Chemistry of Tetrakis(triethyl phosphite)nickel Hydride, $HNi[P(OEt)_3]_4^+$. II. Reaction with 1,3-Butadiene. Catalytic Formation of Hexadienes

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Abstract: The nickel hydride $HNi[P(OEt)_3]_4^+$ catalyzes the coupling of 1,3-butadiene and ethylene to give 1,4-hexadienes. A detailed kinetic study of the reaction of the hydride with 1,3-butadiene shows that the rate-limiting step is ligand dissociation from $HNiL_4^+$ to give $HNiL_3^+$ [$L = P(OEt)_3$], with rate parameters $k_2 = 0.015\ \text{sec}^{-1}$ in CH_3OH at 25°, $\Delta H^{\ddagger} = 17$ kcal/mol, and $\Delta S^{\ddagger} = -10$ eu. The initial products of the reaction are cationic *syn-* and *anti-*π-crotylnickel phosphite complexes with the composition $\pi\text{-}C_4H_7NiL_3^+$, the anti isomer being kinetically preferred by a factor of 7.5:1. An isomerization of anti to syn isomers occurs which is inhibited by excess phosphite ligand. The equilibrium ratio of anti:syn is about 1:19. A slower reaction of the π-crotyl complexes with ethylene gives hexadienes, of which about 60% is the 1,4 isomer. Synthesis and properties are described for the complexes *syn*-π-$C_4H_7NiL_3PF_6$, where $L = P(OEt)_3$, and for *syn*-π-$C_4H_7NiL_2PF_6$, where $L = P(OEt)_3$ or $P(OMe)_3$. Spectroscopic evidence is given for reactions of *syn*-π-$C_4H_7Ni[P(OEt)_3]_2PF_6$ with $P(OEt)_3$ and C_2H_4 to form five-coordinate π-crotyl complexes.

Because of the importance of transition metal hydrides in a variety of homogeneously catalyzed reactions,[1-3] a detailed study was undertaken to understand the chemistry of the cationic nickel phosphite hydride $HNi[P(OEt)_3]_4^+$, recently discovered in these laboratories.[4]

Paper I in this series[5] dealt with the formation and ultimate decomposition of the hydride $HNiL_4^+$ ($L = P(OEt)_3$). A sequence of four steps (Scheme I) was proposed to explain the behavior of NiL_4 and H_2SO_4 in methanol.

Scheme I

$$(1)\quad H^+ + NiL_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HNiL_4^+ \qquad \text{rapid, reversible}$$

$$(2)\quad HNiL_4^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HNiL_3^+ + L \qquad \text{small } K_2$$

$$(3)\quad H^+ + HNiL_3^+ \xrightarrow{k_3} H_2 + Ni(II) + 3L \qquad \text{irreversible}$$

$$(4)\quad L \xrightarrow[H^+]{k_4} HPO(OEt)_2 \qquad \text{irreversible}$$

The ligand dissociation step 2 was proposed on the basis of kinetic data, although there was no spectroscopic evidence for $HNiL_3^+$. A value of k_2 of 0.01 to 0.04 sec^{-1} at 25° was estimated from the fact that reactions 2 and 3 were of comparable rate at high acid concentration.

This paper deals with the reaction of these nickel hydride solutions with 1,3-butadiene and ethylene to give 1,4-hexadiene. An effort has been made to study the catalytic mechanism in detail, to ascertain the order of individual steps, and to determine, as far as possible, the rate and equilibrium constants of each step.

The kinetics of the hydride–diene reaction were followed spectrophotometrically at 0, +10, and +25°, with variations in the concentrations of H_2SO_4, butadiene (BD), and added $P(OEt)_3$ (L). These measurements permitted a determination of k_2 at the three temperatures as well as of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the ligand dissociation process. Rate measurements at 0° with both BD and L added permitted a determination of the relative rates of reaction of $HNiL_3^+$ with BD and with L.

Nmr experiments showed that the reaction of $HNiL_4^+$ with butadiene gave both isomers of the π-crotyl group at 0°, where the isomerization of the kinetically preferred anti isomer to the thermodynamically preferred syn isomer was very slow. The isomerization could be conveniently followed in the nmr from 30 to 50°.

Identification of the products of the hydride–diene reaction was confirmed by the preparation of cationic π-crotylnickel phosphite complexes,[6] precipitated as the PF_6^- salts.

The coordinatively unsaturated complexes,[10] $\pi\text{-}C_4H_7NiL_2^+$, were found to react rapidly with L or C_2H_4 to form five-coordinate complexes, the latter reaction providing a catalytic route to the synthesis of hexadienes from butadiene and ethylene.[12]

In most of the work in this paper, the phosphite ligand (abbreviated L) was $P(OEt)_3$. Data are also presented for the hydride $HNiL_4^+$ and for π-crotyl complexes where the phosphite ligand was $P(OMe)_3$. The trimethyl phosphite ligand was more convenient in some of the proton nmr work because of its simpler spectrum.

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Table I. Proton Nmr Spectra of Isolated π-Crotyl Complexes in $CDCl_3$ (TMS)

Compound	Mp, °C	H_a	H_b	H_c	H_d	*syn*-CH_3	*anti*-CH_3
syn-π-$C_4H_7Ni[P(OEt)_3]_2PF_6$[a]	63–65	4.71 (dt)		7.36 (d)	6.24 (dq)	8.25 (d)	
syn-π-$C_4H_7Ni[P(OEt)_3]_3PF_6$[b]	<25	4.86 (dt)		7.59 (d)	6.28 (dq)	8.40 (d)	8.94 (*d*)[d]
syn-π-$C_4H_7Ni[P(OMe)_3]_2PF_6$[c]	43–44	4.63 (dt)	5.78 (dd)	7.32 (dd)		8.25 (d)	8.82 (d)[e]

[a] τ 5.96 (q, 2, J = 7, $-OCH_2CH_3$), 8.70 (t, 3, J = 7, $-OCH_2CH_3$); $J_{ac} = J_{ad} = 14$, $J_{ab} = 7.5$, $J_{bc} = 2$, $J_{dCH_3} = 6$. [b] τ 5.97 (quintet, 2 J = 7, $-OCH_2CH_3$), 8.71 (t, 3, J = 7, $-OCH_2CH_3$); $J_{ac} = J_{ad} = 12.5$, $J_{ab} = 7$, $J_{bc} \sim 2$, $J_{dCH_3} = 6.5$. [c] τ 6.20 (s, $-OCH_3$); $J_{ac} = J_{ad} = 14$, $J_{ab} = 7.5$, $J_{bc} = 2.5$, $J_{dCH_3} = 6$. [d] 30% anti isomer was present in the second batch of crystals ($J_{eCH_3} = 6$). [e] 10% anti isomer was present in the sample ($J_{eCH_3} = 6$).

Experimental Section

^1H and ^{31}P nmr spectra were recorded on a Varian HA-100 spectrometer. Proton resonances at 100 Mc were measured relative to internal tetramethylsilane, with a precision of ±0.03 ppm for the chemical shifts and ±0.5 cps for the coupling constants. Phosphorus resonances at 40.5 Mc were measured relative to external P_4O_6 in a concentric capillary, using the side-band technique. Chemical shifts (±0.3 ppm) were converted to the more common 85% H_3PO_4 scale by subtracting 112.5 ppm.[14]

Infrared spectra were recorded in KBr on a Perkin-Elmer 221 spectrometer. Melting points were determined in evacuated, sealed capillaries on a Mel-Temp apparatus and are uncorrected.

