

³¹P NMR Study of Active Species for Ethylene Dimerization in σ -Aryl Nickel Complex-AgClO₄

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[NiBr(σ -C₆F₅)(PPh₃)₂] and [NiCl(σ -C₆Cl₅)(PPh₃)₂] are active for ethylene dimerization in the presence of AgClO₄. The activity increases with increase in the amount of AgClO₄ and reaches maximum at AgClO₄/Ni-complex=2. Addition of excess AgClO₄ leads to marked decrease in activity with [NiBr(σ -C₆F₅)(PPh₃)₂] but a little decrease with [NiCl(σ -C₆Cl₅)(PPh₃)₂]. ³¹P NMR spectra of the active solution showed new resonance peaks due to [Ni(ClO₄)(σ -C₆X'₅)(PPh₃)₂] and [Ni(ClO₄)(σ -C₆X'₅)(PPh₃)] (X'=F,Cl), accompanying formation of AgX (X=Br,Cl) and [Ag(ClO₄)(PPh₃)]. Thus the role of AgClO₄ is to abstract halide anion and/or triphenylphosphine. The amount of [Ni(ClO₄)(σ -C₆X'₅)(PPh₃)₂] is in good correlation with the rate of dimerization, which suggests this species to be catalytically active.

It has been shown that σ -aryl(halogeno)bis(triphenylphosphine)nickel(II), [Ni(σ -aryl)X(PPh₃)₂], is active for the dimerization of ethylene¹ and for the codimerization of ethylene with styrene² or 1,3-butadiene³ in the presence of ether-boron trifluoride (1/1), Et₂O·BF₃. During the course of our study on the effect of aryl ligands and Et₂O·BF₃ on the dimerization, it has been found that Et₂O·BF₃ combined with chloro-(σ -pentachlorophenyl) bis (triphenylphosphine) nickel(II), [NiCl(σ -C₆Cl₅)(PPh₃)₂], in the catalyst system can be effectively replaced by silver perchlorate, AgClO₄.⁴ In the [Ni(σ -aryl)X(PPh₃)₂]-Et₂O·BF₃ system, the role of Et₂O·BF₃ was suggested to form BF₃X⁻ and to abstract the phosphine ligand,¹ but no evidence to prove this has been reported. On the other hand, AgClO₄ is not so sensitive to water as Et₂O·BF₃ and [NiCl(σ -C₆Cl₅)(PPh₃)₂] is stabler than other σ -arylnickel(II) complexes such as [NiBr(σ -C₆H₅)(PPh₃)₂] and [NiBr(σ -1-naphthyl)(PPh₃)₂].⁵ The system comprising [NiCl(σ -C₆Cl₅)(PPh₃)₂] and AgClO₄ is suitable to investigate the effects.

When chlorobis(methyldiphenylphosphine or dimethylphenylphosphine) (σ -pentachlorophenyl)nickel(II), [NiCl(σ -C₆Cl₅)(PR₃)₂] (PR₃=PMePh₂ or PMe₂Ph), is treated with AgClO₄ in the presence of the ligand (L) such as lutidine, carbon monoxide, or water the corresponding cationic complex, [Ni(σ -C₆Cl₅)(L)(PR₃)₂]ClO₄ is isolated.^{6,7} The reaction of the triphenylphosphine analogue, [NiCl(σ -C₆Cl₅)(PPh₃)₂], with AgClO₄ is, however, too complicated to isolate the corresponding cationic complex, since the addition of excess AgClO₄ results in formation of triphenylphosphine-silver complex.⁷ This suggests that AgClO₄ replaces the halide anion of the nickel complex with perchlorate anion and at the same time abstracts the triphenylphosphine ligand. Both bromobis(triphenylphosphine) (σ -pentafluorophenyl)nickel(II), [NiBr(σ -C₆F₅)(PPh₃)₂],⁸ and [NiCl(σ -C₆Cl₅)(PPh₃)₂]⁴ are active for the dimerization of ethylene in the presence of AgClO₄. The reaction of AgClO₄ with [NiBr(σ -C₆F₅)(PPh₃)₂] was investigated by means of ³¹P NMR spectroscopy, suggesting a coordinatively unsaturated nickel complex, [Ni(ClO₄)(σ -C₆F₅)(PPh₃)], to be an active species for the dimerization of ethylene.⁸ This report is concerned with investigation of the re-

action of AgClO₄ with [NiCl(σ -C₆Cl₅)(PPh₃)₂] by means of ³¹P NMR spectroscopy in addition to re-examination of the reaction with [NiBr(σ -C₆F₅)(PPh₃)₂]; the active species for the dimerization of ethylene is described.

