Dimerization of Ethylene Catalyzed by σ-Aryl Nickel Compound in the Presence of Trifluoro Boron Etherate

Ken-ichi Maruya, Tsutomu Mizoroki, and Atsumu Ozaki
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo

(Received January 13, 1972)

It was found that σ-aryl nickel(II) complex catalyzes the dimerization of ethylene rapidly and selectively when trifluoro boron etherate is added. The rate of dimerization increases in order Br$\ll$mesityl$<$naphthyl$<$ *o*-tolyl. The aryl ligands remain in the nickel complexes during the course of dimerization, since vinyl naphthalene, butenyl-naphthalene, *etc.*, which are expected to be the reaction products of ethylene with the σ-aryl lingands, were not detected. The isotopic exchange between ethylene and deuteroethylene and the dimerization of deuteroethylene were studied to confirm the active species of this catalyst system. The isotopic exchange is faster than both the dimerization and isomerization of 1-butene formed. No increase in the atomic fraction of hydrogen of deuteroethylene was observed after treatment with the catalyst system. Thus it is concluded that the nickel hydride formed by the dissociative addition of ethylene is the active species of the catalyst system. The role of trifluoroboron etherate was also elucidated by a comparison of its effect on the rate of ethylene dimerization with that of sodium tetraphenyl borate.

Much interest has been shown in the use of transition metal catalysts for the dimerization of monoolefins and has extended recently to homogeneous catalysis. Of the catalysts, complex nickel catalysts are considered to greatest interest.

In solid catalyst systems such as NiO–SiO$_2$ and NiCl$_2$ for ethylene dimerization, the active species was proposed by one of the authors to consist of an exposed nickel ion possibly of low valence and an acid site of the catalyst; the former catalyzes the isotopic exchange of C_2H_4–C_2D_4, but has no activity for the dimerization in the absence of the acid site. In homogeneous catalysis, a wide range of nickel compounds are known to show excellent catalytic activity for olefin dimerization in an organic solvent, when they coexist with certain Lewis acids such as aluminium alkyl halide.[3-6] This indicates that the coexistence of the Lewis acid with the nickel compound is essential for olefin dimerization in heterogeneous as well as homogeneous catalysis. Several mechanisms for olefin dimerization have been proposed, but the real configuration of active species is still obscure.

In a previous paper it was reported that bis(triphenylphosphine)nickel(II) dihalide in organic solvent catalyzes the isotopic exchange of C_2H_4–C_2D_4 in the presence of molecular hydrogen, and that a nickel hydride formed by the heterolytic splitting of molecular hydrogen is responsible for the exchange.[7] However, no dimerization of ethylene was observed. From the characteristics of the catalyst for dimerization the nickel compound is expected to have catalytic activity for ethylene dimerization, in the presence of some Lewis acid. This was realized by using trifluoroboron etherate as the Lewis acid. Dimerization into butenes was observed. The catalytic activity, however, was considerably smaller than that of the catalyst system composed of nickel(II) halide compound and alkyl aluminium halide. In the coexistence of nickel(II) halide with alkyl aluminium halide, it has been proposed that a σ-alkyl nickel complex is formed by the substitution of a halide coordinated to nickel with an alkyl ligand of alkyl aluminium halide, and the σ-alkyl nickel complex thus formed promotes the dimerization of olefin not isolated probably because of its unstability.[4,5] This suggests the use of the well-known stable σ-aryl nickel(II) halide in place of bis(triphenylphosphine)nickel(II) dihalide as a component of the catalyst, leading to the result that both the activity and selectivity are effectively enhanced for ethylene dimerization.[8] This work was undertaken to investigate the active species of the catalyst system composed of bis(triphenylphosphine)σ-arylnickel(II) bromide and trifluoroboron etherate by examining the effect of the amounts of trifluoroboron etherate and σ-aryl ligand of the nickel compound on the catalytic activity for ethylene dimerization and also by using deuteroethylene.

