Mechanistic Studies on the Catalysis of Isomerization of Olefins by $(Ph_3P)_3NiX$

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Abstract: Details of an investigation of the alleged catalysis of olefin isomerization by $(Ph_3P)_3NiX$ are presented; a low concentration of a nickel(II) hydride is responsible for the catalytic activity. The hydride is apparently produced by the reaction 2Ni(I) + olefin ⇌ Ni(II) hydride + Ni(II) allyl. These conclusions are based on several observations including mass spectral analysis of isomerization products of 1-butene-*3,3-d*$_2$ and the similarity of the catalytic and chemical activity of hydrido species produced by reactions of $(Ph_3P)_4Ni$ with HX at −78 °C to that produced from $(Ph_3P)_3NiX$. The hydride produced from $(Ph_3P)_4Ni$ and HCl reacts with 1 equiv of 1,3-butadiene to give $\{(\eta^3\text{-}C_3H_7)Ni(PPh_3)Cl\}$ in good yield and with 0.5 equiv to give Ni(I) and a mixture of butenes.

Introduction

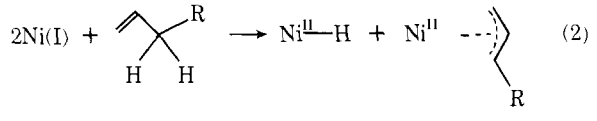
Metal complex catalyzed olefin isomerizations that have been studied thus far proceed by one of two mechanisms. The metal hydride addition–elimination mechanism is most common and has been shown to be operative in catalysis by hydrides such as $HNi[P(OC_2H_5)_3]_4^+$,[2] $HCo(N_2)(PPh_3)_3$,[3] and $HRh(CO)(PPh_3)_3$[4] and in systems where metal hydrides were generated in situ by combination of an inactive metal complex and a cocatalyst. Examples of such systems include $[(C_2H_4)_2RhCl]_2/HCl$,[5] $Co_2(CO)_8/H_2$,[6] and $Ni[Ph_2P(CH_2)_2PPh_2]_2/HCN$.[7] Key features of this mechanism include the effective 1,2-hydrogen shift and the possibility that scrambling of a deuterium label among catalyst, substrate, and, in some cases, protonic solvents can occur. The second mechanism involves oxidative addition of an α C–H bond of the olefinic substrate to the catalytically active species to form an allyl hydride intermediate. Reductive elimination of olefin from this intermediate can then result in isomerization if the hydrogen moves to C_1 instead of returning to C_3 (in the case of a terminal olefin). Characteristic of this mechanism is the requirement that the active species be coordinatively unsaturated and capable of a $2e^-$ oxidation and the fact that a deuterium label will not be lost from substrate in the isomerization process which constitutes a 1,3-hydrogen shift. This mechanism has been convincingly demonstrated in only a limited number of cases. One nickel complex has been shown to undergo intramolecular 1,3 shifts, i.e., (allyl)$Ni(PF_3)H$ ⇌ (propene)$NiPF_3$, but a catalytic cycle was not demonstrated.[8] A recent study has shown that $Fe_3(CO)_{12}$ catalyzes the isomerization of 3-ethyl-1-pentene by this mechanism[9a] and some palladium complexes also appear to catalyze olefin isomerization in this fashion.[9b]

All of the metal-catalyzed olefin isomerizations that have been studied in detail occur by one of the mechanisms outlined above and most catalytic systems may be assumed to operate by one of these mechanisms on the basis of the components of the catalytic mixture. There are, however, a few instances in which a metal complex catalyzed olefin isomerization occurs and it is not obvious that either of the above mechanisms apply. One example is the catalytic activity reported for nickel(I) complexes of the type $(Ph_3P)_nNiX$ reported by Kanai[10] and by Otsuka and co-workers.[11] Kanai reported that solutions prepared according to reaction 1 are active for catalysis of 1-butene isomerization.

$$(Ph_3P)_2NiX_2 + Zn \xrightarrow[\text{THF}]{Ph_3P} \xrightarrow{(Ph_3P)_2NiX_2} \text{active catalyst} \quad (1)$$

The two reactions in this sequence are known to produce nickel(0) and nickel(I) complexes, respectively, so that it is likely that the major part of the nickel was in the univalent form. Such solutions were, in fact, shown to contain paramagnetic species. Additional investigations[10] indicated that an increase in the size of the anion X produced an increase in the cis:trans ratio of the product 2-butene and that addition of stannous chloride increased both the rate and the cis:trans ratio compared to the halo complex alone. Otsuka and coworkers[11] found that toluene solutions of $(Ph_3P)_3NiBr$ were active for the isomerization of 1-hexene to 2-hexene. These observations raised several questions concerning the possible mechanism of the catalyzed reaction. The presence of a metal hydride could not be ruled out on the basis of the evidence available but the source of such a species was not obvious if properly purified materials were used for the experiments described by these researchers. It should be noted that olefin isomerization reported to be catalyzed by a presumed nickel(I) complex, $\{Ni_2[Ph_2P(CH_2)_4PPh_2]_3(CN)_2\}$,[12] is, in fact, due to $[HNi(CN)(Ph_2P(CH_2)_4PPh_2)]$.[7] It also seemed unlikely that Ni(I) would undergo a $2e^-$ oxidative-addition reaction to form an allyl hydride intermediate, which would contain the metal ion formally in the +3 oxidation state. That an alternative mechanism could be operative, perhaps one unique to odd-electron species, was also considered as a possibility.

We present here results that indicate that olefin isomerization by $(Ph_3P)_nNiX$ occurs by a metal hydride pathway (Scheme II) but that the hydride is formed as one product of an unusual reaction involving oxidative addition of an α-CH bond of the olefin to two nickel(I) centers, i.e., eq 2. Kanai has



(2)

also recently concluded that a hydrido species is responsible for the catalytic activity of these systems.[13]

Experimental Section

General. All operations were carried out under a nitrogen atmosphere in oven-dried glassware unless otherwise noted. A Vacuum Atmospheres inert atomsphere box or gas-tight syringes and glassware suitable for maintaining an inert atmosphere were used for handling all reagents.

^1H NMR spectra were recorded on a Varian HA-100 spectrometer operated at 100 MHz with internal Me_4Si as lock. X-Band ESR spectra were obtained on a Varian E9 spectrometer. Mass spectra were obtained on a Varian MAT-CH5 spectrometer at the School of Chemical Sciences, University of Illinois.

A Varian Aerograph Model 2700 gas chromatograph equipped with

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a flame ionization detector was used to monitor olefin concentrations during kinetic runs. A glass 6 ft × 2 mm i.d. column packed with 100/120 mesh Durapack *n*-octane/Porasil C (Waters Associates) was employed for all quantitative olefin separations. This column was operated at ambient temperature, ca. 25 °C, with a N_2 carrier gas flow rate of 20 mL/min, an injector temperature of 150 °C, and a detector temperature of 200 °C. Retention times for the butene isomers under these conditions are: 1-butene, 2.3 min; *trans*-2-butene, 2.9 min; *cis*-2-butene, 3.2 min. Preparative GLC separations were performed on a F & M Model 700 chromatograph equipped with a thermal conductivity detector. Two columns were employed. One was a 3/8 in. × 15 ft copper column packed with 25% 1,2,3-tri(cyanoethoxy)propane (TCEP) on 60/80 mesh Chromosorb P AW. This column was operated at ambient temperature with a N_2 carrier gas flow rate of 100 mL/min and injector and detector temperatures of 100 °C. This TCEP column was used for the removal and collection of butenes (retention time 2 min) from solution. The second column, used only for the separation of the butene isomers, was a 3/8 in. × 22 ft copper column packed with a mixture of glutaronitrile/propylene carbonate (30/70 w/w) on 60/80 mesh Chromosorb P NAW (35% by weight liquid phase). This column, denoted GN/PC hereafter, has been described.[14] It was operated at ambient temperature with a N_2 carrier gas flow rate of 60 mL/min and injector and detector temperatures of 100 °C. Under these conditions, the butene isomers had retention times as follows: 1-butene, 12 min; *trans*-2-butene, 14.5 min; *cis*-2-butene, 16.5 min. Effluents from these columns were collected in a 6 ft × 5 mm glass coil cooled with liquid nitrogen. Both chromatographs were operated with a Houston Instruments variable span recorder equipped with an electronic integrator.