Because the nickel hydrides and π-crotyl compounds are sensitive to air, all solutions were prepared in a drybox under N_2 using deoxygenated solvents and were transferred by syringe.

Complexes. $Ni[P(OEt)_3]_4$[15,16] and $Ni[P(OMe)_3]_4$[16,17] were prepared as described earlier.[18]

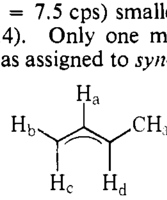
syn-π-**Crotylbis(triethyl phosphite)nickel hexafluorophosphate,** *syn*-π-$C_4H_7Ni[P(OEt)_3]_2PF_6$, was prepared in a 50-ml reaction flask fitted with a standard-taper joint.

To a slurry of 7.23 g of $Ni[P(OEt)_3]_4$ (0.01 mol) in 10 ml of ether at −65° was added 1.1 g of concentrated H_2SO_4 (0.011 mol) in 10 ml of ether at −50°, stirring with a Teflon fluorocarbon resin-coated magnetic stirring bar. The flask was evacuated and 2.0 ml of 1,3-butadiene (0.03 mol) condensed in from a graduated cold trap. A cap was placed on the flask and held tightly with rubber bands.[19] The flask was allowed to warm slowly to room temperature, the solution changing from yellow to orange to deep red. The cap was removed and the solution heated at reflux for 1 hr. Solvent was removed under vacuum and the crude product washed twice with 5 ml of petroleum ether to remove unreacted solid. Drying under vacuum gave a red oil. The flask was washed with 5 ml of H_2O into a chilled solution of 1.63 g of NH_4PF_6 (0.01 mol) in 5 ml of H_2O. A dark red, crystalline solid separated. Washing twice with 3 ml of H_2O and twice with 3 ml of chilled methanol gave 5.30 g of rust-colored product, mp 38–42°.

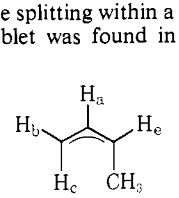
The crude solid was dissolved in methanol to give 6 ml of dark red solution. Chilling in Dry Ice followed by filtration gave a deep red-orange solid. With repeated washings of Dry Ice chilled methanol, the color gradually became lighter until, after 12 2-ml washings, it was yellow-orange. Drying gave 2.06 g (35% yield) of yellow crystals, mp 63–65°.

Anal. Calcd for $C_{16}H_{37}NiF_6O_6P_3$: C, 32.5; H, 6.3; Ni, 9.9; F, 19.3; P, 15.7. Found: C, 32.3; H, 5.7; Ni, 10.3; F, 19.2; P, 15.4.

The proton nmr spectrum of the product (Table I) showed that it was the syn isomer. The central proton H_a showed the characteristic pattern of a pair of triplets, with the splitting between triplets (J_{ab} = 7.5 cps) smaller than the splitting within a triplet ($J_{ac} = J_{ad}$ = 14). Only one methyl doublet was found in the spectrum and was assigned to *syn*-CH_3.



syn-π-crotyl



anti-π-crotyl

The infrared spectrum was very similar to that of $Ni[P(OEt)_3]_4$ or $P(OEt)_3$ with the ν_{PF} of PF_6^- appearing as a very strong band at 845 cm^{-1} (KBr).

syn-π-**Crotyltris(triethyl phosphite)nickel hexafluorophosphate,** *syn*-π-$C_4H_7Ni[P(OEt)_3]_3PF_6$, was prepared as described above except that ethanol was used as the solvent, 5 ml for the slurry of $Ni[P(OEt)_3]_4$ and 5 ml for the H_2SO_4. After the flask has warmed to room temperature and the color had changed from yellow to dark red, the flask was heated for 0.6 hr at 65°. The dark red solution was cooled to 0° and added to a chilled solution of 1.63 g of NH_4PF_6 (0.01 mol) in 15 ml of H_2O. A dark red oil separated. Cooling in Dry Ice, filtering, and washing with chilled methanol gave a deep red-orange solid, 6.24 g, which melted on warming to room temperature to a dark red liquid.

The crude product was dissolved in 5 ml of CH_3OH. Chilling in Dry Ice, filtering, and washing with chilled CH_3OH gave deep red-orange crystals, 5.19 g (68% yield), which again melted below room temperature.

Anal. Calcd for $C_{22}H_{52}F_6NiP_4O_9$: C, 34.9; H, 6.9; F, 15.1; Ni, 7.8; P, 16.4. Found: C, 33.4; H, 6.8; F, 16.9; Ni, 8.7; P, 15.3.

The analysis showed that the compound was not pure. In particular, the P:Ni ratio was low (found, a mole ratio of 3.6:1 or 2.6:1 for $P(OEt)_3$:Ni since the PF_6^- contributes one P per Ni). The integrated proton nmr spectrum (Table I) showed a $P(OEt)_3$:π-allyl ratio of 2.7:1, in good agreement with the analysis. Only the syn isomer was present in the first batch of crystals.

From the mother liquor a second batch of deep red-orange crystals, 1.31 g, was obtained, again melting below room temperature. The nmr spectrum showed that 30% of the π-crotyl was anti and 70% syn; apparently the anti isomer was more soluble.

syn-π-**Crotylbis(trimethyl phosphite)nickel hexafluorophosphate,** *syn*-π-$C_4H_7Ni[P(OMe)_3]_2PF_6$, was prepared from $Ni[P(OMe)_3]_4$. To a chilled slurry of 2.22 g of $Ni[P(OMe)_3]_4$ (4 mmol) in 2 ml of ether at −65° was added a chilled solution of 0.48 g of H_2SO_4 (5 mmol) in 3 ml of ether. Then 1.1 ml of 1,3-butadiene (16 mmol) was condensed in and the vessel was tightly capped. Gradual warming to room temperature with stirring gave a deep red oil insoluble in the ether.

The product was extracted with 3 ml of H_2O and the dark red solution added to 0.66 g of NH_4PF_6 (4 mmol). The salt dissolved and an orange oil separated. Stirring and chilling gave a slurry of ice and orange crystals. When filtered, the crystals melted as the frit warmed. The resulting red oil was dissolved in 5 ml of CH_3OH. Chilling the red methanolic solution in Dry Ice, filtering, and washing once with chilled CH_3OH gave yellow-orange crystals, 0.47 g (23%) yield, mp 43–44°.

Anal. Calcd for $C_{10}H_{25}F_6NiP_3O_6$: C, 23.7; H, 5.0; Ni, 11.6; P, 18.3. Found: C, 23.6; H, 5.0; Ni, 11.4; P, 18.1.

The nmr spectrum (Table I) showed that the compound contained 10% *anti*- and 90% *syn*-π-crotyl. The infrared spectrum was very similar to that of $Ni[P(OCH_3)_3]_4$ or $P(OCH_3)_3$, with the PF_6^- appearing as a very strong additional band at 840 cm^{-1} (KBr).

Kinetic Studies. The kinetics of the reaction of $Ni[P(OEt)_3]_4$, H_2SO_4, and 1,3-butadiene was followed spectrophotometrically using a jacketed 1-mm quartz cell and holder designed for the Cary 14 spectrometer as described earlier.[5] Temperatures in the cell of 0.0, 10.0, and 25.0° were maintained to ±0.1° by circulating water from a constant-temperature bath (Forma Scientific, Inc.) through the cell jacket.