Experimental

Materials. Bis(triphenylphosphine)nickel(II) dibromide (Found: C, 58.2%; H, 4.0%, Calcd C, 58.2%; H, 4.1%) was prepared according to the method of Venanzi.[9] Bis(triphenylphosphine)1-naphthylnickel(II) bromide (Found: C, 69.9%; H, 4.5%. Calcd: C, 69.9%; H, 4.7%), bis(triphenylphosphine)*o*-tolylnickel(II) bromide (Found: C, 67.9%; H, 4.6%. Calcd: C, 68.5%; H, 4.9%) and bis(triphenylphosphine)mesityl nickel(II) bromide (Found: C, 69.1%; H, 4.7%. Calcd: C, 69.1%; H, 5.3%) were prepared by almost the same method as that of Chatt and Shaw.[10] Organic solvents were dried with sodium, magnesium, or molecular sieve before they were distilled under dry nitrogen. Trifluoroboron etherate

---

[1] K. Kimura, H. A-i, and A. Ozaki, *J. Catal.*, **18**, 271 (1970).

[2] K. Maruya, N. Ando, and A. Ozaki, *Nippon Kagaku Zasshi*, **91**, 1125 (1970),

[3] G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kröner, W. Oberkirch, K. Tanaka, E. Steinrücke, D. Walter, and H. Zimmermann, *Angew. Chem.*, **78**, 157 (1966).

[4] M. Uchino, Y. Chauvin, and G. Lefebvre, *Compt. Rend.*, 1967, **C265**, 103.

[5] O. T. Onsager, H. Wang, and U. Blindheim, *Helv. Chim. Acta*, **52**, 187, 196, 215, 224, 230 (1969).

[6] J. R. Jones, *J. Chem. Soc., C*, **1971**, 1117.

[7] N. Ando, K. Maruya, T. Mizoroki, and A. Ozaki, *J. Catal.*, **20**, 299 (1971).

[8] K. Maruya, T. Mizoroki, and A. Ozaki, **43**, 3630 (1970).

[9] L. M. Venanzi, *J. Chem. Soc.*, **1958**, 719,

[10] J. Chatt, and B. L. Shaw, *ibid.*, **1960**, 1718.

TABLE 1. DIMERIZATION OF C_2H_4 CATALYZED BY $NiBrL(P\phi_3)_2$–BF_3OEt_2

No	L[a]-Ni (mmol)	$BF_3 \cdot OEt_2$ / Ni complex (mole ratio)	Solvent[b] (m*l*)	C_2' introduced (m*l*, STP)	React time (hr)	React temp (°C)	Conv of C_2' (%)	Select into C_4 (%)	aryl-H[c] (%)	$(aryl)_2$[c] (%)
1	Br-Ni(1.0)	1	Bz(50)	98	5	30	11	51		
2	n-Ni(0.1)	10	Mc(5)	107	1/5	0	83	92		
3	t-Ni(0.1)	10	Mc(5)	99.1	1/12	0	94	95		
4	m-Ni(0.1)	10	Mc(5)	105	1/2	0	93	99		
5	n-Ni(0.25)	1	Bz(50)	68.6	1	35	92	82	tr.	0
6	n-Ni(0.25)	1	Bz(50)	68.7	20	35	93	95	11	4.0
7	n-Ni(1.0)	1	Mc(5)	69.2	1	0	94	100	1.3	0
8	t-Ni(2.0)	10	Mc(20)	120.8	1/2	0	100	78	0.7	0

a) Br=Br; n=1-naphthyl; t=*o*-tolyl; m=mesityl.
b) Bz=C_6H_6; MC=CH_2Cl_2
c) Based on the amount of σ-aryl-nickel complex used.

obtained from commercial sources was also distilled under dry nitrogen and its benzene solution (10 vol %) was prepared. Moisture in ethylene was trapped by dry ice methanol. Deuteroethylene (C_2D_4 93.3%, C_2D_3H 6.7%) obtained from partial deuteration of deuteroacetylene was purified by means of a gas chromatographic column of silica gel. Deuteroacethylene was obtained from the reaction of heavy water with calcium carbied preevacuated at 800°C for 3 hr.

