

PROCESS FOR PRODUCING 1,4-DIENES

This invention relates to processes for the preparation of 1,4-dienes from the reaction of a conjugated diolefin with an alpha-monoolefin, and more particularly, to such processes involving a catalyst system including a salt of cobalt, a tertiary diphosphine, and an organoaluminum compound.

1,4-Dienes are useful as comonomers in polyolefin polymers since they allow the polymer to be cross linked.

US-A-3,405,194 teaches a method of producing hexadienes by the reaction of an alpha-monoolefin with a conjugated diolefin in the presence of a catalyst system of a salt or cobalt or iron, a tertiary diphosphine, and an organoaluminum compound. The tertiary diphosphines include 1,2-bis(diphenylphosphino) ethane ("dppe") and 1,3 -bis (diphenylphosphino) propane ("dppp").

The examples, and certain contemporaneous and subsequent publications, teach the importance of reacting a conjugated diolefin with an alpha-monoolefin at temperatures of 80° C or more when using a cobalt based catalyst system of the types described. Thus of the 88 examples in the patent, 68 examples (1-53 and 74-88) are directed to a catalyst system of a salt of cobalt, a tertiary diphosphine, and an organoaluminum compound, and 64 of these 68 examples employ a temperature of at least 80° C (example 2 is at 70° C and examples 39, 47 and 76 are at 50° C, all with a catalyst system including a cobalt complex with dppe).

In "A New Process for 1,4-Diene Synthesis", A. Miyake, G. Hata, M. Iwamoto, and S. Yuguchi, *Proceedings of the Seventh World Petroleum Congress*, 1967 volume 5, 317, the authors described the superiority of a cobalt diphosphine system of CoCl₂-dppe in combination with an aluminum trialkyl, specifically, triethylaluminum, at 80° C (each also described in US-A-3,405,194).

The effects of reaction temperature on reaction rate for butadiene conversion are particularly described for the catalyst system of CoCl₂-dppe-Et₃Al in "Reaction of Butadiene with Ethylene. IV. Synthesis of 1,4-Hexadiene by a Cobalt Chloride-Ditertiary Phosphine Complex and an Organolaluminum Compound Catalyst", M. Iwamoto and S. Yuguchi, *Bulletin of the Chemical Society of Japan*, 1968, 41, 150. Apparent optimum reaction temperatures are said to be in the range of 80 to 100° C. Two examples



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achieved 97% selectivity at 80° C. Below 80° C, rate of conversion is shown to fall precipitously, and at temperatures higher than 100° C a considerable loss of selectivity from isomerization of 1,4 hexadiene to conjugated dienes, mainly to 2,4-hexadiene, is reported.

5 Henrici-Oliv et al. in "Codimerization of Butadiene and Ethylene," *Journal of Organometallic Chemistry*, vol. 35, p. 381 (1972), a study of the catalytic system described in the above cited articles by Iwamoto et al. report that temperature of reaction appears critical for high selectivity using CoCl₂-dppe-Et₃Al in dichloroethane. Page 381 expressly states that "between 80° C
10 and 110° C *cis*-1,4-hexadiene is formed in high yield, whereas below 80° C more ethylene than butadiene is consumed with the result that C₈ compounds are produced. Above 110° C 1,4-hexadiene is isomerized to 2,4-hexadiene." Teaching the same is US-A-3,647,902, to Henrici-Oliv et al. (where the catalyst system is CoCl₂-dppe-Et₃Al in a halogenated
15 hydrocarbon solvent), stating that the temperature must be not less than 80° C when ethylene is reacted with 1,3-butadiene, or poor selectivity results (col. 2, lines 13-24).

The foregoing teachings in the prior art on conducting the reaction at temperatures of at least 80° C encompass specific described cobalt catalyst
20 systems where the diphosphine ligand is dppp. In US-A-3,405,194, examples 18-27, 43 and 88 employ dppp as a cobalt catalyst ligand. In examples 18-27, the cobalt complex is CoCl₂ and dppp; in examples 43 and 48, the cobalt complex is the acetyl acetonate of trivalent cobalt, i.e., Co(C₅H₇O₂)₃, with the dppp ligand. (Acetylacetonate is sometimes referred to as "acac"; for
25 example, the acetylacetonate of trivalent cobalt is Co(acac)₃). The organoaluminum compound used in examples 18-27, 43 and 88 is trimethylaluminum ("TMAL") or triethylaluminum ("TEAL") when the cobalt salt is CoCl₂ and is sometimes diethylaluminum chloride ("DEAC") when the cobalt salt is Co(acac)₃. In all these examples employing the dppp ligand,
30 the temperatures are in the range 80° - 102° C.

"Effects of Ditertiary Phosphine Ligands in Co-dimerization of Butadiene and Ethylene Catalyzed by cobalt Chloride-Ditertiary Phosphine-Triethylaluminum" T. Kagawa, Y. Inoue, and H. Hashimoto, *Bulletin of the Chemical Society of Japan*, 1970, 43, 1250, reports results for testing a CoCl₂-
35 Ph₂P(CH₂)_nPPh₂-Et₃Al catalyst system (Ph=phenyl, n=1,2,3,4 etc.) for effect of length of the methylene chain between the two phosphorus atoms on

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cis-1,4-hexadiene formation at 80-90°C. The data presented for the system CoCl₂-dppp-Et₃Al indicate a relatively low yield to 1,4-hexadiene on butadiene.

The temperature teachings in the art have applied whether the conjugated diolefin is butadiene or isoprene. Examples 74-75 and 77-82 of US-A-3,405,194 employ CoCl₂-dppe-Et₃Al at 80°C or 100°C to react isoprene with ethylene. In "Preparation of 3-Methyl-1,4-heptadiene, 3-Ethyl-1,4-hexadiene, and Methyl-1,4-hexadienes" by M. Iwamoto, K. Tani, H. Igaki, and S. Yuguchi, *Journal of Organic Chemistry* 1967, 32, 4148, reaction of isoprene with ethylene is reported rapid and selective (97.2 - 99%) at 80-98°C with the CoCl₂-dppe-Et₃Al catalyst system.

Even variants of the cobalt catalyst systems teach reaction conversion of conjugated diolefins to 1,4-dienes at a 80°C minimum. US-A-3,445,540 uses a triphosphine instead of a diphosphine, and US-A-3,574,139 uses cobalt complexed with two diphosphines, i.e., bis [ethylene bis (diphenylphosphine)] cobalt (0) or bis [ethylene bis (diphenylphosphine)] cobalt (I) hydride. Both of these two patents state that "temperatures below 80°C may be too slow for operating convenience. The preferred temperature range lies between 80 and 120°C..." (US-A-3,574,139, col. 3, lines 70-74; US-A-3,445,540, col. 5, lines 35-39.)