Experimental

Materials. The preparation of nickel complexes and the purification of solvents were conducted in a nitrogen atmosphere, and they were kept under nitrogen. [NiBr(σ -C₆F₅)(PPh₃)₂]⁹ and [NiCl(σ -C₆Cl₅)(PPh₃)₂]¹⁰ were prepared according to the literature. Solvents were dried with diphosphorus pentoxide (dichloromethane, chlorobenzene, and *o*-dichlorobenzene), metallic sodium (tetrahydrofuran and toluene), or metallic magnesium (ethanol) before distillation. Ethylene was distilled *in vacuo* at the Dry Ice temperature. Exact measurement of the amount of AgClO₄ was very hard because of its hygroscopicity. AgClO₄ was evacuated in a two-necked flask (50 ml) of known weight at 60 °C for 5 h, after which the flask was filled with nitrogen and weighed. It was kept as a toluene solution of 0.1, 0.2, or 0.5 mol/l.

Ethylene Dimerization. A typical reaction was performed as follows. To an *o*-dichlorobenzene solution (5 ml) of [NiBr(σ -C₆F₅)(PPh₃)₂] (16.6 mg, 0.02 mmol) was added a toluene solution (0.2 ml) of AgClO₄ (0.1 mol/l). The solution was kept stirred at room temperature for 1 h, during which the color turned from yellow to reddish brown accompanying a formation of white precipitate. Then ethylene was introduced at 0 °C at 67 kPa of initial pressure and the pressure change was followed. After 1 h of the reaction the volatile material in the reaction flask was transferred into a sampling tube cooled at -196 °C *in vacuo* and analyzed by gas chromatography. The products corresponded to a butene mixture of equilibrium composition and no hexene was detected.

³¹P NMR Measurements. ³¹P NMR spectra were obtained on an Electron Optics Laboratory FX-100 spectrometer capable of operating in the pulsed Fourier transform mode at 40.26 MHz. In a typical experiment a toluene solution of AgClO₄ was added to a dichloromethane solution (2 ml) of [NiBr(σ -C₆F₅)(PPh₃)₂] (33.2 mg, 0.04 mmol). The solution was filtered to remove the silver bromide formed before being put into an ampule. The chemical shifts were reported in ppm from the external PPh₃ reference (-5.86 ppm from 85% H₃PO₄).

Quantitative measurements were performed using [NiCl(σ -

$\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2$. To a chlorobenzene solution (2 ml) of the nickel complex (17.3 mg, 0.02 mmol) was added a toluene solution of AgClO_4 . After stirring the solution at room temperature for 1 h, benzene- d_6 (0.2 ml) was added and the solution was filtered to remove the silver chloride. A chlorobenzene solution of triphenylphosphine was sealed into a capillary tube, which was fixed in the NMR tube. The integrated peak area was corrected by use of known concentrations of $[\text{NiCl}(\sigma\text{-C}_6\text{Cl}_5)(\text{PPh}_3)_2]$ in chlorobenzene. Amounts of the complexes and silver-phosphine complexes were evaluated by using the same correction factor as for $[\text{NiCl}(\sigma\text{-C}_6\text{Cl}_5)(\text{PPh}_3)_2]$.