Procedure, All the experiments were carried out under nitrogen atmosphere. One of nickel compounds placed in a flask (50 or 100 m*l*) was dried in a vacuum at 50°C before organic solvents were added in order to dissolve the compound completely. The benzene solution of trifluoro boron etherate was then poured into the flask with stirring. Before ethylene was introduced into the flask at the reaction temperature, the nitrogen gas in the flask was evacuated with the solution cooled to liquid nitrogen temperature. The rate of ethylene absorption was measured with a mercury manometor or a gas burette. After the dimerization had been carried out for a given period of time with vigorous stirring, it was stopped by cooling the flask with liquid nitrogen. All volatile materials (butenes, ethylene, and solvent) were transferred to another flask by means of liquid nitrogen and the amounts of olefins were quantitatively determined by gas chromatography. Non-volatile materials were extracted with *n*-hexane, when necessary.

Isotopic exchange of C_2H_4–C_2D_4 and dimerization of C_2D_4 were also carried out according to the same procedure as described above, where a part of the butenes formed and the residual ethylene were separated from the solvent by gas chromatographic column and subjected to mass spectrometry with an ionization potential of 12 eV.

Results

Dimerization Catalyzed by Bis(triphenylphosphine)-Nickel(II) Dibromide and Trifluoroboron Etherate. When isotopic exchange of C_2H_4–C_2D_4 was catalyzed by bis(triphenylphosphine)nickel(II) dibromide in benzene solution in the presence of molecular hydrogen, no dimerization was observed.[7] In the presence of trifluoroboron etherate, however, a small amount of ethylene was dimerized into butenes even in the absence of hydrogen as shown in Table 1 (Run 1). The effect of the amount of trifluoroboron etherate on the rate of ethylene absorption was examined. The result is plotted against the mole ratio of trifluoroboron etherate to nickel compound ($BF_3 \cdot OEt_2/Ni(P\phi_3)_2Br_2$) in Fig. 1, where the rate was determined by the decrease in ethylene pressure during initial 10 min. It shows that the rate increases with the added amount of trifluoroboron etherate.

Dimerization Catalyzed by Bis(triphenylphosphine)σ-Arylnickel(II) Bromide–Trifluoroboron Etherate. Bis(triphenylphosphine)σ-arylnickel(II) bromide was used in place of the corresponding nickel(II) dibromide. Ethylene dimerization with this catalyst system selectively took place without any induction period at room temperature under atmospheric pressure. The result is also given in Fig. 1. It is seen that the rate of ethylene absorption is considerably faster than that by bis(triphenylphosphine)nickel(II) dibromide catalyst and that the rate increases in the order Br≪mesityl<1-naphthyl<*o*-tolyl. The products of these runs are shown in Table 1 (Run 2, 3, and 4). More than 97% of the consumed ethylene is converted into butenes accompanied only by a small

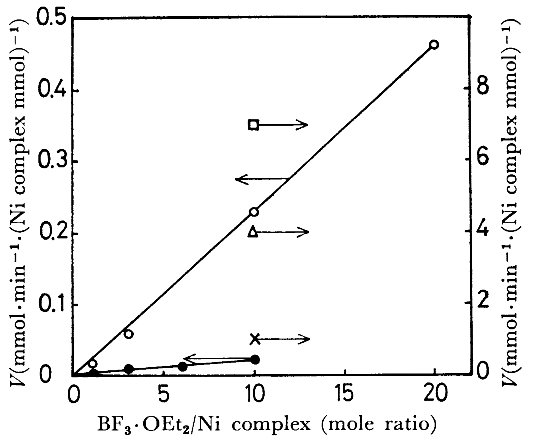


Fig. 1. Rate of ethylene absorption as a function of mole ratio $BF_3 \cdot OEt_2$/Ni-complex.

○: $NiBr(1\text{-naphthyl})(P\phi_3)_2$(1 mmol) in benzene (50 m*l*) soln., react. temp. 35°C, $P_{C_2H_4}$ 45 cmHg.

●: $NiBr_2(P\phi_3)_2$(2 mmol) in benzene (50 ml) soln., react. temp. 42°C, $P_{C_2H_4}$ 50 cmHg.

