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Selective Dimerization of Propene to 2,3-Dimethylbutene Catalyzed by a Nickel Complex in Solution

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A selective, catalytic dimerization reaction of propene to 2,3-dimethylbutene-1 was investigated. The catalyst is prepared *in situ* by the reaction of a nickel coordination complex $R_4P\ [(i-C_3H_7)_3PNiCl_3]$ with ethylaluminumsesquichloride in toluene solution. The active species has to be stabilized by the reacting monomer and is thought to involve a coordinated nickel hydride intermediate. Very high rates of dimerization and a selectivity of ca. 68% are achieved under certain reaction conditions.

INTRODUCTION

Recently Wilke *et al.* (*1*) described a homogeneous catalytic system for the selective dimerization of propene to 2,3-dimethylbutene-1 (2,3-DMB). The system is based on a tertiary phosphine coordinated π-allyl nickel halide in conjunction with a Lewis acid such as aluminum trichloride or ethylaluminumdichloride and a chlorinated hydrocarbon, e.g., chlorobenzene, as a preferred solvent. These authors have shown that the selectivity of the dimerization reaction can be directed by the nature of the tertiary phosphine ligand. A triphenylphosphine ligand produces predominantly methylpentenes while the more basic trialkyl phosphines favor the formation of 2,3-DMB in the dimerizate. The latter olefinic product is maximized by the use of basic phosphines such as trisopropyl or tricyclohexylphosphine. The above-mentioned π-allyl nickel halide catalyst component is not readily available, is highly reactive and difficult to handle. Furthermore, the use of the Al_2Cl_6 or even the $R_2Al_2Cl_4$ cocatalyst can readily lead to a competing acid type oligomerization of the reactant or product olefin. Our search for an alternative system centered first on the readily available dihalogenobis(tertiary phosphine) nickel(II) (*1*) which with ethylaluminumsesquichloride in chlorobenzene solvent also gave a very active catalyst system for the selective dimerization of propylene.

$$NiCl_2(PR_3)_2,\ Et_3Al_2Cl_3,\ C_6H_5Cl \qquad (1)$$

$$(R = \text{isopropyl})$$

During the course of the present work, communications related to this system were published in the literature (*2*). Further development led us to the discovery of R_4P $[(\text{isopropyl})_3PNiCl_3]$ as a catalyst component which is, under the proper conditions, an extraordinarily active and selective catalyst system for the dimerization of propene to 2,3-DMB. The results and data obtained with the above nickel complex catalyst for the dimerization of propene near ambient conditions are presented below.

THE CATALYST

The formation of the active catalytic species from the system components (1) occurs via a chemical reaction sequence with its corresponding activation energy parameter. The optimal development of this active species obviously determines the catalytic effectiveness and reproducibility of the system. We found that optimal results are obtained and lengthy induction periods are avoided when the active species is formed at a temperature of 30–35°C (activation temperature) while the actual propene dimerization reaction may be conducted subsequently at a lower temperature level. The activated catalytic species is not stable for an extended period of time in the absence of the reacting olefin. Therefore, a lower reaction temperature of 0° or below is employed to assure a sizable propene concentration in the solvent near atmospheric pressure. Furthermore, we observed that system (1) can be activated more effectively in the chlorohydrocarbon solvent, as compared to toluene, pointing to a participation of this solvent in the formation of the active species. The selectivity of the catalyst component discovered by Wilke is guided by one tertiary phosphine ligand per Ni atom only, while the nickel complex in system (1), e.g., dichloro-bis(triisopropylphosphine) nickel(II), contains 2 phosphine ligands per complex molecule. The removal of one phosphine ligand in the formation of the active and selective catalyst is therefore considered.

In this context it was noted that according to the literature (*3*) the quaternization of a tertiary phosphine with arylhalides can be catalyzed by nickel salts or Lewis acids under certain conditions. Since the system discussed here contains both these components, a quaternization of one phosphine ligand by the chlorohydrocarbon was suggested as a reaction step leading to the active species under these conditions. The less effective activation of system (1) in hydrocarbon solvents (e.g., toluene) therefore must involve a different, yet undefined mechanism.