Results and Discussion

Ethylene Dimerization with $[\text{NiBr}(\sigma\text{-C}_6\text{F}_5)(\text{PPh}_3)_2]$. Figure 1 shows a typical time course of ethylene dimerization catalyzed by $[\text{NiBr}(\sigma\text{-C}_6\text{F}_5)(\text{PPh}_3)_2]\text{-AgClO}_4$ system. Since the total yield of the butene

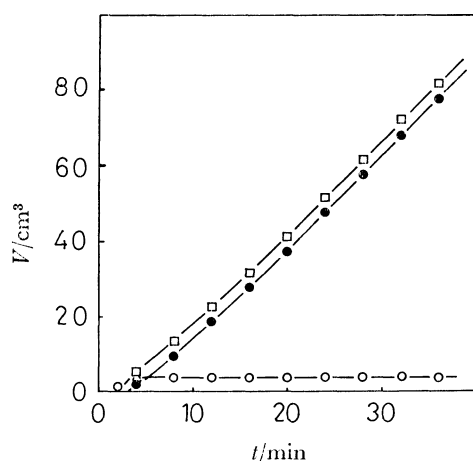


Fig. 1. Time course of ethylene absorption. $[\text{NiBr}(\sigma\text{-C}_6\text{F}_5)(\text{PPh}_3)_2]$ (0.02 mmol) and AgClO_4 (0.04 mmol) in dichloromethane (5 ml) soln, reaction temp 0°C , initial ethylene pressure 67 kPa. ○: Without AgClO_4 , □: with AgClO_4 , ●: reacted ethylene.

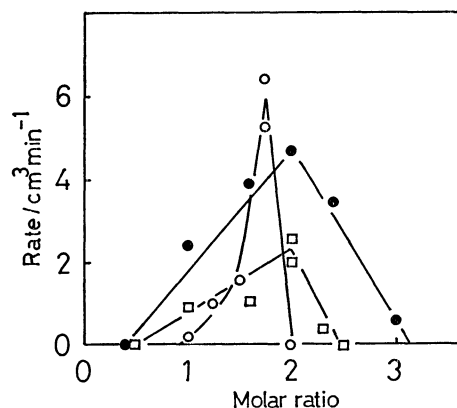
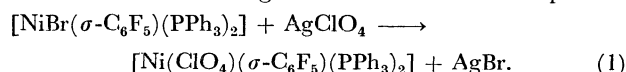


Fig. 2. Rate of ethylene dimerization as a function of molar ratio $\text{AgClO}_4/\text{Ni-complex}$ at 0°C .

a □: $[\text{NiBr}(\sigma\text{-C}_6\text{F}_5)(\text{PPh}_3)_2]$ (0.02 mmol) in *o*-dichlorobenzene (5 ml) soln, b ●: $[\text{NiBr}(\sigma\text{-C}_6\text{F}_5)(\text{PPh}_3)_2]$ (0.05 mmol) in *o*-dichlorobenzene (5 ml) soln, c ○: $[\text{NiBr}(\sigma\text{-C}_6\text{F}_5)(\text{PPh}_3)_2]$ (0.02 mmol) in dichloromethane (5 ml) soln.

mixture exceeded 97% and no other products such as hexene were detected, the rate of the absorption of ethylene corresponds to that of the ethylene dimerization. Thus the rate of dimerization is easily derived from a constant slope in Fig. 1. Figure 2 shows the dependence of the dimerization rate of ethylene in an *o*-dichlorobenzene solvent on the molar ratio of the nickel complex to AgClO_4 . It can be seen that the catalyst does not show any activity at molar ratios smaller than 0.5. The catalytic activity increases with increase in the molar ratio from 0.5 to 2 and reaches the highest value at the molar ratio of 2. Beyond this ratio the catalytic activity decreases with increase in the ratio. The rate of dimerization depends also on the concentration of the nickel complex, but the dependence is not so simple. The higher concentration of the nickel complex results in the wider effective range of molar ratio, where the catalyst system is sufficiently active even at higher molar ratios than 2.5. When the same reaction was carried out in dichloromethane, the effective range was limited to 1 to 2 and the highest activity was obtained at the molar ratio of 1.75 (Fig. 2c). These results show that the molar ratio range for the catalyst system effective for the reaction is dependent on both the concentration of the nickel complex and the solvent used.

