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THERMAL DECOMPOSITION OF *trans*-CHLORO(2-ALLYLPHENYL)BIS(TRIETHYLPHOSPINE)NICKEL(II)*

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Summary

Thermolysis of *trans*-chloro(2-allylphenyl)bis(triethylphosphine)nickel(II), I, in tetrachloroethylene has afforded indene as the major hydrocarbon product along with lesser amounts of allylbenzene and *trans*-β-methylstyrene. Organonickel products were *trans*-chloro(trichlorovinyl)bis(triethylphosphine)nickel(II), II, chloro[2-(*trans*-propenyl)phenyl]bis(triethylphosphine)nickel(II), III, and *trans*-dichlorobis(triethylphosphine)nickel(II). Compound III was the major product from thermolysis of I in benzene. Chloro[2-(*cis*-propenyl)phenyl]bis(triethylphosphine)nickel(II), IV, and III could be synthesized independently by treatment of chloro-2-(*cis*-propenyl)benzene and chloro-2-(*trans*-propenyl)benzene, respectively, with nickel acetylacetonate and triethylaluminium in the presence of triethylphosphine. Thermolysis of I in benzene containing allylbenzene led to the formation of *trans*-β-methylstyrene. The thermolysis of I in benzene in the presence of *cis*-1,4-hexadiene caused the skeletal rearrangement of the diene to *trans*-2-methyl-1,3-pentadiene. A catalyst derived from ethylenebis(triphenylphosphine)nickel(0) and hydrogen chloride isomerized allylbenzene to *trans*-β-methylstyrene.

Introduction

Catalysts derived from reactions of diisobutylaluminium chloride with dihalobis(trialkylphosphine)nickel(II) compounds, and from reactions of hydrogen halides with ethylenebis(triarylphosphine)nickel(0) complexes, have accomplished some remarkable skeletal isomerizations of 1,4-dienes [2]. These rearrangements

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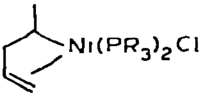
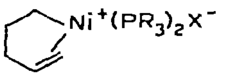
* Some of these results were published in a preliminary communication, see ref. 1. Taken in part from the Ph. D. theses of Darryl R. Fahey, 1968, and Harry J. Golden, 1973, University of North Dakota.

have been postulated to involve the intervention of alkenyl nickel complexes such as A [3] and B [4], derived from the addition of the elements of nickel


(A)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hydride to a double bond of the diene reactant. In this paper we describe the results from some studies of *trans*-chloro(2-allylphenyl)bis(triethylphosphine)-nickel(II), I, in hydrocarbon solvents. The synthesis and characterization of I and its palladium analog have been described elsewhere [5]. The compounds possess the *trans*-planar configuration and the plane of the benzene ring is restricted to orientations roughly perpendicular to the metal bonding plane. This places the *o*-allyl group in positions where the olefinic bond becomes a potential ligand at an apical site in the complexes. Thus I possesses features in common with A and B and its chemistry might be expected to be related to th behavior of reaction intermediates in the diene arrangements.

