

# Chemistry of Tetrakis(triethyl phosphite)nickel Hydride, $\text{HNi}[\text{P}(\text{OEt})_3]_4^+$ . III. A Proton Nuclear Magnetic Resonance Study of Reactions with Dienes

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**Abstract:** The products of the reaction of  $\text{HNiL}_4^+$  ( $\text{L} = \text{P}(\text{OEt})_3$  or  $\text{P}(\text{OMe})_3$ ) with a variety of conjugated dienes are identified as  $\pi$ -allylnickel phosphite complexes by proton nmr. Both structural and electronic factors are shown to affect the rates of the hydride-diene reactions and the rates and equilibria of the subsequent isomerization of the products. Reaction of  $\text{DNi}[\text{P}(\text{OMe})_3]_4^{4+}$  with cyclopentadiene is shown to occur by addition of deuterium and nickel to the same side of the ring. 1,4-Pentadiene isomerizes in the presence of the hydride to 1,3-pentadiene which then reacts to give 1,3-dimethyl- $\pi$ -allyls. Reactions of  $\text{HNi}[\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2]_2^+$  and  $\text{HCo}[\text{P}(\text{OEt})_3]_4$  with 1,3-butadiene are compared with the much faster reaction of the phosphite-nickel hydrides.

In recent years a number of papers<sup>1-5</sup> have dealt with the reaction of monoenes and conjugated dienes to give 1,4-dienes, catalyzed by transition metal complexes. Of particular importance is the reaction of ethylene with 1,3-butadiene to give 1,4-hexadiene. In a number of cases transition metal hydrides have been proposed as intermediates in these reactions,<sup>3a,3c,4,5</sup> but definitive evidence has generally been lacking.

Earlier papers in this series have dealt with the formation of nickel hydrides of the type  $\text{HNiL}_4^+$  (where  $\text{L}$  is triethyl or trimethyl phosphite) from strong acids and the  $\text{NiL}_4$  complexes,<sup>6</sup> and with the role of the hydrides in catalyzing 1,4-hexadiene synthesis.<sup>7</sup> This paper deals with the products and rates of reaction of these nickel hydrides with conjugated acyclic dienes, including 1,3-butadiene, 1,3-pentadienes, *trans*-3-methyl-1,3-pentadiene, isoprene, *trans*-2-methyl-1,3-pentadiene, 2,4-dimethyl-1,3-pentadiene, 2,4-hexadienes, 2,5-dimethyl-2,4-hexadiene, and chloroprene, and with cyclopentadiene and 1,4-pentadiene. The products of the reactions were not isolated, but were characterized in solution as  $\pi$ -allylic nickel phosphite complexes by their proton nmr spectra.

## Experimental Section

Tetrakis(triethyl phosphite)nickel,  $\text{Ni}[\text{P}(\text{OEt})_3]_4$ ,<sup>8,9</sup> and tetrakis(trimethyl phosphite)nickel,  $\text{Ni}[\text{P}(\text{OMe})_3]_4$ ,<sup>10</sup> were prepared as described earlier.<sup>11</sup> Nickel hydrides of the two alkyl phosphite complexes were quite similar both in the rates of reaction with dienes and in the proton nmr spectra of the  $\pi$ -allylic portion of the products. Most of the work was with the trimethyl phosphite complex because of the greater simplicity of the ligand's nmr spectrum.

(1) (a) T. Alderson, U. S. Patent 3013066 (1961); (b) T. Alderson, E. L. Jenner, and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **87**, 5638 (1965).

(2) G. Hata, *ibid.*, **86**, 3903 (1964).

(3) (a) M. Iwamoto and S. Yuguchi, *J. Org. Chem.*, **31**, 4290 (1966);

(b) M. Iwamoto, K. Tani, H. Igaki, and S. Yuguchi, *ibid.*, **32**, 4148 (1967); (c) M. Iwamoto and S. Yuguchi, *Chem. Commun.*, 28 (1968).

(4) R. Cramer, *J. Amer. Chem. Soc.*, **89**, 1633 (1967).

(5) R. G. Miller, T. J. Kealy, and A. L. Barney, *ibid.*, **89**, 3756 (1967).

(6) Paper I in the series: C. A. Tolman, *ibid.*, **92**, 4217 (1970).

(7) Paper II in the series: C. A. Tolman, *ibid.*, **92**, 6777 (1970).

(8) J. R. Leto and M. F. Leto, *ibid.*, **83**, 2944 (1961).

(9) R. S. Vinal and L. T. Reynolds, *Inorg. Chem.*, **3**, 1062 (1964).

(10) H. Bigorgne, *Bull. Soc. Chim. Fr.*, 1986 (1960).

(11) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).

Bis[1,2-bis(diphenylphosphino)ethane]nickel,  $\text{Ni}[\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2]_2$ ,<sup>12</sup> and tetrakis(triethyl phosphite)cobalt hydride,  $\text{HCo}[\text{P}(\text{OEt})_3]_4$ ,<sup>13</sup> were prepared as described in the literature. Nickel hydrides were prepared in solution by the addition of concentrated  $\text{H}_2\text{SO}_4$ . The cobalt hydride was used directly.