The use of a previously synthesized quaternary phosphonium derivative of the appropriate Ni complex was therefore indicated, since the introduction of this class of compounds could offer some advantages. These derivatives of nickel are known in the literature (*4*) and can be readily synthesized.

Compound (2) (see experimental section) was evaluated as a catalyst for the selective dimerization of propene in conjunction with $Et_3Al_2Cl_3$. In summary we found that (2) can be activated under identical conditions with $Et_3Al_2Cl_3$ in chlorobenzene solvent to a system of still higher dimerization rates and unchanged selectivity. It can be activated to these rates even at lower temperatures (0° or lower) after a short induction period. These facts indicate a more ready and complete conversion of the available nickel into an active species. As compared to the dihalogeno bis(trialkylphosphine) nickel(II), the quaternized nickel complex can be activated more effectively in aromatic solvents with $Et_3Al_2Cl_3$ to yield a system of high dimerization rates and, again, unchanged selectivity. The rates of dimerization, once the active species is formed, are apparently not much influenced by the solvent polarity.

$$R_3R'P[(R_3P)NiCl_3] \quad (R = \text{isopropyl}, R' = \text{benzyl}) \qquad (2)$$

Independently we have demonstrated that dichloro-bis(tributylphosphine) nickel (II) in the presence of a tenfold excess of tributylphosphine gives rise to the phenyltributyl phosphonium cation under activation conditions, that is chlorobenzene has quaternized the excess trialkylphosphine.

Experimental Methods

A. Materials

Fischer certified grade toluene, distilled from sodium and stored over molecular sieves, was used as solvent. Sun Oil polymerization grade propylene was a reliable source of monomer without further purification. Ethyl aluminumsesquichloride was obtained from Ethyl Corporation.

B. Reaction Procedure

The following reaction procedure is referred to as "standard reaction condition" so that a direct comparison of results can be made. All equipment is oven dried before use. A 250 ml three-necked Morton flask is equipped with a thermometer, a 15-gauge syringe needle introduced through a rubber syringe cap, a gas outlet leading to a manometer and a mercury valve set at 860 Torr. The propylene is fed through the needle below the liquid level of the solution, which can be rapidly agitated with a magnetic stirrer at ~2500 rmp. The flask, which is continuously swept with a slow stream of purified nitrogen via the gas inlet needle, is charged with 50 ml of toluene solvent and the desired amount of the nickel complex catalyst is added as a solid from a small weighing glass (e.g., 0.01 mM or 5.7 mg). The solvent is measured with a graduated dried syringe. The nickel compound is dissolved under gentle warming (~60°) and stirring. A clear blue solution is obtained after 10–12 min. The nitrogen sweep is now changed to propene to displace all the nitrogen and to saturate the solution. The dimerization reaction is initiated by the addition of the desired amount of ethylaluminumsesquichloride, $(C_2H_5)_3Al_2Cl_3$ (e.g., 0.25 mM for an Al/Ni ratio of 50) at room temperature (22–24°) and rapid stirring. A color change from blue to pale yellow occurs immediately. A temperature rise is noted 10–20 sec later. The temperature rises to 35° within 30–40 sec at which time rapid cooling with dry ice–acetone is applied to obtain a reaction temperature of ca. 0°. This procedure requires ca. 2.5 min. The temperature (±¼°) is maintained throughout the reaction by the cooling bath, and the propene feed is continuously adjusted to maintain a total pressure of 860 Torr. The reaction is terminated by addition of 0.5 ml of isopropanol. The product can be analyzed via VPC technique.

