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PREPARATION AND ISOMERIZATION REACTIONS OF 2-NICKELAHYDRINDANES

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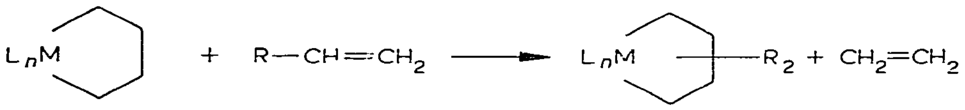
Summary

The *cis* and *trans* isomers of 2-nickelahydrindane have been prepared and characterized by NMR spectroscopy. The more stable *trans* isomer was prepared from 1,7-octadiene and tris(triphenylphosphine)nickelacyclopentane. A sample of the *cis* isomer was prepared from bis(triphenylphosphine)nickel dichloride and *cis*-1,2-dilithiomethylcyclohexane. Each isomer reacts with CO or acids to give products of retained stereochemistry. The *cis* isomer rearranges to the *trans* under the influence of light or excess phosphine.

Introduction

A variety of metallacyclopentanes are now known. The unsubstituted complexes of nickel [1], titanium [2], platinum [3,4], cobalt [5] and rhodium [5] can be prepared by the reaction of a transition metal dihalide with 1,4-dilithiobutane, while those of tantalum [6] and zirconium [7] can be prepared from reduced metallocenes and ethylene. Substituted analogs of the nickel [8], titanium [8], tantalum [9], and zirconium [7] metallacycles can be prepared by treating the parent complex with a primary olefin.



Of the substituted metallacycles prepared by such olefin interchange reactions, the metallahydrindane [9] produced from I and 1,7-octadiene (II) was chosen for further study because of the relative stability of this ring system, its potential synthetic utility and the structural and mechanistic studies made possible by the geometry of the ring juncture.

(I) (II) (III)

Experimental section

General method

All reaction and other manipulations were performed under prepurified argon or welding-grade nitrogen purified before use by a BASF deoxygenation catalyst and molecular sieves (Linde 4A). Toluene, n-hexane, diethyl ether and decalin were dried over sodium (with benzophenone added) under an argon atmosphere and were freshly distilied before use. Chemical reagents such as 1,7-octadiene and 1,6-heptadiene were reagent grade and were distilled over CaH_2 before use and were stored under argon. Tris(triphenylphosphine)nickelacyclopentane, I, [1] and bis(triphenylphospine)nickel(ethylene), IV [10] were prepared by a reported method. Other chemicals were reagent grade and used without further purification.

Analytical methods

Proton NMR spectra were determined on a Brucker WH-180 spectrometer and ^{13}C NMR spectra were measured on a Varian CFT-20 spectrometer using TMS as internal standard. Mass spectra were recorded on a Hitachi—Perkin—Elmer RMV-6 mass spectrometer. Reaction products were analyzed by gas chromatography on a Varian Series 1400 instrument equipped with flame ionization detectors using 1.5% OV-101 (100—120 mesh on Chromosorb), 10% Carbowax (on Chromosorb G, 32 ft.), 5% DC-550 (on Chromosorb G, 25 ft.) and 1% SE-30 (15 ft.). Organic products were purified by gas chromatography on a Varian Model 90-P gas chromatograph and identified by ^1H NMR and mass spectroscopy by comparison with authentic samples. Product yields were determined by response relative to an internal standard. Infrared spectra were measured with a Perkin—Elmer Model 567 instrument using a polystyrene film as a calibration standard.

Preparation of bis(triphenylphosphine)-trans-2-nickelahydrindane, III

To a deep red toluene solution containing I (2.3 g, 2.6 mmol) was added slowly 1,7-octadiene (10 ml, 0.13 mol) below —20° C. While the mixture was stirred below —10° C and maintained at that temperature for about 10 h, the solution slowly turned pale yellow and ethylene was evolved. Cooling the solution after dilution with n-hexane (10 ml) resulted in the formation of a brown-yellow crystalline solid, which was isolated by filtration and dried in vacuum at room temperature (0.95 g, 53% yield). Three samples of the complex were decomposed with hydrogen chloride in toluene and the amount of *trans*-1,2-dimethylcyclohexane (V) produced was determined by GLC. An average yield of 98% of the *trans* isomer was produced. On reaction of the complex (0.497 g, 0.717 mmol) with Br_2 in toluene below —20° C, a 96% yield of *trans*-

1,2-dibromomethylcyclohexane (VI) was obtained. It was identified by comparison to the sample prepared below.