In US-A-3,405,194, toluene is the solvent in examples 18-23 and 43; halogenated hydrocarbon solvents are used in examples 24-27 and 88. Halogenated hydrocarbon solvents are instructed to be used to improve selectivity when the intended hexadiene is 1,4-hexadiene, and to provide the further advantage of easier cobalt catalyst handling, since these solvents dissolve the cobalt complex completely (col. 4, lines 60-67). In the article by Henrici-Oliv et al. cited above, halogenated hydrocarbon solvents are said to be favored, because CoCl₂-dppe is insoluble in toluene and alkylation reactions of transition metal salts with aluminum alkyls are faster and more complete in halogenated solvents than in aromatics. US-A-3,647-902 contain a similar teaching

According to the present invention there is provided a process for producing substantially pure 1,4 dienes, which comprises reacting a conjugated diolefin with an alpha-olefin in a hydrocarbon solvent reaction medium and in the presence of a catalyst system consisting essentially a cobalt compound, a tertiary diphosphine and an organo aluminum

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compound, characterized in that the catalyst system comprises: $\text{Co}(\text{acac})_n$ combined with dppp or a preformed complex of $\text{CoCl}_2(\text{dppp})$, where acac is acetylacetonate, dppp is 1,3-bis (diphenylphosphino) propane, and n is the valence of cobalt; and a dialkylaluminum halide, and in that the reaction is performed at a temperature of less than 70°C to convert the conjugated diolefin to the 1,4-diene with substantially 100% selectivity. It is preferred to perform the process at a temperature of about 60°C . It is also preferred to perform the process at an alpha-olefin partial pressure of from 50 to 10,000 kPa (0.5 to 100 atmospheres). By "pure" is generally meant more than about 99% 1,4-diene, preferably approaching or equaling 100% 1,4-diene.

The highest selectivity, essentially 100 percent selectivity, is desired, in order to maximize production of pure 1,4-dienes, thereby eliminating the difficult separation of 2,4-diene and other by-products to satisfy the commercial need for pure 1,4-dienes. It has been found that substantially 100% selectivity from reaction of conjugated diolefins with an alpha-olefin is possible using the process according to the invention. Preferably the selectivity is greater than 98.5%, more preferably greater than 99%, most preferably 99.5% and ideally 100%. It is also possible by selection of reaction conditions within the specified ranges to provide essentially pure 1,4-dienes from conjugated diolefins at high rates of reaction and/or high catalyst productivity.

In order to obtain highest reaction rates per unit of catalyst, the prior art has employed halogenated hydrocarbon solvents for preformed catalysts, particularly the favored $\text{CoCl}_2\text{-dppe/TEAL}$ catalyst system of the above referenced prior art. However, halogenated solvents are environmentally disfavored, are corrosive to equipment, and consequently are commercially unattractive as a means of improving catalytic reaction rates and product yields. With the process of this invention it is possible to promote reaction of conjugated diolefins and alpha-olefins at high rates of reaction without the use of halogenated hydrocarbon solvents.

Surprisingly, contrary to the teachings of the prior art, such results are achievable at temperatures less than 80°C . Further, exceptional selectivity at these reaction temperatures in this particular catalyst system may be accompanied by vastly increased rates of reaction and catalyst productivity indicative of a very reactive species of catalyst. Still more surprisingly, the results may be accomplished without use of the corrosive

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environmentally disfavored halogenated hydrocarbon solvents that the prior art teaches should be used to improve yields.

The catalysts employed in the process of this invention are $\text{Co}(\text{acac})_n$ combined with dppp and preformed $\text{CoCl}_2(\text{dppp})$, and the cocatalysts are selected from dialkylaluminum halides of the general formula $\text{R}'\text{R}''\text{AlX}$, where R is an alkyl, suitably in the $\text{C}_1 - \text{C}_4$ range, Al is aluminum, and X signifies a halide, for example, dimethylaluminum chloride, diethylaluminum chloride, di-n-propylaluminum halides, di-isopropylaluminum halides, and di-isobutylaluminum halides. Conjugated diolefins employed suitably are 1,3-butadiene (sometimes referred to herein simply as butadiene or "BD") or isoprene, and the alpha monoolefins suitably are ethylene or propylene. Where the reactants are butadiene and ethylene, pure 1,4-hexadiene is produced.

When the cobalt catalyst is $\text{Co}(\text{acac})_n$, preferably from about 0.9 to less than 2 mols of dppp are combined with the $\text{Co}(\text{acac})_n$ in the reaction medium. Advantageously, the mol ratio of dppp to $\text{Co}(\text{acac})_n$ is effective to produce a rate of reaction, at a reaction temperature less than 70°C , preferably around 60°C , of at least about 120 mols of 1,4-hexadiene per mol of cobalt per minute, where the conjugated diene is butadiene or where isoprene or propylene are the reactants, of at least 30 mols of pure product per mol of cobalt per minute. Advantageously, the mol ratio of dppp to $\text{Co}(\text{acac})_n$ is effective for a catalyst productivity, at the reaction temperature less than 70°C , of at least about 1000 mols of 1,4-hexadiene per mol of cobalt.

In a preferred embodiment, the catalyst system is $\text{Co}(\text{acac})_2$ combined with dppp and diethylaluminum chloride or $\text{Co}(\text{acac})_3$ combined with dppp and diethylaluminum chloride.

In another preferred embodiment, the process catalyst system is $\text{CoCl}_2(\text{dppp})$ and diethylaluminum chloride. Using this system in the process, the rate of the reaction suitably exceeds 100 mols of 1,4-hexadiene produced per mol of cobalt per minute. The most preferred embodiment is a process for preparing pure 1,4-hexadiene, which comprises reacting butadiene with ethylene in the presence of a catalyst system consisting of (a) Co (II) (acetylacetonate) $_2$ and 1,3-bis (diphenylphosphino) propane in a preferred mol ratio of about 1:1.5, and (b) diethylaluminum chloride, at a mol ratio of Al/Co of at least 5:1, in a hydrocarbon solvent at reaction conditions controlled in a temperature range from about 50°C to 69°C and an

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alpha-olefin partial pressure range from 50 to 10,000 kPa (.5 to 100 atmospheres), effective to convert the butadiene to 1,4-hexadiene with essentially 100% selectivity at a reaction rate of at least 500 mols of 1,4-hexadiene produced per mol of cobalt per minute.

5 Optionally, the catalyst system employing the $\text{CoCl}_2(\text{dppp})$ preformed complex further includes triethylaluminum, preferably with no more than two molar equivalents of triethylaluminum pre mol of the preformed complex.