In typical experiments with  $\text{HNi}[\text{P}(\text{OMe})_3]_4^+$ , 0.14 g of  $\text{Ni}[\text{P}(\text{OMe})_3]_4$  (0.25 mmol) was weighed into an nmr tube under  $\text{N}_2$ . To this was added 0.25 mmol of diene, 30  $\mu\text{l}$  of  $\text{Me}_4\text{Si}$ , and  $\text{CDCl}_3$  to a volume of 0.5 ml. Liquid dienes were added with a 100- $\mu\text{l}$  syringe. 1,3-Butadiene (6 ml, 0.25 mmol) was added as a gas after freezing the tube in liquid nitrogen and evacuating through a syringe needle inserted through the rubber cap of the tube. The tubes were cooled to  $-78^\circ$  in a Dry Ice chilled trichloroethylene bath before 14  $\mu\text{l}$  of concentrated  $\text{H}_2\text{SO}_4$  (0.25 mmol) was added. Vigorous shaking gave homogeneous yellow solutions. The tubes were quickly placed in the nmr spectrometer precooled to  $-20^\circ$ . Spectra were recorded over the low-field region ( $\tau$  0-10) and the high-field hydride region ( $\tau$  20-30). The samples were then warmed in the spectrometer and spectra recorded at various times at 0, +25, +50, and +70°. The formation of  $\pi$ -allylnickel products was accompanied by a color change from yellow to deep red.

The reaction of 1,3-butadiene with  $\text{HNi}[\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2]_2^+$  and  $\text{HCo}[\text{P}(\text{OEt})_3]_4$  was investigated by allowing solutions to warm in the nmr tube as described for reactions of  $\text{HNi}[\text{P}(\text{OMe})_3]_4^+$ . A solution of 0.2 M  $\text{HNi}[\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2]_2^+$  and 0.4 M butadiene was prepared in  $\text{CDCl}_3$  by adding 6  $\mu\text{l}$  of  $\text{H}_2\text{SO}_4$  (0.1 mmol) to 0.09 g of  $\text{Ni}[\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2]_2$  (0.1 mmol) in 0.5 ml of solution, followed by 5 ml of butadiene gas. The solution of 0.4 M  $\text{HCo}[\text{P}(\text{OEt})_3]_4$  and 0.4 M butadiene in  $\text{CDCl}_3$  was prepared by dissolving 0.15 g of  $\text{HCo}[\text{P}(\text{OEt})_3]_4$  (0.2 mmol) and 5 ml of butadiene gas (0.2 mmol) to give 0.5 ml of solution.

Proton nmr spectra were recorded in most cases at 100 Mc with a Varian HA-100 spectrometer. Varian 60- and 220-Mc instruments were used in a few cases. Tetramethylsilane, about 6% by volume in  $\text{CDCl}_3$  or  $\text{CD}_2\text{Cl}_2$  solvent, was used as an internal reference and lock signal. Temperature control was provided by a Varian V-4343 variable temperature controller. Reported temperatures are accurate to  $\pm 10^\circ$ . Chemical shifts were reproducible to  $\pm 0.03$  ppm and coupling constants to  $\pm 0.5$  cps.

Approximate half-lives were measured for each hydride-diene reaction and for the subsequent product isomerization. In cases where several spectra were measured at one temperature, the reactions appeared to be first order in diene or  $\pi$ -allyl; in others, a half-life was estimated, assuming a first order reaction and the formula

$$\tau_{1/2} = \frac{t \log 2}{\log \left( \frac{x_0 - x_e}{x - x_e} \right)}$$

where  $t$  is the time in hours and  $x$  is the concentration of a species approaching an equilibrium value  $x_e$  from an initial value  $x_0$ .

(12) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

(13) W. Kruse and R. H. Atalla, *Chem. Commun.*, 921 (1968).

Table IA. <sup>1</sup>H Nmr Data:  $\pi$ -Allyl-Ni[P(OEt)<sub>3</sub>]<sub>2</sub>HSO<sub>4</sub> in CDCl<sub>3</sub> at 25° (τ)<sup>a</sup>

$\pi$ -Allyl	Middle -H	End -H				End -CH <sub>3</sub>				Coupling constants, cps
		Syn		Anti		Syn		Anti		
		-CH <sub>3</sub>	-H	-CH <sub>3</sub>	-H	-CH <sub>3</sub>	-H	-CH <sub>3</sub>	-H	
<i>anti</i> -1-Methyl <sup>b</sup>	4.91 (dt)		6.44 (d)		7.01 (d)				8.91 (d)	$J_{ac} = 12, J_{nb} = J_{ae} = 6,$ $J_{eCH_3} = 7$
<i>syn</i> -1-Methyl <sup>b</sup>	4.87 (dt) <sup>c</sup>		6.69 (d)	5.70 (m)	7.75 (d)		8.51 (d)			$J_{ac} = J_{ad} = 11.5, J_{ab} = 6.5,$ $J_{dCH_3} = 6.5$
<i>anti,syn</i> -1,3-Dimethyl	5.34 (m) <sup>d</sup>						8.41 (d)		8.98 (d)	$J_{eCH_3} = 6, J_{cCH_3} = 6.5$
<i>syn,syn</i> -1,3-Dimethyl	5.04 (t)			6.51 (dq) <sup>e</sup>			8.75 (d)			$J_{ac} = J_{ad} = 12,$ $J_{eCH_3} = J_{dCH_3} = 6$

<sup>a</sup> Key: s, singlet; d, doublet; t, triplet; dt doublet of triplets; dq, doublet of quartets; m, unresolved multiplet. <sup>b</sup> Data in CD<sub>2</sub>Cl<sub>2</sub> solvent from ref 7. <sup>c</sup> At 50°. <sup>d</sup> At 0°. <sup>e</sup> Overlapping quartets appeared as six lines.