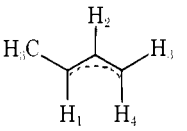
Diethyl ether, medium petroleum ether, and pentane were refluxed over $LiAlH_4$ under a N_2 atmosphere overnight and distilled immediately prior to use. Benzene and tetrahydrofuran (THF) were refluxed over the sodium ketyl of benzophenone under a N_2 atmosphere and distilled. Two further distillations of THF and benzene from the same reagent were performed when these solvents were used in kinetic experiments.

Preparations. Preparations of tetrakis(triphenylphosphine)nickel(0)[15] and dichlorobis(triphenylphosphine)nickel(II)[16] have been described. The nickel(II) complex was recrystallized from *n*-butyl alcohol before use and exhaustively dried in vacuo. Anhydrous tin(II) chloride was prepared by the method of Williams[17] and recrystallized from THF/ether. Triphenylphosphine was recrystallized once from medium petroleum ether. Anhydrous tetraethylammonium trichlorostannate(II) was prepared by the method of Jones[18] and recrystallized from a mixture of THF/ether before use.

Chlorotris(triphenylphosphine)nickel(I).[19] A 6.1-g (5.5 mmol) portion of $(PPh_3)_4Ni$ and 1.0 g of PPh_3 were dissolved in 100 mL of benzene. The red solution was stirred vigorously as 3.3 g (5.0 mmol) of $(PPh_3)_2NiCl_2$ was added. A yellow solid formed after ca. 5 min. The reaction mixture was heated gently until all the solid dissolved. Filtration and cooling gave yellow crystals which were collected and washed on the frit with three 30-mL portions of ether. Drying in vacuo gave 5.3 g (63%) of $(Ph_3P)_3NiCl$. Anal. Calcd for $C_{54}H_{45}ClP_3Ni$: C, 73.61; H, 5.14; Cl, 4.02; Ni, 6.66. Found: C, 73.16; H, 5.37; Cl, 4.03; Ni, 6.52. Samples of $(PPh_3)_3NiCl$ used for kinetic runs were recrystallized from benzene prior to use.

Trichlorostannitotris(triphenylphosphine)nickel(I). A 4.4-g (4 mmol) portion of $(PPh_3)_4Ni$ and 1.0 g of PPh_3 were dissolved in 150 mL of benzene. A 2.6-g (4 mmol) portion of $(PPh_3)_2NiCl_2$ was added with stirring and the solution heated. All of the nickel(II) compound dissolved to give a yellow solution of $(PPh_3)_3NiCl$. This solution was treated with 2.0 g (10 mmol) of $SnCl_2$ and stirred for 10 min. The hot solution was filtered to remove excess $SnCl_2$ and then evaporated to ca. 100 mL on a rotary evaporator. Addition of 100 mL of medium petroleum ether gave an orange solid. Two recrystallizations from 100-mL portions of benzene with 1 g of PPh_3 added gave yellow-orange crystals. These were filtered and washed with three 30-mL portions of ether and dried in vacuo to yield 3.0 g (35%) of $(PPh_3)_3NiSnCl_3$. This material was used in kinetic runs without further purification. Anal. Calcd for $C_{54}H_{45}Cl_3P_3SnNi$: C, 60.50; H, 4.24; Cl, 9.95; Ni, 5.48. Found: C, 60.48; H, 4.29; Cl, 9.99; Ni, 5.59.

Chloro(η^3-1-methylallyl)triphenylphosphinenickel(II). A slurry of 5.0 g (4.5 mmol) of $(PPh_3)_4Ni$ in 50 mL of ether, containing 20 mL of liquid 1,3-butadiene, was treated at −78 °C with 50 mL of ether containing 4.5 mmol of anhydrous HCl. The HCl solution was added dropwise over a period of 1.5 h. The reaction mixture was stirred for an additional 2 h at −78 °C, and then allowed to warm to room temperature. The solvent and excess 1,3-butadiene were evaporated under vacuum and the residue was redissolved in 200 mL of ether. A small amount of gray residue was removed by filtration and the filtrate evaporated to ca. 50 mL. Red-brown crystals formed as the volume was reduced. The slurry was treated with 25 mL of medium petroleum ether and filtered. The solid was washed with two 15-mL portions of medium petroleum ether and dried in vacuo to give 1.2 g (60%) of $(\eta^3\text{-}C_4H_7)Ni(PPh_3)Cl$. Anal. Calcd for $C_{22}H_{22}ClPNi$: C, 64.21; H, 5.39; Cl, 8.62; Ni, 14.26. Found: C, 63.89; H, 5.36; Cl, 8.62; Ni, 14.06. NMR τ(Me_4Si, C_6D_6) *o*-C_6H_5, 2.38, multiplet; *m*, *p*-C_6H_5, 2.97, multiplet;



H_1, 6.28, doublet of quartets, $J_{1,CH_3} = 6$, $J_{1,2} = 13$ Hz; H_2, 5.20, doublet of triplets, $J_{2,3} = 7$, $J_{2,1} = J_{2,4} = 13$ Hz, H_3, 8.08, doublet of doublets, $J_{3,2} = 7$, $J_{3,4} = 2.5$ Hz; CH_3, 8.61, doublet, $J_{CH_3,1} = 6$ Hz; H_4, 8.67, overlapped with CH_3 doublet. The patterns observed for the crotyl group proton resonance (in particular the doublet of triplets observed for H_2) are consistent with the syn isomer shown. This complex has been prepared by an alternative route.[20] The anti isomer was not detected at any time.

Tetraethylammonium Trichlorostannitotris(triphenylphosphine)nickelate(0). A solution of 1.1 g (1.0 mmol) of $(Ph_3P)_4Ni$ and 0.5 g of PPh_3 in 25 mL of THF was treated with 0.36 g (1.0 mmol) of $(C_2H_5)_4NSnCl_3$. The solution color changed from red to orange immediately and the solution was stirred at room temperature for 15 min. The solution was then filtered and evaporated to ca. 10 mL on a rotary evaporator. An orange solid began to form and crystallization was completed by slow addition of 5 mL of ether. The product was collected and washed with three 30-mL portions of ether and dried in vacuo. This procedure gave 1.0 g (84%) of $[(C_2H_5)_4N][(PPh_3)_3NiSnCl_3]$. Anal. Calcd for $C_{62}H_{65}NCl_3P_3SnNi$: C, 62.01; H, 5.46; N, 1.17; Cl, 8.86; Ni, 4.89. Found: C, 62.82; H, 5.79; N, 1.14; Cl, 8.59; Ni, 4.79.

