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^{31}P NMR Study of Active Species for Ethylene Dimerization in σ-Aryl Nickel Complex–$AgClO_4$

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$[NiBr(\sigma\text{-}C_6F_5)(PPh_3)_2]$ and $[NiCl(\sigma\text{-}C_6Cl_5)(PPh_3)_2]$ are active for ethylene dimerization in the presence of $AgClO_4$. The activity increases with increase in the amount of $AgClO_4$ and reaches maximum at $AgClO_4$/Ni-complex=2. Addition of excess $AgClO_4$ leads to marked decrease in activity with $[NiBr(\sigma\text{-}C_6F_5)(PPh_3)_2]$ but a little decrease with $[NiCl(\sigma\text{-}C_6Cl_5)(PPh_3)_2]$. ^{31}P NMR spectra of the active solution showed new resonance peaks due to $[Ni(ClO_4)(\sigma\text{-}C_6X'_5)(PPh_3)_2]$ and $[Ni(ClO_4)(\sigma\text{-}C_6X'_5)(PPh_3)]$ (X'=F,Cl), accompanying formation of AgX (X=Br,Cl) and $[Ag(ClO_4)(PPh_3)]$. Thus the role of $AgClO_4$ is to abstract halide anion and/or triphenylphosphine. The amount of $[Ni(ClO_4)(\sigma\text{-}C_6X'_5)(PPh_3)]$ 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), $[Ni(\sigma\text{-aryl})X(PPh_3)_2]$, is active for the dimerization of ethylene[1] and for the codimerization of ethylene with styrene[2] or 1,3-butadiene[3] in the presence of ether-boron trifluoride (1/1), $Et_2O \cdot BF_3$. During the course of our study on the effect of aryl ligands and $Et_2O \cdot BF_3$ on the dimerization, it has been found that $Et_2O \cdot BF_3$ combined with chloro(σ-pentachlorophenyl) bis (triphenylphosphine) nickel(II), $[NiCl(\sigma\text{-}C_6Cl_5)(PPh_3)_2]$, in the catalyst system can be effectively replaced by silver perchlorate, $AgClO_4$.[4] In the $[Ni(\sigma\text{-aryl})X(PPh_3)_2]$–$Et_2O \cdot BF_3$ system, the role of $Et_2O \cdot BF_3$ was suggested to form BF_3X^- and to abstract the phosphine ligand,[1] but no evidence to prove this has been reported. On the other hand, $AgClO_4$ is not so sensitive to water as $Et_2O \cdot BF_3$ and $[NiCl(\sigma\text{-}C_6Cl_5)(PPh_3)_2]$ is stabler than other σ-arylnickel(II) complexes such as $[NiBr(\sigma\text{-}C_6H_5)(PPh_3)_2]$ and $[NiBr(\sigma\text{-1-naphthyl})(PPh_3)_2]$.[5] The system comprising $[NiCl(\sigma\text{-}C_6Cl_5)(PPh_3)_2]$ and $AgClO_4$ is suitable to investigate the effects.

When chlorobis(methyldiphenylphosphine or dimethylphenylphosphine) (σ-pentachlorophenyl)nickel(II), $[NiCl(\sigma\text{-}C_6Cl_5)(PR_3)_2]$ ($PR_3=PMePh_2$ or PMe_2Ph), is treated with $AgClO_4$ in the presence of the ligand (L) such as lutidine, carbon monoxide, or water the corresponding cationic complex, $[Ni(\sigma\text{-}C_6Cl_5)(L)(PR_3)_2]ClO_4$ is isolated.[6,7] The reaction of the triphenylphosphine analogue, $[NiCl(\sigma\text{-}C_6Cl_5)(PPh_3)_2]$, with $AgClO_4$ is, however, too complicated to isolate the corresponding cationic complex, since the addition of excess $AgClO_4$ results in formation of triphenylphosphine–silver complex.[7] This suggests that $AgClO_4$ 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), $[NiBr(\sigma\text{-}C_6F_5)(PPh_3)_2]$,[8] and $[NiCl(\sigma\text{-}C_6Cl_5)(PPh_3)_2]$[4] are active for the dimerization of ethylene in the presence of $AgClO_4$. The reaction of $AgClO_4$ with $[NiBr(\sigma\text{-}C_6F_5)(PPh_3)_2]$ was investigated by means of ^{31}P NMR spectroscopy, suggesting a coordinatively unsaturated nickel complex, $[Ni(ClO_4)(\sigma\text{-}C_6F_5)(PPh_3)]$, to be an active species for the dimerization of ethylene.[8] This report is concerned with investigation of the reaction of $AgClO_4$ with $[NiCl(\sigma\text{-}C_6Cl_5)(PPh_3)_2]$ by means of ^{31}P NMR spectroscopy in addition to reexamination of the reaction with $[NiBr(\sigma\text{-}C_6F_5)(PPh_3)_2]$; 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. $[NiBr(\sigma\text{-}C_6F_5)(PPh_3)_2]$[9] and $[NiCl(\sigma\text{-}C_6Cl_5)(PPh_3)_2]$[10] were prepared according to the literature. Solvents were dried with diphosphorus pentaoxide (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 $AgClO_4$ was very hard because of its hygroscopicity. $AgClO_4$ 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 $[NiBr(\sigma\text{-}C_6F_5)(PPh_3)_2]$ (16.6 mg, 0.02 mmol) was added a toluene solution (0.2 ml) of $AgClO_4$ (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.