The reported half-lives are uncertain for a number of reasons. Their computation assumed instantaneous changes in the reported temperatures, so that the uncorrected half lives are somewhat overestimated.<sup>14</sup> A more serious difficulty is the estimated uncertainty of  $\pm 10^\circ$  in the temperature. Two different probes and two different V-4343 control units were used during the course of the work and it was only near the end that we realized that each combination of probe and control unit must be individually calibrated. Because of these factors, reported half-lives may be uncertain by as much as a factor of 2. No attempt was made to determine rate constants, especially since it has been shown that rates of both the hydride-butadiene reaction and *anti*- to *syn*-1-methyl- $\pi$ -allyl isomerization depend on the concentration of free phosphite ligand.<sup>7</sup>

## Results and Discussion

**Reaction of HNiL<sub>4</sub><sup>+</sup> with Conjugated Acyclic Dienes.** At -20° the reactions of HNiL<sub>4</sub><sup>+</sup> (L = P(OEt)<sub>3</sub> or P(OMe)<sub>3</sub>) with dienes were very slow, so that the spectra consisted of resonances characteristic of the unreacted diene and nickel hydride.<sup>15</sup> At 0°, however, the hydride-diene reactions proceeded at a moderate rate, in several cases with a half-life of 0.5 hr or less. Resonances of HNiL<sub>4</sub><sup>+</sup> and diene disappeared at an equal rate and were replaced by new ones, assignable to  $\pi$ -allylic products. In no cases were resonances due to other hydride species or  $\sigma$ -allyl intermediates detected in the spectra. In several cases marked spectral changes occurred after completion of the hydride-diene reaction, usually at higher temperatures. These changes are attributed to isomerization reactions of the initial  $\pi$ -allylic products. In most cases the solutions were held at a high temperature long enough to approach an equilibrium distribution of the isomers.

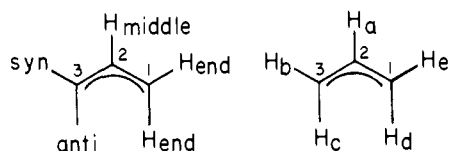


Figure 1. Designation of the protons on the  $\pi$ -allyl.

Assignments of the proton nmr spectra of the  $\pi$ -allylic products were made on the basis of spin-spin coupling patterns, consistency of chemical shifts for protons of a given type, and by analogy with earlier work on  $\pi$ -allyl-Co(CO)<sub>3</sub>.<sup>16</sup>

(14) This systematic error does not affect a comparison of the relative rates between different compounds.

(15) Proton spectra of the hydrides are given in ref 7.

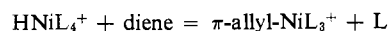
(16) J. A. Bertrand, H. B. Jonassen, and D. W. Moore, *Inorg. Chem.*, **2**, 601 (1963).

The nmr data are presented in Tables IA and IB. The chemical shifts are listed by type, generally progressing to high field from left to right. A major division is made depending on whether a proton is directly attached to the  $\pi$ -allyl framework or to a carbon in an attached -CH<sub>3</sub> group, and whether the point of attachment is at the middle (position 2) or at the end (positions 1 and 3) of the  $\pi$ -allyl. Further divisions are made depending on whether an end position is *syn* or *anti* with respect to the unique middle position<sup>17</sup> and whether the other group on the end is -CH<sub>3</sub> or -H. These distinctions and the lettering system for the coupling constants are shown in Figure 1.

It can be seen in Tables IA and IB that this scheme of classification separates the resonances into rather well-defined regions of the spectrum. Invariably single protons are found at lower field ( $\tau$  4.8-7.7) than methyl groups ( $\tau$  8.1-9.1), with the middle position of the  $\pi$ -allyl lying lowest,  $\tau$  4.8-5.4 for -H and 8.1-8.2 for -CH<sub>3</sub>, respectively. The resonance for an end position is at lower field for *syn* than for *anti*, and is generally lower with -CH<sub>3</sub> as a partner than with -H. The coupling constants, generally accurate to  $\pm 0.5$  cps, are quite uniform throughout the series regardless of starting diene, with  $J_{ac} = J_{ad} \sim 13, J_{ab} \sim 7, J_{bc} \lesssim 2, J_{dCH_3} = J_{eCH_3} \sim 6.5$  cps.

Assignments for methyl groups could be made rather easily in all cases, whereas several entries are missing for single hydrogens. Not only were the single hydrogen resonances weaker and split into more components, but they frequently occurred in regions of the spectrum containing ligand and unreacted diene resonances.

The phosphite ligand resonances indicated the presence of only one type of ligand in the spectrum, rather than two as might be expected from free and complexed ligand, according to the reaction



The reason is that free and complexed ligand exchange so rapidly that only an average spectrum is observed. Thus triethyl phosphite appeared in the  $\pi$ -allyl solutions as a methylene quintet ( $J = 7$ ) at 5.98 and a methyl triplet at  $\tau$  8.73 ( $J = 7$ ); trimethyl phosphite appeared as a simple doublet at  $\tau$  6.30 ( $J_{P-CH_3} = 11$  cps).<sup>7</sup>

It has already been mentioned that the initial distributions of products of the hydride-diene reactions

(17) This designation was suggested by W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muettterties, and B. W. Howk, *J. Amer. Chem. Soc.*, **83**, 1601 (1961).