A portion (0.505 g) of the complex was decomposed with hydrogen peroxide/sulfuric acid for analysis. Nickel was determined as the dimethylglyoxime complex and triphenylphosphine as its oxide. Three samples were analyzed. Found: Ni, 8.45; PPh_3, 76.8%; PPh_3/Ni, 2.06. Calculated: Ni, 8.46; PPh_3, 75.6%; PPh_3/Ni, 2.00.

The same complex, III, could be prepared from bis(triphenylphosphine)nickel-(ethylene), IV, and 1,7-octadiene (10 ml, 0.13 mol) at —10° C. The mixture was stirred below —10° C for about 12 h until a pale yellow solution was obtained. After dilution with n-hexane (15 ml) and cooling, a brown-yellow solid precipitate was isolated and dried in vacuum (0.47 g, 32% yield). Found: Ni, 8.44; PPh_3, 74.9%; PPh_3/Ni, 1.98. On protonolysis of the complex, 94% of *trans*-1,2-dimethylcyclohexane was obtained.

Preparation of bis(triphenylphosphine)-trans-2-nickelahydrindane-1,1,3,3-d_4

The deuterated complex, III-d_4, was prepared by the same method described above except using 1,7-octadiene-1,1,8,8-d_4 [11].

Preparation of cis-1,2-dilithiomethylcyclohexane, VIII [2]

To a THF (200 ml) suspension of lithium aluminum hydride (15 g, 0.4 mol) was added slowly a THF (50 ml) solution containing *cis*-1,2-cyclohexanedicarboxylic anhydride (30 g, 0.19 mol). After work-up, the resulting diol (21 ml) [16] was converted to *cis*-1,2-dibromomethylcyclohexane by bromination with 48% HBr (50 ml) and H_2SO_4 (80 ml). 44.6 g (87% yield); b.p. 123—125° C/4 mmHg; NMR ($CDCl_3$) [2] δ 3.25 (d, 4 H), 1.2—2.3 (m, 10 H).

trans-1,2-Dibromomethylcyclohexane was prepared in an analogous manner, 92% yield, b.p. 105—107° C/4 mmHg; NMR ($CDCl_3$) [2] δ 3.50 (m, 4 H), 1.2—2.0 (m, 10 H).

cis-1,2-Dilithiomethylcyclohexane VIII was obtained by lithiation of the dibromide with fresh lithium chips. A solution of *cis*-1,2-dibromomethylcyclohexane (15 ml) in 50 ml of diethyl ether was added dropwise to 7 g (1.2 mol) of lithium chips in 80 ml of ether at 0° C. The mixture was stirred at 0° C overnight. A white-gray precipitate was removed by filtration using Celite filter aid. The concentration was determined by GLC analysis after disilylation with trimethylchlorosilane (0.76 *M*, 90% yield). During this preparative process, no *cis*—*trans* isomerization was observed.

trans-1,2-Dilithiomethylcyclohexane was prepared in the same manner in 92% yield.

Preparation of bis(triphenylphosphine)-cis-2-nickelahydrindane VII

To an ether suspension of bis(triphenylphosphine)nickel dichloride (2.3 g, 3.5 mmol) was added slowly VIII (5.4 mmol) below —40° C. The mixture was slowly warmed to 0—10° C and stirred at this temperature for several hours until a brown-yellow crystalline solid precipitated. After filtration, the solid was recrystallized from ether or toluene/n-hexane (1.2 g, 48% yield).

On protonolysis of complex VII with hydrogen chloride, only *cis*-1,2-dimethylcyclohexane (IX) was produced in a 94.5% yield (average of three experiments).

Bromination of VII in toluene below —40° C afforded *cis*-1,2-dibromomethylcyclohexane (96% yield) which was purified by GLC and identified by ^1H NMR and mass spectroscopy and comparison to a sample prepared by an alternate route (see above). Ni and PPh_3 were determined by the method described above. Found: Ni, 8.33; PPh_3, 76.0%; PPh_3/Ni, 1.98; *cis*-1,2-dimethylcyclohexane/Ni, 0.95. Calcd.: Ni, 8.46; PPh_3, 75.6%; PPh_3/Ni, 2.00; *cis*-1,2-dimethylcyclohexane/Ni, 1.00.