Solutions for the kinetic runs were prepared by adding 1 ml of Dry Ice chilled (−78°) methanolic H_2SO_4 by syringe to a chilled 1-ml solution of 10^{-2} *M* $Ni[P(OEt)_3]_4$. The tube was then evacuated with a hypodermic needle through the serum cap, and 1,3-butadiene gas condensed in from a syringe. These solutions could be kept at Dry Ice temperature for several hours without changing color from yellow to orange, indicating that the nickel hydride and

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[19] This permitted a pressure in the flask greater than 1 atm without danger of rupture.

butadiene did not react appreciably in that time at −78°. To begin each run, a 0.2-ml portion of the solution was injected into the precooled cell using a chilled syringe. Air was excluded by a stream of nitrogen through a side arm on the cell.[5]

The concentration of sulfuric acid for each kinetic run was determined by titration of the stock solution with 0.1 *M* aqueous sodium hydroxide.

Thermocouple tests showed that the injected solutions came to reaction temperature within 1 min.

The effect of added ligand on the *anti-* to *syn*-π-crotyl isomerization was determined by proton nmr. Solutions were prepared in nmr tubes by dissolving 0.11 g of $Ni[P(OMe)_3]_4$ (0.2 mmol) and 50 μl. of TMS in CD_3CN and diluting to a volume of 0.3 ml. The tubes were chilled in Dry Ice and 0.2 ml of 1 *M* H_2SO_4 (0.4 mmol) in CD_3CN was added. The tubes were then capped, evacuated, and loaded with 5 ml of BD gas (0.2 mmol). Shaking and warming the tubes to 0° in an ice–water bath caused the color to change from yellow to deep red. The tubes were kept at 0° for 1 hr to ensure completion of the hydride–butadiene reaction before various amounts of neat $P(OMe)_3$ were added by syringe. Earlier experiments had shown that the half-life of the hydride–diene reaction was about 9 min at 0° in CD_3CN.

The tubes were then warmed in a water bath to 30° and inserted into the probe of the HA-100 at 30°.

Reaction of *syn*-π-$C_4H_7Ni[P(OEt)_3]_2^+$ with C_2H_4. Into an nmr tube was weighed 0.05 g of *syn*-π-$C_4H_7Ni[P(OEt)_3]_2PF_6$ (0.1 mol), and 0.4 ml of CD_2Cl_2 was added to give a yellow solution. The tube was capped, chilled in Dry Ice, and evacuated through a hypodermic needle. A pressure of 10 psig of C_2H_4 gas was applied and the tube allowed to warm with shaking. The color appeared to change slightly to gold. The nmr spectrum of the solution showed, in addition to the resonances expected from the starting complex and a sharp peak assigned to free C_2H_4 at τ 4.60, a new multiplet consisting of about six lines (8 cps wide) centered at τ 8.38, assigned to complexed ethylene. Comparison of the integrated intensity with that of the ligand $-CH_3$ showed that the area represented about one C_2H_4 unit per nickel atom. The appearance of the multiplet was different at 60 Mc from that at 100 Mc, indicating a second-order spectrum.

Catalytic Formation of Hexadienes. Both preformed *syn*-π-$C_4H_7Ni[P(OEt)_3]_2PF_6$ (0.38 g, 0.5 mmol) and a mixture of $Ni[P(OEt)_3]_4$ (0.36 g, 0.5 mmol) and H_2SO_4 (0.06 g, 0.6 mmol) were tested as catalysts, with CH_3OH and CH_3CN, respectively, as solvents.

The reactions were carried out in an 80-ml stainless steel tube equipped with a pressure gauge and thermocouple. The tube was charged with the catalyst in an evacuated sealed ampoule (two when $Ni[P(OEt)_3]_4$ and H_2SO_4 were both added). Then 10 ml of solvent was added, followed after cooling and degassing by 4 g of 1,3-butadiene (70 mmol) and 2 g of ethylene (70 mmol).

During the reaction the tubes were agitated to break the vials and to keep the contents mixed. There was no reaction at 50° over 2 hr, as evidenced by the absence of a pressure drop. A reaction occurred in both cases at 100°. At the end of 8 hr the tubes were cooled, vented, and washed with two 10-ml portions of solvent.

The volatile product was distilled under vacuum and analyzed by gas chromatography through a 2-m column of 20% 2,4-dimethyltetramethylene sulfone on Gas Chrom R (60–80 mesh) at 60° and a helium flow rate of 10 cc/6.1 sec. Retention times were determined on authentic samples of 2-methyl-1,4-pentadiene, 1,5-hexadiene, *trans*-1,4-hexadiene, *cis*-1,4-hexadiene, *trans*-1,3-hexadiene, and mixed 2,4-hexadienes (three isomers). The results are given in Table VIII.

Results and Discussion

The Reaction of $HNi[P(OEt)_3]_4^+$ with Butadiene. If $Ni[P(OEt)_3]_4$, sulfuric acid, and 1,3-butadiene (BD) are mixed together in methanol at room temperature, the initial yellow color of the hydride $HNi[P(OEt)_3]_4^+$ rapidly changes to deep red. The red color is associated with an absorption maximum at about 370 mμ (ε ~1.1 × 10³ cm⁻¹ M^{-1}). A maximum absorbance at 370 mμ was achieved when the three reagents were added in equimolar quantities. In the presence of excess acid the color gradually changed to yellow-orange. The absorption maximum at 370 mμ disappeared and was replaced by a new one at 295 mμ (ε 2.6 × 10³). During the process isosbestic points were maintained at 290 and 340 mμ, showing that conversion of one chromophoric species to another was involved.

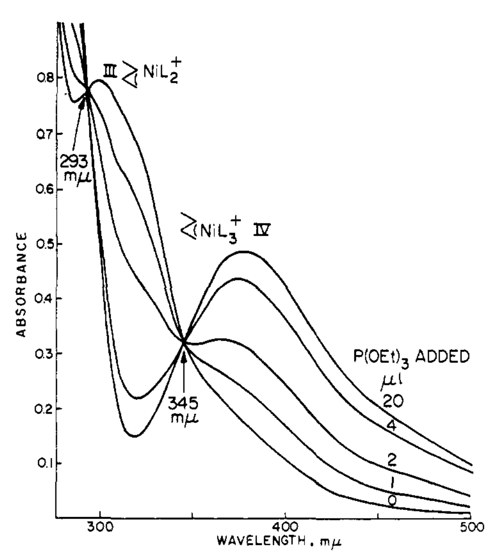

Figure 1. Ultraviolet spectra on adding $P(OEt)_3$ to 1 ml of 0.03 *M* methanolic *syn*-π-$C_4H_7Ni[P(OEt)_3]_2PF_6$; 0.1-mm cell.

Initial attempts to isolate the red species on a preparative scale using H_2SO_4 led to dark red oils of variable composition, with P:Ni ratios in the range of 2.5–3. It was possible to precipitate the cationic complex using the hexafluorophosphate anion. The deep red precipitate from an ethanol–water mixture melted below room temperature and analyzed approximately for [π-$C_4H_7NiL_3$]PF_6 [L = $P(OEt)_3$]. Precipitation with NH_4PF_6 from water and repeated washings of the red crystals with cold methanol leached out the red color and gave a pure yellow compound, mp 63–65°, of composition [π-$C_4H_7NiL_2$]PF_6.