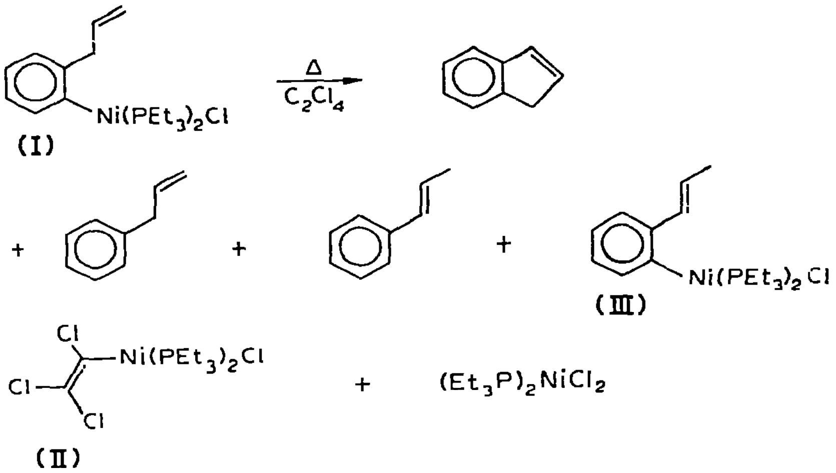
Results and discussion

Thermolyses in tetrachloroethylene and benzene

Solutions of I in tetrachloroethylene and benzene were warmed in the absence of air and products from its decomposition were isolated and characteriz During 2.5 h at 80-85° in tetrachloroethylene, 96% of I was converted to produ Two nickel compounds could be isolated from the product mixture; *trans*-chlor (trichlorovinyl)bis(triethylphosphine)nickel(II), II, 46% yield, and chloro[2-(*trans*-propenyl)phenyl]bis(triethylphosphine)nickel(II), III, 6%. The identifiabl hydrocarbon products were indene, 52% yield, allylbenzene, 5%, and *trans*-β-methylstyrene, 2%. In analogous experiments conducted on a larger scale and during an 18 h period, the above products were afforded in similar yields along with an additional nickel compound, *trans*-dichlorobis(triethylphosphine)nickel (II), 2% yield. No other monomeric products derived from the allylphenyl ligan in I were detected. Indane and 2,2'-diallylbiphenyl were specifically shown not to be present in > 1% yields.

When I was warmed in benzene at 60-70° for 16 h, 56% was converted to products. Of the material reacted, 39% was converted to III. GLPC analysis of the hydrocarbon products showed that the corresponding percentages of indene, *trans*-β-methylstyrene and allylbenzene were 11, 1.6 and 1.4% respectively. Thermolysis of I in benzene containing small amounts of tetrachloroethylene (Ni/C_2Cl_4 molar ratio = 3/1) resulted in the conversion of 96% of I to products during 24 h at 60-70°. Of the I reacted, 24% was converted to III and 28, 8.5 and 1% of the 2-allylphenyl ligand was converted to indene, *trans*-β-methylstyren and allylbenzene respectively. The amount of II formed was 75% of the theoreti amount possible.

trans-Chloro(2-allylphenyl)bis(triethylphosphine)palladium(II) exhibited a much greater stability when its solutions were heated. No detectable decomposition occurred in tetrachloroethylene solution during 48 h at 90-100°.



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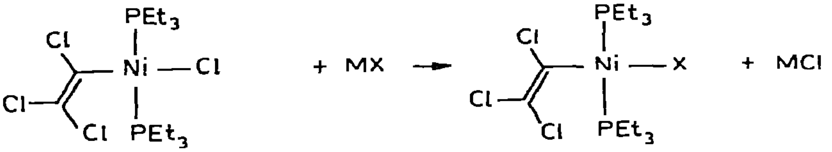
Characterization of II and III

Compound II is a yellow diamagnetic solid, m.p. 92.0-92.8° (dec. 190-200°), which is monomeric in benzene solution. The assignment of the trichlorovinylnickel chloride structure as distinguished from that of a π complex such as in tetrachloroethylenebis(triphenylphosphine)platinum(0) [6] was based upon both spectral and chemical evidence. The PMR spectrum ($CDCl_3$) consisted of partially overlapping multiplets centered near τ 8.3 and 8.75 ppm, the high field resonance (CH_3 protons) being an apparent 1/4/6/4/1 quintet characteristic of *trans*-bis(triethylphosphine) transition metal complexes [5, 7, 8]. The dipole moment was found to be 1.95D, providing further evidence for the *trans* configuration. The compound exhibited a marked resistance to attack by atmospheric oxygen, and it was recovered in 95% yield after its ether solution was treated with HCl for two days. The halogen ligand could be replaced in metathetical displacement reactions (eqn. 2) employing NaI, LiBr, *o*-tolyllithium [5], and phenylethynylmagnesium bromide [9].