In order to clarify the effective component in the catalyst system, the reaction of the nickel complex with AgClO_4 was examined. When a toluene solution (0.2 ml) of AgClO_4 (0.1 mmol) was added to a dichloromethane solution (4 ml) of $[\text{NiBr}(\sigma\text{-C}_6\text{F}_5)(\text{PPh}_3)_2]$ (83 mg, 0.10 mmol), 16.0 mg of AgBr (85% based on the nickel complex) was precipitated. This shows that the following reaction is almost completed:



An addition of more than 0.2 mmol of AgClO_4 resulted in a formation of light greenish brown precipitate and a decoloration of the solution. The aqueous solution of the precipitate reacted with dimethylglyoxime to give a reddish brown precipitate. These results suggest that the addition of excess AgClO_4 decomposes the nickel complex to reduce the dimerization activity.

^{31}P NMR Spectra of $[\text{NiBr}(\sigma\text{-C}_6\text{F}_5)(\text{PPh}_3)_2]\text{-AgClO}_4$ System.

The dichloromethane solution of $[\text{NiBr}(\sigma\text{-C}_6\text{F}_5)(\text{PPh}_3)_2]$ with or without AgClO_4 was monitored by ^{31}P NMR at -30 and -80°C . As shown in Fig. 3b, the addition of an equimolar amount of AgClO_4 to the nickel complex leads to the disappearance of the resonance peak at 30.5 ppm due to the original nickel complex and to the appearance of a new resonance peak at 27.1 ppm. Since the reaction of AgClO_4 with the nickel complex at this molar ratio is expressed by Reaction 1, the new resonance peak at 27.1 ppm can be assigned to $[\text{Ni}(\text{ClO}_4)(\sigma\text{-C}_6\text{F}_5)(\text{PPh}_3)_2]$. Further addition of AgClO_4 up to 1.5 of molar ratio resulted in both the decrease in the resonance peak at 27.1 ppm and the increase in a resonance peak at 34.7 ppm along with the appearance of three broad resonance peaks at 13.3, 21.7, and 25.4 ppm (Fig. 3c). At the ratio of 2, the resonance peak

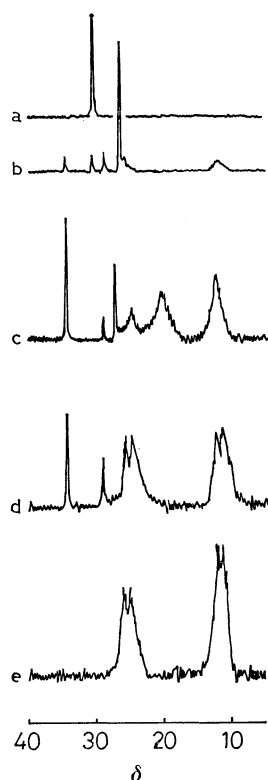


Fig. 3. ^{31}P NMR spectra of catalyst solution (0.02 mmol cat. ml) with different molar ratio $\text{AgClO}_4/\text{Ni-complex}$ at -30°C in dichloromethane (2 ml) soln. Molar ratios are as follows: a; zero, b;1, c;1.5, d;2, e;3.

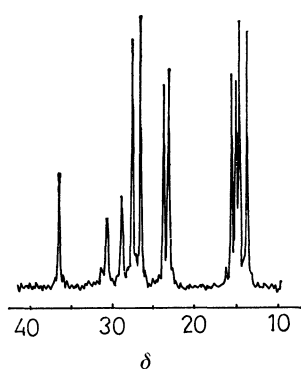


Fig. 4. ^{31}P NMR spectrum of Fig. 3 (c) at -80°C .