The presence of a π-crotyl group in the products was clearly shown by the proton nmr spectra, data for which are shown in Table I. The assignments were easily made based on the reported spectra of π-C_4H_7-$Co(CO)_3$.[7b] The isomers are named syn or anti according to whether the methyl group is near or away from the central proton H_a.[20]

One interesting feature of the nmr spectra of the isolated complexes was the ligand resonance. The methyl group of $P(OEt)_3$ for both complexes in Table I appeared as a single very strong triplet.[21] The methylene resonance of π-$C_4H_7Ni[P(OEt)_3]_3PF_6$ appeared as a quintet, because of accidental equal coupling with the three methyl protons and the phosphorus. In the spectrum of π-$C_4H_7Ni[P(OEt)_3]_2PF_6$, however, the methylene appeared only as a quartet, the coupling to phosphorus having disappeared. Similar behavior in a bis(phosphite) complex was observed with π-C_4H_7-$Ni[P(OMe)_3]_2PF_6$, where the ligand methyl appeared as an uncoupled singlet.

The electronic spectrum of a yellow solution of *syn*-π-$C_4H_7Ni[P(OEt)_3]_2PF_6$ in methanol (Figure 1,

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[20] This designation was suggested in ref 8.

[21] The complex listed as *syn*-π-$C_4H_7Ni[P(OEt)_3]_3PF_6$ had an analysis suggesting a mixture of π-$C_4H_7NiL_3PF_6$ and π-$C_4H_7NiL_2PF_6$; nevertheless, only one type of ligand apeared in the nmr spectrum. The explanation is a rapid ligand exchange leading to an averaged ligand spectrum.

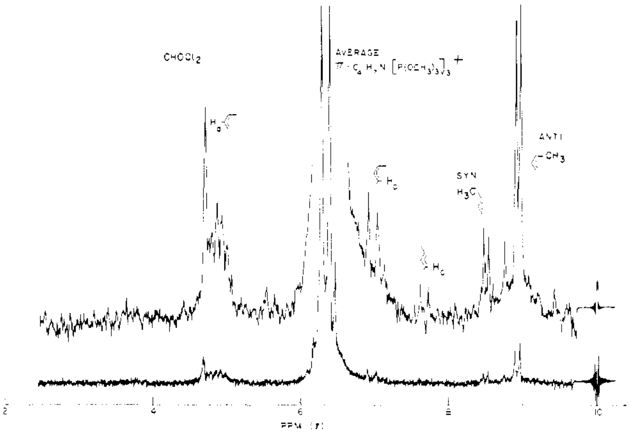

Figure 2. Proton nmr spectrum at 100 Mc after 0.2 hr at +50°, 80% *anti*- and 20% *syn*-π-$C_4H_7Ni[P(OMe)_3]_3^+$ in CD_2Cl_2.

curve III) showed an absorbance maximum at 300 mμ (ε 2.7×10^3). Addition of $P(OEt)_3$ to the solution changed the color rapidly, the solution turning to deep red with successive additions. The final spectrum (curve IV in Figure 1) was unaffected by the further addition of ligand and showed a maximum absorbance at 380 mμ (ε 1.6×10^3). Well-defined isosbestic points at 293 and 345 mμ indicate that only two chromophoric species were involved in the reaction. A plot of the absorbance at 380 mμ against $P(OEt)_3$ added gave a titration curve with a sharp end point at a 1:1 ratio of added ligand to starting complex. The sharpness of the end point, which occurred with 5 μl of added $P(OEt)_3$, shows that the reaction lies far to the right with an equilibrium constant $K \gtrsim 10^3\ M^{-1}$.

$$\underset{\text{III}}{syn\text{-}\pi\text{-}C_4H_7NiL_2^+} + L \overset{K}{\rightleftharpoons} \underset{\text{IV}}{syn\text{-}\pi\text{-}C_4H_7NiL_3^+}$$

The spectra shown in Figure 1 are similar to but not exactly the same as those described at the beginning of the discussion. The maxima and isosbestic points in Figure 1 are shifted 5–10 mμ to longer wavelength relative to the corresponding spectral features of the *in situ* generated π-crotyl solutions. The explanation of these differences lies in the distribution among the four π-crotyl species present, *viz.*, *anti*-π-$C_4H_7NiL_3^+$ (I), *anti*-π-$C_4H_7NiL_2^+$ (II), *syn*-π-$C_4H_7NiL_2^+$ (III), and *syn*-π-$C_4H_7NiL_3^+$ (IV). The complex first formed in solution is predominantly I,[22] characterized by λ_{max} 370 mμ. Decomposition of phosphite ligand in the presence of acid causes the red color to turn yellow, giving a mixture of bis(phosphite) complexes, largely II (λ_{max} 295 mμ). The limiting spectra in Figure 1 are those of pure III (λ_{max} 300 mμ) and IV (λ_{max} 380 mμ).

The rapid rate of ligand exchange in these solutions was shown by an experiment using ^{31}P nmr, where $P(OEt)_3$ was added to a $CDCl_3$ solution of *syn*-π-$C_4H_7Ni[P(OEt)_3]_2PF_6$, which showed a resonance at −129.8 ppm (H_3PO_4). The addition of $P(OEt)_3$ caused no new resonance in the position of free ligand; rather, the one resonance observed became stronger and shifted downfield, asympototically approaching the position expected for free ligand at −138.3 ppm. This is the behavior expected for a very rapid ligand-exchange process which gives only an average resonance. The average lifetime of a phosphite ligand in the complexes must be $\leqslant 2 \times 10^{-3}$ sec.

One proton nmr experiment using $Ni[P(OMe)_3]_4$ was particularly instructive in showing the sequence of reactions in the system in the absence of ethylene, and will be described in some detail. A solution of 0.14 g of $Ni[P(OMe)_3]_4$ (0.25 mmol) and 6 cc of BD gas (0.25 mmol) in 0.5 ml of CD_2Cl_2 solution showed resonances of butadiene and $Ni[P(OMe)_3]_4$ (a broad multiplet at τ 6.56).[23] There was no evidence for reaction before acid was added. The solution was chilled to −78° and 13 μl of H_2SO_4 (0.25 mmol) injected. Shaking gave a homogeneous yellow solution which was placed in the spectrometer at −20°. The spectrum showed resonances of unreacted butadiene and those characteristics of the hydride $HNi[P(OMe)_3]_4^+$, a very strong singlet due to the ligand $-OCH_3$ at τ 6.38 and a clean sharp quintet of the hydride at τ 24.0 (J_{PH} = 29.5 cps).[24] The spectrometer was warmed to 0°. Repeated sweeps of both low- (τ 0–10) and high-field (τ 20–30) regions of the spectrum showed that resonances of the diene and the hydride were disappearing at the same rate with a half-life of about 30 min and that new resonances characteristic of the π-crotyl products were appearing. There was no spectral evidence for $HNiL_3^+$, expected to appear as a quartet in the hydride region. Nor was there evidence for σ-bonded allyls.[25]

The ligand methyl group of the π-crotyl products gave only one resonance, a doublet at τ 6.28 (J_{POCH_3} = 11 cps), as expected for exchange of free and complexed ligand.

The remainder of the spectrum was complicated by the presence of both syn and anti forms of the π-crotyl. After the spectrometer was warmed to 25°, no trace of either $HNiL_4^+$ or BD remained. The π-crotyl resonances (Table II) had the same relative intensities as at 0°. The ratio of syn to anti was 1:7.5, corresponding to 12% syn and 88% anti isomer.

At 50° the spectrum gradually changed as the anti isomer was isomerized to the more stable syn in a reaction with a 2-hr half-life at 50°. Figure 2 shows the spectrum after 0.2 hr at 50°, at which point 80% of the π-crotyl groups were still in the anti form (highest field CH_3 doublet).

Heating at 70° for 1.5 hr gave the equilibrium distribution of the isomers, a 19:1 ratio of syn to anti, corresponding to 95% syn and 5% anti. The greater thermal stability of the syn isomer as well as the lower solubility of its complexes probably account for its isolation. We have been unable to isolate pure salts of the anti isomer. A similar isolation of only the syn isomer has been reported for the reaction of BD with $HCo(CO)_4$,[7b] indicating that a greater stability for the syn isomer may be a general phenomenon.