C. The Preparation of the Nickel Catalyst Complex

The nickel coordination compound, used in this study as a catalyst component, is synthesized according to:

$$NiCl_2\,(PR_3)_2 + C_6H_5CH_2Cl \rightarrow [R_3PCH_2C_6H_5] \oplus [(R_3P)NiCl_3] \ominus \quad (R = \text{isopropyl})$$

The dichloro-bis(triisopropylphosphine) nickel(II) was prepared according to the literature (*4*). Benzylchloride is chosen as a quaternizing agent because of its availability and reactive chloride. Thirty g of $(NiCl_2(PR_3)_2$ were dissolved in 500 ml of toluene and 5.7 g of benzylchloride were added. The red solution was refluxed for 20 hr under N_2 gas protection to produce a deep blue solution which is slowly cooled; upon filtration 25 g of deep blue crystals are obtained. The crystals are washed with dry toluene and dried *in vacuo*. The yield is 72% based on benzylchloride. The compound appears as two crystalline structures with the following melting characteristics (hot stage under N_2): small birefringent needles: 147.5–148.5°C; large isotropic plates: 161.5–162.5°C; analysis: C, H, Cl—calc: 52.07, 8.56, 18.44%; found: 52.00, 8.68, 18.20%. Solutions of the above compound in toluene are not indefinitely stable. A disproportionation according to:

$$2R_4P[(R_3P)NiCl_3] \rightleftarrows NiCl_2(PR_3)_2 + [R_4P]_2[NiCl_4]$$

occurs slowly within days. Catalyst solutions therefore have to be freshly prepared. The solid compound, however, can be stored under N_2 indefinitely and handled for short times in the air. The above synthesis procedure uses a 30% molar excess of $(NiCl_2(PR_3)_2$ to counteract the disproportionation by mass law effect.

D. Quaternary Phosphonium Cation Identification

Tributylphosphine is quaternized with bromobenzene according to the literature (*3b*). The phenyltributyl phosphonium cation is precipitated from aqueous solution with sodium tetraphenylborate and recrystallized from toluene/alcohol to give $(C_4H_9)_3PC_6H_5\ [B(C_6H_5)_4]$ of mp 223°C. In another experiment 0.1 mM (tributylphosphine)$_2$NiCl$_2$ and 1.5 mM tributylphosphine is activated at room temperature in 50 ml of chlorobenzene with 6 mM $Et_3Al_2Cl_3$. The clear yellow color of the resulting solution lasted for several minutes before darkening occurred.

At this point methanol is added and all the volatiles are removed *in vacuo*. The dry residue is digested with 1 *m* aqueous sodium carbonate solution. The metal hydroxides are filtered off and washed several times with hot distilled water. A white precipitate is obtained from the filtrate after addition of $NaB(C_6H_5)_4$. This precipitate is identical with above compound by

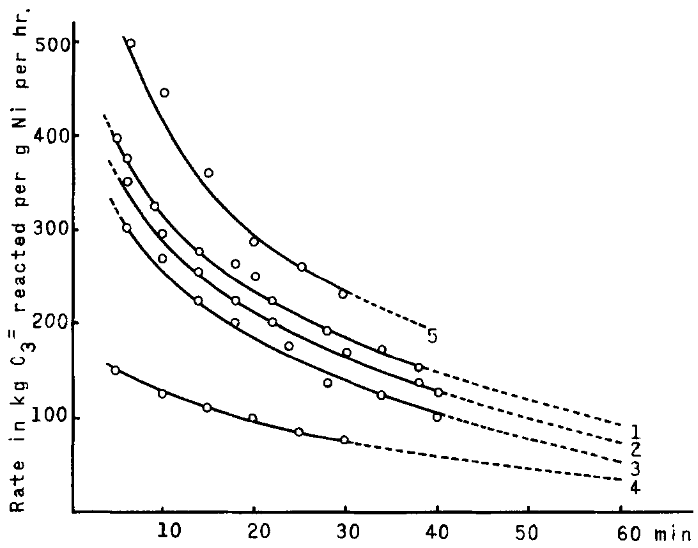


FIG. 1. The rate of propene dimerization with the $R'R_3P$ [(R_3P) $NiCl_3$]/$R_3Al_2Cl_3$ system at 0° and 860 mm Hg pressure and an initial Ni concentration of 2×10^{-4} *m*. (1,2,3,4) represent Al/Ni atomic ratios of 100, 50, 25, 12 in toluene; (5) a ratio of 100 in chlorobenzene.

mp and infrared spectra. The yield was ca. 90% of the theoretical based on the total phosphine present.