□: $NiBr(o\text{-tolyl})(P\phi_3)_2$, △: $NiBr(1\text{-naphthyl})(P\phi_3)_2$, ×: $NiBr(mesityl)(P\phi_3)_2$ in dichloromethane (5 m*l*) soln., react. temp. 0°C, $P_{C_2H_4}$ 60 cmHg.

amount of hexene. Propylene seems to be less reactive than ethylene. When an equimolar amount of triphenylphosphine was added to the solution of bis(triphenylphosphine)-1-naphthylnickel(II) bromide ($BF_3 \cdot OEt_2/1\text{-}C_{10}H_7Ni(P\phi_3)_2Br=1$), the rate of ethylene absorption under the same reaction conditions as shown in Fig. 1 decreased to about one-seventh of that in the absence of triphenylphosphine. Acrylonitrile as well as butadiene strongly inhibited the ethylene dimerization, while a trace amount of hexadiene was detected on addition of butadiene.

Whether the olefin reacts with the aryl ligand of the nickel complex or not was examined by using a large amount of σ-arylnickel(II) compound. It can be expected that the reaction of olefin with the aryl ligands results in the formation of vinylnaphthalene, vinyltoluene, butenylnaphthalene *etc*. However, none of them was detected by gas chromatography and only a small amount of decomposed products of the complex such as naphthalene, 1,1′-dinaphthyl and triphenylphosphine were detected in the solution after dimerization, as is shown in Table 1 (Run 5, 6, 7, and 8). This means that the aryl ligand remains in the nickel complex during the course of dimerization.

Effect of Trifluoroboron Etherate. When bis(triphenylphosphine)nickel(II) dibromide was used as a catalyst, no activity for ethylene dimerization was observed in the absence of trifluoroboron etherate. However, it was found with bis(triphenylphosphine)σ-arylnickel(II) bromide that it slowly catalyzes ethylene dimerization even in the absence of trifluoroboron etherate. The rate of ethylene absorption was, for example, 1.8×10^{-2} (m*l* min^{-1}mmol-cat^{-1}) at 0°C under atmospheric pressure, when a methylene chloride solution (30 m*l*) of bis(triphenylphosphine)1-naphthylnickel(II) bromide (1 mmol) was used as a catalyst. Under the same conditions, the rate was surprisingly accelerated up to 44.9 [m*l* min^{-1}mmol-cat^{-1}] by the addition of trifluoroboron etherate (1 mmol), *viz*, the rate is increased to 2.6×10^3 times as much with one mole of trifluoroboron etherate and increases linearly with the mole ratio of trifluoroboron etherate to σ-arylnickel(II) complex as shown in Fig. 1.

We examined sodium tetraphenyl borate in place of trifluoroboron etherate to get information on the interaction between σ-arylnickel(II) compound and trifluoroboron etherate. Sodium tetraphenyl borate is known to take off anionic ligand from dihalide complexes of platinum(II) and nickel(II) giving cationic complexes as follows. $2M(P\phi_3)_2X_2 + 2NaB\phi_4 \rightarrow [M_2(P\phi_3)_4X_2][B\phi_4]_2 + 2NaX$ (M=Pd(II), Pt(II), Ni(II); X=Cl, Br).[11,13] Dried bis(triphenylphosphine)-1-naphthyl nickel(II) bromide (1 mmol) and sodium tetraphenyl borate (2 mmol) were dissolved in methylene chloride (50 m*l*) and the solution was kept at 0°C for 10 hr with stirring. It was filtered to separate the sodium bromide formed and the residual sodium tetraphenyl borate. Ethylene (40 cmHg) was introduced into the filtrate at 0°C and kept at the temperature for 2 hr with vigorous stirring. No dimerization was observed. The solution no longer showed any activity for dimerization in the presence of trifluoroboron etherate.

Isotopic Exchange of C_2H_4–C_2D_4 and Dimerization of C_2D_4. We examined the isotopic exchange of C_2H_4–C_2D_4 to investigate the active species of the catalyst system of σ-arylnickel compound-trifluoroboron etherate. The isotopic distribution (mol fraction) in the residual ethylene is given in Table 2.