Propanal-2-d_2. A 250-mL pressure bottle was charged with 17.4 g (0.3 mol) of freshly distilled propanal, 2.4 mL (0.03 mol) of dry pyridine, and 50 mL of D_2O. The bottle was then sealed and maintained at 100 °C with stirring for 4 h. After this time, the bottle was cooled and the aldehyde-water azeotrope removed by distillation, bp 47 °C. An NMR spectrum indicated 80% incorporation of deuterium at the α carbon. The exchange was repeated a second time with 37 mL of fresh D_2O and 1.8 mL of pyridine. A final distillation through a 50-cm column packed with 2-mm glass helices gave 8.5 g (47%) of propanal-2-d_2 as a 2% azeotrope with water. This azetrope was dried over 4A molecular sieves before further reaction. NMR τ (Me_4Si, C_6D_6) —CH_3, 8.98, quintet, $J_{H-D} = 1.3$ Hz, 3 H; -C(0)H, 0.25, singlet, 1 H; residual -CH_2-, 7.55. Deuterium incorporation was 97% by integration.

Preparation of Sodium Methylsulfinyl Methylide Stock Solution. Sodium methysulfinyl methylide ($NaMe_2SO$) was prepared according to literature methods[21] as follows. A 500-mL three-necked flask was charged with 12 g of a sodium hydride/mineral oil dispersion (50% NaH by weight). The hydride was washed three times with 100-mL portions of ether to remove the mineral oil, after which it was thoroughly dried in vacuo. Dimethyl sulfoxide (220 mL) was added and the mixture maintained at 60 °C with sitrring for 4 h. Filtration through a coarse frit gave a dark solution which was standardized by titrating 2-mL aliquots dissolved in 25 mL of H_2O with 0.1 M HCl to a bromthymol blue end point. This procedure gave about 250 mL of a 1.0-1.1 M $NaMe_2SO$ solution.

1-Butene-3-d_2. A three-necked 100-mL flask was charged with 25 mL of a 1.065 M $NaMe_2SO/Me_2SO$ solution (0.027 mol of $NaMe_2SO$). Solid Ph_3PCH_3Br (11.9 g, 0.03 mol, 25% excess), prepared by the method of Wittig and Schoellkopf,[22] was added with stirring. The yellow slurry was stirred for 0.5 h. The flask was fitted to a trap with a short length of gum rubber tubing attached to one neck, and a serum cap was placed in the second neck. The trap was purged thoroughly with nitrogen and cooled to −196 °C with liquid nitrogen. A slow purge of N_2 was maintained through the entire system. The flask containing the ylide was then heated to 100 °C, whereupon the yellow solid dissolved, to give a homogeneous solution. To the vigor-

ously stirred solution was injected a solution of 1.6 g (0.027 mol) of propanal-2-d_2 in 15 mL of Me_2SO as quickly as possible without causing excessive frothing of the solution. Typically, 1 or 2 min were required. The olefin was evolved as the aldehyde was introduced. The N_2 purge was continued for ca. 10 min after completion of the aldehyde addition. The product was isolated using standard vacuum line techniques. Distillation from a −95 °C trap (toluene slush) gave 1.3 g (84%) of 1-butene-3-d_2. The product was further purified by preparative GLC on the TCEP column described above: NMR τ (Me_4Si,C_6D_6) $-CH_3$, 9.02, quintet, J_{H-D} = 1.3 Hz, 3 H; $=CH_2$, 5.04, multiplet, 2 H; =CH; 4.14, two doublets of quintets, J_{H-D} = 0.9 Hz, 1 H; residual $-CH_2-$, 7.92; 95% incorporation by integration. Mass spectrum (8.6 eV) 0.5% d_0, 8.8% d_1, 84.5% d_2, 5.9% d_3, 0.4% d_4.

Kinetics. All solutions were prepared by weight in volumetric flasks under a N_2 atmosphere. Solutions of unlabeled 1-butene in THF or benzene were prepared by adding the gaseous olefin, which was purified by passage through activated alumina on a vacuum line, to a tared volumetric flask half-filled with solvent and ca. an equimolar amount of *n*-pentane as internal standard. The flask employed for kinetic runs was either a 10-mL or 25-mL round-bottom single neck, 14/20 flask with a side arm stopcock. The end of the stopcock was fitted with a serum cap through which aliquots could be withdrawn with a syringe. The neck of the flask was fitted with a three-way stopcock, which allowed addition of reactant solutions by syringe under a N_2 purge.

The general procedure for the kinetic runs was as follows. The Ni(I) complex was weighed to 0.1 mg in a tared vial and the contents of the vial were then transferred into the isomerization vessel in the inert atmosphere box. If PPh_3 was used in a run, it was also weighed and added to the flask at this point. A Teflon-coated magnetic stirring bar was added and the three-way stopcock was then put into place. The flask was brought out of the inert atmosphere box and the 1-butene solution added via a 50-mL buret fitted with a stainless steel needle tip which was inserted into the flask. The reaction flask was placed in a thermostated water bath at 25.0 ± 0.2 °C and the stirrer started. A timer was started as soon as the Ni(I) complex had completely dissolved, typically ca. 0.5 min. Samples of the solution, ca. 1 μL, were withdrawn through the side arm at regular intervals with a N_2-flushed 10-μL syringe and immediately injected into the gas chromatograph. Changes in the gas-phase concentration of 1-butene correlated well with those in solution, indicating that catalyst pyrolysis products formed in the chromatograph injection port did not affect the butene isomer ratio.

The 1-butene concentrations were calculated from the expressions

$$[B]_t = (A_B/A_P)_t R$$

$$R = (A_P/A_B)_0[B]_0$$

where $(A_P/A_B)_0$ is the ratio of peak areas for pentane and 1-butene in the starting solution with known 1-butene concentration, $[B]_0$. Similarly, $(A_B/A_P)t$ is the ratio of peak areas at any time during the reaction and $[B]_t$ the corresponding molar concentration of 1-butene.

Isomerization of 1-Butene-d_2. Isomerization reactions involving 1-butene-d_2 were conducted in benzene with $(Ph_3P)_3NiSnCl_3$ as catalyst in the same fashion as regular kinetic runs except that transfer of solvent and olefin to the isomerization vessel was carried out on a vacuum line using standard vacuum techniques and the reactions were stopped by evaporation of the solvent and olefin mixture once the desired degree of conversion was reached. The butenes were isolated from the solvent by preparative GLC on the TCEP column. The isomers were separated on the GN/PC column by injecting several 10-mL samples of the gaseous mixture. Portions of each isomer were transferred, on a vacuum line, to NMR tubes containing degassed 6% (v/v) Me_4Si/benzene-d_6 and their NMR spectra recorded; portions were also utilized for mass spectral analysis as described below.