Table IB. <sup>1</sup>H Nmr Data: π-Allyl-Ni[P(OMe)<sub>3</sub>]<sub>2</sub>HSO<sub>4</sub> in CDCl<sub>3</sub> at 25° (τ)<sup>a</sup>

π-Allyl	Middle -H	End -H				Middle -CH <sub>3</sub>	End -CH <sub>3</sub>				Coupling constants, cps	
		Syn		Anti			Syn		Anti			
		-CH <sub>3</sub>	-H	-CH <sub>3</sub>	-H		-CH <sub>3</sub>	-H	-CH <sub>3</sub>	-H		
<i>anti</i> -1-Methyl <sup>a</sup>	4.80 (m)				6.95 (d)						8.95 (d)	$J_{ac} = 12, J_{eCH_3} = 6.5$ $J_{ac} = J_{ad} = 12, J_{ab} = 7$ $J_{dCH_3} = 6.5$
<i>syn</i> -1-Methyl <sup>a</sup>	4.82 (dt) <sup>b</sup>			6.08 (m) <sup>b</sup>	7.68 (d)			8.52 (d)				
<i>anti,syn</i> -1,3-Dimethyl	5.32 (t) <sup>c</sup>							8.48 (d)			9.01 (d)	$J_{ac} = 14, J_{ae} = 7, J_{eCH_3} = 6$ $J_{eCH_3} = 7$ $J_{ac} = J_{ad} = 11.5$ $J_{eCH_3} = J_{dCH_3} = 6.5$
<i>syn,syn</i> -1,3-Dimethyl	5.13 (t)			6.53 (dq) <sup>d</sup>				8.62 (d)				
<i>anti,syn</i> -1,2,3-Trimethyl		5.27 q				8.18 (s)		8.44 (d)			8.98 (d)	$J_{eCH_3} = 6, J_{eCH_3} = 6.5$ $J_{eCH_3} = J_{dCH_3} = 6.5$
<i>syn,syn</i> -1,2,3-Trimethyl						8.18 (s)		8.57 (d)				
<i>anti</i> -1,2-Dimethyl					7.08 (d)	8.16 (s)					8.90 (d)	$J_{eCH_3} = 6.5, J_{bc} = 2.5$ $J_{dCH_3} = 6.5, J_{bc} = 3$
<i>syn</i> -1,2-Dimethyl			6.72 (d)		7.42 (d)	8.16 (s)		8.47 (d)				
1,1-Dimethyl					7.61 (d)		8.24 (s)		8.78 (s)			$J_{ac} = 14$
<i>syn</i> -1,1,3-Trimethyl	4.96 (d)			6.56 (dq) <sup>d</sup>			8.33 (s)	8.53 (d)	8.84 (s)			$J_{ac} = 13, J_{eCH_3} = 6$
1,1,3,3-Tetramethyl	5.34 (s)						8.45 (s)		8.61 (s)			None
<i>anti</i> -1-Ethyl- <i>syn</i> -3-methyl <sup>e</sup>								8.37 (d)				$J_{eCH_3} = 7$
<i>syn</i> -1-Ethyl- <i>syn</i> -3-methyl <sup>f</sup>	5.04 (t)							8.52 (d)				$J_{ac} = J_{ad} = 12, J_{eCH_3} = 6$
1,1-Dimethyl-3-isopropyl <sup>g</sup>							8.42 (s)		8.77 (s)			
<i>syn</i> -1-Methyl-2-chloro				5.79 (q)				8.40 (d)				$J_{dCH_3} = 6$

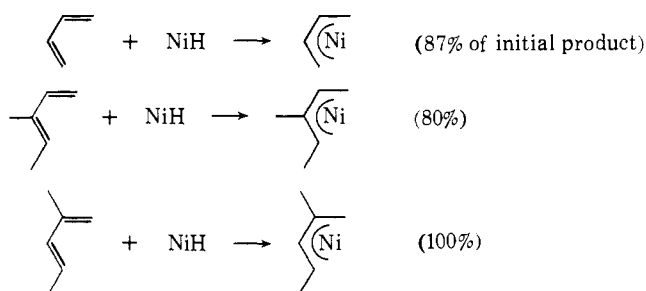
<sup>a</sup> Data in CD<sub>2</sub>Cl<sub>2</sub> from ref 7. <sup>b</sup> At 75°. <sup>c</sup> At 0°. <sup>d</sup> Overlapping quartets appeared as six lines. <sup>e</sup> The 220-Mc spectrum showed the ethyl group as a broad methylene resonance at τ 8.26 and the methyl as a triplet at τ 9.00 ( $J = 7$ ). <sup>f</sup> The 220-Mc spectrum showed the ethyl group as a broad methylene resonance at τ 8.07 and the methyl as a triplet at τ 8.86 ( $J = 6.5$ ). <sup>g</sup> The 220-Mc spectrum showed the methyl resonance of the isopropyl group as a doublet at τ 9.13 ( $J_{H-CH_3} = 6.5$ ). The orientation of this isopropyl group is uncertain but probably *syn*. A questionable very weak doublet at τ 9.50 ( $J = 6.5$ ) is assigned to a trace of *anti*-isopropyl isomer. <sup>h</sup> Key: s, singlet; d, doublet; t, triplet; q, quartet; dt, doublet of triplets; dq, doublet of quartets; m, unresolved multiplet.