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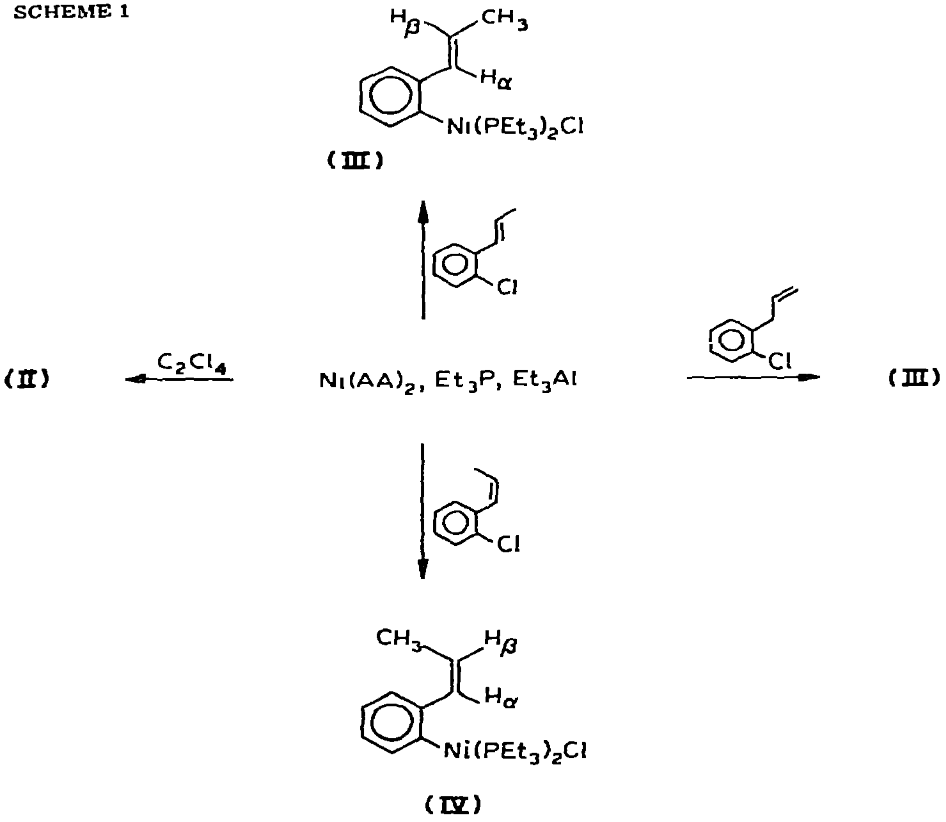
The structure assignment for III was also based upon a combination of spectral and chemical evidence. The *trans*, or *E*, configuration about the olefinic bond was evident from the vinyl carbon—hydrogen out-of-plane deformation vibration at 968 cm^{-1} ($CHCl_3$ solution) and from features of the PMR spectrum. Both vinyl proton resonances were deshielded to the extent that they overlapped with those of the aromatic protons to give a complex array of peaks from τ 2.26 to 3.45 ppm. This was expected [5] for the isomer with the *trans* double bond since rotation of the propenyl group would cause both vinyl protons to experience environments in close proximity to the metal above the bonding plane in a planar complex. Only the α proton in the corresponding *cis*-β-methylstyrylnickel complex can reside near the metal. The propenyl methyl proton resonance in

III consisted of a doublet at τ 8.03 ppm, $J(CH_3, H_\beta)$ = 5.9 Hz. *trans*- and *cis*-β-Met styrene were found to have corresponding coupling constants of 6.0 and 6.7 H respectively. The compound presumably exists in the *trans*-planar configuratio along with other complexes of this type [5], although this could not be deduce from the PMR spectrum which exhibited overlapping CH_3 and CH_2 proton reso es of the Et_3P ligands. Treatment of III with hydrogen chloride in ether afforde a hydrocarbon with a GLPC retention time identical with that of *trans*-β-methy styrene. When III was warmed in tetrachloroethylene for 18 h at 80-90°, 90% could be recovered unchanged.

Compounds II, III, and chloro[2-(*cis*-propenyl)phenyl]bis(triethylphosphi nickel(II), IV, could be synthesized independently by the oxidative additions o tetrachloroethylene [1, 5], chloro-2-(*trans*-propenyl)benzene, and chloro-2-(*cis*-propenyl)benzene, respectively to nickel(0) generated in situ in the presence of triethylphosphine. Nickel(0) complexes possessing triarylphosphine or tricyclohexylphosphine ligands, with either ethylene or nitrogen also bonded to the met had previously been synthesized by treatment of nickel acetylacetonate with a trialkylaluminium compound in the presence of the potential ligands [10-14]. We have used this general procedure to generate a nickel(0) complex in situ through the reaction of triethylaluminium with nickel acetylacetonate in the presence of triethylphosphine and the desired chlorocarbon substrate. The observed oxidative addition reactions employing the above-mentioned chlorocarbo are shown in Scheme 1. The first application of this procedure to the synthesis

SCHEME 1



of arylnickel compounds was reported by Fahey [15]. Subsequent work has provided other routes to arylnickel compounds via oxidative addition reactions [16-19].