REACTION RATE AND YIELD

The compound $R'R_3P$ [$(R_3P)NiCl_3$], (R = isopropyl, R′ = benzyl) was used as a catalyst component under standard reaction conditions in toluene solvent as described in the experimental part. It should be emphasized that in all cases the catalytic species was formed at a higher activation temperature (35°) while the experiment was subsequently conducted at lower temperature of ca. 0°.

This procedure resulted from a detailed experimental study to achieve optimal catalytic activity. However, the percentage of nickel complex (2) converted into the active catalytic species under these condi-

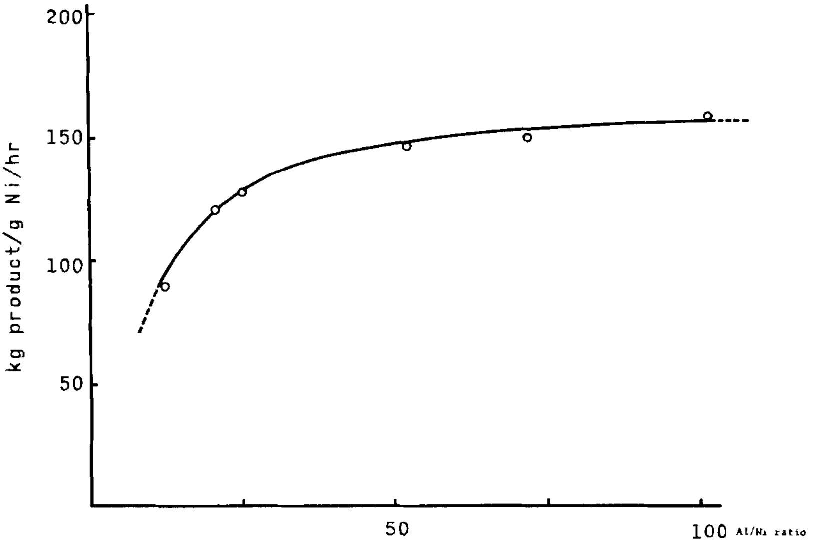


FIG. 2. Hourly product yield per gram of Ni as function of Al/Ni ratio as calculated from Fig. 1.

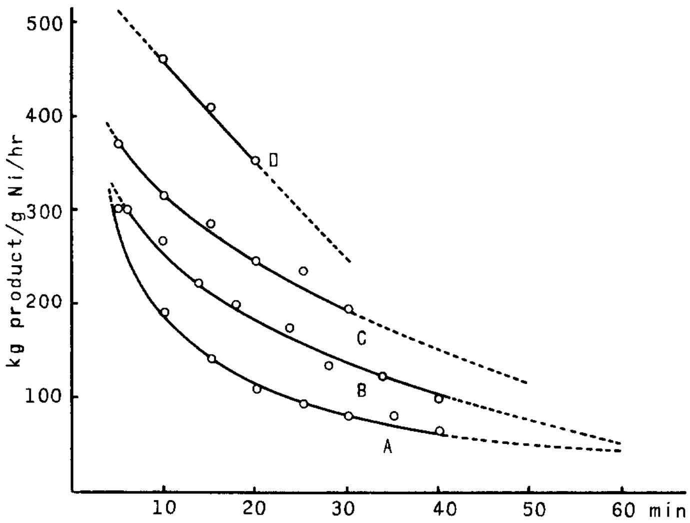


FIG. 3. The rate of propene dimerization as in Fig. 1 at different temperature levels (°C): A, +10; B, 0; C, −10; D, −20. Al/Ni ratio 50, at standard reaction conditions in toluene solvent.

tions is not known. The very high reaction rates of the system necessitate the use of very dilute catalyst solutions to avoid diffusion control. At these dilution levels a high purity of reagents and apparatus is an absolute requirement to obtain reproducible results. A nickel concentration of 2×10^{-4} *m* (0.01 m*M* in 50 ml of toluene) proved to be a reasonable choice under the given experimental conditions. All the data points have been duplicated.