Table II. Reaction of  $\text{HNi}[\text{P}(\text{OMe})_3]_4\text{HSO}_4$  with Dienes in  $\text{CDCl}_3$ 

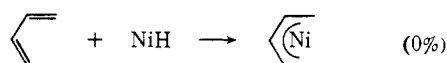
Diene	$\pi$ -Allyl products	Initial distribution, %	Final distribution, %	Hydride-diene reaction $\tau_{1/2}$ (1), hr, °C	Product isom $\tau_{1/2}$ (2), hr, °C	Final conditions, hr, °C
1,3-Butadiene <sup>a</sup>	<i>anti</i> -1-Methyl	88	5	0.5, 0	2, 50	1.4, 70
	<i>syn</i> -1-Methyl	12	95	<0.1, 25	0.3, 70	
1,3-Pentadienes	<i>anti,syn</i> -1,3-Dimethyl	100	20	0.3, 0	0.2, 25	0.4, 50
68% <i>trans</i> , 32% <i>cis</i>	<i>syn,syn</i> -1,3-Dimethyl	0	80	<0.1, 25		
<i>trans</i> -3-Methyl-1,3-pentadiene	<i>anti,syn</i> -1,2,3-Trimethyl	80	80	0.5, 0	<0.2, 25	0.4, 50
	<i>syn,syn</i> -1,2,3-Trimethyl	20	20	<0.1, 25		
2-Methyl-1,3-butadiene	<i>anti</i> -1,2-Dimethyl	62	24	0.3, 0	0.3, 75	0.9, 75
	<i>syn</i> -1,2-Dimethyl	18	59	<0.1, 25		
	1,1-Dimethyl	20 <sup>e</sup>	17 <sup>e</sup>			
<i>trans</i> -2-Methyl-1,3-pentadiene	<i>syn</i> -1,1,3-Trimethyl	100	100	>1.5, 0	<i>b</i>	0.6, 50
				0.2, 25		
2,4-Dimethyl-1,3-pentadiene <sup>c</sup>	1,1,3,3-Tetramethyl	100	100	>1.5, 0;	<i>b</i>	0.6, 50
				0.4, 25		
2,4-Hexadienes	<i>anti,syn</i> -1-Ethyl-3-methyl	50	30	0.5, 25	<0.5, 25	0.5, 50
43% <i>trans,trans</i> ; 40% <i>cis,trans</i> ;	<i>syn,syn</i> -1-Ethyl-3-methyl	50	70			
14% <i>cis,cis</i>						
2,5-Dimethyl-2,4-hexadiene <sup>d</sup>	1,1-Dimethyl-3-isopropyl	? <sup>d</sup>	?	1.5, 25	?	1.5, 50
2-Chloro-1,3-butadiene	<i>syn</i> -1-Methyl-2-chloro	100	100	6.0	<i>b</i>	0.9, 50
				0.4, 25		

<sup>a</sup> In  $\text{CD}_2\text{Cl}_2$  solvent. <sup>b</sup> No product isomerization detected. <sup>c</sup> The reaction of the diene with the hydride did not go to completion. <sup>d</sup> The configuration of the isopropyl group is uncertain. <sup>e</sup> The fraction of 1,1-dimethyl- $\pi$ -allyl in the products did not change significantly on heating at 75° and is regarded as kinetically controlled.

were modified in several cases by subsequent isomerization. Table II shows the initial and final distributions of products detected from the reaction of various conjugated dienes with  $\text{HNi}[\text{P}(\text{OMe})_3]_4^+$ . The products are listed in the same order as in Table I, the kinetically preferred product from each diene being listed first. It can be seen that the *anti* isomers are kinetically preferred, suggesting rotation of the diene into a *cisoid* configuration as  $\text{NiH}$  is added. This is illustrated below for addition of  $\text{Ni-H}$  to 1,3-butadiene, *trans*-3-methyl-1,3-pentadiene, and *trans*-2-methyl-1,3-pentadiene.



Addition to *cisoid* diene appears to be preferred, but only in the absence of a *cis* substituent on one of the double bonds. Thus *cisoid cis*-1,3-pentadiene would give *anti,anti*-1,3-dimethyl- $\pi$ -allyl, which was not observed.<sup>18</sup>



The *syn* isomers tend to be thermodynamically preferred, becoming less so in the highly substituted  $\pi$ -allyls. Thus the *syn:anti* ratios at equilibrium were 19:1, 4:1, 2.5:1, and 0.25:1 for 1-methyl-, 1,3-dimethyl-, 1,2-dimethyl-, and 1,2,3-trimethyl- $\pi$ -allyls. The decreasing *syn:anti* ratios in this series are probably

(18) *cis*-1,3-Pentadiene was present to the extent of 32% in a mixture of the isomers.

the result of steric crowding. Destabilization of highly crowded products was also indicated by the extent of the hydride-diene reaction. Though in most cases the reaction of  $\text{HNi}[\text{P}(\text{OMe})_3]_4^+$  and conjugated diene was quantitative, the highly hindered 1,1,3,3-tetramethyl and 1,1-dimethyl-3-isopropyl- $\pi$ -allyls were only incompletely formed, leaving unreacted hydride and diene in solution; in the latter case about 80% of the starting diene and hydride remained at the end of the reaction.

The experiments show that the  $\pi$ -allylic products formed invariably corresponded to  $\text{Ni-H}$  addition across a terminal double bond, if present. Thus 1,3-pentadiene gave 1,3-dimethyl- $\pi$ -allyls but no detectable 1-ethyl- $\pi$ -allyls.<sup>19</sup> *trans*-3-Methyl-1,3-pentadiene gave no 1-ethyl-1-methyl- $\pi$ -allyl.

If no terminal  $\text{C}=\text{C}$  was present, an addition reaction still occurred, but at a much slower rate, as in the case of the 2,4-hexadienes.

The effect of an internal methyl group as in isoprene was to hinder addition to that double bond, but only by a factor of about 5:1. Thus isoprene gave both 1,1-dimethyl- $\pi$ -allyl and 1,2-dimethyl- $\pi$ -allyls in a 1:5 ratio.

A competition between internal and terminal methyl blockage is shown in the case of 2-methyl-1,3-pentadiene. Only 1,2 addition was observed with a rate approximately one-fifth that of 1,3-pentadiene, as expected.