Mass Spectral Analysis of Labeled Butenes. The olefins were transferred from the GLC collection coil to 25-mL bulbs on a vacuum line and submitted for mass spectral analysis. Samples of each of the unlabeled butenes were run under the same conditions as standards. All samples were run at 8.6 eV. Higher ionization potentials result in fragmentation of the sample, giving peaks at M − 1, M − 2, and M − 3, which correspond to the loss of hydrogen atoms from the parent ion, M. Such fragmentation makes the analysis of a mixture of deuterated molecules impossible. At 8.6 eV, however, only the M and M + 1 (due to ^{13}C) peaks were present in the m/e range of 52–62 for the standard unlabeled butenes. The height of the M + 1 peak was calculated as a percentage of the M peak by averaging the results from three slow-scan mass spectrometer oscillograph traces. The values obtained (1-butene, 5.07; *cis*-2-butene, 4.97; *trans*-2-butene, 5.05) were used to correct the peak heights in the labeled butene spectra for M + 1 contributions from the next lower m/e peak, i.e.,

$$(M + n)_{cor} = (M + n)_{obsd} - X(M + n - 1)_{cor};\ n = 0, 1, 2, \ldots$$

where X is the fractional percentage of M + 1 formation corresponding to the butene isomer under analysis. This correction was applied consecutively starting with the peak at lowest m/e. Once the corrected peak heights were calculated, the percent composition of the mixture was calculated by

$$\%\, d_n = I_n/I_t \times 100\%$$

where I_n is the corrected peak height for a molecule with n deuteriums and I_t is the sum of all corrected peak heights. This method of analysis was carried out on three separate slow scan mass spectrometer oscillograph traces for each sample and the results averaged. The values of % d_n were in agreement within ±0.1% for the three scans.

Reactions of Ni(0)/Cocatalyst Systems. The general procedure for generating the hydrides was to treat a THF or toluene solution of $(PPh_3)_4Ni$ at −78 °C with 1 equiv of a solution of anhydrous HCl or $HSnCl_3$–(HCl + $SnCl_2$) in THF or toluene (toluene-d_8 for NMR studies). For NMR studies, 1 equiv of gaseous HCl or a toluene solution of HCl or $HSnCl_3$ was added at −78 °C and the spectrum then recorded at −60 °C. A similar investigation was conducted with $[Et_4N][(PPh_3)_3NiSnCl_3]/CF_3COOH$.

Isomerization reactions with 1-butene were carried out by adding 1-butene solutions to the hydride generated at −78 °C as outlined above. The solution was then allowed to warm to room temperature and the concentration of 1-butene followed by GLC.

Reactions of the Ni(0)/acid systems with 1,3-butadiene were carried out in a fashion similar to that of the isomerization reactions. The production of butenes by the stoichiometric reaction of 0.5 equiv of 1,3-butadiene with 1 equiv of nickel hydride, prepared from $(PPh_3)_4Ni(0)$/HCl or $HSnCl_3$, was observed in two ways. A solution of the hydride (either by HCl or $HSnCl_3$) was treated with 0.5 equiv (based on the amount of $(PPh_3)_4Ni$ used) of a 1,3-butadiene solution at −78 °C and allowed to warm to room temperature. GLC of the solution indicated that a mixture of C_4 hydrocarbons was formed. Stripping the volatile material from this solution and analyzing it by GLC gave the same distribution of hydrocarbons and indicated that pyrolysis in the chromatograph injection port did not generate the mixture. The formation of butenes was also observed when a solution of the π-crotyl complex was treated with 1 equiv of nickel hydride. In these experiments, the π-crotyl complex was generated in situ by treating a sample of the hydride with an excess of 1,3-butadiene at −78 °C. When the solution was allowed to warm to room temperature a brown solution of the π-crotyl complex formed. The solution was partially evaporated to remove excess 1,3-butadiene and then cooled to −78 °C. One equivalent of the hydride solution was added and the solution again warmed to room temperature. GLC analysis showed that a mixture of C_4 hydrocarbons was formed similar to that obtained by the first method.

Detection of Hydrocarbon-Containing Metal Products in Ni(I)-Catalyzed Isomerizations. A 0.2-g sample of $(PPh_3)_3NiSnCl_3$ was dissolved in a minimum of THF and gaseous 1-butene was introduced until the complex began to crystallize. A minimum amount of THF was then added until the complex redissolved. The reaction mixture was allowed to stand overnight. The solvent and olefin were then evaporated and the dark residue was placed under a dynamic vacuum for ca. 2 h. Recrystallization of the residue from warm benzene gave some nickel metal and ca. 0.15 g of $(PPh_3)_3NiSnCl_3$. The filtrate from the recrystallization was evaporated on a rotary evaporator and the brown residue pumped on at 10^{-5} Torr overnight. The residue was dissolved in ca. 0.25 mL of THF and 1-μL samples of the resulting brown solution were pyrolyzed in the gas chromatograph injection port at 200 °C. A mixture of C_4 olefins was evolved which was similar to that obtained under the same conditions with an authentic sample of $(\eta^3\text{-}C_4H_7)Ni(PPh_3)Cl$. A similar experiment conducted with $(PPh_3)_3NiCl$ and 1-butene gave the same results.

Table I. Mass Spectral Analyses of Deuterated Butenes

Isomer	% conversion	% composition d_0	d_1	d_2	d_3	d_4	d_5	d_6	Deuterium no.[b]
1-	0	0.5	8.8	84.5	5.9	0.4			1.97
	7.9	0.4	8.0	79.7	11.1	0.7			2.04
	47.4	0.6	5.9	50.4	36.8	5.8	0.4		2.44
	Complete	10.6	26.5	31.5	20.5	8.4	2.3	0.4	1.99
cis-2-	47.4	3.1	55.6	32.1	8.1	1.1	0.1		1.49
	Complete	10.8	26.7	30.1	20.5	8.9	2.5	0.5	2.00
trans-2-	47.4	3.5	53.3	32.7	8.9	1.5			1.51
	Complete	10.2	27.4	30.7	20.2	8.4	2.4	0.4	1.97
Statistical distribution (calcd)[a]		10.4	27.7	31.1	20.3	8.3	2.2	0.4	

[a] $\%d_n = [8!/(8-n)!n!]P_D{}^n(1-P_D)^{8-n} \times 100$; $P_D = 0.246$. [b] Deuterium no. $= \Sigma_n (n \times \% d_n)/100$.

Results

Preliminary Investigations. Our initial approach was to verify Kanai's conclusion and Otsuka's observation that triphenylphosphine-nickel(I) complexes catalyze or serve as catalyst precursors for the isomerization of olefins. Preformed and purified $(Ph_3P)_3NiCl$ and $(Ph_3P)_3NiSnCl_3$ were utilized for these studies. The latter complex, which has not been previously reported, was prepared by reaction of the chloro complex with $SnCl_2$. Survey experiments indicated that solutions of the chloro complex catalyzed the isomerization of 1-butene and that the cis/trans product ratio was about 2 until nearly all of the 1-butene was consumed. Prolonged reaction times (24 h) resulted in an equilibrium mixture of butenes. Initially these experiments were conducted in highly purified THF but were later done in benzene as well. Isomerization rates were greater in benzene but there was no change in the product distribution. A noticeable darkening of solutions in both solvents occurred after about 2 h and they often became heterogeneous after a few hours with reduction in the rate of isomerization.

Since $(Ph_3P)_3NiCl$ is prepared by a comproportionation reaction between $(Ph_3P)_4Ni$ and $(Ph_3P)_2NiCl_2$ the possibility existed that either of these complexes might be formed by the reverse reaction and that one might serve as the catalyst or its precursor. Control experiments indicated that the nickel(II) complex was totally inactive and that the zerovalent complex catalyzed isomerization at a rate that was much slower than the nickel(I) system ($t_{1/2} \sim 1$ week under similar conditions).