Carbonylation of bis(triphenylphosphine)-2-nickelahydrindane

Dry carbon monoxide was slowly bubbled into a deep yellow toluene solution of III (0.512 g, 0.738 mmol). The temperature was initially —10° C and subsequently was raised gradually to 10° C, at which time the solution turned dark brown. Subsequently a white-gray precipitate appeared. After 4 h, oxygen gas was bubbled gently through the reaction solution for 15 min. The resulting colorless solution was analyzed by GLC.

The white-gray solid produced on this reaction was identified as $Ni(CO)_2(PPh_3)_2$ by IR spectroscopy and its physical properties (m.p. 208—210° C (dec.); Lit. [12] 210—215° C (dec.)) [12]. The organic product was purified by GLC and identified as *trans*-2-hydrindanone (X) (0.694 mmol, 94% yield based on Ni). ^1H NMR: δ 0.92, 1.25 (m, 8 H), 1.83 ppm (m, 4 H). Mass spectrum; M^+, 138; $M^+ - CO$, 110. IR spectrum [13]: 1745 s, 884m, 830s cm^{-1}. M.p. —15 to —12.5° C (cf. *trans*-isomer, —12° C; *cis*-isomer, 10° C) [13].

Isomerization reaction of bis(triphenylphosphine)-cis-2-nickelahydrindane, VII

In a 50 ml Schlenk tube equipped with a vacuum stopcock were placed VII (0.332 mmol) and triphenylphosphine (6.6 mmol) which was dissolved in 10 ml of toluene (below —20° C). The sample tube then was placed in a constant temperature bath (0 ± 0.3° C) and stirred for about 6 h. The tube was connected to a vacuum line (0.002 Torr) and all the liquid was distilled. The distillate contained 0.139 mmol of 1,7-octadiene (42% yield based on Ni). The remaining brown-yellow solid was decomposed with sulfuric acid and the organic products were extracted with 5 ml of toluene and analyzed by GLC. The toluene extract contained 0.143 mmol of *trans*-1,2-dimethylcyclohexane (V) (43% yield) and 0.023 mmol of *cis*-isomer (7% yield), respectively. When the reaction was carried out for 20 h the products, 1,7-octadiene (86% yield) and 2-methylenemethylcyclohexane (2%), were isolated by GLC and identified by NMR.

Photolysis of VII

Four 45 ml quartz Schlenk tubes containing 0.315 mmol of VII dissolved in 10 ml of toluene were placed in a cold bath maintained below —40° C. Two samples were irradiated with 450 W high pressure mercury lamp while the other two samples were covered with aluminum foil. After 6 h, dry hydrogen chloride gas was bubbled into each sample. The resulting colorless solution was analyzed by GLC. The irradiated samples gave 0.117 mmol of 1,7-octadiene (II) (37% based on VII), 0.047 mmol of *trans*-1,2-diemthylcyclohexane (15%) and 0.129 mmol of the *cis*-isomer (41%), while the unirradiated samples afforded 0.293 mmol of the *cis*-isomer (93%) and a small amount of *trans*-isomer (less than 0.3%).