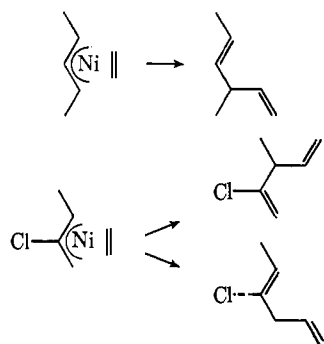
The half-lives of the reactions of various dienes with  $\text{HNi}[\text{P}(\text{OMe})_3]_4^+$  [ $\tau_{1/2}$ (1)] are given in column 5 of Table II, ranked in order of increasing half-life. The rate differences between the dienes with terminal double bonds are not judged to be significant.<sup>20</sup> Dienes without terminal double bonds reacted much more slowly, consistent with the products when one double bond was ter-

(19) A similar result was reported for the reactions of  $\text{HCo}(\text{CO})_4$ .<sup>16</sup>

(20) It was shown earlier<sup>7</sup> that the rate of reaction of  $\text{HNi}[\text{P}(\text{OEt})_3]_4^+$  with butadiene in  $\text{CH}_3\text{OH}$  was independent of diene concentration, implying that ligand dissociation was the rate-limiting step in this case.

minally substituted and the other not. The importance of electronic effects is shown by comparison of the rates of reaction of chloroprene and isoprene, where steric effects are probably comparable. The reaction of chloroprene was slower by a factor of 20 at 0°, giving exclusively the product of Ni-H addition to the non-chlorinated double bond.

The  $\pi$ -allylic complexes observed in the reaction of  $\text{HNi}[\text{P}(\text{OMe})_3]_4^+$  with dienes are in full accord with the major products of the ethylene-diene coupling reactions reported by Miller, Kealy, and Barney,<sup>5</sup> using a catalyst consisting of dichlorobis(tri-*n*-butylphosphine)nickel (II) and chlorodiisobutylaluminum. Thus 1,3-pentadiene and ethylene gave 3-methyl-1,4-hexadiene, while 2-chloro-1,3-butadiene and ethylene gave mostly 4-chloro-1,4-hexadiene with some 2-chloro-3-methyl-1,4-pentadiene. These are just the products expected from ethylene coupling to the 3 and 1 positions of the 1,3-dimethyl- $\pi$ -allyl or 1-methyl-2-chloro- $\pi$ -allyl intermediates of the kind which we identified in the nmr spectra.<sup>21</sup>



The ethylene-diene coupling products reported by Alderson, Jenner, and Lindsey<sup>1b</sup> using a rhodium chloride catalyst can also be understood in terms of the complexes we have observed. For example, ethylene and 2,4-hexadienes gave 3-ethyl-1,4-hexadiene and 3-methyl-1,4-heptadiene, just the products expected by coupling of an ethylene to the 1 or 3 position, respectively, of the 1-ethyl-3-methyl- $\pi$ -allyl complex like that we observed.

Most of the products of the ethylene-diene coupling reactions reported in the literature with a variety of catalysts can be rationalized in terms of coupling ethylene to  $\pi$ -allylic complexes of the type we have observed in the reactions of  $\text{HNiL}_4^+$  with various dienes. The one result which is inconsistent is the report by Hata<sup>2</sup> that ethylene and 1,3-pentadiene in the presence of a catalyst consisting of tris(acetylacetonato)-iron(III) and triethylaluminum gave 1,4-heptadiene as the major product. This could form by addition of ethylene to the 3 position of a 1-ethyl- $\pi$ -allyl complex. This type of  $\pi$ -allyl was not observed in the nickel system.

**Reaction of  $\text{HNiL}_4^+$  with Cyclopentadiene.** The products of reaction of the nickel hydrides with acyclic conjugated dienes suggested reaction of the diene in a cisoid orientation. In cyclopentadiene the diene is held in this position by the ring. The rate of reaction of cyclopenta-

(21) The coupling reactions are considered to occur by way of olefin insertion to the  $\pi$ -allyl to give an intermediate metal alkyl-olefin complex, <sup>4</sup> followed by abstraction of a  $\beta$ -hydrogen to give 1,4-diene product with the liberation of metal hydride.

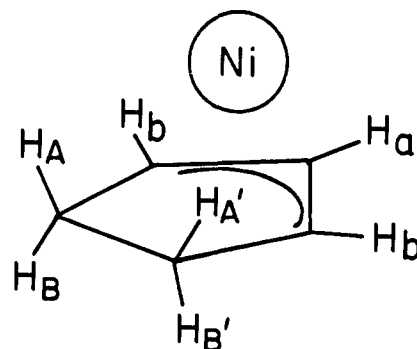


Figure 2. Cyclopentenylnickel.

diene with  $\text{HNi}[\text{P}(\text{OMe})_3]_4^+$  was rapid, comparable to that of dienes with a terminal double bond. The proton nmr spectrum at 100 Mc showed the typical  $\text{P}(\text{OCH}_3)_3$  resonance as a doublet at  $\tau$  6.34 ( $J_{\text{PH}} = 10.5$  cps). The  $\pi$ -allyl fragment contained three resonances in a 1:2:4 ratio. Singlets were found at 4.52 and 5.86 and a four-line AA'BB' pattern at  $\tau$  8.48, with  $\delta_{\text{AB}} = 0.44$  ppm and  $J_{\text{AB}'} = 16$  cps. This interpretation of the strongest feature was confirmed by spectra at 60, 100, and 220 Mc. The three resonances are assigned to  $\text{H}_a$ ,  $\text{H}_b$ , and the ethylene bridge protons  $\text{H}_A$  and  $\text{H}_B$ , as shown in Figure 2.