It is noteworthy that the oxidative additions of the chloro-2-(propenyl)-benzenes to nickel(0) occurred with predominant retention of configuration about the olefinic bond. The PMR spectrum (C_6D_6) of IV exhibited an octet resonance for H_β centered at τ 4.24, a doublet of multiplets for H_α at τ 2.28, and the propenyl CH_3 quartet resonance at τ 8.10 ppm; $J(CH_3, H_\beta) = 7.0$, $J(CH_3, H_\alpha) = 1.8$, $J(H_\alpha, H_\beta) = 11.6$ Hz. The selective pronounced antishielding of H_α by the metal [5] served as a verification of the structure assignment.

Generation of alkene isomerization catalysts

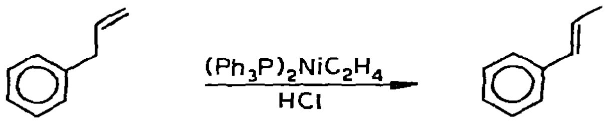
(a) Isomerization of allylbenzene. Treatment of allylbenzene with I in benzene solution at 60-70° (alkene/I molar ratio = 2.2) afforded a 79% conversion of I to products during 26 h. Of the I reacted, 54% was converted to III and 22% to indene. During the reaction period, 97% of the allylbenzene was consumed and 64% of the reacted material was isomerized to *trans*-β-methylstyrene.

Appreciable isomerization of allylbenzene was not observed in analogous experiments conducted in tetrachloroethylene. Solutions of I in tetrachloroethylene were heated at 85-90° for 10 h in the presence of allylbenzene. Three experiments in which molar ratios of allylbenzene/I of 0.5, 1.0 and 2.0 were employed all afforded product mixtures in which the *trans*-β-methylstyrene yields were in the 0-2% range and most of the allylbenzene was recovered unchanged.

(b) Skeletal rearrangement of cis-1,4-hexadiene. Treatment of *cis*-1,4--hexadiene with I in benzene solution at 60-70° (diene/Ni molar ratio = 0.85) for 45 h caused 56% of the diene to be converted to products. Of the material reacted, 56% was converted to *trans*-2-methyl-1,3-pentadiene, 21% to *cis, trans*-2,4-hexadiene, and 21% to *cis, cis*-2,4-hexadiene. Analysis showed that 37% of I had reacted with 35% of this amount being converted to III. No rearrangement of *cis*-1,4-hexadiene was observed and $<$ 1% of I had reacted when its benzene solution was treated with I for 24 h at room temperature. However, an active catalyst for the isomerization of *cis*-1,4-hexadiene to the above-mentioned products was generated when a toluene solution of I and the diene was treated with diisobutylaluminium chloride at room temperature.

To investigate the possibility that *cis*-1,4-hexadiene was being isomerized by HCl, generated in the decomposition of I, a toluene solution of the diene was saturated with HCl and warmed at 60-70° for a 6 h period. No diene isomerization products were detected.

(c) Isomerization of allylbenzene by HCl and ethylenebis(triphenylphosphine)nickel(0). Allylbenzene in benzene solution remained unchanged when it was treated with ethylenebis(triphenylphosphine)nickel(0) (alkene/Ni ratio = 10) for 3.5 h at room temperature. On addition of a benzene solution of hydrogen chloride (Ni/HCl ratio = 5/1), an amber solution formed and the allylbenzene was quantitatively converted to *trans*-β-methylstyrene during the next 3.5 h (eqn. 3). A control experiment demonstrated that HCl did not isomerize allylbenzene during 20.5 h at 60-70° in benzene.