^{31}P NMR Measurements. ^{31}P 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 $AgClO_4$ was added to a dichloromethane solution (2 ml) of $[NiBr(\sigma\text{-}C_6F_5)(PPh_3)_2]$ (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 PPh_3 reference (−5.86 ppm from 85% H_3PO_4).

Quantitative measurements were performed using [NiCl(σ-

$C_6Cl_5)(PPh_3)_2$]. 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 [NiCl(σ-C_6Cl_5)$(PPh_3)_2$] in chlorobenzene. Amounts of the complexes and silver–phosphine complexes were evaluated by using the same correction factor as for [NiCl(σ-C_6Cl_5)$(PPh_3)_2$].

Results and Discussion

Ethylene Dimerization with [NiBr(σ-C_6F_5)$(PPh_3)_2$]. Figure 1 shows a typical time course of ethylene dimerization catalyzed by [NiBr(σ-C_6F_5)$(PPh_3)_2$]-$AgClO_4$ system. Since the total yield of the butene 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.

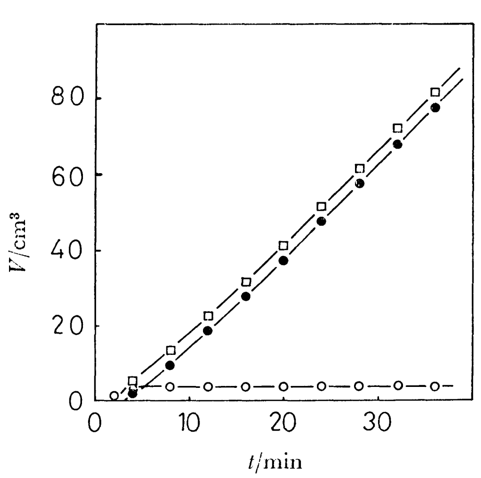

Fig. 1. Time course of ethylene absorption.
[NiBr(σ-C_6F_5)$(PPh_3)_2$] (0.02 mmol) and $AgClO_4$ (0.04 mmol) in dichloromethane (5 ml) soln, reaction temp 0 °C, initial ethylene pressure 67 kPa.
○: Without $AgClO_4$, □: with $AgClO_4$, ●: reacted ethylene.

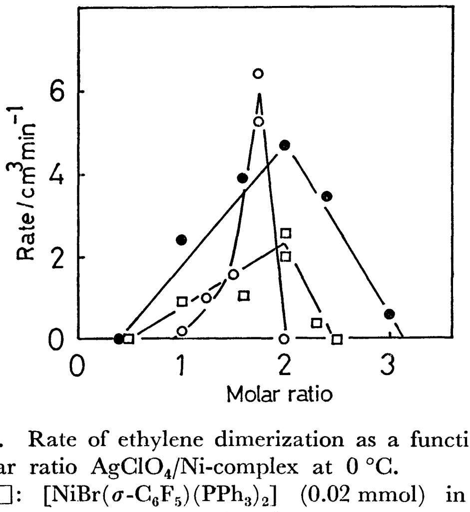

Fig. 2. Rate of ethylene dimerization as a function of molar ratio $AgClO_4$/Ni-complex at 0 °C.
a □: [NiBr(σ-C_6F_5)$(PPh_3)_2$] (0.02 mmol) in *o*-di chlorobenzene (5 ml) soln, b ●: [NiBr(σ-C_6F_5)$(PPh_3)_2$] (0.05 mmol) in *o*-dichlorobenzene (5 ml) soln, c ○: [NiBr(σ-C_6F_5)$(PPh_3)_2$] (0.02 mmol) in dichloromethane (5 ml) soln.