The rate of reaction was followed as a function of time at different Al/Ni ratios as shown in Fig. 1. The propene uptake was measured with a standardized flow meter. The solid line represents the part of the curve actually measured. The rapid initial rate decline reflects primarily the gradual build up of product. This, due to its added vapor pressure (~150 mm), decreases the propene partial pressure in the system and thus its effective concentration in solution. The subsequent more steady decline of the rate suggests a continuous deactivation of the catalyst. The Al/Ni ratio has a pronounced effect on the reaction rate particularly at lower values as shown in Figure 1. The product yield/g of Ni/hr calculated from these and other data as a function of the Al/Ni ratio is shown in Fig. 2. A sharp increase is noted at lower ratios, while at larger ratios (> 25) only small incremental effects are seen. This dependency may reflect the following factors: (i) a stoichiometric requirement, (ii) mass law action, and (iii) losses related to trace solvent impurities. Thus excess of the $R_3Al_2Cl_3$ cocatalyst leads to a more complete formation of the catalyst species by the chemical reactions involved; a plateau value of the reaction rate is reached.

Figure 3 shows the rate of reaction at various temperatures. The higher initial rates at lower temperature reflect the increased propene solubility. The initial decline period is less pronounced in the lower temperature range because of a proportionately decreased vapor pressure contribution of the formed dimer. However, the slope of the subsequent more linear decline of the rate increases and is apparently related to the absolute amount of monomer reacted. The source of this rate decline is most likely trace impurities, introduced with the monomer, which gradually deactivate the catalyst. In this context, Fig. 4 shows the rate of reaction of 0° with polymerization grade propene as a monomer compared with the same propene feedstock distilled from diisobutylaluminum hydride before use. The highly purified monomer gives rise, after vapor pressure adjustments, to a more steady rate of reaction; increased yields are obtained at equal time intervals.

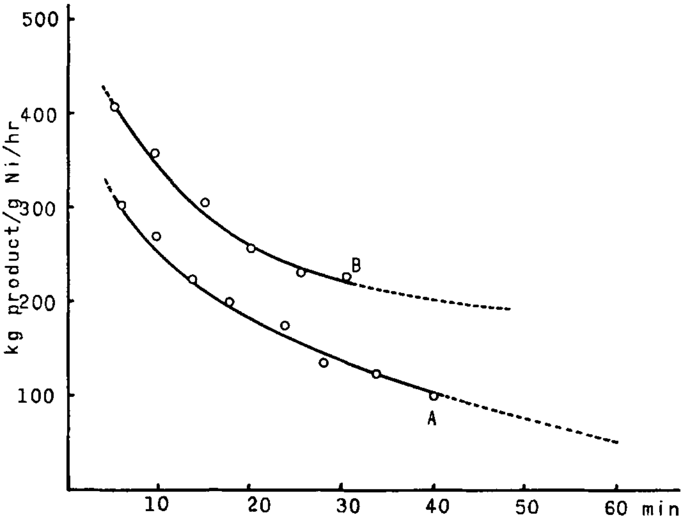


FIG. 4. A, Polymerization grade propene; B, same propene distilled from DIBAL Al/Ni ratio 50; conditions as in Fig. 1.

These results suggest that once the catalytic species is optimally developed, it is thermally stable under the experimental conditions, yet very susceptible to poisoning by trace impurities of undefined nature. These impurities are probably mainly water, which is very effectively removed by the distillation of the reagent from aluminum alkyls. These catalyst poisons apparently react with the activated nickel catalyst site directly, since a large excess of the $R_3Al_2Cl_3$ cocatalyst does not increase product yields above a plateau value (Fig. 2). Also incremental addition of the cocatalyst has no effect on yield or rate once this plateau value is reached.