Comparison of the chemical shifts due to π-C_4H_7 in Tables I and II shows that the resonances of the isolated compounds are generally at lower fields. For ex-

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[22] Nmr evidence for the distribution between anti and syn isomers is given later.

[23] Proton nmr spectrum reported in ref 18.

[24] The hydride resonance of $HNi[P(OEt)_3]_4^+$ under these conditions was a quintet at τ 24.3 (J_{PH} = 26.5 cps).[5]

[25] This can be contrasted with the behavior of $HMn(CO)_5$[8] and $HCo(CN)_5^{3-}$ [26] in reacting with butadiene, where σ-bonded species were observed as intermediates.

[26] J. Kwiatek and J. K. Seyler, *Advan. Chem. Ser.*, **No.** 70, 207 (1968).

Table II. Proton Nmr Spectra of π-$C_4H_7NiL_3^+$ Generated in Solution in CD_2Cl_2 (TMS)[a]

Ligand	Isomer	H_a	H_b	H_c	H_d	*syn*-CH_3	*anti*-CH_3
$P(OEt)_3$	Syn[b]	4.87 (dt)	6.69 (d)	7.75 (d)	5.70 (m)	8.51 (d)	
	Anti[c]	4.91 (dt)	6.44 (d)	7.01 (d)			8.91 (d)
$P(OMe)_3$	Syn[d]	4.82 (dt)		7.68 (d)	6.08 (m)	8.52 (d)	
	Anti[e]	4.80 (m)		6.95 (d)			8.95 (d)

[a] By the reaction of NiL_4, H_2SO_4, and 1,3-butadiene. [b] $J_{ac} = J_{ad} = 11.5, J_{ab} = 6.5, J_{dCH_3} = 6.5$ cps. [c] $J_{ac} = 12, J_{ab} = J_{ae} = 6, J_{eCH_3} = 7$. [d] $J_{ac} = J_{ad} = 12, J_{ab} = 7, J_{dCH_3} = 6.5$. [e] $J_{ac} = 12, J_{eCH_3} = 6.5$.

Table III. Proton Chemical Shifts of Phosphites in Some Nickel Complexes in CD_2Cl_2 (TMS)

Ligand	Group	NiL_4[d]	$HNiL_4^+$	π-$C_4H_7NiL_3^+$ [a]	Free L
$P(OEt)_3$	$-OCH_2-$	6.13	6.00[b]	5.98 (5.93)	6.12
	$-CH_3$	8.86	8.73	8.73 (8.72)	8.76
$P(OMe)_3$	$-OCH_3$	6.56	6.38[c]	6.30 (6.23)	6.52

[a] As generated in solution with NiL_4, H_2SO_4, and 1,3-butadiene. The resonance observed is really the average of that for π-$C_4H_7NiL_3^+$ and displaced free L. The value in parentheses is the true chemical shift of ligand in the complex, such that $\tau_{obsd} = {}^1/_4(3\tau_{complex} + \tau_{free})$. [b] The hydride proton appeared as a quintet at τ 24.3 ($J_{PH} = 26.5$ cps) at −20° (ref 5). [c] The hydride proton appeared as a quintet at τ 24.0 ($J_{PH} = 29.5$ cps) at −20°. [d] Reference 18.

ample, the resonance of the *syn*-CH_3, where L = $P(OEt)_3$, was observed at τ 8.25 in the isolated *syn*-π-$C_4H_7NiL_2PF_6$ and at 8.51 for *syn*-π-$C_4H_7NiL_3$-HSO_4 generated in solution. The difference reflects the effect of coordination of the third phosphite ligand, which appears to act as an electron donor (increased shielding). Incidentally the *syn*-CH_3 resonance of the material isolated with an elemental analysis corresponding to *syn*-π-$C_4H_7NiL_{2.6}PF_6$ (second entry in Table I) was τ 8.40, just six-tenths of the way between 8.25 and 8.51.

The ligand proton resonance in the π-crotylnickel phosphite solutions are shown in Table III. The downfield shift of the ligand protons on going from NiL_4 to $HNiL_4^+$ to π-$C_4H_7NiL_3^+$ is consistent with electron withdrawal from the ligand as the Ni is oxidized from Ni(0) in NiL_4 to Ni(II) in the other two complexes. The fact that the π-crotyl complexes show ligand proton resonances at lower fields than the hydrides suggests that the electron density on nickel is less in the π-crotyl complexes than in the hydrides. The position of free ligand between those of the Ni(0) and Ni(II) complexes suggests that the net flow of electrons is into the ligand in the Ni(0) complexes and out of the ligand in the Ni(II) complexes.

Kinetics of the Hydride–Diene Reaction. The kinetics of the reaction of $Ni[P(OEt)_3]_4$, H_2SO_4, and butadiene in methanol was studied spectrophotometrically at 0, 10, and 25°. In most cases the reaction was followed at 340 mμ, thus avoiding the complication of conversion of π-$C_4H_7NiL_3^+$ to π-$C_4H_7NiL_2^+$ *via* ligand degradation. Spectra at the completion of the hydride–diene reaction indicated substantial conversion to π-$C_4H_7NiL_2^+$, especially in runs with higher acid concentrations or at higher temperatures. After many hours at 0° or less than an hour at 25°, at the higher acid concentrations, the absorbance at 340 mμ began to drop and the solutions gradually decolorized. This is attributed to decomposition of the π-$C_4H_7NiL_2^+$ complexes by excess H^+, possibly to give butenes and Ni(II).

Table IV. Rates of H_2SO_4 + $Ni[P(OEt)_3]_4$ + BD Reaction in CH_3OH at 0°, Variable H_2SO_4 Concentrations, 0.5×10^{-2} *M* $Ni[P(OEt)_3]_4$, 0.5 *M* BD, 1-mm Cell, 340 mμ

Initial $[H_2SO_4]$	A_0 (340)[a]	A_∞ (340)	κ,[b] min^{-1}	$f(H^+)$[c]	$\kappa/f(H^+)$, min^{-1}
0.01	0.29	0.44	0.0128	0.23	0.056
0.02	0.32	0.44	0.0224	0.37	0.060
0.03	0.46	0.58	0.0219	0.48	0.046
0.05	0.54	0.59	0.0366	0.61	0.060
0.10	0.59	0.57	~0.069[d]	0.76	~0.09[d]
0.20	0.69	0.59	0.074	0.87	0.085
0.47	0.83	0.64	0.062	0.94	0.066
					0.062 ± 0.009

[a] Absorbance at 340 mμ at the beginning of recording, uncorrected. [b] From slope of semilog plots. [c] The fraction of nickel in the form of $HNiL_4^+$, calculated from the quadratic equation using the initial concentration of H_2SO_4 and $K = 33\ M^{-1}$.[5] [d] Very little absorbance change at 340 mμ.

The reaction was most conveniently followed at 0° where it was reasonably slow, the half-life of the reaction of nickel hydride with diene being about 8 min in the most concentrated acid solution (0.47 *M* H_2SO_4). Plots of log $|A(340) - A_\infty(340)|$ against time were approximately linear over two to four half-lives. Table IV summarizes the effect of varying the acid concentration while keeping the butadiene concentration fixed at 0.5 *M*.