Experiments with $(Ph_3P)_3NiSnCl_3$ indicate that it catalyzes 1-butene isomerization at a rate nearly 15 times that of the chloro complex and that the cis:trans product ratio is about 30. These results are in agreement with the observations of Kanai. Isomerizations of 1-pentene, 1-hexene, 3-methyl-1-butene, and 1,5-cyclooctadiene are all catalyzed by this complex. Solutions in both THF and benzene did not change color or precipitate solids for several hours. In no cases involving either the chloro or trichlorostannite complex as catalyst was oligomerization of the olefin detected.

Our initial intent was to perform a complete study of the kinetics of the isomerization reaction of 1-butene using both the chloro and trichlorostannite complexes as catalysts. Our initial studies with the chloro complex, however, showed that the rate of decomposition of the catalyst was too high to make careful rate measurements over more than 1 half-life; however, the disappearance of 1-butene was consistently zero order in the early stages of the reaction. Typical rate constants for the zero-order disappearance of 1-butene follow. $(PPh_3)_3niCl$, 5×10^{-2} M in THF; 5×10^{-4} mol L^{-1} min^{-1}; $(PPh_3)_3NiSnCl_3$, 5×10^{-2} M in THF; 7×10^{-3} mol L^{-1} min^{-1}. There was no detectable difference in the electronic spectrum of the nickel(I) complex in the presence and absence of 1-butene. This indicates, in agreement with other information, that the concentrations of other species involved in the catalytic process are very low. The $SnCl_3$ complex appeared more promising since equilibration of butene isomers could be achieved without a visually detectable change in the reaction mixture. Unfortunately, despite repeated attempts using highly purified chemicals and maximum precautions in the preparation and handling of samples, completely reproducible results could not be obtained. However, the results of these studies do indicate certain trends which any proposed mechanism must obey. These are summarized below.

Table II. ^1H NMR Analysis of the Deuterated Butenes

% conversion	1-Butene Integrals (CH_3 = 3.00) CH_3	$-CH_2-$	$=CH_2$	$=CH$
0	3.00	0.072	1.98	1.03
7.9	3.00	0.073	1.92	0.93
47.4	3.00	0.117	1.89	0.63

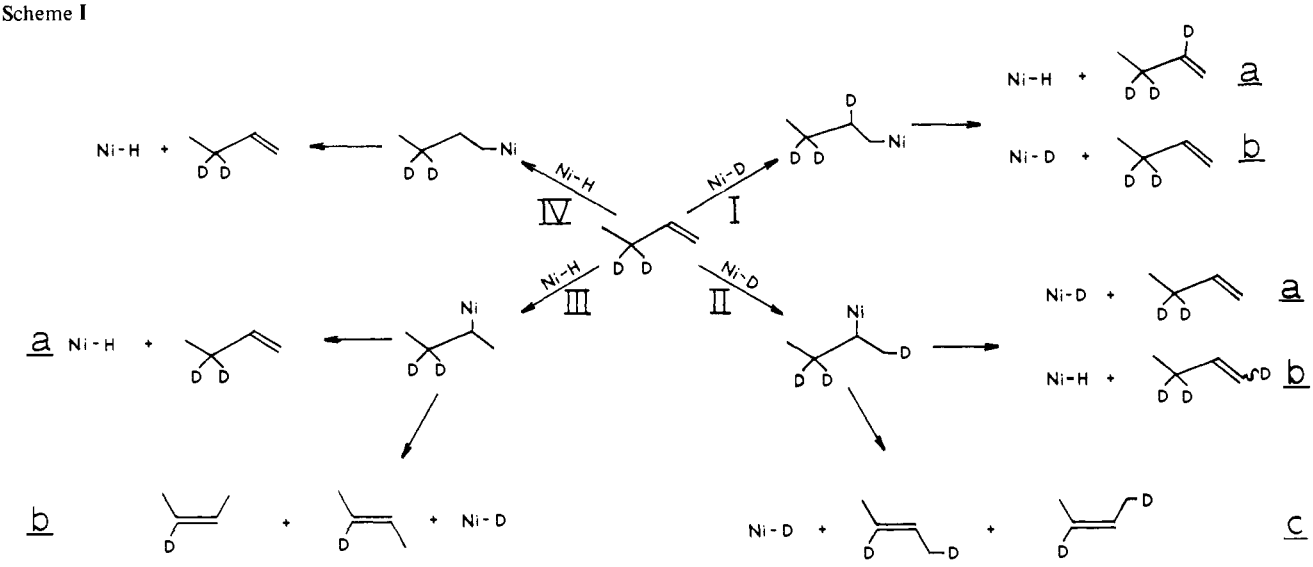
Isomer	Product Integral Ratios % conversion	$CH_3/=CH$
cis-2-Butene	47.4	6.93
	Complete	3.00
trans-2-Butene	Complete	3.30

The zero-order dependence on 1-butene mentioned above was observed over a 1-butene concentration range of 0.5–0.025 M with 1-butene: $(PPh_3)_3NiSnCl_3$ ratios of 10 to less than 1. Plots of the concentration of 1-butene vs. time were linear in all cases and remained so over at least 3 half-lives regardless of the specific rate of the reaction which varied by as much as 50% in some cases for duplicate reactions. Induction periods were not observed, although close examination of the first 10 min of a given run was not possible by the GLC technique. The order with respect to $(PPh_3)_3NiSnCl_3$ varied among runs but was always in the range of 1.8–3.3. There appeared to be an inverse dependence on added PPh_3, but this was not examined in detail. Rates of isomerization were at least four times faster in benzene than in THF.

In addition to the kinetic studies, a series of chemical studies were also conducted. These shed considerable light on the nature and method of formation of the catalytic species and provide some evidence on the mechanism of the isomerization reaction. These results are described in subsequent sections.

Isomerization of 1-Butene-*3-d*$_2$. Products of the catalyzed isomerization of 1-butene-*3-d*$_2$, by both the chloro and trichlorostannite complexes, showed deuterium migrations and distributions at various stages of the isomerization reaction that are only consistent with the action of a metal hydride as the catalytically active species. Mass spectral and NMR analyses of the products of the $(Ph_3P)_3NiSnCl_3$-catalyzed isomerization of 1-butene-*3-d*$_2$ at 7.9 and 47.4% conversion and at equilibrium, which are given in Tables I and II, justify this conclusion.

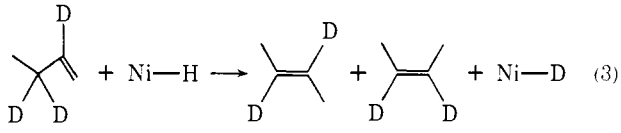
Scheme I



Examination of the mass spectral data indicates that intermolecular deuterium exchange has occurred. Deuterium numbers (given in the last column of Table I), which indicate the average number of deuterium atoms per molecule, are a convenient aid in illustrating the intermolecular transfer of deuterium among molecules. These data show that the amount of deuterium increases in the unisomerized 1-butene at the expense of the product 2-butenes in the early stages of reaction. At equilibrium, however, there is an equal distribution of deuterium among all molecules. No significant amount of deuterium is lost from the olefins since the initial and final deuterium numbers are the same. At complete conversion there is both an equal distribution of deuterium among isomers and a statistical distribution of deuterium within each isomer. The latter is evident by comparison of the observed final distributions with that calculated using the theoretical expression. That a statistical distribution of deuterium is present in the olefins can also be shown on the basis of the ^{1}H NMR integrals. A statistical distribution of two deuterium atoms in either *cis*- or *trans*-2-butene would result in a $CH_3/{=}CH$ integral ratio of 3.0. As can be seen from Table II, reasonable agreement is observed. The 1-butene sample was too dilute for accurate integration, but resonances were observed for each type of proton in the molecule.