Figure 5 shows the dependency of the initial dimerization rate (av rate for 12 min after catalyst activation according to the standard procedure) as a function of the initial nickel concentration in toluene solution. The rate is fairly independent of

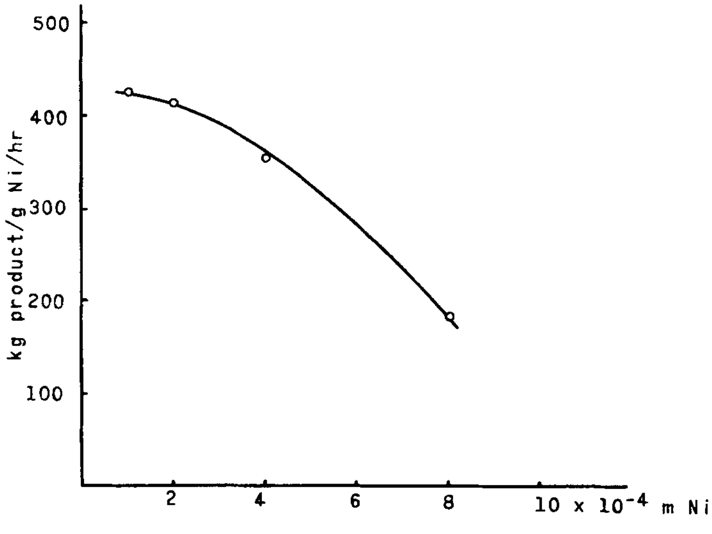


FIG. 5. Initial rate of dimerization under standard reaction conditions as a function of the Ni molarity.

nickel concentrations at dilution levels below 4×10^{-4} *m*. The rate decline at higher concentration levels is attributed to diffusion control by the gas feed into the liquid phase. This diffusion control level is determined by the mechanics of the apparatus. However, the data discussed previously were measured at a dilution (2×10^{-4} *m* Ni initially) where diffusion control can be neglected.

SELECTIVITY

The selectivity of the system with respect to the optimization of 2,3-DMB is dependent on guidance by the basicity of the tertiary phosphine ligand bonded to the nickel atom, as originally found by Wilke (*1*). The nickel compound under investigation containing a triisopropylphosphine ligand, shows a maximum 2,3-DMB selectivity of 65–70% based on the total propylene reacted.

Table 1 shows the composition of the total product obtained under standard reaction conditions at various temperatures and high yield levels. The selectivities represent typical values from many experiments, which show slight deviations individually. The product gradually formed stays in contact with the active catalyst while the relatively lower propene concentration (determined by its partial pressure, i.e., 860 mm Hg minus solvent and product vapor pressure) is maintained throughout the reaction. No major composition change is noted at different yield levels indicating that the deactivating catalyst (Figs. 2 and 3) is not affecting the selectivity. The increasing reaction temperature results in a slight general deterioration of the selectivity (−20 to +20°C). It is particularly noted that the percentage of the C_9 olefins increases at the expense of 4-methylpentene-1. This relationship suggests a secondary codimerization of the product olefin with propene. Because of lower propene concentration at higher temperatures the olefins can compete more successfully at the catalyst site. Other olefins apparently do not compete in this reaction for structural reasons.

Most of the product olefins are the thermodynamically less favored α-olefins indicating the absence of a rapid double-bond isomerization activity under these conditions. The Al/Ni ratio, although having a pronounced effect on reaction rate and yield at low values (see Figs. 3 and 4), has no influence on the catalyst selectivity. Different cocatalysts such as $R_2Al_2Cl_4$ or $R_4Al_2Cl_2$ produce a comparable catalyst with a somewhat decreased activity. Other solvents such as benzene or chlorobenzene also do not produce any major changes in the product composition.