The increasing initial absorbance in the second column of Table IV reflects the increasing percentage of nickel as $HNiL_4^+$, as the acid concentration is increased. That fraction is shown in column 5. In the more concentrated acid solutions the *A*(340) actually decreased with time as hydride was converted to product. It can be seen that the reaction rates increase with acid concentration, though not linearly. Thus an increase in acid concentration by a factor of about 50 caused only a fivefold increase in rate. If, however, one divides the pseudo-first-order rate constant κ by the fraction of nickel in the form of $HNiL_4^+$, calculated from the previously determined hydride formation constant,[5] the result is a constant, as shown in the last column.

Thus κ is given by the equation

$$\kappa = f(H^+)k_2$$

where $k_2 = 0.062 \pm 0.009\ min^{-1}$. We shall see later that k_2 is the rate constant for ligand dissociation from $HNiL_4^+$.

Similar measurements at 10 and 25° gave results which are included in Table V.[27]

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(27) The values of equilibrium constant used to calculate $f(H^+)$ at 25 and 10° were 48 and 39 M^{-1}, respectively. The *K* at 25° was determined from the initial absorbance in hydride solutions with various H_2SO_4 concentrations (Figure 1, ref 5). The value at 10° was calculated from the values at 0 and 25° by interpolation of log *K* *vs.* 1/*T*.

Table V. Rates of H_2SO_4 + $Ni[P(OEt)_3]_4$ + BD Reaction in CH_3OH at Various Temperatures

Temp, °C	k_2, min$^{-1\,a}$	$10^3 + k_2$, sec^{-1}
0	0.062 ± 0.009	1.0 ± 0.15
10	0.15 ± 0.03	2.5 ± 0.5
25	0.9 ± 0.3	15 ± 5

[a] Determined by dividing κ at each temperature for each acid concentration by the fraction of nickel initially in the form of $HNiL_4^+$, as in Table II. Equilibrium constants used were 33, 39, and 48 M^{-1} at 0, 10, and 25°, respectively.[27]

The experiments cited above were all carried out with an initial butadiene concentration of 0.5 *M;* in other experiments at 0° the initial concentration of H_2SO_4 was kept fixed at 0.05 *M*, while the concentrations of BD and added ligand were varied. Because of the small absorbance change at 340 mμ with this acid concentration, the reactions were followed at 400 mμ. Some data of this sort are given in Table VI.

Table VI. Rates of H_2SO_4 + $Ni[P(OEt)_3]_4$ + BD Reaction in CH_3OH at 0°, Variable BD and Ligand Concentrations, 0.5 × 10^{-2} *M* $Ni[P(OEt)_3]_4$, 0.05 *M* H_2SO_4, 1-mm Cell, 400 mμ

$[BD]_{initial}$	$[L]_{initial}$	Initial slope,[a] min^{-1}	k_{-2}/k_3[b]
1	0	0.052	
1	0.05	0.028	19
1	0.1	0.017	22
0.2	0.05	0.021	6
0.2	0.1	0.009	10
0.04	0	0.055	
0.04	0.1	0.002	11
			14 ± 6

[a] Taken from plots of log $\Delta A(400)$ *vs.* time. [b] The value of κ in the absence of added ligand was taken to be 0.055 ± 0.022 min^{-1}, the average of four runs.

The value of the initial slope is given in Table VI because many of the semilog plots showed negative curvature. This behavior is believed to be due to ligand decomposition in the solution, converting π-$C_4H_7NiL_3^+$ to π-$C_4H_7NiL_2^+$.

In the absence of added ligand the reaction rate is independent of BD concentration, as shown by the initial slopes with 1 and 0.04 *M* BD. This behavior suggests that the rate-determining step is ligand dissociation from $HNiL_4^+$, followed by a rapid reaction with BD. For fixed BD concentrations the rate is decreased by added ligand. Comparison of the three runs with 0.1 *M* added $P(OEt)_3$ shows that the rate does depend on BD concentration if added ligand is present. This type of behavior is given by an expression of the form

$$\frac{k_3(\mathrm{BD})}{k_{-2}(\mathrm{L}) + k_3(\mathrm{BD})} = \frac{1}{1 + k_{-2}(\mathrm{L})/k_3(\mathrm{BD})}$$

The values of k_{-2}/k_3 in Table VI were obtained from the initial slopes, *s*, using the formula

$$\frac{k_{-2}}{k_3} = \frac{(\mathrm{BD})}{(\mathrm{L})}\left[\frac{0.055}{s} - 1\right]$$

where 0.055 min^{-1} is the initial slope without added ligand.

The pseudo-first-order rate constant can be seen to be a product of terms as follows

$$\kappa = k_2 f(\mathrm{H}^+)\frac{k_3(\mathrm{BD})}{k_{-2}(\mathrm{L}) + k_3(\mathrm{BD})}$$

where the third term involving (BD) is approximately 1.0 in the absence of added ligand because $k_3(\mathrm{BD}) \gg k_{-2}(\mathrm{L})$.

A mechanism which is consistent with the data is shown in Scheme II.

Scheme II

$$(1)\quad \mathrm{H^+ + NiL_4 \overset{K_1}{\rightleftharpoons} HNiL_4^+} \qquad \text{rapid, reversible}$$

$$(2)\quad \mathrm{HNiL_4^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HNiL_3^+ + L} \qquad \text{slow, rate determining}$$

$$(3)\quad \mathrm{HNiL_3^+ + BD \xrightarrow{k_3} \pi\text{-}C_4H_7NiL_3^+} \qquad \text{very fast}$$

$$(4)\quad \underset{\text{red}}{\mathrm{\pi\text{-}C_4H_7NiL_3^+}} \rightleftharpoons \underset{\text{yellow}}{\mathrm{\pi\text{-}C_4H_7NiL_2^+}} + \mathrm{L} \qquad \text{rapid, reversible}$$

$$(5)\quad \mathrm{L \xrightarrow[(H^+)]{} HPO(OEt)_2} \qquad \text{slow}$$

Steps 1, 2, and 5 have been proposed in paper I of this series,[5] based on the behavior of the hydride solutions in the absence of butadiene. The oxidation of $HNiL_3^+$ to give H_2 and Ni(II) found in the absence of butadiene (Scheme I) is unimportant in the presence of excess BD because $HNiL_3^+$ is rapidly removed from solution by reaction with BD in step 3.

By following the reaction at 340 mμ the complication of reaction 4 was avoided, because of equal extinction coefficients for the chromophores of step 4. Letting P represent the π-allyl products and applying the steady-state approximation to $HNiL_3^+$, one obtains the following equations.

$$(\mathrm{HNiL_3^+}) = \frac{k_2(\mathrm{HNiL_4^+})}{k_{-2}(\mathrm{L}) + k_3(\mathrm{BD})}$$

$$\frac{d\mathrm{P}}{dt} = k_3(\mathrm{BD})(\mathrm{HNiL_3^+})$$

$$(\mathrm{HNiL_4^+}) = f(\mathrm{H^+})[(\mathrm{Ni})_{total} - \mathrm{P}]$$

$$\frac{d\mathrm{P}}{dt} = k_2 f(\mathrm{H^+})\frac{k_3(\mathrm{BD})}{k_{-2}(\mathrm{L}) + k_3(\mathrm{BD})}[(\mathrm{Ni})_{total} - \mathrm{P}]$$

The solution of the last equation, in the absence of ligand decomposition, is a first-order appearance of product with a pseudo-first-order rate constant given by

$$\kappa = k_2 f(\mathrm{H^+})\frac{k_3(\mathrm{BD})}{k_{-2}(\mathrm{L}) + k_3(\mathrm{BD})}$$

the same expression as determined experimentally. It can now be seen that k_2 is the rate constant for ligand dissociation from $HNiL_4^+$ and becomes the experimental κ for large (H^+) and small (L).