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 [NiBr(σ-C_6F_5)$(PPh_3)_2$] (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:

$$[NiBr(\sigma\text{-}C_6F_5)(PPh_3)_2] + AgClO_4 \longrightarrow [Ni(ClO_4)(\sigma\text{-}C_6F_5)(PPh_3)_2] + AgBr. \qquad (1)$$

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 [NiBr(σ-C_6F_5)$(PPh_3)_2$]-$AgClO_4$ System. The dichloromethane solution of [NiBr(σ-C_6F_5)$(PPh_3)_2$] 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 [Ni(ClO_4)(σ-C_6F_5)$(PPh_3)_2$]. 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

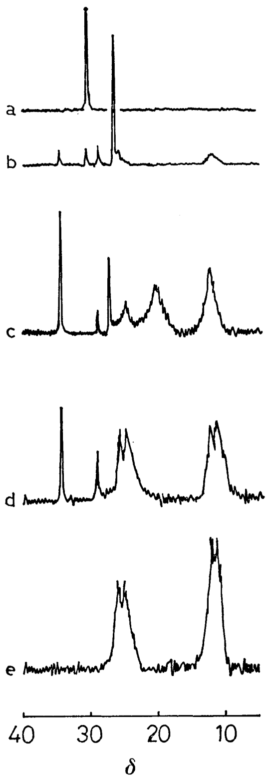

Fig. 3. ^{31}P NMR spectra of catalyst solution (0.02 mmol cat. ml) with different molar ratio $AgClO_4$/Ni-complex at −30 °C in dichloromethane (2 ml) soln. Molar ratios are as follows: a; zero, b;1, c;1.5, d;2, e;3.

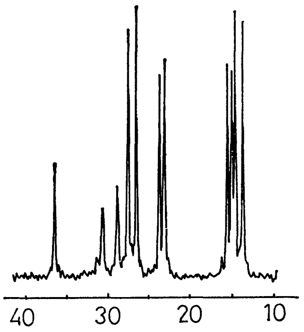

Fig. 4. ^{31}P NMR spectrum of Fig. 3 (c) at −80 °C.

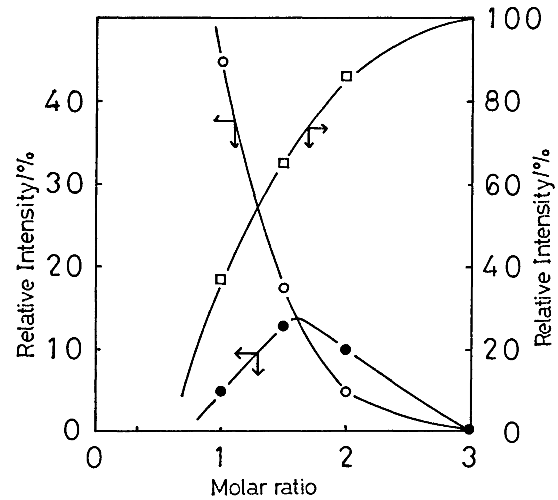

Fig. 5. Changes in relative intensities of resonances as a function of molar ratio $AgClO_4$/Ni-complex. □: Broad resonance peaks, ○: 27.1 ppm, ●: 34.7 ppm.

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), $[Ag(ClO_4)(PPh_3)]$, at 20.5 ppm (${}^1J_{{}^{107}Ag,P}=499.24$ Hz, ${}^1J_{{}^{109}Ag,P}=577.34$ Hz) and (perchloro)bis(triphenylphosphine)silver(I), $[Ag(ClO_4)(PPh_3)_2]$, at 19.2 ppm (${}^1J_{{}^{107}Ag,P}=317.97$ Hz, ${}^1J_{{}^{109}Ag,P}=367.80$ Hz) according to the litterature,[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 of $[Ag(ClO_4)(PPh_3)_2]$ into $[Ag(ClO_4)(PPh_3)]$ 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:

$$[Ni(ClO_4)(\sigma\text{-}C_6F_5)(PPh_3)_2] + AgClO_4 \longrightarrow [Ni(ClO_4)(\sigma\text{-}C_6F_5)(PPh_3)] + [Ag(ClO_4)(PPh_3)]. \quad (2)$$

Thus, the sharp resonance peak at 34.7 ppm in Figs. 3b, c, and d would be assigned to $[Ni(ClO_4)(\sigma\text{-}C_6F_5)(PPh_3)]$. 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 $[Ni(ClO_4)(\sigma\text{-}C_6F_5)(PPh_3)]$ 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 $[NiCl(\sigma\text{-}C_6Cl_5)(PPh_3)_2]$. $[NiCl(\sigma\text{-}C_6Cl_5)(PPh_3)_2]$ as well as $[NiBr(\sigma\text{-}C_6F_5)(PPh_3)_2]$ 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 $[Ni(ClO_4)(\sigma\text{-}C_6Cl_5)(PPh_3)_2]$, and reaches the highest at around 2 of the ratio in a similar manner as $[NiBr(\sigma\text{-}C_6F_5)(PPh_3)_2]$. However, differing from $[NiBr(\sigma\text{-}C_6F_5)(PPh_3)_2]$, the rate decreases only slightly with increase in the ratio up to 5. ^{31}P NMR spectra of the chlorobenzene solution of $[NiCl(\sigma\text{-}C_6Cl_5)(PPh_3)_2]$ 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 $[Ag(ClO_4)(PPh_3)]$. The resonance peak at 26.4 ppm is the one of the original nickel complex. As with