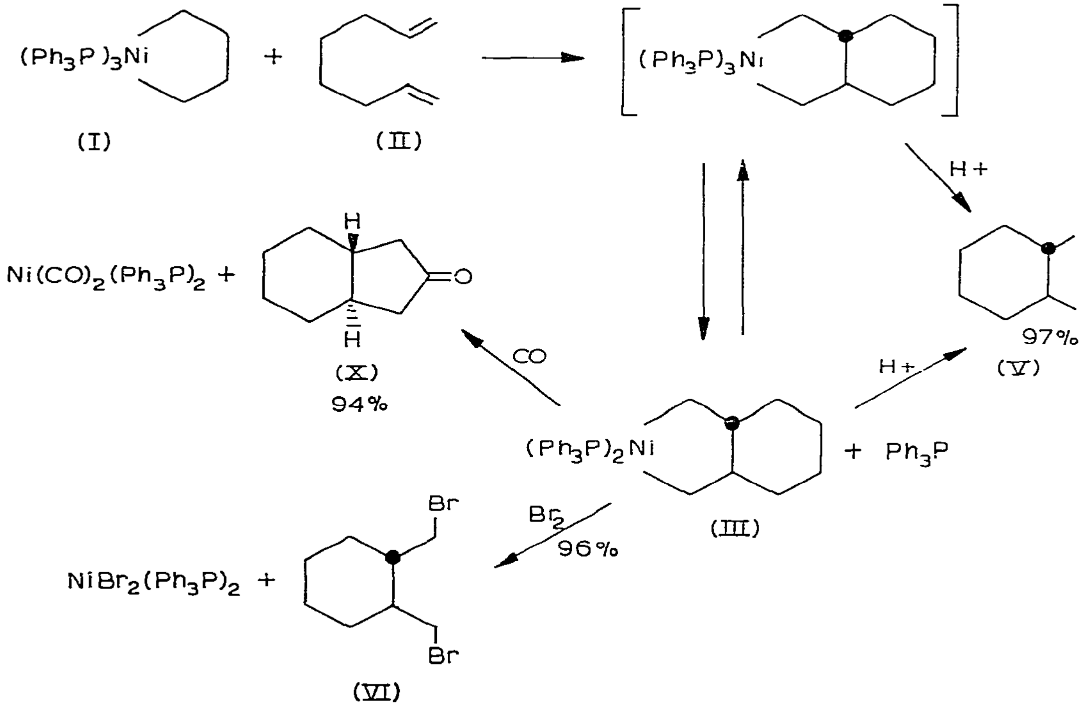
Reaction of 1,6-heptadiene with I and carbonylation

To a deep red toluene solution of I (3.1 g, 3.44 mmol) was added slowly 10 ml of 1,6-heptadiene (0.13 mol) at —25° C. After 15 h at —10° C, the original deep red solution turned to brown-yellow. A dry carbon monoxide stream was passed through the reaction solution at —10° C. After the solution had been maintained at this temperature for 4 h under a CO atmosphere, the reaction solution was decomposed with oxygen at 50° C. The resulting colorless solution was analyzed by GLC. Two major products were obtained and identified as *trans*-bicyclo[3.3.0]octan-2-one, XI and the *cis*-isomer, XII. *trans*-Isomer (0.653 mmol, 19% yield): ^{1}H NMR, δ 2.0 (m, 2 H), 1.9 (m, 4 H), 1.5 (m, 6 H) ppm; IR, 1748vs cm^{-1}; mass spectrum, M^+, 124; M^+ — CO, 108; m.p., 17—19°C (Lit. [13b] 18—20°C); b.p., 186—187°C/760 mmHg (Lit [13b] 189°C/755 mmHg). *cis*-Isomer: mass spectrum, M^+, 124; M^+ — CO, 108; IR 1751vs cm^{-1}; m.p. —30 to —33°C (Lit. [13b] —28— —29°C); b.p. 199—202°C/760 mmHg (Lit. [13b] 195°C/755 mmHg).