 The improved catalyst preferably uses diethylaluminum chloride as the dialkylaluminum halide cocatalyst. This is used alone when the catalyst is
10 formed in situ from $\text{Co}(\text{acac})_3$ or $\text{Co}(\text{acac})_2$. When the improved preformed complex $\text{CoCl}_2(\text{dppp})$ is used, triethylaluminum, preferably up to two equivalents ($\text{Et}_3\text{Al}:\text{Co}$ not more than 2), may be added with the diethylaluminum chloride.

 The temperature of the reaction has a dramatic effect on the
15 selectivity of the reaction to the desired 1,4-diene with the catalyst systems employed in the process of the present invention. The process temperature is less than 70°C , preferably from 50°C to less than 70°C , and most preferably from 55°C to 65°C , eg about 60°C . In examples 1 through 3 and 5 through 10 below of the present improved process, the temperature of reaction is 60°C .
20 Selectivity to 1,4-hexadiene in these Examples approaches 100%. The reaction rate and catalyst productivity are very high with the improved catalyst despite the improvement in selectivity by use of a lower temperature.

 The improved process may use a hydrocarbon solvent such as toluene or xylene or the 1,4-diene product of the reaction, e.g. 1,4-hexadiene from the
25 reaction of butadiene with ethylene. No separation of a solvent from the product is needed when the product is used as the solvent for the reaction. Halogenated solvents are usable but unnecessary for adequate results.

 The present invention is illustrated by the following Examples 1 through 3 and 5 through 10. In all of these examples except Example 5, data
30 is given on (1) conversion of the charged conjugated diene by a catalyst system, i.e., the percent conversion of a conjugated diene charge to all products of reaction, (2) productivity of a catalyst system, i.e., yield of the desired 1,4-diene product per mol of cobalt catalyst, (3) selectivity of the catalyst system for the desired 1,4-diene, i.e., the percent of all the products
35 which is the desired 1,4-diene, (4) the observed first order rate constant of the catalyst system, and (5) the overall reaction rate of the catalyst system.

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Thus, "conversion" of diene (expressed as a percentage) is mols of diene converted to all products divided by mols of diene charged (for 1,3-butadiene, percent conversion is the percent of mol 1,3-butadiene converted to all products/mol 1,3-butadiene charged). "Selectivity" (expressed as percentage) is the mols yield of a particular diene product divided by the mols of diene converted to all products. Thus, selectivity of the catalyst system for 1,4-hexadiene with a charge of ethylene and 1,3-butadiene is mols of 1,4-hexadiene yield/mols 1,3-butadiene converted to all products. "Yield" of a desired product results from multiplying the selectivity percentage of the catalyst system for that desired product under the conditions of the reaction times the aggregate mols of all the products into which the charge diene is converted.

The first order rate constant in the Examples is helpful for within system comparisons. As is shown, the first order reaction rate constant per mmole of cobalt can be about 15. Ethylene pressure in a 500 mL vessel was recorded vs. time during the reaction as the ethylene was fed to the reactor to keep the pressure constant. The reaction was permitted to proceed for a long enough time to determine the pressure of ethylene remaining after all butadiene had been consumed. The $P_{\text{time}} - P_{\text{final}}$ is then proportional to the amount of butadiene remaining in the autoclave. The reaction is first order for butadiene, and a plot of $\ln(P_{\text{time}} - P_{\text{final}})$ vs. time yields a straight line, the slope of which is the observed rate constant.

Example 1

In a nitrogen-filled glove box 6 mg (0.01 mmole) of a preformed complex of CoCl_2 (1,3-bis (diphenylphosphino) propane) was dissolved in 80 mL anhydrous toluene. To this was added with stirring a 25 wt% solution of diethylaluminum chloride in toluene (0.6 mL, 1.0 mmole). This solution was transferred under nitrogen to a 300 mL stirred autoclave and heated to 60° C. With the stirrer stopped, butadiene (20.8 g, dried and with *t*-butylcatechol inhibitor removed by passing through a column of 3A molecular sieve and a column of basic alumina) was pressured into the autoclave using ethylene and the total pressure brought to 2089 kPa with the ethylene. The stirrer was started, and the total pressure in the autoclave was kept constant at 1400 kPa (200 psig) by feeding ethylene through a pressure regulator from a 500 mL vessel containing ethylene at a higher pressure. The rate of the reaction was

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monitored by the drop in pressure in this vessel. After the consumption of ethylene had essentially stopped (71 minutes) the autoclave was cooled rapidly in an ice bath. The autoclave was vented, opened, and the contents removed and analyzed by gas chromatography. Conversion of butadiene was 97%. Selectivity to *cis*-1,4-hexadiene was 99.9%. The only other product of the reaction was 2,4-hexadiene. Vinylcyclohexene, which is an impurity in the butadiene, was also found. The observed first-order rate constant for the reaction was 0.106 min^{-1} . The rate constant per mmole Co is 10.6

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Example 2

This example illustrates that the rate of the reaction doubles when the amount of starting cobalt complex is doubled. The reaction was carried out in a similar manner and at the same temperature and pressure as in Example 1.

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11 mg (0.02 mmole) of the preformed complex of $\text{CoCl}_2(1,3\text{-bis (diphenylphosphino) propane})$ was dissolved in 80 mL anhydrous toluene. To this was added with stirring a 25 wt% solution of diethylaluminum chloride in toluene (0.6 mL, 1.0 mmole). Only 11.8 g of butadiene was added to the autoclave, and consumption of ethylene stopped after 37 minutes. Conversion of butadiene was 94%. Selectivity to *cis*-1,4-hexadiene was 100%. A trace of 2,4-hexadiene (less than 0.1%) was found. The observed first-order rate constant for the reaction was 0.206 min^{-1} . The rate constant per mmole Co is 10.3.

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Example 3

This example illustrates the use of two equivalents of triethylaluminum per cobalt in addition to an excess of diethylaluminum chloride.

The reaction was carried out in a similar manner and at the same temperature and pressure as Example 1. The preformed complex $\text{CoCl}_2(1,3\text{-bis (diphenylphosphino) propane})$ (11 mg, 0.02 mmole) was dissolved in 80 mL anhydrous toluene. To this was added with stirring a 25 wt% solution of diethylaluminum chloride in toluene (0.5 mL, 0.96 mmole) and also a 2.5 wt% solution of triethylaluminum in toluene (0.2 mL, 0.04 mmole). Butadiene (22.7 g) was added to the autoclave, and consumption of ethylene stopped after 25 minutes. Conversion of butadiene was 98%. Selectivity to



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cis-1,4-hexadiene was 100%. A trace of 2,4-hexadiene (less than 0.1%) was found. The observed first-order rate constant for the reaction was 0.206 min^{-1} . The rate constant per mmole Co is 10.3.