at 27.1 ppm disappeared accompanying the decrease in the resonance peak at 34.7 ppm with the growth of the broad resonance peaks remaining (Fig. 3e). This sample gave eight sharp resonance peaks at -80°C instead of broad ones. These resonance peaks are assigned to a couple of double doublet peaks due to (perchloro)(triphenylphosphine)silver(I), $[\text{Ag}(\text{ClO}_4)(\text{PPh}_3)]$, at 20.5 ppm ($^1J_{107\text{Ag},\text{P}}=499.24\text{ Hz}$, $^1J_{109\text{Ag},\text{P}}=577.34\text{ Hz}$) and (perchloro)bis(triphenylphosphine)silver(I), $[\text{Ag}(\text{ClO}_4)(\text{PPh}_3)_2]$, at 19.2 ppm ($^1J_{107\text{Ag},\text{P}}=317.97\text{ Hz}$, $^1J_{109\text{Ag},\text{P}}=367.80\text{ Hz}$) according to the literature,^{11,12} where the broadness was induced by rapid exchange of the coordinated PPh_3 . The disappearance of the resonance peak at 21.7 ppm in Figs. 3d and 3e may be ascribable to the transformation

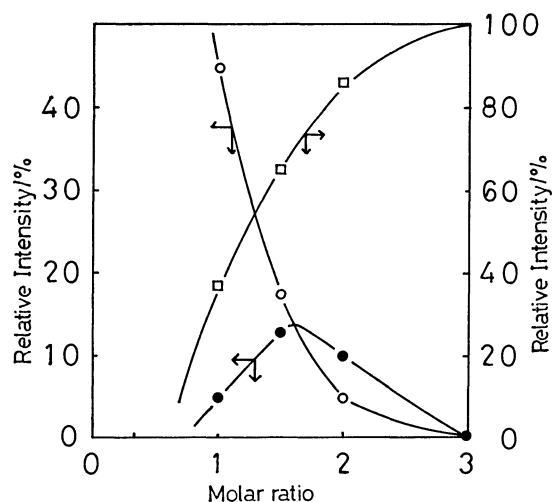
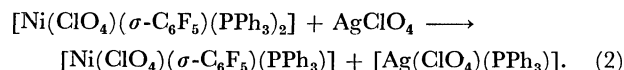


Fig. 5. Changes in relative intensities of resonances as a function of molar ratio $\text{AgClO}_4/\text{Ni-complex}$. $\square$: Broad resonance peaks, $\circ$: 27.1 ppm, $\bullet$: 34.7 ppm.

of $[\text{Ag}(\text{ClO}_4)(\text{PPh}_3)_2]$ into $[\text{Ag}(\text{ClO}_4)(\text{PPh}_3)]$ with increase in AgClO_4 . The formation of these silver-phosphine complexes suggests the presence of a coordinatively unsaturated nickel complex according to the following reaction:



Thus, the sharp resonance peak at 34.7 ppm in Figs. 3b, c, and d would be assigned to $[\text{Ni}(\text{ClO}_4)(\sigma\text{-C}_6\text{F}_5)(\text{PPh}_3)]$. The changes in relative intensity of the resonance peaks shown in Fig. 3 with increase in AgClO_4 added are summarized in Fig. 5. The intensity change of the resonance peak at 34.7 ppm well corresponds to the change in the dimerization rates shown in Fig. 2, suggesting that $[\text{Ni}(\text{ClO}_4)(\sigma\text{-C}_6\text{F}_5)(\text{PPh}_3)]$ would be an active species. The decrease in the active species must come from the abstraction of the second PPh_3 accompanied by the decomposition of the nickel complex, because the addition of excess AgClO_4 resulted in the formation of the precipitate of Ni(II) salts. The reason for the dependences of the dimerization rate on the solvent and the concentration of the nickel complex in higher molar ratios than 2 is not clear.