TABLE 1

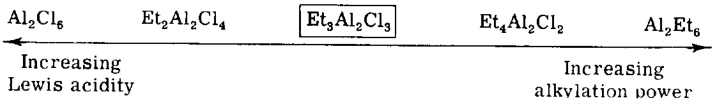
TOTAL PRODUCT COMPOSITION OBTAINED AT VARIOUS TEMPERATURES WITH THE $R_3R'P[(R_3P)NiCl_3]/(C_2H_5)_3Al_2Cl_3$ CATALYST SYSTEM IN TOLUENE SOLVENT UNDER STANDARD REACTION CONDITIONS

(°C):	−20	−10	0	+10	+20
2,3-Dimethylbutene-1	67.5	66.5	65.0	62.5	61.0
-2	0.1	0.1	0.1	0.2	0.3
2-Methylpentene-1	11.3	11.5	11.7	12.6	13.8
4-Methylpentene-1	8.6	6.3	5.0	4.4	4.0
-2	2.5	2.8	3.3	3.0	3.6
Hexene-1 -2	1.8	1.7	1.9	2.4	3.2
C_9 Olefins	8.1	11.0	12.3	14.6	13.1
C_{12} Olefins	0.1	0.1	0.7	0.3	1.0

MECHANISM

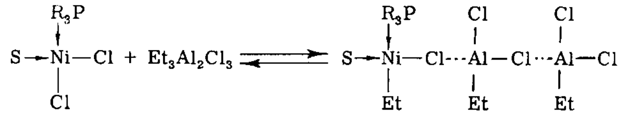
A complete picture of the reaction mechanism cannot be given on the basis of the available information. The high reactivity and lability of the activated catalyst species makes its isolation very difficult. The precipitation of the species with other chemical agents would yield secondary products with a questionable relationship to their origin. However, on the basis of indirect evidence some thoughts can be considered.

The mechanistic connection between the nickel complexes $NiCl_2(PR_3)_2$ and $R_4P[NiCl_3(PR_3)]$ has been discussed above. The activation of the latter complex also necessitates the addition of $Et_3Al_2Cl_3$ which is both a Lewis acid and an alkylating agent. It was found experimentally that in this context ethylaluminumsesquichloride is the most efficient cocatalyst, while Al_2Cl_6 or Al_2Et_6 alone are ineffective. An excess of Al_2Cl_6, of course, catalyzes a Friedel Craft type propylation of the aromatic solvent under these conditions. The cocatalyst of choice therefore combines an optimum balance both of Lewis acidity and alkylation power. The contact of both catalyst components in solution results in an instantaneous reaction as indicated by the color change to yellow, typical for square planar nickel complexes. This reaction most likely consists of an electrophilic attack of the Lewis acid on the nickelate anion, an illustrated by the equation:



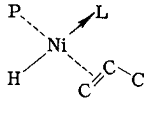
$$R_4P^{\oplus}[NiCl_3(PR_3)]^{\ominus} + Et_3Al_2Cl_3 \longrightarrow R_4P^{\oplus}[Et_3Al_2Cl_4]^{\ominus} + (R_3P)NiCl_2$$

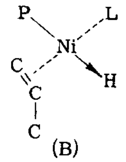
resulting in an acid displacement of the $(R_3P)NiCl_2$ entity. This coordinatively unsaturated, hypothetical species would be stabilized by the olefinic reactant or solvent (S) and simultaneously subjected to a reaction with additional $Et_3Al_2Cl_3$, e.g., resulting in both the alkylation of the Ni and the complexing of the halide with excess Lewis acid.



$$\mathrm{S\rightarrow \overset{R_3P\downarrow}{\underset{Cl}{Ni}}-Cl + Et_3Al_2Cl_3 \rightleftharpoons S\rightarrow \overset{R_3P\downarrow}{\underset{Et}{Ni}}-Cl\cdots\overset{Cl}{\underset{Et}{Al}}-Cl\cdots\overset{Cl}{\underset{Et}{Al}}-Cl}$$

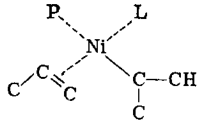
A ready equilibrium between metal alkyl and metal hydride plus coordinated olefin is well known and of key importance in many catalytic olefin reactions (hydrogenation, dimerization, hydroformylation, etc.). The equilibrium leads us to two hypothetical square planar isomer catalyst species (A) and (B) with the olefin and hydrogen ligand in *cis* position.