Closer examination of the data of Tables I and II allows deduction of additional details of the processes which lead to the extensive intermolecular exchange of deuerium. The results in the early stages of isomerization are readily accounted for by consideration of the results of all of the ways that a nickel hydride or deuteride can interact with the labeled 1-butene. These are illustrated in Scheme I. Of prime importance in the early stages of reaction are pathways I and III. As shown in pathway III every isomerization involving a nickel hydride will result in the formation of Ni–D and d_1 product. This assumes that the initial isomerization is followed by rapid decomplexation of the olefin. Reversal along IIIb could lead to d_2 products. The extent to which this occurs cannot be ascertained with certainty but it appears to be low. The retention of well-defined methyl-d_2 coupling in the NMR spectrum of recovered 1-butene (vide infra) at low conversion indicates that multiple processes do not involve the terminal olefin. In the early stages of the reaction where 1-butene-*3*-d_2 is the major component, nickel deuteride will be converted to nickel hydride by the degenerate reaction Ia which produces 1-butene-d_3. It should be noted that the third deuterium is introduced at C-2 by this process and that this is substantiated by the NMR results. The rate along path I is expected to be several times faster than that along path II, thus ensuring that path II is of relatively little importance in the early stages of the isomerization process. Path IV is of no significance as it does not affect the isotope distribution. This scheme predicts that at substantial levels of conversion unisomerized 1-butene should consist predominately of *3*-d_2 and *2,3,3*-d_3 species. If these are assumed to be the d_2 and d_3 molecules indicated by the mass spectral analysis at 47.4% conversion the $={CH}/CH_3$ integral should be 0.6. The observed value of 0.63 is in good agreement with this value. Consistent with this interpretation is the appearance of the methyl resonance which shows well-defined coupling to two α-deuterium atoms.

The products at 47.4% conversion are mostly d_1 and d_2 materials. As indicated by the above discussion, the d_1 material is probably *cis*- and *trans*-2-butene-*2*-d_1. The d_2 molecules can arise in two ways (in addition to the reversal of IIIb). As the isomerization proceeds, increasing amounts of 1-butene-*2,3,3*-d_3 will be present and will undergo isomerization to yield *cis*- and *trans*-2-butene-*2,3*-d_2, i.e.,



(3)

Also, the increasing amount of 1-butene-*2,3,3*-d_3 will effectively increase the lifetime of the Ni–D species, thus increasing the probability that it will serve as catalyst to produce *cis*- and *trans*-2-butene-*1,3*-d_2, as shown by path IIc of Scheme I, and interact in a similar fashion with the lesser amounts of other d_n species. The NMR integral ratio of the *cis*-2-butene formed at 47.4% conversion can be approximated if it is assumed that the d_1 material is *cis*-2-butene-*2*-d_1 and the d_2 material is a mixture of equal amounts of *cis*-2-butene-*2,3*-d_2 and *cis*-2-butene-*1,3*-d_2. Such a mixture will display a $CH_3/{=}CH$ integral ratio of 7.1, which is in good agreement with the observed ratio of 6.9.

All of the above processes seem to be occurring at significant levels prior to the first half-life of 1-butene-*3*-d_2. Thus it is easy to see how continual addition of Ni–D and Ni–H gives rise to statistical deuterium distributions after prolonged contact with the catalyst solution.

A significant piece of chemical evidence was discovered during the labeled 1-butene experiments. Traces of butane, about 0.1%, were formed during isomerization. This was not noted during the kinetic studies since the 1-butene employed contained 0.5% butane and a small increase in its GLC peak was not detected so readily. The formation of butane can also

be accounted for by a metal hydride mechanism and is considered below.

Chemical Evidence for a Nickel Hydride Mechanism. The results of the labeled butene studies strongly indicate that a nickel hydride is responsible for isomerization in the Ni(I) systems but provide no evidence regarding its composition or method of formation. This section outlines the results of several experiments designed to define the nature of the catalytically active species and the process(es) by which it is formed from the Ni(I) precursor. The general thrust of these experiments was to generate nickel hydrides by known processes and compare their chemical properties and behavior as isomerization catalysts to those of the Ni(I) systems.

A variety of Ni(II) hydrides have been formed by the protonation of phosphine or phosphite nickel(0) complexes; in several cases the hydride complexes can be isolated.[7,23] The products have generally been of the type $[L_4NiH]Y$, where Y is a weakly coordinating anion, or L_2NiHX or L_3NiHX, where X is a ligating anion. Each type of complex has been shown to function as an isomerization catalyst for olefins. Catalysis of olefin isomerization by $\{HNi[P(OC_2H_5)_3]_4\}^+$ has been studied in detail and is one of the most completely understood examples of a hydride catalyzed process.[2] It seemed possible that a neutral hydride with L = PPh_3 and X = Cl or $SnCl_3$ might be generated in the Ni(I)-catalyzed isomerization reactions, although the formation of such a species for chemical studies was in doubt since it had been reported[24] that the addition of strong acids to solutions containing $(PPh_3)_4Ni$ yielded hydrogen and Ni(II) salts. However, the strong implication of the presence of a hydride that was obtained from the experiments with labeled butene prompted a reinvestigation of the $(PPh_3)_4Ni$/acid system.

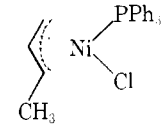
Treatment of a THF solution of $(PPh_3)_4Ni$ with dilute (0.1-0.5 M) solutions of anhydrous HCl, $HSnCl_3$(HCl + $SnCl_2$), or H_2SO_4 at −78 °C gave bright red solutions which decomposed rapidly with gas evolution when warmed to room temperature. An NMR investigation of the $(PPh_3)_4Ni$/HCl reaction product in toluene-d_8 at −60 °C revealed a broad, featureless resonance at τ 39.4 which disappeared irreversibly on warming the sample. This high-field line suggested that a nickel hydride was present, but the absence of phosphorus coupling prevented any determination of structure. The sample became paramagnetic at room temperature and displayed a single, strong ESR line at g = 2.975, characteristic of $(PPh_3)_3NiCl$. This suggests that the hydride decomposes by homolysis of the Ni-H bond:

$$2HNi(PPh_3)_nCl \rightarrow H_2 + 2(PPh_3)_nNiCl \qquad (4)$$

Similar NMR experiments with $HSnCl_3$ were not performed since this acid could not be isolated in pure form. An alternate route to a nickel hydride derived from $HSnCl_3$ would be protonation of the Ni(0) anion, $[(PPh_3)_3NiSnCl_3]^-$. A complex of this type was readily prepared by treatment of $(PPh_3)_4Ni$ with $[Et_4N][SnCl_3]$. Protonation of this species was carried out at −78 °C in toluene-d_8 by addition of CF_3CO_2H. The sparingly soluble complex dissolved slowly, giving an orange-red solution with precipitation of a colorless oil, probably $[Et_4N][CF_3COO]$. Gas evolution was not observed; however, no hydride resonance could be detected in the NMR spectrum obtained on such a solution. The sample evolved hydrogen and became paramagnetic on warming, and exhibited an ESR signal typical of $(PPh_3)_3NiSnCl_3$. The overall evidence indicates that a hydride formed.