The plane of symmetry implied by the single resonance of the  $\text{H}_b$  protons makes  $\text{H}_A$  chemically equivalent to  $\text{H}_A'$  and  $\text{H}_B$  to  $\text{H}_B'$ . The higher field doublet of the second-order pattern is assigned to the A protons by analogy with the higher fields found for anti than for syn protons in other  $\pi$ -allyl complexes, proximity to the metal apparently giving rise to an upfield shift. This assignment was confirmed by spectra on cyclopentenyl solutions made using  $\text{D}_2\text{SO}_4$ . The high-field component of the AA'BB' pattern was reduced in intensity by a factor of about 2 by the use of  $\text{D}_2\text{SO}_4$ . This result means that Ni and D add to the same side of the cyclopentadiene ring, giving one D and one H in the A positions. The product excludes as an intermediate a loosely associated ion pair of Ni(II) and cyclopentenyl anion, which would lead to scrambling of deuterium between A and B positions on the ring.

The ready formation of a cyclopentenylnickel complex is interesting in view of the report that cyclopentadiene could not be coupled with ethylene to form 3-vinylcyclopentene<sup>5</sup> under conditions where 1,3-butadiene readily gave 1,4-hexadienes. The difficulty presumably arose in the coupling step rather than in the formation of a  $\pi$ -allyl. It may be that the ethylene bridge effectively hinders attack by ethylene on the terminal carbons of the  $\pi$ -allyl.

**Reaction of  $\text{HNiL}_4^+$  with 1,4-Pentadiene.** The reaction with 1,4-pentadiene was of interest since it provided an example of olefin isomerization and  $\pi$ -allyl formation in the same system where it was possible to determine the relative rates of the two reactions.

The reaction proceeded at a convenient rate at 0°. As 1,4-pentadiene reacted, 1,3-pentadiene and the syn-anti isomer of 1,3-dimethyl- $\pi$ -allyl (I) were detected in early stages of the reaction. Later the syn,syn isomer II formed, finally becoming preferred at higher temperatures. Figure 3 shows how the concentrations changed with time. At times corresponding to the ver-

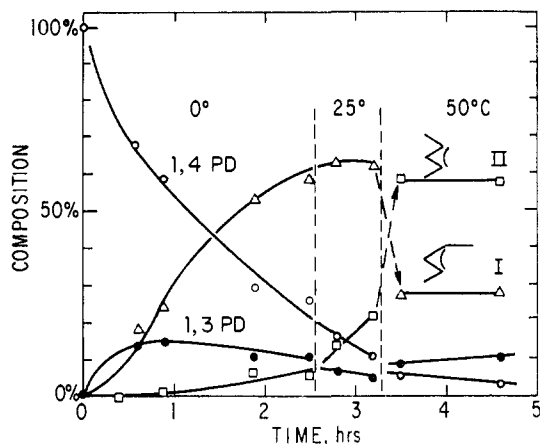
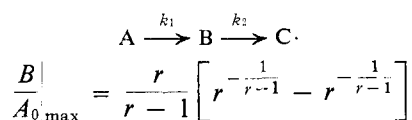


Figure 3. Reaction of  $\text{HNi}[\text{P}(\text{OMe})_3]_4^+$  with 1,4-pentadiene (1,4 PD), each 0.5 M in  $\text{CDCl}_3$ . Formed in the reaction are 1,3-pentadiene (1,3 PD), *anti,syn*-1,3-dimethyl- $\pi$ -allyl (I), and *syn,syn*-1,3-dimethyl- $\pi$ -allyl (II).

tical dashed lines the temperature was raised by 25° to accelerate the reaction.

The half-life for disappearance of 1,4-pentadiene was 1.2 hr at 0°. In a separate experiment starting with 1,3-pentadiene, the half-life for  $\pi$ -allyl formation from the conjugated diene was 0.3 hr at 0°. Thus 1,3-pentadiene formed from 1,4- at about one-quarter of the rate at which 1,3-pentadiene itself reacted with the hydride to give 1,3-dimethyl- $\pi$ -allyl. An independent measure of the relative rates comes from the maximum concentration achieved by the intermediate 1,3-pentadiene. In consecutive first-order reactions



where  $r = k_1/k_2$ . For the observed  $B/A_{0,\text{max}} = 0.15$  a graphical solution gives  $r = 0.23$ , in good agreement with the factor of 0.25 obtained above.

The observation of  $\pi$ -allyl products in the addition of nickel hydride to the conjugated diene, but not of the  $\sigma$ -alkyl intermediates presumed formed in the isomerization of 1,4-pentadiene to 1,3-, illustrates the far greater stability of  $\pi$ -allyl complexes of nickel compared to the  $\sigma$ -alkyls.<sup>22</sup>

The observed 1,3-dimethyl- $\pi$ -allyl products, the presence of 1,3-pentadiene in the solution, and the behavior of the concentrations with time strongly recommend a process involving double bond migration followed by  $\pi$ -allyl formation in the presence of  $\text{HNi}[\text{P}(\text{OMe})_3]_4^+$ .<sup>23</sup> The more rapid reaction of the hydride with the conjugated than with the unconjugated diene explains why 1,4-hexadienes can be obtained in about 70% yields in the catalytic coupling of ethylene with 1,3-butadiene.<sup>7</sup> The nickel hydride preferentially reacts with 1,3-butadiene, rather than with product 1,4-hexadiene to give the less desirable 2,4-hexadienes.<sup>24</sup>

(22) Unstable alkylnickel complexes which decomposed and were not isolated were described by J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1718 (1960).