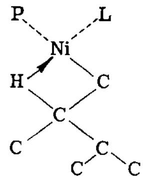

(A)


(B)

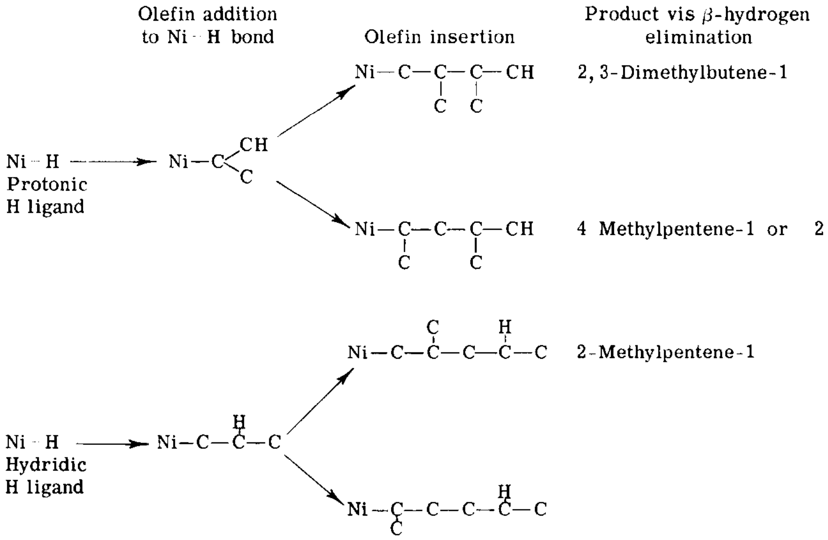
(P = Triisopropyl phosphine; L = Lewis acid complexed halide ligand)

The hydrogen ligand in (A) or (B) is either under the electron withdrawing *trans* effect of L or under the electron donating *trans* effect of P as indicated by arrows. A protonic shift of the hydrogen ligand in A to the coordinated olefin will result in an isopropyl ligand as shown in (C):


(C)


(D)

The coordination of a second olefin molecule is followed by an insertion reaction leading from (C) to (D). The well-known abstraction of a β-hydrogen by the metal



closes the catalytic cycle and releases the product 2,3-DMB-1. The isomer species (B) would lead to the formation of a *n*-propyl ligand via a hydridic shift which after an olefin insertion yields 2-methylpentene-1. The olefin insert reaction can also occur in the reverse sense as illustrated in the scheme shown above. The subsequent β-hydrogen abstraction can occur in 2 ways yielding either 4-methylpentene-1 or -2. All the product components observed can be derived from such a scheme. The total product composition reflects a summation of all the relative selectivities and rates involved. The proposed scheme rationalizes the picture in the context of known organometallic reactions and it accounts for the prime features of the catalyst system: selectivity guidance through the phosphine basicity, Lewis acidity and alkylation power of the cocatalyst. The high rates of reaction in nonpolar solvents make the presence of ionic intermediates unlikely.

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REFERENCES

1. WILKE, G., *et al., Angew. Chem. Intern. Ed. Engl.* **5,** 151 (1966); AND BOGDANOVIC, B., presented: 152nd meeting of the ACS, Sept. 1966, New York; and *Advan. Chem. Ser.* **70,** 250 (1968).
2. (a) EWERS, J., *Angew. Chem. Intern. Ed. Engl.* **5,** 584 (1966); and *Erdoel und Kohle* **21,** 763 (1968); (b) UCHINO, M., CHANVIN, Y., AND LEFEBVRE, G., *Compt. Rend.* **265,** 103 (1967); (c) ONSAGER, O. T., WANG, H., AND BLINDHEIM, U., *Helv. Chim. Acta* **52,** 187-250 (1969).
3. (a) CHATT, J., AND MANN, F. G., *J. Chem. Soc.* **1940,** 1192; (b) HIRUSAWA, Y., OKU, MO, AND YAMAMOTO, K., *Bull. Chem. Soc. Japan* **30,** 667 (1957).
4. GIACOMETTI, G., AND TURCO, A., *J. Inorg. Nucl. Chem.* **15,** 242 (1960).