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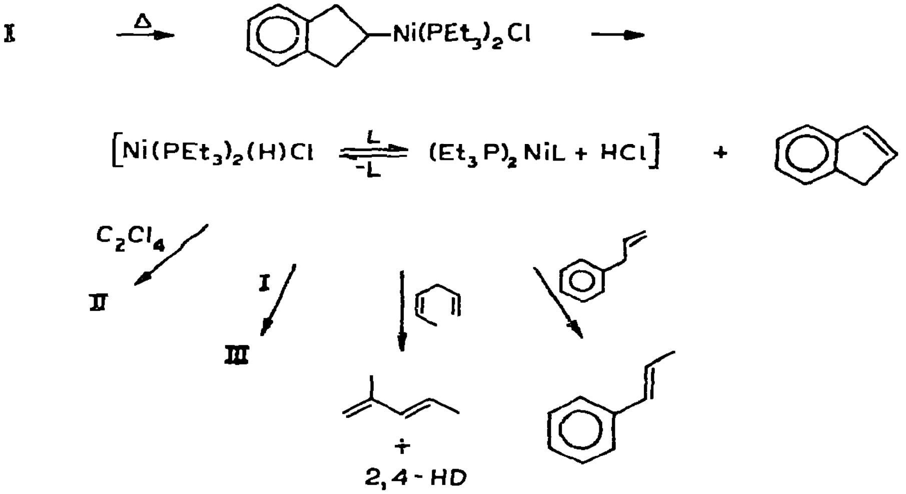
Mechanism of the thermal decomposition of I

The results provide chemical evidence that the thermal decomposition of I in hydrocarbon media affords the same type of catalyst species that is generated on treatment of ethylenebis(triphenylphosphine)nickel(0) with HCl. We propose that the catalyst generation proceeds as depicted in Scheme 2. The L designation represents an electron pair donor present in solution such as alkene or solvent. The first step generates an indanylnickel intermediate via an intramolecular carbon—nickel addition to the allyl double bond. β-Elimination of nickel hydride would afford the alkene isomerization catalyst system. Both of these types of transformations have been proposed as important steps in nickel-promoted 1,4-diene rearrangements [3], although the intramolecular carbon—nickel addition to coordinated alkenyl group via complex A in the type I diene rearrangement [3] is believed to generate a three-membered cycloalkane ring. The geometric restrictions imposed by the benzene ring, and the additional carbon atom in the alkenyl chelate system must make five-membered ring formation a more favorable process in I.

SCHEME 2



Reactions characteristic of both nickel(0) and of hydridonickel(II) complexes by species generated in the thermolysis of I have been observed. Thus, the oxidative addition of tetrachloroethylene to the nickel(0) complex (Scheme 2) explains the formation of II on thermolysis of I in tetrachloroethylene. Support for this route to II is found in its independent synthesis via oxidative addition to $(Et_3P)_2NiL$ generated in situ[*], (Scheme 1). The presence of the $(Et_3P)_2$-NiL/HCl system is also supported by the observed isomerizations of allylbenzene

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[*] For a detailed description of the experimental procedure for the synthesis of II by this route, see ref. 5.

and *cis*-1,4-hexadiene, both of which have been accomplished independently by the $(Ph_3P)_2NiC_2H_4/HCl$ catalyst system*. The formation of III from I is explained by the catalysis of double bond migration in I by the $(Et_3P)_2NiL/HCl$ system. Allylbenzene, *trans*-β-methylstyrene and $(Et_3P)_2NiCl_2$ are the expected products from the reaction of HCl with I and III.

The facile generation of arylnickel complexes III and IV through reactions of chlorostyrene derivatives with the $Ni(AA)_2—Et_3P—Et_3Al$ system provides a further illustration of the general applicability of this synthetic route [1, 5, 15, 22]. The formation of III on treatment of I with this system emphasizes one drawback to the synthetic utility of the generation of the nickel(0) complex in situ. The double bond migration in this case was presumably accomplished by an intermediate hydridonickel species [10, 14] which serves as a precursor in nickel(0) complex formation [23, 24].

Experimental

All experiments, including column chromatographic separations, were conducted under nitrogen unless indicated otherwise. Solvents were purified by conventional methods and were deoxygenated before use.

Elemental analyses and molecular weight determinations were performed by Spang Microanalytical Laboratories, Ann Arbor, Michigan. Melting points are uncorrected. The IR spectra were recorded on Beckman IR 12 and Perkin—Elmer 137 spectrophotometers, and the PMR spectra were obtained using a Varian A-60 spectrometer, tetramethylsilane being employed as an internal standard. The dipole moment of II was determined by a method described previously [5]. Diene separations were accomplished by a Varian Aerograph 90-P3 instrument utilizing a 20′ × 3/8″ 20% β,β′-oxydipropionitrile on Firebrick 60/80 column. The aromatic hydrocarbons were analyzed on a 20′ × 3/8″ 20% 1,2,3-tris(2-cyanoethoxy)propane (TCEP) on 60/80 Chromosorb P column and on a 10′ × 1/4″ 20% SE-30 on 60/80 Chromosorb W column.