The value of 1.5 × 10^{-2} sec^{-1} for the ligand-dissociation rate constant (Table V) at 25° compares favorably with the value of 1-4 × 10^{-2} sec^{-1} estimated from a study of the hydride decomposition reaction.[5]

A value of 14 for k_{-2}/k_3 in Table VI indicates that $HNiL_3^+$ is 14 times as likely to recombine with L as it is to react with butadiene to form products at 0°.

A logarithmic plot of k_2 (Table V) against $1/T$ gives the activation parameters

Table VII. Effect of Added Ligand on Anti–Syn Isomerization, 0.4 M π-$C_4H_7Ni[P(OMe)_3]_3^+$ in CD_3CN at 30°

$[P(OMe)_3]_{\mathrm{added}}$, M	Initial slope, hr^{-1}
0	1.9
0.2	0.26
0.5	0.14
0.8	0.09

Table VIII. Products of Hexadiene Synthesis with π-Crotylnickel Phosphite Catalysts. Peak Areas by Gas Chromatography[a]

Retention time, min	2.0	2.5	3.0	3.2	4.4	5.8	6.5	6.8	2–7[d]	7–25[e]
Products										
Catalyst	3M1,4P	1,5H	T1,4H	C1,4H	T1,3H	TT2,4H	CT2,4H	CC2,4H	Unidentified	
syn-π-$C_4H_7Ni[P(OEt)_3]_2PF_6$[b]	8.2	1.6	107.4	16.4	0.8	27.0	13.6	20.2	3.8	3.6
$Ni[P(OEt)_3]_4 + H_2SO_4$[c]	16.6	0.7	131.6	10.5	1.7	14.8	12.9	Trace	1.8	6.5

[a] With 10-μl injection into 2-m column of 20% 2,4-dimethyltetramethylene sulfone on Gas Chrom R (60–80 mesh) at 60° with He flow rate of 10 cc/6.1 sec. 10^{-6} mol of diene gives about 50 area units. Abbreviations: 3M1,4P, 3-methyl-1,4-pentadiene; 1,5H, 1,5-hexadiene; T1,4H, *trans*-1,4-hexadiene; etc. [b] 0.5 mmol of catalyst in CH_3OH solvent. [c] 0.5 mmol NiL_4 and 0.6 mmol H_2SO_4 in CH_3CN solvent. [d] Probably includes *cis*-1,3-hexadiene, 3-methyl-*trans*-1,3-pentadiene, 3-methyl-*cis*-1,3-pentadiene, and 2-ethyl-1,3-butadiene. [e] Probably includes octadienes or higher oligomers.

$$\Delta H^{\ddagger} = 17 \pm 2.5 \quad \text{kcal/mol}$$

$$\Delta S^{\ddagger} = -10 \pm 10 \quad \text{eu}^{28}$$

The activation enthalpy of 17 kcal/mol for ligand dissociation from $HNiL_4^+$ can be compared with a value of $\Delta H^{\ddagger} = 27$ kcal/mol for ligand dissociation from NiL_4 in benzene determined by the kinetics of ligand exchange.[29] Labilization of dissociation of a triethyl phosphite ligand is one of the important functions of the hydride ligand in this system. A similar labilization of CO dissociation by a hydride is implied by the acid-catalyzed exchange of ^{14}CO with $Fe(CO)_5$.[30]

The fact that hydride $HNiL_4^+$ does not react with butadiene until one of the original phosphite ligands has come off indicates that a free coordination position on nickel is required before addition of Ni–H to the diene can occur. The first step of the reaction of $HCo(CO)_4$ with olefins has also been shown to be CO dissociation.[31] We again see here the importance of coordinative unsaturation.[10]

Anti → Syn Isomerization of the π-Allyl. In the preceding section the π-allyl products have been written as π-$C_4H_7NiL_3^+$ or π-$C_4H_7NiL_2^+$. This was admissible for the spectrophotometric experiments, since the optical spectra were only slightly dependent on the distribution between syn and anti isomers of the 1-methyl-π-allyl products. Since the optical spectra did not provide a convenient means for following the isomerization, an nmr method was used. $Ni[P(OMe)_3]_4$ was chosen because of the greater simplicity of its proton nmr spectrum; essentially similar results were obtained when $Ni[P(OEt)_3]_4$ was used.

The series of kinetic measurements was carried out by nmr at 30° in CD_3CN solvent. Spectra of π-$C_4H_7Ni[P(OMe)_3]_3^+$ were scanned repeatedly in solutions containing various concentrations of added $P(OMe)_3$. The first spectrum of each solution showed 15–25% syn isomer, approximately the percentage given by kinetic control in the hydride–diene reaction. After equilibration, which required about 1 hr in the absence of added ligand, there was about 95% syn isomer. In the presence of added ligand, the isomerization reaction was much slower, as shown by the data in Table VII.

Though no attempt has been made to analyze these data in detail,[32] it is clear that added ligand decreases the isomerization rate. This is not the result one would expect if the isomerization were passing through a σ-crotyl intermediate, whose concentration ought to increase with added ligand,[33] and suggests that the reaction goes by way of a coordinatively unsaturated intermediate, as shown in Scheme III.

Scheme III

$$\underset{\text{I}}{anti\text{-}\pi\text{-}C_4H_7NiL_3^+} \rightleftharpoons \underset{\text{II}}{anti\text{-}\pi\text{-}C_4H_7NiL_2^+} + L \qquad \text{fast}$$

$$\underset{\text{II}}{anti\text{-}\pi\text{-}C_4H_7NiL_2^+} \rightleftharpoons \underset{\text{III}}{syn\text{-}\pi\text{-}C_4H_7NiL_2^+} \qquad \text{slow}$$

$$\underset{\text{III}}{syn\text{-}\pi\text{-}C_4H_7NiL_2^+} + L \rightleftharpoons \underset{\text{IV}}{syn\text{-}\pi\text{-}C_4H_7NiL_3^+} \qquad \text{fast}$$

The rate of the anti–syn isomerization may be important in determining the product distribution in hexadiene catalysis, particularly in the distribution between *cis*- and *trans*-1,4-hexadiene.

Catalytic Formation of Hexadienes. The reaction of $HNiL_4^+$ with butadiene, the anti–syn isomerization, and the reaction of the π-$C_4H_7NiL_2^+$ with C_2H_4 all proceed readily at or below 50°. At higher temperatures and in the presence of excess butadiene and ethylene, hexadienes were produced in a catalytic reaction.[34] The results of two reactions at 100° using either *syn*-π-$C_4H_7Ni[P(OEt)_3]_2PF_6$ or simply a mixture of $Ni[P(OEt)_3]_4$ and H_2SO_4 are given in Table VIII. About 10 mmol of hexadienes were recovered from 70 mmol of BD with a catalyst charge of 0.5 mmol.

It can be seen from Table VIII that *trans*-1,4-hexadiene was the predominant product, representing 60–70% of the hexadienes formed. Smaller amounts of 3-methyl-1,4-pentadiene and *cis*-1,4-hexadiene (each about 10% of the largest peak) were also found.

A picture of the overall reaction system is given in Figure 3a. A simplified sketch is shown in Figure 3b, where each dot represents a nickel complex. Writing the mechanism in this way rather than as a

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[28] The large uncertainty is mostly due to the uncertainty in k_2 at 25°, where the reaction was inconveniently fast.

[29] M. Meier, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, 8, 795 (1969).