Olefins are rapidly isomerized by solutions of the nickel hydrides generated from $(PPh_3)_4Ni$/HCl, H_2SO_4, or $HSnCl_3$. The rate of isomerization at −78 °C could not be determined by GLC since the small sample required (1 μL) was rapidly warmed to near room temperature in the sampling syringe. At room temperature the isomerization was too fast to follow at initial hydride concentrations of ca. 0.03 M in THF. Isomerization stopped after ca. 15 min when solutions were allowed to stand at room temperature. However, this was a sufficient amount of time for a mixture of butenes to approach equilibrium. Addition of more 1-butene at this point did not result in further isomerization. The cis/trans product ratios measured near the first half-life of 1-butene for the Ni(0)/HCl and Ni(0)/$HSnCl_3$ systems were lower than those observed for $(PPh_3)_3NiSnCl_3$. Significant amounts of butane were formed in both Ni(0)/HX systems, amounting to around 1.5% of the C_4 mixture near equilibrium. The formation of butane was also observed with $(PPh_3)_3NiSnCl_3$ during the labeled olefin experiments, vide supra, and probably is the result of reaction between nickel hydride and nickel alkyl moieties.

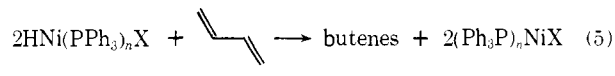
The isomerization catalysts derived from the Ni(0)/HX systems are extremely sensitive to poisoning by 1,3-butadiene. Addition of 1 equiv of diene per nickel hydride at −78 °C in the presence of 1-butene followed by warming of the mixture to room temperature resulted in less than 5% isomerization. The reaction of nickel hydrides with dienes to yield η^3-allyl complexes is well documented.[25] In fact, the reaction of butadiene with the product of $(Ph_3P)_4Ni$ and HCl at −78 °C is a better synthetic procedure for the preparation of the crotyl



complex than the previously reported method.[20] This method should be applicable to a variety of substituted dienes and may provide access to a variety of new allylic complexes.

Catalysis of isomerization of 1-butene by $(PPh_3)_3NiSnCl_3$ is also strongly affected by the addition of 1,3-butadiene. Figure 1A illustrates the poisoning effect of 0.01 equiv of 1,3-butadiene per equiv of $(PPh_3)_3NiSnCl_3$ in a typical isomerization experiment in THF. As can be seen, this addition effectively halts isomerization. An important implication of this experiment is that the concentration of the hydride moiety in the Ni(I) isomerization mixture is at least two orders of magnitude more dilute than the Ni(I) complex, i.e., $<5 \times 10^{-4}$ M. Figures 1B and 1C illustrate the effect of added butadiene on isomerizations conducted in benzene. A 50:1 nickel:butadiene mole ratio results in almost complete inhibition for a 0.008 M $(PPh_3)_3NiSnCl_3$ solution in benzene. A ratio of 100:1, however, causes a significant inhibition which eventually is overcome with an increase in the rate of isomerization. The rate approaches that of an isomerization reaction run under the same initial conditions without addition of 1,3-butadiene (Figure 1D). A reasonable conclusion is that the concentration of the catalytically active species (nickel hydride) is maintained by an equilibrium process and it is likely that it is the same process by which it was originally formed.

Evidence for the possible nature of this process was obtained in two ways. When 0.5 equiv of 1,3-butadiene per equiv of Ni was added to a solution containing the nickel hydride generated from $(PPh_3)_4Ni$/HCl or $HSnCl_3$, reaction 5 occurred. The



mixture of butenes formed was detected by sampling the gas phase over the reaction mixture and by sampling the liquid phase after removal in vacuo. The Ni(I) complex was detected by its ESR spectrum. The hydrogenation of 1,3-butadiene to butenes probably occurs via attack of the nickel hydride moiety on the π-crotyl complex (eq 6). This process has been postulated[26] to account for the catalytic hydrogenation of 1,3-butadiene to butenes by $Co(CN)_5^{3-}/H_2$. If this reaction is re-

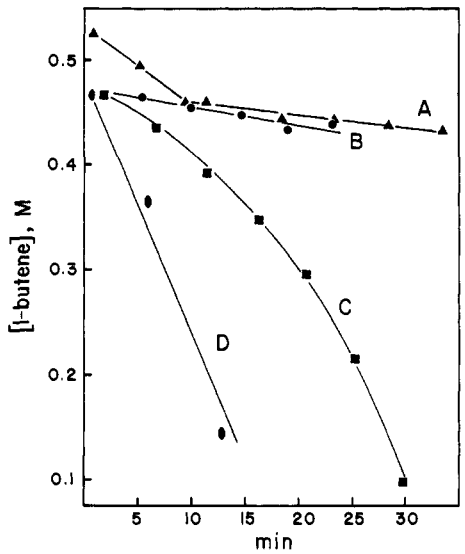
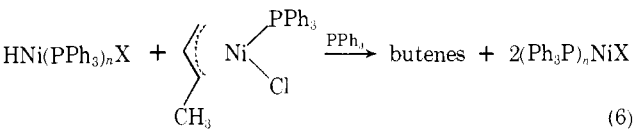


Figure 1. Effect of 1,3-butadiene on the $(Ph_3P)_3NiSnCl_3$-catalyzed isomerization of 1-butene: A, THF, 0.05 M catalyst, 1,3-butadiene added at t = 10 min, [butadiene] = 5×10^{-4} M; B, benzene, 8×10^{-3} M catalyst, 1.6×10^{-4} M 1,3-butadiene; C, benzene, 8×10^{-3} M catalyst, 8×10^{-5} M 1,3-butadiene; D, benzene, 8×10^{-3} M catalyst, no 1,3-butadiene added.



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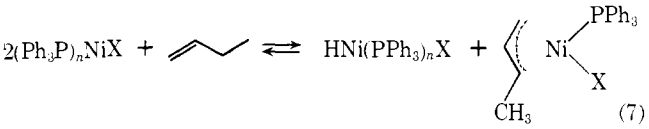
versible, then the equilibrium of eq 7 may be responsible for



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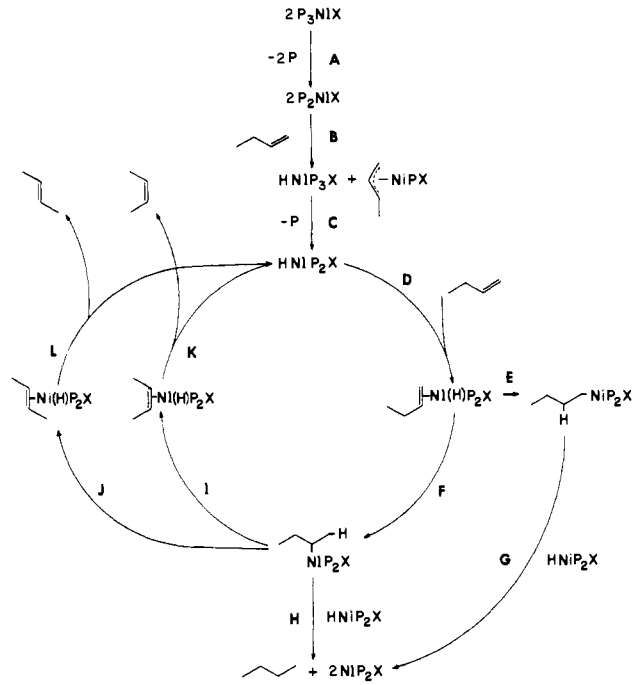
the formation of the nickel hydride in Ni(I) isomerization systems. The equilibrium constant is apparently quite small in the direction that the reaction is written in view of the hydrogenation of 1,3-butadiene mentioned above and the results of the catalysis poisoning experiments described earlier. Evidence for the presence of π-crotyl complex in catalyst recovered from an isomerization reaction was obtained by comparison of the gaseous pyrolysis products of the recovered complexes with those of authentic $[(\eta^3\text{-}C_4H_7)Ni(PPh_3)Cl]$. Nearly identical mixtures of C_4 hydrocarbons were obtained. This indicates that a π-crotyl complex is formed during the isomerization; the most likely source of this complex is the equilibrium shown above.