Preparation of trans-chloro(2-allylphenyl)bis(triethylphosphine)nickel(II), I

The title compound was prepared in tetrahydrofuran by treatment of 4.75 g (0.013 mol) of *trans*-dichlorobis(triethylphosphine)nickel(II) with a sample of a Grignard reagent derived from 3.35 g (0.022 mol) of 2-allylchlorobenzene and 0.54 g (0.022 mol) of magnesium, according to a procedure described previously [5]. The product was isolated by chromatography of the product mixture under nitrogen on Baker alumina (pH 3.8), eluting with ether—hexane mixtures. The yield of I, m.p. 64-65°, after recrystallization from cold benzene—methanol was 3.5 g (61%).

The following procedures are typical of those employed in the thermolysis reactions.

Thermolysis of trans-chloro(2-allylphenyl)bis(triethylphosphine)nickel(II), I, in tetrachloroethylene

(a) A mixture of 0.218 g (0.487 mmol) of I in 1 ml of tetrachloroethylene

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* The isomerization of *cis*-1,4-hexadiene by this catalyst is described in refs. 2 and 20. Also, see ref. 21 for related catalysts.

was stirred at 85-90° for 18 h. The yellow solution turned red, and some green insoluble material was deposited on the walls of the flask. The hydrocarbon yields in the crude product mixture could be determined by GLPC on a TCEP column operated at 150°, helium flow rate 60 ml/min. 1-Bromo-2-chlorobenzene and toluene were employed as internal standards and relationships between recorder signal areas and sample weights of the hydrocarbon products were determined by analysis of standard mixtures. The yields of allylbenzene, *trans*-β-methylstyrene and indene were found to be 4.5, 2 and 51% based on the moles of I employed.

A larger scale experiment was conducted to enable isolation of the organonickel products. A mixture of 2.23 g (4.98 mmol) of I in 5 ml of tetrachloroethylene was stirred at 85-90° for 18 h. The crude product mixture was then concentrated in vacuo and then chromatographed on alumina. The PMR spectrum of the hydrocarbon products eluted with 2% ether in pentane showed that indene composed > 80% of the mixture. The indene was collected by GLPC and conclusively identified by its PMR and IR spectra. The allylbenzene and *trans*-β-methylstyrene were identified by comparisons of GLPC retention times with thos of authentic samples on three columns. The presence of *trans*-β-methylstyrene could also be confirmed by its PMR spectral identification in a mixture with indene derived from column chromatography. A control experiment demonstrated that allylbenzene did not isomerize to β-methylstyrene on the alumina column. *trans*-Chloro(trichlorovinyl)bis(triethylphosphine)nickel(II), II, was eluted from the alumina column with 20% ether in pentane. Recrystallization of the product from methanol afforded 0.868 g (40%) of II, m.p. 91-92°. (Found: C, 36.29; H, 6.80; Cl, 30.68; Ni, 12.79; P, 13.58; mol. wt., cryoscopic in benzene, 459. $C_{14}H_{30}Cl_4NiP_2$ calcd.: C, 36.48; H, 6.56; Cl, 30.77; Ni, 12.74; P, 13.44%; mol. wt., 461.) Recrystallization from pentane (−10°) of the orange-brown solid, eluted with 50% ether in pentane afforded 0.243 g (11%) of yellow crystals of III, m.p. 94-96°. (Found: C, 56.55; H, 8.85. $C_{21}H_{39}ClNiP_2$ calcd.: C, 56.32; H, 8.78%.) Elution with ether afforded 0.039 g (2.2%) of red crystals of *trans*-dichlorobis(triethylphosphine)nickel(II), identity confirmed by its PMR spectrum.

(b) A similar experiment was conducted in 10 ml of tetrachloroethylene at 80-85° for 2.5 h employing 0.85 g of I. The products were isolated and identified as described in (a) with the exception that the hydrocarbon product yields were determined by GLPC, employing *o*-dibromobenzene as an internal standard, after isolation of the mixture by column chromatography. The yield data are presented in Results and discussion.