Tables 1, 2 and 3

5 The data of Examples 1, 2 and 3 for *cis*-1,4-hexadiene production using a preformed cobalt chloride-dppp catalyst and DEAC cocatalyst at a temperature less than 70°C are set forth in Table 1, arranged in descending order of overall rate of reaction. The surprising difference between these
10 results and those using the same catalyst but with a TEAL cocatalyst at temperatures above 70°C are seen by comparison of the data of Table 1 with the data of following Table 2, a tabulation of data from examples contained in US-A-3,405,194, also arranged in the same descending order. There is an order of magnitude greater rate of reaction when using a preformed cobalt
15 chloride-dppp catalyst and DEAC cocatalyst at less than 70°C in accordance with the invention, compared to using a preformed cobalt chloride-dppp catalyst and TEAL cocatalyst at more than 70°C ; further, the selectivity to 1,4-hexadiene is essentially 100% when using the preformed cobalt chloride-dppp catalyst and DEAC cocatalyst at less than 70°C , but is less than 90%
20 with the prior art catalyst system at the higher temperatures. The same improvement exists whether the prior art process CoCl_2 -dppp is preformed or not. Table 3 tabulates data calculated from examples in the US-A-3,405,194 patent in which the CoCl_2 -dppp catalyst was formed *in situ* and used in the presence of TEAL at temperatures above 70°C . Reaction rates
25 are on the same order as the preformed catalyst set out in Table 2. In Tables 1, 2 and 3, "Al" is aluminum, "Co" is cobalt, "Cmpd" is compound, "BD" is butadiene, "Di" is diene, and "1,4-HD" is 1,4-hexadiene. "Prod'ty" is catalyst productivity. "Conv" is conversion of butadiene to 1,4-hexadiene, and "Select'y" is selectivity of conversion of butadiene to 1,4-hexadiene. "TMAL"
30 is Trimethyl Aluminum.

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Table 1

Preformed $\text{CoCl}_2(\text{dppp})$ Catalyst, DEAC Cocatalyst
Less Than 70° C

Ex	3	1	2
Co Compd	CoCl_2 (dppp)	CoCl_2 (dppp)	CoCl_2 (dppp)
Organo-Aluminum Compd	DEAC+ TEAL	DEAC	DEAC
Al (mmol)	1.00	1.00	1.00
Al/Co	50	100	50
Solvent	toluene	toluene	toluene
BD (gms)	22.70	20.80	11.80
BD (mmol)	420	385	219
Di/Co	21,019	38,519	10,926
Time (min)	25	71	37
Temp (°C)	60	60	60
1,4-HD Yield (gms)	33.78	30.61	16.84
1,4-HD Yield (mols)	0.41	0.37	0.21
Prodt'y (mol/mol)	20,563	37,262	10,253
Rate (mol/mol/min)	823	525	277
Observed 1st Order Rate K (min^{-1})	0.206	0.106	0.206
Rate per mmol Co	10.30	10.60	10.30
Conv (%)	98	97	94
Select'y (%)	100	99.9	100

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Table 2

U.S. Patent 3,405,194: Preformed $\text{CoCl}_2(\text{dppp})$ Catalyst
TEAL Cocatalyst, More Than 70° C

Ex.	23	24	21	22	20	19	18
Co Cmpd	CoCl_2 (dppp)	CoCl_2 (dppp)	CoCl_2 (dppp)	CoCl_2 (dppp)	CoCl_2 (dppp)	CoCl_2 (dppp)	CoCl_2 (dppp)
Co (mmol)	0.25	0.18	0.25	0.13	0.50	0.50	0.50
Organo-Aluminum Cmpd	TMAL	TEAL	TEAL	TEAL	TEAL	TEAL	TEAL
Al (mmol)	15.65	8.47	10.95	10.95	1.46	5.11	5.11
Al/Co	63	46	44	88	3	10	10
Solvent	toluene	ethylene chloride	toluene	toluene	toluene	toluene	toluene
BD (gms)	114	85.7	100	100	100	20.5	20.5
BD (mmol)	2,111	1,587	1,852	1,852	1,852	380	380
Di/Co	8,444	8,625	7,4017	14,815	3,704	759	759
Time (min)	180	120	180	180	156	60	1140
Temp (°C)	80-90	98-102	80-90	80-90	80-90	80-90	80-90
1,4-HD Yield (g)	161.80	67.20	116.70	51.80	105.80	24.40	13.40
1,4-HD Yield (mols)	1.97	0.82	1.42	0.63	1.29	0.30	0.16
Prod'ty (mol/mol)	7,879	4,446	5,683	5,045	2,576	594	326
Rate (mol/mol/min)	43.77	37.05	31.57	28.03	16.51	9.90	0.29
Conv (%)	107.41	65.05	89.25	40.41	93.87	112.59	149.37
Select'y (%)	87.01	79.37	86.11	84.41	74.22	69.61	28.82

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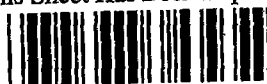
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Table 3
U.S. Patent 3,405,194: In Situ CoCl₂(dppp) Catalyst
TEAL Cocatalyst, More Than 70° C

Ex.	27	26	25
Co Cmpd	CoCl ₂ + dppp	CoCl ₂ + 0.5 dppp	CoCl ₂ + dppp
Co (mmol)	0.13	0.25	0.50
Organo- Aluminum Cmpd	TEAL	TEAL	TEAL
Al (mmol)	7.27	7.30	7.30
Al/Co	58	29	15
Solvent	ethylene chloride	chloro- benzene	chloro- benzene
BD (gms)	67	67	67
BD (mmol)	1,241	1,241	1,241
Di/Co	9,926	4,963	2,481
Time (min)	180	180	180
Temp (°C)	80-90	80-90	80
1,4-HD Yield (g)	83.70	78.50	85.00
1,4-HD Yield (mols)	1.02	0.96	1.04
Prod'y (mol/mol)	8,151	3,822	2,069
Rate (mol/mol/min)	45.28	21.23	17.24
Conv (%)	85.75	92.72	96.80
Select'y (%)	95.93	83.21	86.30

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Comparative Example 4 and Example 5 which follow demonstrate that use of excess triethylaluminum (TEAL) as cocatalyst at less than 70°C yields unsatisfactory results with the preformed cobalt chloride-dppp catalyst system of the present invention compared to the use of excess diethylaluminum chloride (DEAC) as cocatalyst. In these two examples the preformed complex $\text{CoCl}_2(\text{dppp})$ is initially dissolved in a small amount of chlorobenzene in order to assure it is completely dissolved before addition of the cocatalyst.