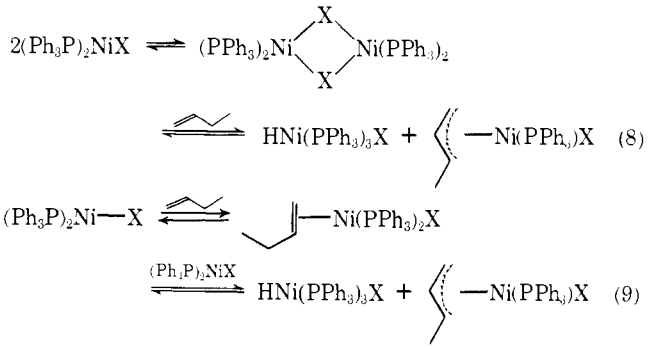
Discussion

The results of the experiments described above clearly indicate that a hydrido species is responsible for the catalytic activity of $(Ph_3P)_3NiX$ systems and that this hydrido complex is probably the same as that obtained from the reaction of HX with $(Ph_3P)_4Ni$. An overall mechanism that is generally consistent with our observations on this system and the known behavior of metal hydride catalysts is shown in Scheme II. There are several interesting features to this scheme that merit brief discussion. Although the paramagnetic species does not itself behave as an olefin isomerization catalyst, its reversible reaction with olefin to form the hydridonickel and allylnickel complexes (B) represents a novel reaction for formation of hydride and illustrates reactivity unique to low-valent odd-electron systems. Because of the problems with reproducibility of the rate measurements, and the small equilibrium constant inferred for reaction B, very little can be said about the

Scheme II



mechanism of the abstraction reaction. The *apparent* second-order dependence of the rate of isomerization on [Ni(I)] is in agreement with two plausible mechanisms which can be written for the reaction (eq 8 and 9). It should be noted that



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(9)

the parent complex $(Ph_3P)_3NiX$ (X = halide) is extensively dissociated in solution[19] as shown in step A. The exact nature of the hydrido species could not be determined. Both $L_2Ni(H)X$ and $L_3Ni(H)X$ species have been identified. Recent work by Tolman and co-workers on L_4Ni + HCN systems shows unambiguously that trigonal bipyramidal $L_3Ni(H)CN$ species are formed for a wide range of phosphorus ligands, that these undergo rapid ligand exchange, and that they function as isomerization catalysts. It is entirely reasonable that the $SnCl_3$ and Cl complex would behave similarly. If, as expected, the catalytically active species for the isomerization is the 16-electron $(Ph_3P)_2Ni(H)X$ formed by phosphine dissociation, then the inverse dependence of the rate of isomerization on added phosphine is explicable. It should be pointed out that an inverse dependence on phosphine would also be observed as a result of reaction A.

The zero-order dependence of the rate of isomerization in butene concentration that is observed cannot be explained on the basis of information presently available. Because of the instability of the catalyst system reaction rate measurements were not considered to be reliable for more than a few half-lives. The expected complexity of the rate law could cancel a rate dependence at high substrate concentrations. Measurements made at subambient temperatures might provide a more stable system from which further information could be obtained.

An additional feature that is unique to this catalyst system is the fact that reactions which destroy the catalytically active hydrido complex, such as homolytic cleavage of the Ni–H bond and reactions G and H, produce the catalyst precursor. Thus, the net result of these side reactions would only be to remove catalyst precursor in the form of the crotyl complex. The detection of this complex in the spent catalyst would probably not have been possible if these reactions were not operative.

An important result of this work is the observation that a nickel(II) hydride can react with a nickel(II) allyl to produce olefin and nickel(I) as products. To our knowledge a corresponding reaction has only been demonstrated for the $Co^{III}(CN)_5H^{3-}/Co^{III}(CN)_5(allyl)^{3-}$ system where the products are olefin and $Co^{II}(CN)_5^{3-}$. The importance of such a reaction to nickel chemistry must yet be assessed. Butene apparently is not formed by reaction of phosphite nickel hydrides with the corresponding crotyl complex.[25] This is not surprising since phosphite nickel(I) complexes are unstable with respect to disproportionation, which makes their formation by such a reaction rather less likely.[19,27] It seems quite possible, however, that the reaction may provide a clean route to new tris*phosphine*nickel(I) complexes from readily available (in most cases) phosphine nickel(0) starting materials.

Our observations on the reaction of the nickel(II) hydride formed by protonation of $(Ph_3P)_4Ni$ with butadiene to give the *syn*-η^3-crotyl complex are also interesting in light of Tolman's work on related reactions which shows that the reaction rate of pentacoordinate nickel hydrides can be directly related to the ease with which a vacant coordination site is achieved. The fact that the crotyl complex is formed rapidly indicates that phosphine exchange is rapid if the hydrido species exists in solution as $(Ph_3P)_3Ni(H)X$.

The fact that no C_8 hydrocarbon products, which might arise from metal hydride catalyzed coupling of butene molecules, were ever observed is probably a result of the presence of the large excess of phosphine relative to hydrido complex (recall that 1 mol of phosphine is liberated per mol of catalyst precursor utilized in reaction A).[28] This phosphine would compete for the coordinatively unsaturated $(Ph_3P)_2Ni(butyl)X$ species that could produce C_8 products by coordination and insertion of butene followed by elimination of olefin.

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Stannylation/Destannylation. Preparation of α-Alkoxy Organolithium Reagents and Synthesis of Dendrolasin via a Carbinyl Carbanion Equivalent

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Abstract: Tributylstannyllithium (I) is a valuable reagent for the preparation of oxyfunctional organolithium reagents and is readily prepared by deprotonation of tributyltin hydride with lithium diisopropylamide. Addition of I to an alkyl or aryl aldehyde yields an α-hydroxystannane ($RCH(OH)Sn(Bu)_3$) which is then protected with α-chloroethyl ethyl ether to give the ethoxyethyl derivative (II) in >90% yield. On treatment with butyllithium, II yields the corresponding α-alkoxy organolithium reagent ($RCH(OR')Li$). These reagents are synthetically useful as carbinyl carbanion equivalents. Application of the new organolithium reagents to natural product synthesis is illustrated by a simple synthesis of dendrolasin and (±)-9-hydroxydendrolasin from furan-3-carboxaldehyde.

Addition reactions in which a carbonyl group behaves like a hydroxyl-substituted carbocation i characterize some of the most widely used synthetic methods for carbon–carbon bond formation. In contrast, only a few synthetic operations based on the opposite charge affinity pattern are known. The main problem with the latter approach centers on the relative un-

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