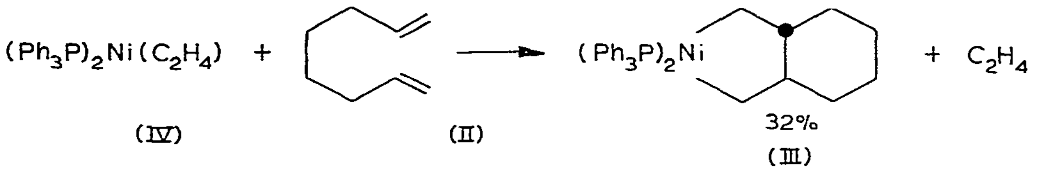
Results

Preparation

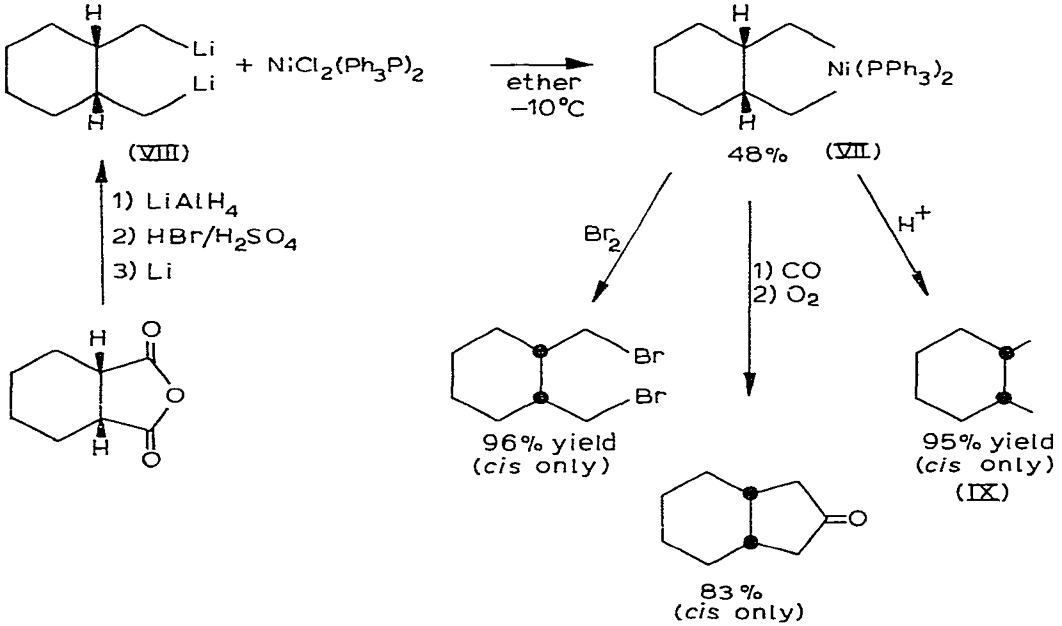
The reaction of an excess of 1,7-octadiene with tris(triphenylphosphine)nickelacyclopentane (I) at —10° C for 10 h resulted in the evolution of ethylene. The resulting solution was treated with dry hydrogen chloride to produce a 94% yield (based on nickel) of *trans*-1,2-dimethylcyclohexane (V). Cooling the reaction mixture before protonolysis, gave a brown-yellow solid in 53% yield which was shown to be *trans*-2-[bis(triphenylphosphine)]nickelahydrindane (III) by chemical and elemental analysis. The three products (V, VI and X) of metal car-



bon bond cleavage were all of *trans* stereochemistry. The nickel/phosphine ratio of 2.09 showed that the isolated complex had lost one phosphine to produce the bisphosphine complex. Addition of excess phosphine to a solution of the isolated complex in an attempt to produce the trisphosphine complex induced decomposition to 1,7-octadiene. The same complex also could be prepared in 32% yield by reaction of an excess of 1,7-octadiene with bis(triphenylphosphine)·ethylenenickel(0), (IV).



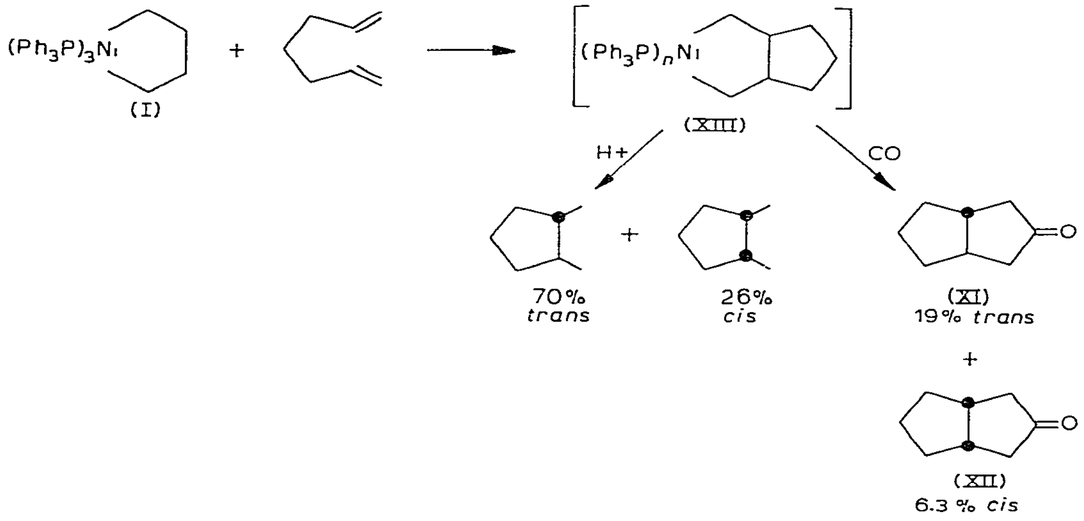
cis-2-[Bis(triphenylphosphine)]nickelahydrindane, VII, could be prepared from the corresponding dilithium reagent (VIII) and bis(triphenylphosphine)-nickel dichloride.