Comparative Example 4

The reaction was carried out in a similar manner and at the same temperature and pressure as in Example 1. The preformed complex $\text{CoCl}_2(\text{dppp})$ (27 mg, 0.05 mmole) was dissolved in 10 mL anhydrous chlorobenzene. To this was added with stirring a 25 wt% solution of triethylaluminum (TEAL) in toluene (0.8 mL, 1.5 mmole). Anhydrous toluene (70 mL) was then added to this solution. Butadiene (21.6 g) was added to the autoclave at 60°C, which was pressured with ethylene, and the reaction was allowed to proceed for 14 minutes. No significant uptake of ethylene was observed during this time. Conversion of butadiene to *cis*-1,4-hexadiene was less than 1%. No other product of the reaction was observed.

Example 5

The reaction was carried out in a similar manner and at the same temperature and pressure as in Example 1. The preformed complex $\text{CoCl}_2(\text{dppp})$ (27 mg, 0.05 mmole) was dissolved in 10 mL anhydrous chlorobenzene. To this was added with stirring a 25 wt% solution of diethylaluminum chloride (DEAC) in toluene (0.8 mL, 1.5 mmole). Anhydrous toluene (70 mL) was then added to this solution. Butadiene (21.1 g) was added to the autoclave at 60°C, which was pressured with ethylene, and the reaction was allowed to proceed for 30 minutes. During the first few minutes the reaction rate was so fast that the temperature could not be controlled. Consumption of ethylene had essentially ceased after 6 minutes. Conversion of butadiene was greater than 99%. Selectivity to *cis*-1,4-hexadiene was 99.4%, the only other product of the reaction was 2,4-hexadiene.

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Example 6

This Example illustrates the use of $\text{Co}(\text{acac})_3$ as the starting cobalt compound component of the complex. Twice as much of this cobalt compound is needed to achieve essentially the same observed first-order rate constant as with the preformed complex.

The reaction was carried out in a similar manner and at the same temperature and pressure as Example 1. Cobalt(III) acetylacetonate (14 mg, 0.04 mmole), and 1,3-bis (diphenylphosphino) propane (19 mg, 0.045 mmole) were dissolved in 80 mL anhydrous toluene. To this was added with stirring a 25 wt% solution of diethylaluminum chloride in toluene (0.6 mL, 1.0 mmole). Butadiene (24.0 g) was added to the autoclave, which was pressured with ethylene, and consumption of ethylene stopped after 27 minutes. Conversion of butadiene was 99%. Selectivity to *cis*-1,4-hexadiene was 99.9%. The only other product of the reaction was 2,4-hexadiene. The observed first-order rate constant for the reaction was 0.195 min^{-1} . The rate constant per mmole Co is 4.9.

Example 7

This Example illustrates the use of $\text{Co}(\text{acac})_2$ as the starting cobalt compound component of the complex. Use of this cobalt compound in the same relative molar amounts results in a rate of reaction about one and a half times that found when the preformed complex $\text{CoCl}_2\text{-dppp}$ is used (as in Example 1).

The reaction was carried out in a similar manner and at the same temperature and pressure as in Example 1. Cobalt(II) acetylacetonate (2.6 mg, 0.01 mmole) and dppp (6.2 mg, 0.015 mmole, dppp = 1,3-bis (diphenylphosphino) propane) were dissolved in 80 mL anhydrous toluene. This was accomplished by using 2 mL of a stock solution made by dissolving $\text{Co}(\text{acac})_2$ (26 mg, 0.10 mmole) and dppp (62 mg, 0.15 mmole) in 20 mL of anhydrous toluene. To the 80 mL catalyst solution was added with stirring a 25 wt% solution of DEAC in toluene (0.6 mL, 1.0 mmole). Butadiene (22.5 g) was added to the autoclave at 60°C , which was pressured with ethylene, and consumption of ethylene stopped after 32 minutes. Conversion of butadiene was 98%. Selectivity to *cis*-1,4-hexadiene was 100%; a trace of 2,4-hexadiene (less than 0.1%) was found. The observed first-order rate constant for the reaction was 0.150 min^{-1} . The rate constant per mmole Co is 15.00.

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Example 8

This Example illustrates the use of the product *cis*-1,4-hexadiene as solvent for the reaction.

5 The reaction was carried out in a similar manner and at the same temperature and pressure as in Example 1. Cobalt(II) acetylacetonate (10 mg, 0.04 mmole) and dppp (19 mg, 0.045 mmole) were dissolved in 80 mL *cis*-1,4-hexadiene (dried by passing through a column of 3A molecular sieve and alumina under nitrogen). To this was added with stirring a 25 wt% solution
10 of DEAC in toluene (0.6 mL, 1.0 mmole). Butadiene (22.9 g) was added to the autoclave at 60°C, which was pressured with ethylene, and consumption of ethylene stopped after 23 minutes. Conversion of butadiene was 99%. Selectivity to *cis*-1,4-hexadiene (based on product formed in the reaction) was 99.9%; the only other product of the reaction was 2,4-hexadiene. The
15 observed first-order rate constant for the reaction was 0.095 min⁻¹. The rate constant per mmole Co is 2.38.

Example 9

20 This example illustrates the use of isoprene as the conjugated diene reactant. In the reaction of isoprene with ethylene, the product is a mixture of 4-methyl-1,4-hexadiene and 5-methyl-1,4-hexadiene.

 The reaction was carried out in a similar manner and at the same temperature and pressure as in Example 1. Cobalt(II) acetylacetonate (31 mg, 0.12 mmole) and dppp (52 mg, 0.125 mmole) were dissolved in 80 mL
25 anhydrous ortho-xylene. To this was added with stirring at 25 wt% solution of DEAC in toluene (3.3 mL, 6 mmole). Isoprene (23.6 g, dried by passing through a column of 3A molecular sieve and alumina) was added to the autoclave at 60°C, which was pressured with ethylene, and consumption of ethylene stopped after 33 minutes. Conversion of isoprene was 99%.
30 Selectivity to 4-methyl-1,4-hexadiene (88%) and 5-methyl-1,4-hexadiene (12%) was essentially 100%. The observed first-order rate constant for the reaction was 0.218 min⁻¹. The rate constant per mmole Co is 1.82.

Example 10

35 The Example shows that using a molar ratio of dppp ligand to Co(acac)_n that is less than two is preferred. In this example, even though the

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amount of the cobalt salt of highest activity was quadrupled and a 2:1 ratio of dppp ligand to $\text{Co}(\text{acac})_2$ was used, a much slower rate of reaction resulted. A molar ratio of dppp ligand of from a little less than unity to less than 2 is preferred, as in Example 7, which uses a dppp:Co ratio of 1.5:1, yet achieves significantly greater activity with one-fourth the amount of cobalt.