[30] F. Basolo, A. T. Brault, and A. J. Poe, *J. Chem. Soc.*, 676 (1964).

[31] R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, 83, 4023 (1961).

[32] Any complete analysis must take into account any ligand decomposition which may occur.

[33] A higher concentration of σ-allyl in the presence of higher CN^- concentration has been reported in the cobalt cyanide system.[26]

[34] A preliminary account of this work was given in C. A. Tolman, Product Licensing Index, July 1969, p 25.

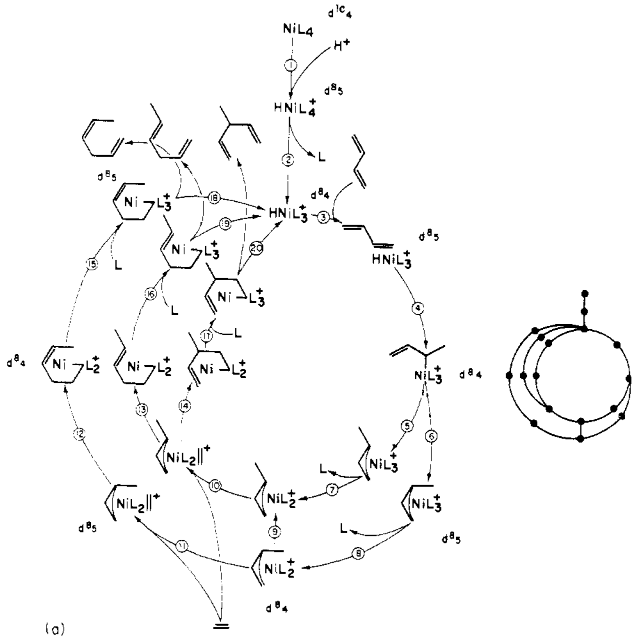

Figure 3. Mechanism of hexadiene formation from butadiene and ethylene using nickel phosphite catalysts: (a) detailed reaction, (b) simplified sketch. The phosphite ligand is designated as L. Electron configurations and coordination numbers (*e.g.*, d⁸4) of nickel are indicated near representative complexes.

list of chemical reactions makes the sequence of the reactions more apparent and emphasizes the cyclic character of the catalytic process. Converging arrows as in step 1 are used to indicate a bimolecular reaction, in this case the reaction of NiL_4 with H^+ to give $HNiL_4^+$. Diverging arrows as in step 2 indicate a unimolecular reaction (in the forward direction) to give two species. All the 20 reactions shown are assumed to be reversible in principle, but the arrows are drawn to indicate the forward course of the reaction. The evidence for the various steps in Figure 3 will now be summarized.

The rapid and reversible hydride formation reaction (1) has been described in detail.[5] Evidence for ligand dissociation (2) to give $HNiL_3^+$ has been given there and in this paper. Reactions 3, 4, 5, and 6 are so rapid that ligand dissociation (2) is rate limiting. The ratio k_6/k_5 at 0° is 7.5:1, the *anti*-π-crotyl being kinetically preferred. Reactions 7 and 8 are so rapid as to average free and bound resonances in the ^{31}P spectrum. It is the gradual conversion of π-$C_4H_7NiL_3^+$ to π-$C_4H_7NiL_2^+$ *via* reactions 7 and 8 as ligand is slowly destroyed by acid that accounts for the color change from red to yellow-orange. Reaction 9 was proposed to account for the effect of added ligand in the isomerization of *anti*- to *syn*-π-crotyl (Scheme III). The equilibrium constant K_9 is about 19, the *syn*-π-crotyl being thermodynamically preferred. Reactions 10 and 11 form π-crotyl–ethylene complexes like that observed in the nmr. Steps 12, 13, and 14, the ethylene insertion reactions, are rate determining. The predominance of *trans*-1,4-hexadiene in the product is attributed to the slowness of these three steps relative to (9), so that ethylene coupling takes place with an equilibrium mixture of *syn*- and *anti*-π-crotyl complexes. Judging from the hexadiene products in Table VIII, about 80% of the reaction goes by (13) with about 10% each by (12) and (14).

The remainder of the scheme in Figure 3 is more speculative. We have been unable to obtain nmr evidence for the alkyl complexes shown,[35] but they are expected to be very unstable, especially at elevated temperatures. There was no experimental evidence requiring coordination of a phosphite ligand in steps 15–17 prior to β-hydrogen abstraction. The reaction was written this way in order to avoid generating $HNiL_2^+$, regarded as a highly unlikely species since nickel would have only 14 electrons.[36]

A nice symmetry emerges in Figure 3 when electrons and occupied coordination sites are counted. The electron configuration and coordination number for each nickel complex are lightly indicated near each complex,[37] for example, d⁸4 by $HNiL_3^+$ means four-coordinate d⁸. All complexes on a given radius line of the loop have the same designation. Each step of the reaction can be seen to involve a change in electron configuration by two electrons or a change in coordination number by one, the nickel oscillating for the most part between d⁸4 and d⁸5, 16- and 18-electron complexes, respectively, returning ultimately to $HNiL_3^+$ to start the cycle anew. Accessibility of these two electronic configurations and the ability to accommodate coordination numbers of 4 or 5 are essential to nickel's catalytic role in the reaction. These phenomena may be quite general in homogeneous transition metal catalysis.[2,10]

Figure 3 has been simplified by the omission of several other reactions which must occur in the system: (a) catalyst deactivation by attack of H^+ on $HNiL_3^+$ to give H_2 or on other nickel complexes present to give butenes or hexenes; (b) ligand decomposition, which will affect the rates of all reactions involving free L; (c) olefin isomerization of the primary products to give conjugated hexadienes.

A detailed account of olefin isomerization in these nickel hydride solutions will be given in a later paper in the series.[38]

Acknowledgment. The author is indebted to Professor C. G. Swain for helpful discussion concerning the kinetics of the nickel hydride–butadiene reaction, and to Drs. R. A. Clement, R. D. Cramer, and L. W. Gosser for providing the dienes used for determining the gc retention times. Thanks also go to Mr. D. K. Nickerson and Mr. P. D. Baiocco for running nmr spectra.

(35) Chelated olefin–alkyl complexes in the rhodium system have been proposed earlier by Cramer.[9]

(36) All the species for which there is experimental evidence leave nickel with 16 or 18 electrons.

(37) The usual convention which regards hydrides, alkyls, and π-allyls as negatively charged has been used in determining the electron configuration; note, however, that the total number of electrons on the metal is not affected by this convention.

(38) Note Added in Proof. One of the referees pointed out the relationship of this work to recently published work of J. P. Durand, F. Dawans, and Ph. Teyssie, *J. Polymer Sci. Part A-1*, 8, 979 (1970), who found that Ni(0) compounds such as $Ni[P(OPh)_3]_4$ or Ni(1,5-cyclooctadiene)$_2$ with protonic acids give stereospecific polymerization of 1,3-butadiene. Previously, F. Dawans, J. C. Marechal, and Ph. Teyssie, *J. Organometal. Chem.*, 21, 259 (1970), had shown that isolated bis(π-allylnickel) haloacetates were efficient catalysts for 1,4-stereospecific polymerization.

In the absence of ethylene, but in a reaction otherwise similar to that described in the Experimental Section, we found that 0.5 mmol of *syn*-π-$C_4H_7Ni[P(OEt)_3]_2PF_6$ completely polymerized 70 mmol of butadiene in 5 hr at 100°. The polybutadiene formed was insoluble in H_2O, CH_3OH, and acetone, but was not further characterized. Similar solids were formed in the presence of ethylene, but to a lesser extent.