Confirmation of the stereochemistry of the complex came from observing only *cis*-cleavage products.

The reaction of 1,6-heptadiene with I resulted in the evolution of ethylene. Attempts to isolate the intermediate, XIII, were unsuccessful. However, the presence of a metallacycle as an unstable intermediate could be demonstrated by protonolysis of the reaction mixture to produce a 96% yield of a mixture of the two isomers of 1,2-dimethylcyclopentane and by carbonylation to produce a 25.0% yield of bicyclo[3.3.0]octan-3-ones.

The stereochemistry of the products demonstrated that the intermediate was a near 3/1 mixture of *trans/cis* ring juncture isomers (XI/XII).



Spectroscopic characterizations

Table 1 gives the ^{13}C and ^{1}H NMR data for the isolated complexes. The 180 MHz ^{1}H spectra were broadened even at —30° C. The ^{13}C spectra of the two isomers showed similar but distinguishably different chemical shifts.

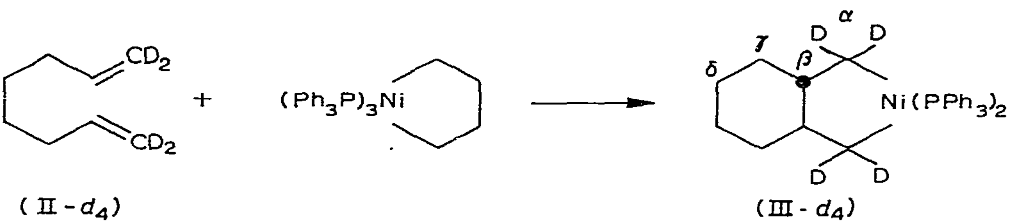
The assignments in Table 1 are based on the results of labeling, splittings and analogy to reported systems. A sample of the *trans* isomer (III) was prepared from 1,7-octadiene-1,1,8,8-d_4. The intensity of the signal at δ 4.9 ppm in the ^{13}C [^{1}H] spectrum of this complex was greatly decreased due to the ^{2}H coupling and the lack of the Overhauser effect. The δ 1.65 ppm signal in the ^{1}H spectrum vanished. These data clearly identify the α-carbons and α-hydrogens. The carbons at the ring juncture should show the only doublet in the ^{13}C spectrum. Assigning the remaining two signals in the ^{13}C spectrum is more difficult. The assingment is based on the pattern observed for organic analogs. The signals of the *cis* compound (VII) were assigned by analogy to the *trans*.

TABLE 1

NMR DATA OF BIS(TRIPHENYLPHOSPHINE)NICKELAHYDRINDANE

	trans-Isomer, III		*cis*-Isomer, VII	
$^{13}C[^{1}H]$ [a]				
Cα	4.9 ppm [b]	(t, 122 Hz) [c]	4.0 ppm	(t, 124 Hz)
Cβ	37.6	(d, 117)	40.9	(d, 112)
Cγ	36.0	(t, 129)	33.2	(t, 129)
Cδ	27.9	(t, 131)	25.7	(t, 133)
^{1}H [d]				
Hα	1.65 ppm [b]	(m, 4 H)	1.75 ppm	(m, 4 H)
Hβ	1.13	(broad, 2 H)	1.21	(broad, 2 H)
Hγ } Hδ	0.89	(m, 8 H)	0.91	(m, 8 H)
PPh$_3$	6.89	(m, 30 H)	6.90	(m, 30 H)

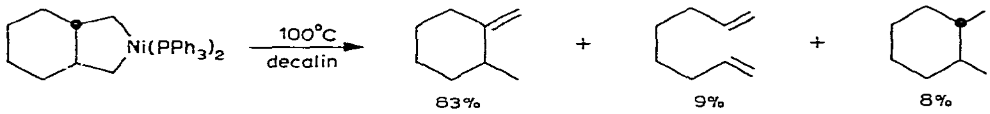
[a] Toluene solution at —90° C. [b] Chemical shifts are relative to internal TMS. [c] Proton coupled spectrum data. [d] Toluene-d_8 solution at —30° C.