Ethylene Dimerization with $[\text{NiCl}(\sigma\text{-C}_6\text{Cl}_5)(\text{PPh}_3)_2]$. $[\text{NiCl}(\sigma\text{-C}_6\text{Cl}_5)(\text{PPh}_3)_2]$ as well as $[\text{NiBr}(\sigma\text{-C}_6\text{F}_5)(\text{PPh}_3)_2]$ is active for the ethylene dimerization in the presence of AgClO_4 . As shown in Fig. 6, the rate of dimerization increases with increase in the molar ratio of AgClO_4 to $[\text{Ni}(\text{ClO}_4)(\sigma\text{-C}_6\text{Cl}_5)(\text{PPh}_3)_2]$, and reaches the highest at around 2 of the ratio in a similar manner as $[\text{NiBr}(\sigma\text{-C}_6\text{F}_5)(\text{PPh}_3)_2]$. However, differing from $[\text{NiBr}(\sigma\text{-C}_6\text{F}_5)(\text{PPh}_3)_2]$, the rate decreases only slightly with increase in the ratio up to 5. ^{31}P NMR spectra of the chlorobenzene solution of $[\text{NiCl}(\sigma\text{-C}_6\text{Cl}_5)(\text{PPh}_3)_2]$ and AgClO_4 showed three sharp resonance peaks at 25.0, 26.4, and 28.6 ppm due to nickel complexes along with two broad ones due to $[\text{Ag}(\text{ClO}_4)(\text{PPh}_3)]$. The resonance peak at 26.4 ppm is the one of the original nickel complex. As with

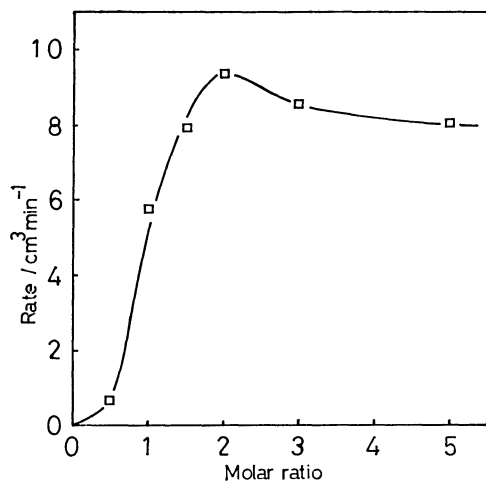


Fig. 6. Rate of ethylene dimerization as a function of molar ratio $\text{AgClO}_4/\text{Ni-complex}$. $[\text{NiCl}(\sigma\text{-C}_6\text{Cl}_5)(\text{PPh}_3)_2]$ (0.02 mmol) in chlorobenzene (2 ml) soln, react. temp 0°C , initial ethylene pressure 67 kPa.

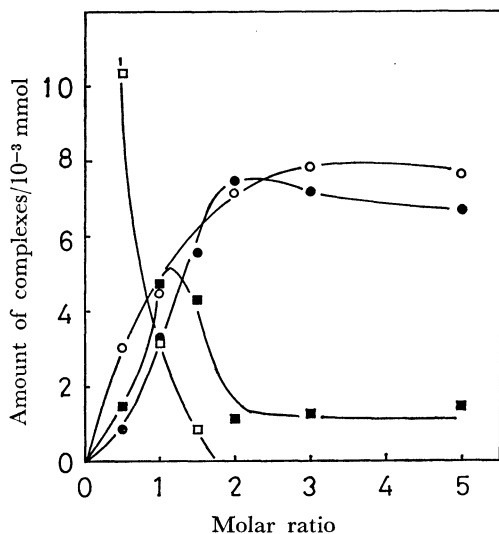


Fig. 7. Changes in the amount of complexes as a function of molar ratio $\text{AgClO}_4/\text{Ni-complex}$.

□: $[\text{NiCl}(\sigma\text{-C}_6\text{Cl}_5)(\text{PPh}_3)_2]$, ■: $[\text{Ni}(\text{ClO}_4)(\sigma\text{-C}_6\text{Cl}_5)(\text{PPh}_3)_2]$, ●: $[\text{Ni}(\text{ClO}_4)(\sigma\text{-C}_6\text{Cl}_5)(\text{PPh}_3)]$, ○: $[\text{Ag}(\text{ClO}_4)(\text{PPh}_3)]$.

the case of $[\text{NiBr}(\sigma\text{-C}_6\text{F}_5)(\text{PPh}_3)_2]$, the resonance peak at 25.0 ppm can be assigned to $[\text{Ni}(\text{ClO}_4)(\sigma\text{-C}_6\text{Cl}_5)(\text{PPh}_3)_2]$ because the peak intensity was the highest at the molar ratio of 1. The resonance peak at 28.6 ppm would be assigned to $[\text{Ni}(\text{ClO}_4)(\sigma\text{-C}_6\text{Cl}_5)(\text{PPh}_3)]$, because the intensity increases with compensation of the resonance peak at 25.0 ppm. Figure 7 shows the dependence of the intensity of the resonance peak at 28.6 ppm on the molar ratio, where the material balances of PPh_3 as estimated from each resonance peak