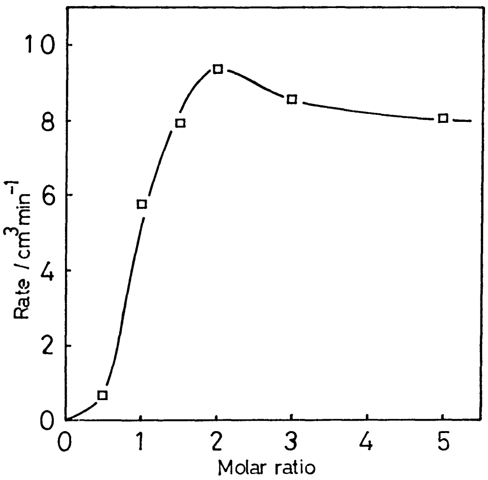

Fig. 6. Rate of ethylene dimerization as a function of molar ratio $AgClO_4$/Ni-complex.
$[NiCl(\sigma\text{-}C_6Cl_5)(PPh_3)_2]$ (0.02 mmol) in chlorobenzene (2 ml) soln, react. temp 0 °C, initial ethylene pressure 67 kPa.

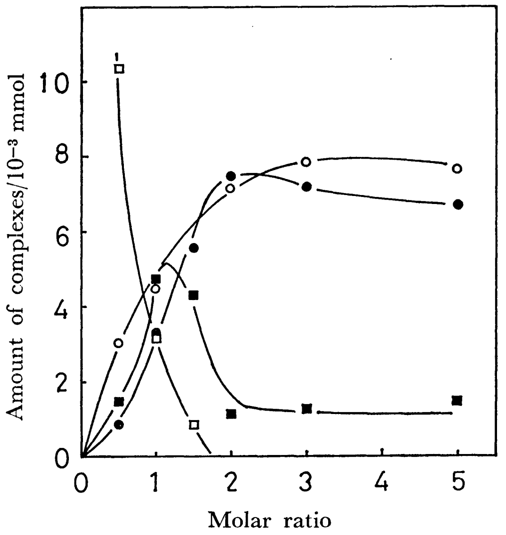

Fig. 7. Changes in the amount of complexes as a function of molar ratio $AgClO_4$/Ni-complex.
□: $[NiCl(\sigma\text{-}C_6Cl_5)(PPh_3)_2]$, ■: $[Ni(ClO_4)(\sigma\text{-}C_6Cl_5)(PPh_3)_2]$, ●: $[Ni(ClO_4)(\sigma\text{-}C_6Cl_5)(PPh_3)]$, ○: $[Ag(ClO_4)(PPh_3)]$.

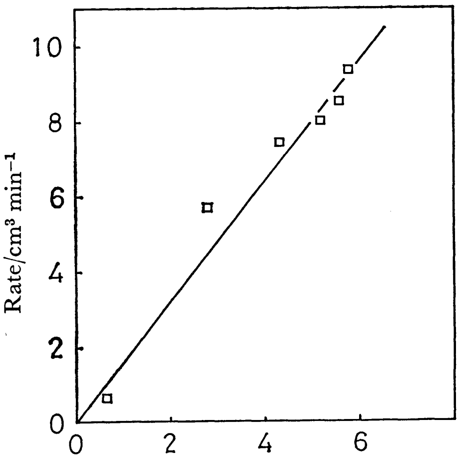

Fig. 8. Relationship between amount of $[Ni(ClO_4)(\sigma\text{-}C_6Cl_5)(PPh_3)]$ and the rate of ethylene dimerization.

the case of $[NiBr(\sigma\text{-}C_6F_5)(PPh_3)_2]$, the resonance peak at 25.0 ppm can be assigned to $[Ni(ClO_4)(\sigma\text{-}C_6Cl_5)(PPh_3)_2]$ because the peak intensity was the highest at the molar ratio of 1. The resonance peak at 28.6 ppm would be assigned to $[Ni(ClO_4)(\sigma\text{-}C_6Cl_5)(PPh_3)]$, 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 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 $[Ni(ClO_4)(\sigma\text{-}C_6Cl_5)(PPh_3)]$ 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 $[Ni(ClO_4)(\sigma\text{-}C_6Cl_5)(PPh_3)]$. The clear linear relationship would suggest that $[Ni(ClO_4)(\sigma\text{-}C_6Cl_5)(PPh_3)]$, 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 $[Ni(\sigma\text{-aryl})X(PPh_3)_2]\text{-}Et_2O\cdot BF_3$ system,[1] we have no evidence for the presence of any hydride species at present.

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