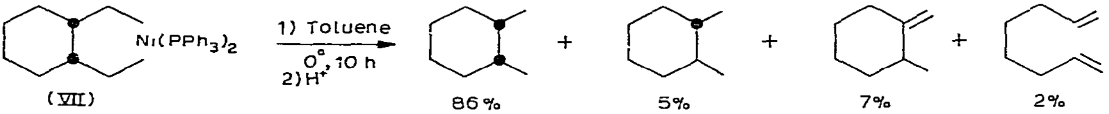
Decomposition studies

Earlier studies of simple metallacycles showed a pronounced effect of ligand concentration and light on the mode of decomposition [1,14]. The reactions of the two isomeric metallacycles also were influenced by similar factors.

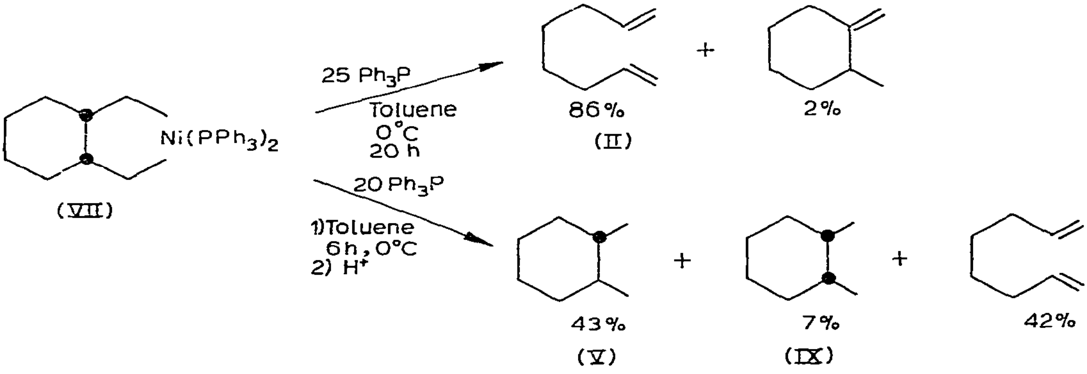
Ligand concentration. In the absence of light or excess ligand, the two nickelahydrindane isomers were reasonably stable. The *trans* isomer, III, decomposed rapidly at 100° C in decalin to produce 2-methylenemethylcyclohexane by a hydride rearrangement pathway.



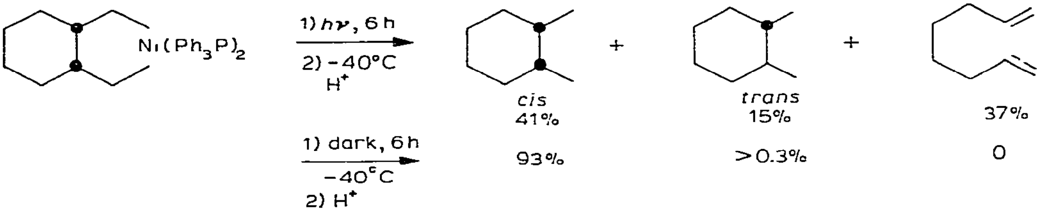
After 10 h at 0° C, only 9% of the *cis* complex had decomposed and 5% had isomerized. The major decomposition product resulted from *β*-hydride elimination to produce 2-methylenemethylcyclohexane. Different results were obtained when the complex was maintained at 0° C in the presence of an excess of phosphine; after 20 h 88% of the complex had decomposed. The major product was 1,7-octadiene, the product of *β*-carbon—carbon bond cleavage.



If the reaction mixture was quenched before extensive decomposition had occurred, an intermediate could be detected. When 42% of the starting complex had decomposed to 1,7-octadiene, 86% of the remaining metallacycle was the *trans* isomer.