Thermolysis of I in benzene

A solution of 0.895 g (2.00 mmol) of I was warmed at 60-70° in 10 ml of benzene for 16 h. The mixture was then allowed to cool and was chromatographed on alumina. The products were isolated and characterized as in (b) above. Unreacted I and product III were eluted from the alumina column as a mixture. The ratios of III to I in fractions afforded in this manner could be determined by PMR integration of the allylic proton resonance in I [5] vs the β-CH_3 proton resonance in III. Yield data are given in Results and discussion.

The thermolyses of I in benzene containing allylbenzene or tetrachloroethylene were conducted in this same manner.

Thermolysis of I in benzene containing cis-1,4-hexadiene

The general procedure for the thermolysis of I was followed and 1.06 g (2.4 mmol) of I, 10 ml of benzene, and 2.0 mmol of *cis*-1,4-hexadiene were employed. The mixture was stirred at 60-70° for 45 h. The progress of the diene isomerization reaction was followed by GLPC analyses of reaction aliquots which were removed periodically. The dienes were analyzed on the β,β'-oxydipropionitrile column. Aromatic hydrocarbons were analyzed on the TCEP column, as described above. The diene products were collected by GLPC and identified by their PMR spectra [3]. The organonickel products were isolated by column chromatography on alumina.

Treatment of allylbenzene and cis-1,4-hexadiene with hydrogen chloride

Solutions of allylbenzene (15 mmol) and of *cis*-1,4-hexadiene (2 mmol) in 6 ml of benzene were saturated with HCl by constantly passing the gas through the mixtures. The reaction flasks were fitted with reflux condensers and the HCl-saturated solutions were warmed to 60-70°. No isomeric hydrocarbon products were detected.

Treatment of allylbenzene with ethylenebis(triphenylphosphine)nickel(0) and hydrogen chloride

Ethylenebis(triphenylphosphine)nickel(0) [2, 11], 0.14 g (0.23 mmol), was treated with 5 ml of benzene and 2.28 mmol of allylbenzene at 0-5°. The resulting solution was then stirred at room temperature under a nitrogen atmosphere for 3.5 h. GLPC analyses of reaction aliquots indicated that no isomerization of allylbenzene had occurred. The mixture was then treated with 0.16 ml of a 0.29 *M* solution of HCl in benzene (allylbenzene/Ni/HCl molar ratio = 10/1/0.2). An amber solution formed and the allylbenzene was quantitatively isomerized to *trans*-β-methylstyrene within 3.5 h.

Treatment of I and III with hydrogen chloride

Hydrogen chloride was slowly bubbled into a tetrahydrofuran solution of I. After 2-4 min, the solution turned green and the mixture was analyzed by GLPC on a silicon rubber column operated at 150°, 65 ml/min helium flow rate. The only hydrocarbon detected had a retention time identical with that of allylbenzene.

Hydrogen chloride was slowly bubbled into an ether solution of III. The yellow solution turned colorless during 20 min, after which it was analyzed by GLPC on a TCEP column, operated at 150° with a helium flow rate of 100 ml/min. The only hydrocarbon detected had a retention time identical with that of *trans*-β-methylstyrene.

Treatment of II with sodium iodide

A solution of 0.25 g (0.54 mmol) of II and 1.5 g (10 mmol) of sodium iodide in 40 ml of acetone was stirred at room temperature for 72 h, after which the solvent was removed. The residue was triturated with 40 ml of hexane, the extract solution was filtered, and it was then evaporated to dryness. Recrystallization of the solid residue from methanol—ether afforded 0.151 g (53%) of gold-brown crystals of *trans*-iodo(trichlorovinyl)bis(triethylphosphine)nickel(II), m.p. 148-149°. (Found: C, 30.15; H, 5.44. $C_{14}H_{30}Cl_3INiP_2$ calcd.: C, 30.44; H, 5.48 ppm.) The PMR spectrum ($CDCl_3$) consisted of a 1/4/6/4/1 quintet at τ 8.78 (Et_3P, CH_3 protons) and a multiplet at τ 8.13 ppm (Et_3P, CH_2 protons).