TABLE 2. ISOTOPIC EXCHANGE[a] OF C_2H_4–C_2D_4

No		1	2	3
Ni complex[b]	(mmol)	0.01	0.21	0.2
$BF_3 \cdot OEt$	(mmol)	0.01	0.29	0
$C_2H_4+C_2D_4$[c]	(mmol)	2.14	1.05	1.12
Time	(min)	10	10	30
Conv. into C_4'	(%)	0	46.5[d]	0
Isotopic distribution in residual ethylene (%)	d_0	34.3	7.4	43.9
	d_1	8.1	26.4	5.4
	d_2	6.7	36.8	1.1
	d_3	12.7	23.4	9.1
	d_4	38.2	6.0	40.5

a) CH_2Cl_2 10 m*l*, Temp. 0°C.

b) $1\text{-}C_{10}H_7NiBr(P\phi_3)_2$.

c) $C_2H_4/C_2D_4=1.0$ (isotopic distribution of reactant ethylene, $d_0=50$, $d_1=d_2=0$, $d_3=4.0$, $d_4=46.0$).

d) Isomer distribution; 1-C_4', 55.8%; *trans*-2-C_4', 29.9%; *cis*-2-C_4', 14.3%

In Run 2, 46.5% of the ethylene used is dimerized into butenes, where the isomer distribution is far from its equilibrium, whereas the isotopic distribution is in good agreement with the equilibrium distribution ($d_0=6.7$, $d_1=25.9$, $d_2=37.5$, $d_3=24.0$, $d_4=5.9$) in the residual ethylene as well as in the butenes formed. In Run 1 where the catalyst concentration was extremely small and Run 3 where no trifluoroboron etherate was added, only isotopic exchange and no butene was detected. This shows that the isotopic exchange between C_2H_4 and C_2D_4 is sufficiently faster than ethylene dimerization or butene isomerization and that one hydrogen atom undergoes exchange in one act. Thus there should be an active hydrogen atom which catalyzes the exchange reaction.

The source of active hydrogen was examined by means of dimerization using C_2D_4 (atomic fraction of hydrogen (f_H)=0.020). If the active hydrogen is supplied from the substances contained in the catalyst system except for ethylene, hydrogen would be taken up into butene and ethylene, leading to the result that f_H becomes higher than that of the starting ethylene. f_H's of olefins obtained under the various reaction conditions are shown in Table 3, where the amount of C_2D_4 used is approximately fixed. No appreciable increase of f_H is observed, independent of reaction time, the amount of catalyst and that of solvent. This means that no hydrogen is supplied from the solvent, diethylether, triphenylphosphine, or 1-naphthyl ligand present in the catalyst system.

---

[11] H. C. Clark and K. K. Dixon, *J. Amer. Chem. Soc.*, **91**, 596 (1969).

[12] J. Powell and B. L. Shaw, *J. Chem. Soc.*, *A*, **1968**, 774.

[13] P. M. Druce, M. F. Lappert, and P. N. K. Riley, *Chem. Commun.*, **1967**, 486.

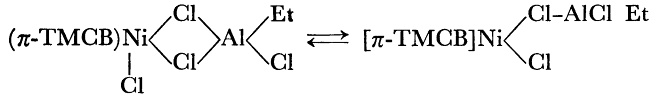
TABLE 3. ATOMIC FRACTION OF HYDROGEN (f_H) IN ETHYLENE OR BUTENES AFTER DIMERIZATION OF C_2D_4[a]

Ni[b] complex (mmol)	$BF_3\cdot OEt_2$ (mmol)	React time	f_H
0.20[c]	0.79	3 hr	0.022[e]
0.20[c]	0.72	10 hr	0.024[e]
0.20[c]	0.72	150 hr	0.023[e]
0.20[d]	0.72	5 min	0.020[f]
1.0[d]	0.72	5 min	0.021[f]
2.0[d]	0.72	5 min	0.020[e,f]
1.0[d]	3.6	5 min	0.020[f]
2.0[d]	7.2	5 min	0.022[f]

a) React. temp., 0°C; C_2D_4=24 m*l* (at STP).
b) (1-naphthyl)NiBr$(P\phi_3)_2$.
c) 20 m*l* of CH_2Cl_2.
d) 30 m*l* of CH_2Cl_2.
e) Calculated from the butenes formed.
f) Calculated from the residual ethylene.