(23) The behavior of  $\text{HNiL}_4^+$  in the reaction with 1,4-pentadiene contrasts with that reported for  $\text{HCo}(\text{CO})_3$ .<sup>16</sup> In the cobalt system the reaction product was (1-ethyl- $\pi$ -allyl)cobalt with 1,4-pentadiene but (1,3-dimethyl- $\pi$ -allyl)cobalt with 1,3-pentadiene.

(24) 1,4-Hexadienes are desirable in terpolymers with ethylene and propylene. The terminal double bond is incorporated into the polymer chain while the less reactive internal double bond remains to provide a site for cross-linking by vulcanization.

This observation also explains why Miller, Kealy, and Barney<sup>5</sup> found increasing fractions of 2,4-hexadienes as the concentration of 1,3-butadiene decreased.

**Reaction of Other Hydrides with 1,3-Butadiene.** Complexes  $\text{HNi}[\text{P}(\text{OEt})_3]_4^+$  and  $\text{HNi}[\text{P}(\text{OMe})_3]_4^+$  reacted rapidly with 1,3-butadiene, complete reaction requiring less than 0.1 hour at 25°. The reaction of  $\text{HNi}[\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2]_2^+$ <sup>25</sup> was considerably slower, with a half-life of about 8 hr at 50° or 0.4 hr at 80°. The product was identified as a *syn*-1-methyl- $\pi$ -allyl complex by the  $-\text{CH}_3$  doublet resonance at  $\tau$  8.65 ( $J_{\text{dCH}_3} = 6$  cps). The reaction of  $\text{HCo}[\text{P}(\text{OEt})_3]_4^+$ <sup>27</sup> was so slow that it could not be detected. Spectra of the solution showed no evidence of reaction up to 75°. After 0.5 hr at 75° the cobalt complex decomposed, giving a deep blue paramagnetic solution. The limited reactivity of the latter two hydrides is attributed to the difficulty in getting a free coordination position *via* ligand dissociation. A detailed kinetic study of the reaction of  $\text{HNi}[\text{P}(\text{OEt})_3]_4^+$  showed that one phosphorus ligand must be dissociated before reaction with butadiene can occur.<sup>7</sup> It is interesting in this regard that Iwamoto and Yuguchi<sup>3c</sup> have reported that  $\text{HCo}[\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2]_2$  is ineffective in hexadiene catalysis in the absence of cocatalysts. They attributed the lack of reactivity to the absence of a free coordination position.

The lack of reactivity of  $\text{HCo}[\text{P}(\text{OEt})_3]_4$  compared to  $\text{HNi}[\text{P}(\text{OEt})_3]_4^+$  is of particular interest since the two compounds are isoelectronic, differing only by one proton in the metal nuclei. The lack of reactivity of the cobalt hydride with butadiene suggests that ligand exchange on  $\text{HCo}[\text{P}(\text{OEt})_3]_4$  is very slow. In this respect  $\text{HCo}[\text{P}(\text{OEt})_3]_4$  is more like  $\text{Ni}[\text{P}(\text{OEt})_3]_4$ <sup>28</sup> than  $\text{HNi}[\text{P}(\text{OEt})_3]_4^+$ . Slow exchange by a dissociative process in the case of  $\text{Ni}[\text{P}(\text{OEt})_3]_4$  has been shown by Meier, Basolo, and Pearson.<sup>29</sup> Triethyl phosphite dissociates much more rapidly from  $\text{HNi}[\text{P}(\text{OEt})_3]_4^+$ .<sup>7</sup>

The marked differences in reaction rates of  $\text{HNi}[\text{P}(\text{OEt})_3]_4^+$  and  $\text{HCo}[\text{P}(\text{OEt})_3]_4$  with 1,3-butadiene, and the great differences in ligand exchange rates in Ni(0)-phosphorus complexes,<sup>11</sup> indicate that both electronic and steric effects are involved in determining the rates of ligand dissociation reactions in transition metal complexes. Ligand exchange steps are essential in catalytic processes for forming coordinatively unsaturated species capable of reaction with substrates present in solution. The importance of coordinative unsaturation in catalytically active systems has recently been emphasized by Collman.<sup>30</sup>

**Acknowledgments.** The author is indebted to Drs. R. D. Cramer, L. W. Gosser, R. J. Harder, H. E. Holmquist, and W. Shear for diene samples, and to R. A. Schunn for the samples of  $\text{Ni}[\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2]_2$  and  $\text{HCo}[\text{P}(\text{OEt})_3]_4$ . Particular thanks go to Mr. D. K. Nickerson for running the many nmr spectra required in this research.

(25) The hydride resonance appeared as a quintet at  $\tau$  23.1,  $J_{\text{PH}} = 5.5$  cps. Isolation of nickel hydride complexes of this type has been described by Schunn.<sup>26</sup>

(26) R. A. Schunn, *Inorg. Chem.*, **9**, 394 (1970)

(27) The hydride resonance in  $\text{CDCl}_3$  appeared as a quintet at  $\tau$  25.7,  $J_{\text{PH}} = 20$  cps.<sup>6</sup> The complex was first reported by Kruse and Atalla, who gave a considerably lower value for  $J_{\text{PH}}$  of 12 cps in  $\text{CS}_2$ .<sup>13</sup>

(28) The proton nmr spectra of  $\text{HCo}[\text{P}(\text{OEt})_3]_4$  and  $\text{Ni}[\text{P}(\text{OEt})_3]_4$  are indistinguishable in the region of  $\tau$  0–10, showing that the electron density in the ligands is very similar.

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

(30) J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).