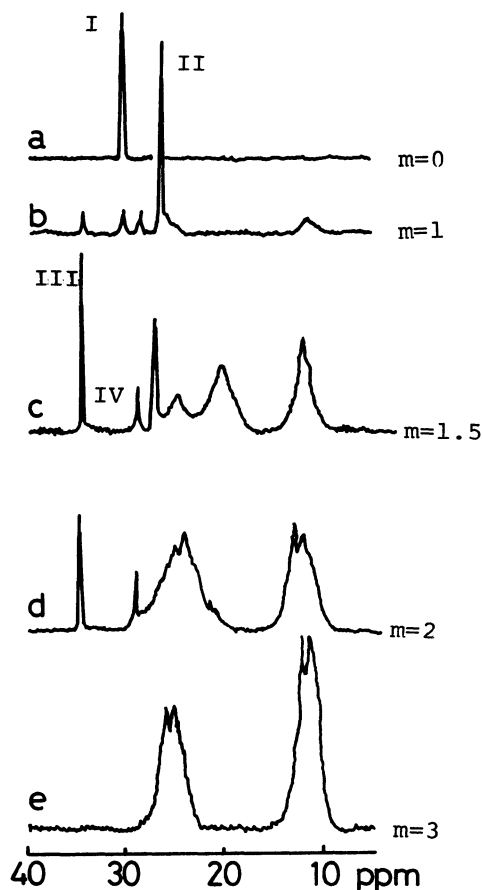


Fig. 3. NMR spectra of catalyst solution ( $0.02 \text{ mol cat. dm}^{-3}$ ) with different  $m$  at  $-30^\circ\text{C}$ .

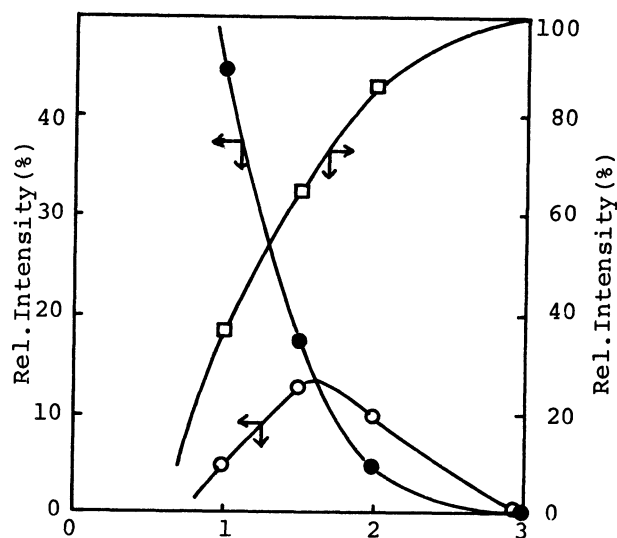


Fig. 4. Variation of relative peak intensity with  $m$ .

Peaks: ● II ○ III □ broad peaks

total peak area). The intensity of peak II decreases as  $m$  is increased beyond 1, demonstrating that C-2 is subjected to a further reaction. Since the peaks III and IV appear in this region of  $m$  with their intensities increasing with  $m$ , the two peaks may be ascribed to products of the reaction of C-2.

If the reaction(2) given above is the case with C-2, C-4 should be one of the products. Thus the  $^{31}\text{P}$ -NMR study was made at  $-80^\circ\text{C}$  with the mixture of  $m=1.5$  to obtain sharp signals. The three broad peaks given in Fig. 3-c were changed to two different doublet doublets which are in agreement with known sharp spectra for  $(\text{PPh}_3)\text{AgClO}_4$ <sup>6)</sup> and  $(\text{PPh}_3)_2\text{AgClO}_4$ <sup>7)</sup> with respect to the chemical shift as well as the coupling constants. The formation of C-4 is clearly demonstrated, giving an evidence for the reaction(2). It is also indicated, however, that another reaction to give  $(\text{PPh}_3)_2\text{AgClO}_4$  takes place concurrently. The relative peak intensity given in Fig. 4 represents the sum of  $(\text{PPh}_3)\text{AgClO}_4$  and  $(\text{PPh}_3)_2\text{AgClO}_4$ , although the relative amounts of them were not determined.

In view of the formation of C-4 at  $m=1.5$ , the peak III seems to be ascribed to C-3 because it appears in parallel with the formation of C-4 as is clear from

Fig. 4 and C-3 is the product of the reaction (2) in addition to C-4. Figure 4 shows that the relative intensity of peak III passes a maximum at around  $m=1.5$ , while the peak assigned for  $(PPh_3)_n AgClO_4$  ( $n=1$  and/or 2) continues to grow with increase in  $m$ . Since the reaction (3) expects a decrease in C-3 as well as an increase in C-4, the above result is consistent with the stoichiometry assumed above. One of the reaction products of the reaction (3), C-5, has no more  $PPh_3$  ligand so that it must be unstable, and liable to decompose. In fact, when  $m$  was increased beyond 2, the orange color of solution characteristic of nickel complex was lost and a precipitate other than  $AgBr$  was formed.

Although another peak IV was observed when  $m=1$ , the relative intensity of IV was almost constant up to  $m=2$ , in contrast to the peak III. Since all the phosphine compounds given in the reactions (1) to (3) are already assigned to other peaks, no particular complex can be assigned to the peak IV, while it might be ascribed to a binuclear complex<sup>8)</sup>.

In summary, it seems clear that C-3 is formed by the reaction between C-1 and  $AgClO_4$ , giving its maximum concentration when  $m=1.5 \sim 2$ . Thus it can be deduced that the catalytic activity almost runs parallel with the concentration of C-3 in the solution, suggesting C-3 to be the active species. The coordinatively unsaturated state of C-3 would be one of the reasons why it can act as the active species. In this way, the role of  $AgClO_4$  can be found in the removal of halogen and  $PPh_3$  from the original complex C-1, although excessive removal of ligands results in the inactive complex, thus giving rise to an optimum value of  $m$ . The stoichiometry in the range of  $m$  larger than 2 may be more complex than that given by the reaction (3), forming different variety of  $(PPh_3)_n AgClO_4$  ( $n=1$  and/or 2) in addition to unstable complex. Once  $m$  exceeded 3 to give the inactive complex, further addition of  $PPh_3$  did not restore the activity, suggesting an irreversible decomposition of complex. Thus when  $m$  is larger than 2, the activity is not solely determined by  $m$  as is seen from Fig. 1.

## References

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