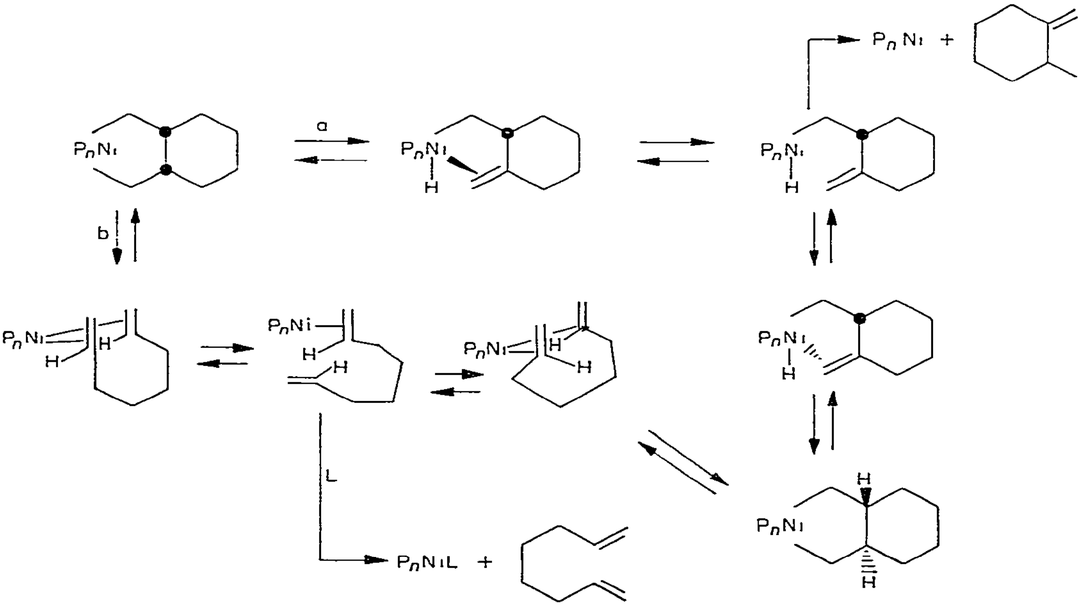
Photochemical reactions. Two samples of the *cis* isomer were dissolved in toluene and placed in a bath maintained below —40° C. One sample was irradiated while the second was covered with aluminum foil. After 6 h, dry hydrogen chloride was added to each sample. The unirradiated sample appeared to have undergone little reaction since only *cis*-dimethylcyclohexane was isolated after protonolysis. However, 37% of photolyzed sample had decomposed and 29% of the remaining metallacycle had isomerized to the *trans* isomer.



Discussion

The thermodynamically more stable isomer of the 2-nickelahydrindane, III, is the *trans* isomer. None of the *cis*-isomer, VII, was detected in any of the reactions which produced this metallacycle from 1,7-octadiene, while the *cis*-isomer converted to the *trans* isomer in a number of the reactions. This was surprising since *trans*-hydrindane is only slightly more stable than the *cis*-isomer [15] and the other reported 2-metallahydrindanes of Ta [9] and Ti [8] are reported to occur as mixtures of the *cis* and *trans* isomers.

With samples and specific reactions of each stereoisomer, reactions which may induce isomerization were explored. Since the *trans* isomer appears to be much more stable, isomerization reactions were carried out with the metallacycle with the *cis* ring juncture.



Two mechanisms of *cis—trans* isomerization are consistent with known reactions of metallacycles. Each produces an intermediate olefin complex which inverts the stereochemistry by dissociation and recomplexation of the olefin from the opposite side.

The most reasonable side reaction for the most important intermediates should be the production of 2-methylenemethylcyclohexane by the β-hydride mechanism (path a) and the production of 1,7-octadiene by the β-carbon—carbon bond cleavage reaction (path b). Consequently, the decomposition product found in those reactions which also result in extensive *cis* to *trans* isomerization should provide a guide to the mechanism of isomerization. From these and earlier studies, it is apparent that decomposition of the complexes in the presence of excess ligand or light results in C—C-bond cleavage [1,14]. These are exactly the conditions which also induce *cis* → *trans* isomerization. Path b, the C—C-bond cleavage route, appears to be the mode of *cis—trans* isomerization. Also consistent with path b was the observation that the olefin products were not isomerized. In most cases reactions involving hydride mechanisms result in the isomerization of olefins.

The *trans*-nickelahydrindane appears to be at least 2.5 kcal/mol more stable than the *cis*. This is in contrast to the Ta [9] and Ti [8] analogs where there is a mixture of *cis* and *trans* isomers. The comparison with the carbocyclic systems suggest that the conformational requirements of the nickelacyclopentane are similar to that of cyclohexane while the metallacyclopentanes of Ti [8] and Ta are similar to the analogous carbocyclic compound. As a further confirmation of this conclusion, 3-nickelabicyclo[3.3.0]octane was prepared. The products XI and XII obtained from this complex were a 3/1 mixture of *trans* and *cis* isomer, as would be expected for a 6—5 carbocyclic system.

Acknowledgments

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