The reaction was carried out in a similar manner and at the same temperature and pressure as in Example 7 but with a 2:1 dppp:Co mol ratio. Cobalt(II) acetylacetonate (10 mg, 0.04 mmole) and dppp (33 mg, 0.08 mmole) were dissolved in 80 mL anhydrous toluene. To this was added with stirring a 25 wt% solution of DEAC in toluene (0.6 mL, 1.0 mmole). Butadiene (20.3 g) was added to the autoclave at 60°C, which was pressured with ethylene, and the reaction was allowed to proceed for 60 minutes. At this time conversion of butadiene was only 76%. Selectivity to *cis*-1,4-hexadiene was 99.9%; the only other product of the reaction was 2,4-hexadiene. The observed first-order rate constant for the reaction was 0.040 min^{-1} . The rate constant per mmole Co is 1.00.

Tables 4 and 5.

Table 4 sets forth the data of Examples 6 - 10, in descending order of rate of reaction. The rate of reaction for butadiene to 1,4-hexadiene is at least about 120 (119) mols of 1,4-hexadiene per mol of cobalt catalyst pre minute. When less than 2 mols of dppp are used per mol of $\text{Co}(\text{acac})_2$ or $\text{Co}(\text{acac})_3$, rates of reaction are from about 4 (Examples 6,8) to about 11 (Example 7) times higher than with 2 mols of dppp per mol of $\text{Co}(\text{acac})_2$ or $\text{Co}(\text{acac})_3$. In all instances, selectivity to 1,4-hexadiene is essentially 100%.

Table 5 tabulates data from the comparable examples of US-A-3,405,194 (these use a $\text{Co}(\text{acac})_3$ combined with dppp catalyst). In Example 43 of the patent, a DEAC cocatalyst is used at a temperature above 70°C. Rate of reaction was very slow, about one fifth that of the minimum preferred rate for the $\text{Co}(\text{acac})_n$ combined with dppp system at less than 70°C. In patent Example 88, the monoolefin is propylene and the rate is about a third that of Example 43 of the patent.

In the tables, "IP" is isoprene, "C2" is ethylene, "C3" is propylene, and other abbreviations are the same as in Tables 1, 2 and 3.

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Table 4

Co(acac)₃ Combined With dppp Catalyst, DEAC Cocatalyst
Less Than 70° C

Ex.	7	8	6	10	9
Co Compd	Co(acac) ₂ + 1.5 dppp	Co(acac) ₂ + dppp	Co(acac) ₃ + dppp	Co(acac) ₂ + 2 dppp	Co(acac) ₂ + dppp
Co (mmol)	0.01	0.04	0.04	0.04	0.12
Organo-Aluminum Compd	DEAC	DEAC	DEAC	DEAC	DEAC
Al (mmol)	1.00	1.00	1.00	1.00	6.00
Al/Co	100	25	25	25	50
Solvent	toluene	1,4-HD	toluene	toluene	o-xylene
Di	BD	BD	BD	BD	IP
Di (gms)	22.5	22.9	24.00	20.3	23.6
Di (mmol)	417	424	444	376	350
Di/Co	41,667	10,602	11,111	9,398	2,917
C=	C2	C2	C2	C2	C2
Time (min)	32	23	27	60	33
Temp (°C)	60	60	60	60	60
1,4-HD Yield (g)	33.48	34.39	36.04	23.40	32.99
1,4-HD Yield (mols)	0.41	0.42	0.44	0.29	0.34
Prodt'y (mol/mol)	40,764	10,468	10,970	7,123	2,858
Rate (mol/mol/min)	1,274	455	406	119	87
Observed 1st Order Rate K (min ⁻¹)	0.15	0.095	0.195	0.04	0.218
Rate/mmol	15.00	2.38	4.90	1.00	1.82
Conv (%)	98	99	99	76	99
Select'y (%)	100	99.9	99.9	99.9	100

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Table 5

U.S. Patent 3,405,194: Co(acac)₃ Combined With dppp Catalyst
Organoaluminum Cocatalyst, More Than 70° C

Ex.	43	88
Co Compd	Co(acac) ₃ + dppp	Co(acac) ₃ + 2 dppp
Co (mmol)	0.50	0.10
Organo- Aluminum Compd	DEAC	TEAL
Al (mmol)	8.0	7.3
Al/Co	16	73
Solvent	toluene	ethylene chloride
Di	BD	BD
BD (gms)	16.2	21.1
BD (mmol)	0.31	0.39
Di/Co	620	3900
C =	C2	C3
Time (min)	25	300
Temp (° C)	80	90-100
1,4-HD Yield (g)	23.70	22.10
1,4-HD Yield (mols)	0.29	0.23
Prod'ty (mol/mol)	577	2298
Rate (mol/mol/min)	23.08	7.66
Conv (%)	97.96	79.33
Select'y (%)	98.34	74.26

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In the following Examples 11 through 14, results of using a catalyst system having a 1,2-bis (diphenylphosphino)ethane (dppe) catalyst ligand at a temperature less than 70°C are shown.

Comparative Examples 11 and 12 show that a substantially slower rate of reaction results when dppe is combined with Co(acac)₂ and DEAC at a temperature of 60°C. This is the case with a molar ratio of dppe:Co of either 1:1 or 2:1.

Comparative Example 11

The reaction was carried out in a similar manner and at the same temperature and pressure as in Example 1. Cobalt(II) acetylacetonate (10 mg, 0.04 mmole) and dppe (16 mg, 0.04 mmole) were dissolved in 80 mL anhydrous toluene. To this was added with stirring a 25 wt% solution of diethylaluminum chloride in toluene (0.6 mL, 1.0 mmole). Butadiene (22.3 g) was added to the autoclave at 60°C, which was pressured with ethylene, and the reaction was allowed to proceed for 60 minutes. Conversion of butadiene was 99%. Selectivity to *cis*-1,4-hexadiene was 99.4%; the only other product of the reaction was 2,4-hexadiene. The observed first order rate constant for the reaction was 0.073 min⁻¹. (Rate constant) / (mmole Co) = 1.83.

Comparative Example 12

The reaction was carried out in a similar manner and at the same temperature and pressure as in Example 1. (Cobalt(II) acetylacetonate (10 mg, 0.04 mmole) and dppe (32 mg, 0.08 mmole) were dissolved in 80 mL anhydrous toluene. To this was added with stirring a 25 wt% solution of diethylaluminum chloride in toluene (0.6 mL, 1.0 mmole). Butadiene (20.6 g) was added to the autoclave at 60°C, which was pressured with ethylene, and the reaction was allowed to proceed for 60 minutes. Conversion of butadiene was 99%. Selectivity to *cis*-1,4-hexadiene was 99.6%; the only other product of the reaction was 2,4-hexadiene. The observed first-order rate constant for the reaction was 0.116 min⁻¹. (Rate constant) / (mmole Co) = 2.90.