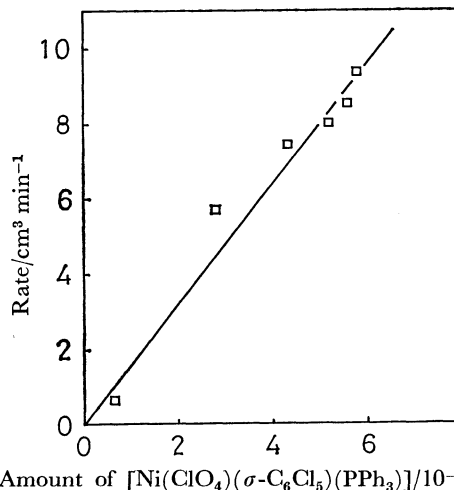


Fig. 8. Relationship between amount of $[\text{Ni}(\text{ClO}_4)(\sigma\text{-C}_6\text{Cl}_5)(\text{PPh}_3)]$ and the rate of ethylene dimerization.

are not complete. This incompleteness is probably because of a loss caused in the procedure of filtration of the solution followed by ampuling the samples.

The dependence of the amount of $[\text{Ni}(\text{ClO}_4)(\sigma\text{-C}_6\text{Cl}_5)(\text{PPh}_3)]$ on the molar ratio is analogous to the rate change shown in Fig. 6. Figure 8 shows the dependence of the rate on the amount of $[\text{Ni}(\text{ClO}_4)(\sigma\text{-C}_6\text{Cl}_5)(\text{PPh}_3)]$. The clear linear relationship would suggest that $[\text{Ni}(\text{ClO}_4)(\sigma\text{-C}_6\text{Cl}_5)(\text{PPh}_3)]$, which can afford two vacant sites on the nickel atom by dissociating the perchlorate anion, is an active species for the dimerization of ethylene. Although a real active species may be such a nickel hydride complex as has been assumed in the $[\text{Ni}(\sigma\text{-aryl})\text{X}(\text{PPh}_3)_2]\text{-Et}_2\text{O}\cdot\text{BF}_3$ system,¹⁾ we have no evidence for the presence of any hydride species at present.

References

- 1) K. Maruya, T. Mizoroki, and A. Ozaki, *Bull. Chem. Soc. Jpn.*, **45**, 2255 (1972).
- 2) N. Kawata, K. Maruya, T. Mizoroki, and A. Ozaki, *Bull. Chem. Soc. Jpn.*, **47**, 413 (1974).
- 3) N. Kawata, K. Maruya, T. Mizoroki, and A. Ozaki, *Bull. Chem. Soc. Jpn.*, **47**, 2003 (1974).
- 4) T. Koike, K. Kawakami, K. Maruya, T. Mizoroki, and A. Ozaki, *Chem. Lett.*, **1977**, 551.
- 5) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, **1960**, 1718.
- 6) M. Wada, *Inorg. Chem.*, **14**, 1415 (1975).
- 7) M. Wada and K. Oguro, *Inorg. Chem.*, **15**, 2346 (1976).
- 8) Y. Ishimura, K. Maruya, Y. Nakamura, T. Mizoroki, and A. Ozaki, *Chem. Lett.*, **1981**, 675.
- 9) J. R. Phillips, D. T. Rosevear, and F. G. A. Storn, *J. Organomet. Chem.*, **2**, 455 (1964).
- 10) J. M. Coronas and J. Sales, *J. Organomet. Chem.*, **94**, 107 (1975).
- 11) R. G. Goel and P. Pilon, *Inorg. Chem.*, **17**, 2876 (1978).
- 12) E. L. Muetterties and C. W. Alegranti, *J. Am. Chem. Soc.*, **95**, 6386 (1972).