Discussion

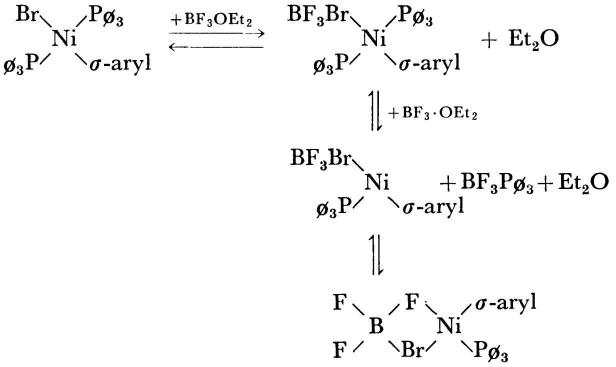
Effect of Trifluoroboron Etherate. It is known that boron trifluoride reacts with $PdCl_2(PR_3)_2$ or $PtCl_2(PR_3)_2$ (R=alkyl, aryl) in organic solvent to give an ionized species such as $[Pd_2Cl_2(P\phi_3)_4]2BF_4$[11-13] or $[(Pt_2Cl_2(P\phi_3)_4]2BF_4$,[11-14] respectively. The corresponding ionized species will be formed from nickel compounds and boron trifluoride. In the case of $Ni(\pi\text{-TMCB})Cl_2\text{-}AlEtCl_2$ (TMCB=tetramethylcyclobutadiene) catalyst, for example, the following equilibrium is usually assumed during the course of olefin dimerization.[5]



$$\rightleftarrows [(\pi\text{-TMCB})NiCl]^+[AlC_3(Et)]^-$$

Similar ionized intermediates have also been suggested for the other nickel halides-ethyl aluminium compounds systems.[3,6] An ionized species, $[Ni(\sigma\text{-aryl})(P\phi_3)_2]^+$ might be formed in the present catalyst system. Thus $Ni(\sigma\text{-aryl})(P\phi_3)_2Br$ was treated with $NaB\phi_4$ for preparation of the species. However, no activity for ethylene dimerization was found even in the presence of trifluoroboron etherate. This indicates that such ionized species which has no halogen ligand is inactive for ethylene dimerization. It might be concluded that the active species should have at least one halogen ligand through which boron trifluoride can interact with nickel atom.

Boron trifluoride has so far been regarded as an acceptor for halide ion. However, it is more probable that it acts as an acceptor for phosphine ligand. It is known that a tertiary phosphine can coordinate to a Lewis acid to give salts such as $AlCl_3\cdot P(Et)_3$ and $AlEtCl_2\cdot P(Et)_3$[5] and that the coordinated tertiary phosphine, such as triethylphosphine of $PdI_2\cdot(PEt_3)_2$, can also be removed by a strong Lewis acid, boron trifluoride,[10] as follows. $2[PdI_2(PEt_3)_2]+2BF_3\rightarrow[Pd_2I_4(PEt_3)_2]+2BF_3\cdot PEt_3$. Thus the addition of triphenylphosphine to the catalyst solution reduces the rate of dimerization, and the activity increases linearly with the mole ratio of $BF_3\cdot OEt_2$ to σ-arylnickel compound as shown in Fig. 1. This suggests that the presence of trifluoroboron etherate is favorable for the dissociation of triphenylphosphine from bis(triphenylphosphine)σ-arylnickel(II) halide to give free coordination site on nickel available for the coordination of ethylene molecule. The role of trifluoroboron etherate can be summarized by the following scheme (Scheme 1).



Scheme 1.

Reaction Scheme. The dimerization of lower olefin by the catalyst composed of nickel(II) complex and alkylaluminum has been explained in terms of a nickel-hydride-complex formed by catalyst components.[4,5] No alkyl aluminum compound, however, is involved in the present catalyst system. There are two points to be clarified; (a) whether a nickel hydride acts as an intermediate, and (b) what substance supplies hydrogen to nickel. The result of isotopic exchange of C_2H_4–C_2D_4 as shown in Table 2 indicates that a nickel hydride has to be taken into account as an intermediate in the course of ethylene dimerization. Neither cyclobutane intermediate accepted in olefin metathesis,[15] nor carbonium ion observed in acid catalysis[7] offers satisfactory explanation for one hydrogen atom being exchanged in one act of the exchange and its rate being exceedingly faster than the isomerization of butenes formed.