Treatment of II with lithium bromide

A solution of 0.50 g (1.1 mmol) of II and 2.0 g (26.8 mmol) of lithium bromide in 50 ml of acetone was refluxed for 2 h, after which the solvent was removed in vacuo. The yellow residue was washed with 100 ml of water and then dried in air. Recrystallization from methanol afforded 0.38 g, 69%, of gold-brown crystals of *trans*-bromo(trichlorovinyl)bis(triethylphosphine)nickel-(II), m.p. 122-124°. (Found: C, 33.29; H, 5.97. $C_{14}H_{30}BrCl_3NiP_2$calcd.: C, 33.27; H, 5.98%.) The PMR spectrum ($CDCl_3$) consisted of a 1/4/6/4/1 quintet at τ 8.76 and a multiplet at τ 8.27 ppm.

Syntheses of III and IV by reactions of chloro-2-(propenyl)benzenes with nickel-(0)

(a) Syntheses of chloro-2-propenylbenzenes. Chloro-2-(*trans*-propenyl)-benzene was prepared by the method of Interrante, Bennett and Nyholm [25]; 6.81 g of product was obtained from 9.85 g of 2-allylchlorobenzene, 2.0 g KOH and 20 ml of amyl alcohol. GLPC analysis showed the presence of minor amounts of impurities. The material was further purified by preparative GLPC before use in the oxidative addition reaction or for conversion to the *cis* isomer.

Chloro-2-(*cis*-propenyl)benzene was prepared by a modification of the general procedure of Caldwell and Scvocool [26]. A solution of 1.23 g of chloro--2-(*trans*-propenyl)benzene in 5 ml of pentane and 500 ml of benzene containing 0.5 g of fluorenone was irradiated with ultraviolet light in an apparatus possessing a cortex filter. GLCP analysis after 2 h indicated the presence of a ca. 1/1 mixture of the *cis* and *trans* isomers of chloro-2-propenylbenzene. Irradiation for an additional 2 h resulted in an almost total conversion to the *cis* isomer. After removal of the solvents in vacuo, the residual oil was chromatographed on acid-washed alumina. Elution with hexane afforded 1.08 g (88%) of the crude product, which was purified by preparative GLPC. The PMR spectrum (CCl_4) consisted of an aromatic proton multiplet centered near τ 2.82, a doublet of multiplets centered at τ 3.49 attributed to H_α, $J(H_\alpha, H_\beta) = 12.0$ Hz, an octet centered at τ 4.15 assigned to H_β, and a quartet resonance at τ 8.22 ppm (doublet of doublets) due to the CH_3 proton resonance, $J(CH_3, H_\beta) = 6.7$ Hz, $J(CH_3, H_\alpha) = 1.7$ Hz.

(b) Synthesis of III. Chloro-2-(*trans*-propenyl)benzene, 0.34 g (2.22 mmol), and bis(acetylacetonato)nickel(II), 0.40 g (1.56 mmol), were placed in 12 ml of toluene under an argon atmosphere. Triethylphosphine, 0.46 ml (1.56 mmol), was then added and the resulting mixture was cooled to −55°. Triethylaluminium, 3.51 mmol (1.25 ml of a 2.81 *M* solution in toluene), was then added dropwise. The cooling bath was removed upon commencement of Et_3Al addition, and the addition was complete before the temperature reached −10°. The resulting solution was then stirred at room temperature for 6.5 h, after which the mixture was treated with 2 ml of 2-propanol. The solvent was then removed in vacuo, the residue was treated with 10% ether in hexane, and the resulting solution was chromatographed on alumina, eluting with ether—hexane mixtures. This procedure afforded 0.35 g (50%) of III which was recrystallized from methanol (m.p.

97-97.5°). The PMR spectrum of the product was identical with that of III derived from the thermal decomposition of I.

(c) Synthesis of IV. The procedure employed was the same as that described for the preparation of III in (b) with the exception that 0.36 g (2.3 mmol) of chloro-2-(*cis*-propenyl)benzene and 13 ml of toluene were used. This afforded 0.45 g, 65% yield, of IV, m.p. 50-51°. (Found: C, 56.18; H, 8.71. $C_{21}H_{39}ClNiP_2$ calcd.: C, 56.32; H, 8.78%.)

(d) Treatment of 2-allylchlorobenzene with Ni(AA)$_2$, Et$_3$P and Et$_3$Al. The same procedure as that described in (b) was employed. This afforded 0.34 g (48%) of III, m.p. 94-95°.

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