The equilibrium values of f_Hs of total olefins in the dimerization of C_2D_4 are calculated by assuming that hydrogen is supplied to nickel from one of the substances involved in the reaction mixture, *i.e.* methylene chloride, triphenylphosphine, diethylether, and 1-naphthyl. They are given in Table 4. It is shown that the f_H value should increase, at lowest to 0.07, .if isotopic scrambling is accomplished between these substances. However, since f_H remains at the starting value 0.02 within experimental error as shown in Table 3, it is clear that hydrogen is supplied to nickel from ethylene molecule.

Two processes can be expected for the formation of nickel hydride from ethylene molecule, one is an inser-

---

[14] H. C. Clark, K. R. Dixon, and W. J. Jacobs, *Chem. Commun.*, **1968**, 93.

[15] N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, and K. W. Scotto, *J. Amer. Chem. Soc.*, **90**, 4133 (1968).

TABLE 4. CALCULATED VALUES[a)] OF f_HS IN OLEFIN ASSUMING THE OCCURENCE OF ISOTOPIC SCRAMBLING OF C_2D_4

Substances supplying hydrogen	f_H
Solvent (CH_2Cl_2)	1
$P\phi_3$	0.40[b)]
$(C_2H_5)_2O$	0.19[c)]
1-naphthyl	0.07[d)]
C_2D_4	0.02[e)]

a) Calculated values, when (1-naphthyl)NiBr$(P\phi_3)_2$ (0.20 mmol), $BF_3 \cdot OEt_2$ (0.8 mmol) and C_2D_4 (1 mmol) are used CH_2Cl_2 solvent.

b) With orthohydrogen atom of phenyl in $P\phi_3$ ligand.

c) With one hydrogen atom per one diethylether molecule.

d) With one hydrogen atom per one naphthyl ligand.

e) f_H of the C_2D_4 used.

tion process in which ethylene is inserted between nickel-carbon bond of 1-naphthyl nickel complex to give Ni–CH_2–CH_2–$C_{10}H_7$, followed by elimination of β-hydrogen to give Ni–H and 1-vinyl naphthalene. However, this seems to be unlikely, because neither vinylnaphthalene nor butenylnaphthalene was detected, and σ-aryl ligand was proved to remain in the nickel complex after ethylene dimerization. The other process is a dissociative addition of ethylene to give H–Ni–CH=CH_2. A similar addition was proposed by one of the authors (A.O.) for the mechanism of ethylene dimerization catalyzed by NiO–SiO_2 catalyst,[1)] or by bis(benzonitrile) palladium(II) dichloride.[16)]

The following course of reaction would account for the rapid hydrogen exchange of ethylene and its dimerization. The dissociative addition of ethylene takes place on the nickel complex shown in scheme 1, and another ethylene then attacks the nickel hydride to form a σ-ethyl-nickel complex reversibly, which is responsible for the rapid hydrogen exchange. 1-Butene may be formed from σ-ethyl-nickel complex by two processes. One is the coupling of ethyl and vinyl attached to the complex. The other is the insertion of another ethylene molecule into ethyl-nickel bond to form primary butyl-nickel complex followed by elimination of β-hydrogen to give 1-butene and nickel hydride. In the former, nickel hydride must be renewed or the next dimerization, while in the latter the hydride is always reproduced the vinyl being kept behind. Discrimination between these two processes is difficult at present.

The variation in activity among σ-aryl nickel compounds supports the view that the σ-aryl ligand is effectively involved in the catalytic species. A combination of steric and inductive factors seems to be responsible for the activity and selectivity for the dimerization. The exact function of the σ-aryl ligands, however, is obscure.

[16)] T. Kitamura, K. Maruya, Y. Moro-oka, and A. Ozaki, This Bulletin, **45**, 1457 (1972).