Comparative Examples 13 and 14 which follow show that a substantially slower rate of reaction results when dppe is combined with

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Co(acac)₃ and DEAC at a temperature less than 70°C. This is the case with a dppe:Co molar ratio of either 1:1 or 2:1.

Comparative Example 13

5 The reaction was carried out in a similar manner and at the same temperature and pressure as in Example 1. Cobalt(III) acetylacetonate (14 mg, 0.04 mmole) and dppe (16 mg, 0.04 mmole) were dissolved in 80 mL anhydrous toluene. To this was added with stirring a 25 wt% solution of DEAC in toluene (0.6 mL, 1.0 mmole). Butadiene (20.1 g) was added to the
10 autoclave at 60°C, which was pressured with ethylene, and the reaction was allowed to proceed for 60 minutes. Conversion of butadiene was 99%. Selectivity to *cis*-1,4-hexadiene was 99.6%; the only other product of the reaction was 2,4-hexadiene. The observed first order rate constant for the reaction was 0.114 min⁻¹. (Rate constant) / (mmole Co) = 2.85.

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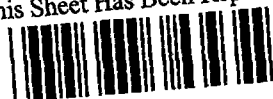
Comparative Example 14

 The reaction was carried out in a similar manner and at the same temperature and pressure as in Example 1. Cobalt(III) acetylacetonate (14 mg, 0.04 mmole) and dppe (32 mg, 0.08 mmole) were dissolved in 80 mL
20 anhydrous toluene. To this was added with stirring a 25 wt% solution of DEAC in toluene (0.6 mL, 1.0 mmole). Butadiene (23.6 g) was added to the autoclave at 60°C, which was pressured with ethylene, and the reaction was allowed to proceed for 49 minutes. Conversion of butadiene was 76%. Selectivity to *cis*-1,4-hexadiene was 99.75; the only other product of the
25 reaction was 2,4-hexadiene. The observed first order rate constant for the reaction was 0.020 min⁻¹. (Rate constant) / (mmole Co) = 0.50.

Tables 6 and 7

 The data of Examples 11, 12 13 and 14, all obtained at a reaction
30 temperature less than 70°C, are set forth in Table 6, in descending order of rate of reaction. The following Table 7 sets forth tabulations of data calculated from the patent examples of US-A-3,405,194 obtained at a reaction temperature less than 70°C. The quantities of Co(acac)_n employed in Examples 11 through 14 are the same as the quantities employed in
35 Example 6 for Co(acac)₃ combined with dppp (toluene solvent) and Example 8 for Co(acac)₂ combined with dppp (1,4-hexadiene solvent). As seen from

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Table 6, a catalyst system employing the ligand 1,2-bis (diphenylphosphino) ethane, or "dppe" as abbreviated herein, in combination with $\text{Co}(\text{acac})_2$ or $\text{Co}(\text{acac})_3$, even in the presence of a dialkylaluminum halide, and even at the same temperatures as used in Examples 6 and 8, is less than half as catalytically active as Examples 6 and 8. The reaction rates for the comparable patent examples shown in table 7 show an extremely slow reaction rate, more than 30 times slower than the rates of Examples 11 through 14. In Table 7, "EASC" is ethyl aluminum sesquichloride.

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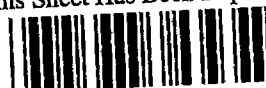
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Table 6

Co(acac)₃ Combined With dppe Catalyst
DEAC Cocatalyst, Less Than 70° C

Ex.	11	14	12	13
Co Compd	Co(acac) ₂ + dppe	Co(acac) ₃ + dppe	Co(acac) ₂ + 2 dppe	Co(acac) ₃ + dppe
Co (mmol)	0.01	0.01	0.04	0.04
Organo-Aluminum Compd	DEAC	DEAC	DEAC	DEAC
Al (mmol)	1.00	1.00	1.00	1.00
Al/Co	25	25	25	25
Solvent	toluene	toluene	toluene	toluene
BD (gms)	22.3	23.6	20.6	20.1
BD (mmol)	413	437	381	372
Di/Co	10,324	10,926	9,537	9,306
Time (min)	60	49	60	60
Temp (°C)	60	60	60	60
C=	C2	C2	C2	C2
1,4-HD Yield (g)	33.32	27.15	30.84	30.10
1,4-HD Yield (mols)	0.41	0.33	0.38	0.37
Prod't'y (mol/mol)	10,142	8,265	9,388	9,160
Rate (mol/mol/min)	169	169	156	153
Observed 1st Order Rate K (min ⁻¹)	0.073	0.02	0.116	0.114
Rate/mmol	1.83	0.50	2.90	2.85
Conv (%)	99	76	99	99
Select'y (%)	99.4	99.7	99.6	99.6

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Table 7

U.S. Patent 3,405,194: Co(acac)_n Combined With dppp Catalyst
Organoaluminum Cocatalyst, Less Than 70° C

Ex.	39	47
Co Cmpd	Co(acac) ₃ + 2.2 dppp	Co(acac) ₃ + 2.2 dppp
Co (mmol)	1.00	1.00
Organo-Aluminum Cmpd	DEAC	EASC
Al (mmol)	15.9	17.6
Al/Co	15.9	17.6
Solvent	ethane	toluene
BD (gms)	32.4	16.7
BD (mmol)	0.60	0.31
Di/Co	600	310
Time (min)	120	1380
Temp (°C)	50	50
C=	C2	C2
1,4-HD Yield (g)	42.50	11.30
1,4-HD Yield (mols)	0.52	0.14
Prodt'y (mol/mol)	517	138
Rate (mol/mol/min)	4.31	0.10
Conv (%)	91.31	47.71
Select'y (%)	94.60	93.39

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Claims:

1. A process for producing substantially pure 1,4 dienes, which comprises reacting a conjugated diolefin with an alpha-olefin in a hydrocarbon solvent reaction medium and in the presence of a catalyst system consisting essentially a cobalt compound, a tertiary diphosphine and an organo aluminum compound, characterized in that the catalyst system comprises:
 1. $\text{Co}(\text{acac})_n$ combined with dppp or a preformed complex of $\text{CoCl}_2(\text{dppp})$, where acac is acetylacetonate, dppp is 1,3-bis(diphenylphosphino) propane, and n is the valence of cobalt; and
 2. a dialkylaluminum halide,wherein the reaction is performed at a temperature of less than 70°C to convert the conjugated diolefin to the 1,4-diene with substantially 100% selectivity.
2. The process of Claim 1, wherein the temperature is at least 50°C and less than 70°C , preferably about 60°C .
3. The process of Claim 1 or 2, wherein the halide is chloride.
4. The process of any preceding claim, when performed at an alpha-olefin partial pressure of from 50 to 10,000 kPa (0.5 to 100 atmospheres).
5. The process of any preceding claim, wherein the hydrocarbon solvent is non-halogenated.
6. The process of Claim 5, wherein the solvent is toluene, xylene, a 1,4-diene which is the product of the reaction, or a mixture of any two or more thereof.
7. The process of any preceding claim, wherein the conjugated diolefin is butadiene or isoprene, the alpha-olefin is ethylene or propylene and



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the 1,4-diene is 1,4-hexadiene, 2-methyl-1,4-hexadiene, or a mixture of 4-methyl-1,4-hexadiene and 5-methyl-1,4-hexadiene.

8. The process of any preceding claim, wherein the selectivity is greater than 99.5%.
9. The process of any preceding claim, in which the rate of reaction is at least 100 mols of 1,4-diene per mol of cobalt per minute.
10. The process of Claim 9, wherein conjugated diolefin is butadiene and the alpha-olefin is ethylene, and wherein the cobalt catalyst system and the reaction conditions are effective to produce a rate of reaction of at least 500 mols of 1,4-hexadiene produced per mol of cobalt per minute.
11. The process of any of Claims 1 to 8, wherein the conjugated diolefin is butadiene and the alpha-olefin is propylene and wherein the cobalt catalyst system and the reaction conditions are effective to produce a rate of reaction of at least 30 mols of 2-methyl-1,4 hexadiene per mol of cobalt per minute.
12. The process of any of Claims 1 to 8, wherein the conjugated diolefin is isoprene and the alpha-olefin is ethylene and wherein the cobalt catalyst system and the reaction conditions are effective to produce a rate of reaction of at least 30 mols of a mixture of 4-methyl-1,4-hexadiene and 5-methyl-1,4-hexadiene per mol of cobalt per minute.
13. The process of any preceding claim, wherein the dialkylaluminum halide is diethylaluminum chloride.
14. The process of any preceding claim, when performed at a catalyst productivity of at least 1000 mols of 1,4-diene per mol of cobalt.
15. The process of any preceding claim, wherein the cobalt catalyst system comprises $\text{Co}(\text{acac})_n$ and wherein from 0.9 to less than 2 mols of dppp are combined with the $\text{Co}(\text{acac})_n$.



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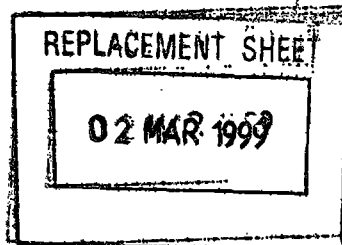
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16. The process of any preceding claim, wherein the cobalt catalyst system comprises $\text{Co}(\text{acac})_2$ combined with dppp and wherein the first order reaction rate constant per mmole of cobalt is at least 15.
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17. The process of any of Claims 1 to 14, wherein the catalyst system comprises $\text{CoCl}_2(\text{dppp})$ and further includes triethylaluminum with no more than two molar equivalents of triethylaluminum per mol $\text{CoCl}_2(\text{dppp})$.
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18. The process of any preceding claim, wherein the catalyst system has an Al/Co molar ratio of at least 5:1.
- 15
19. The process in accordance with any one or more of the preceding claims, comprising the further step of using the produced 1,4-dienes in a polymerization process.
20. Polyolefin polymers manufactured with 1,4-dienes produced according to any one or more of the preceding claims.

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CLAIMS

1. A process for preparing pure 1,4 dienes without the use of halogenated hydrocarbon solvents, which comprises: reacting a conjugated diolefin with an alpha-olefin in the presence of a cobalt catalyst system consisting essentially of:
 1. $\text{Co}(\text{acac})_n$ combined with dppp or $\text{CoCl}_2(\text{dppp})$, where acac is acetylacetonate, n equals the valence of cobalt, and dppp is 1,3-bis(diphenylphosphino)-propane, and
 2. a dialkylaluminum chloride, present at a molar ratio of Al/Co of at least 5:1,in a non-halogenated hydrocarbon solvent reaction medium, at reaction conditions controlled in a temperature range less than 70°C . and an alpha-olefin partial pressure range from about 0.5 to about 100 atmospheres, effective to convert the conjugated diolefin to a 1,4-diene with essentially 100% selectivity.
2. The process of claim 1, in which said conjugated diolefin is butadiene, said alpha-olefin is ethylene and said 1,4-diene is 1,4-hexadiene.
3. The process of claim 2, in which said cobalt catalyst system is said $\text{Co}(\text{acac})_n$ combined with dppp and wherein from about 0.9 to less than 2 mols of dppp are combined with the $\text{Co}(\text{acac})_n$ in the reaction medium.
4. The process of claim 2, in which said cobalt catalyst system is said $\text{Co}(\text{acac})_n$ combined with dppp and wherein, the mol ratio of dppp to $\text{Co}(\text{acac})_n$ is effective to produce a rate of reaction, at the reaction temperature less than 70°C ., of at least about 120 mols of 1,4-hexadiene per mol of cobalt per minute.
5. The process of claim 2, in which said cobalt catalyst



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system is said $\text{Co}(\text{acac})_n$ combined with dppp and where, the mol ratio of dppp to $\text{Co}(\text{acac})_n$ is effective for a catalyst productivity, at the reaction temperature less than 70°C ., of at least about 1000 mols of 1,4-hexadiene per mol of cobalt.

6. The process of claim 1, in which said cobalt catalyst system is $\text{Co}(\text{acac})_2$ combined with dppp and diethylaluminum chloride.
7. The process of claim 1, in which said cobalt catalyst system is $\text{Co}(\text{acac})_3$ combined with dppp and diethylaluminum chloride.
8. The process of claim 6, in which the first order reaction rate constant per mmole of cobalt is at least about 15.
9. The process of claim 1, in which said cobalt catalyst system is $\text{CoCl}_2(\text{dppp})$ and diethylaluminum chloride.
10. The process of claim 9 in which the rate of the reaction exceeds 100 mols of 1,4-hexadiene produced per mol of cobalt per minute.
11. The process of claim 9, in which said cobalt catalyst system further includes triethylaluminum with no more than two molar equivalents of triethylaluminum per mol $\text{CoCl}_2(\text{dppp})$.
12. The process of claim 1, in which said non-halogenated hydrocarbon solvent is selected from one or more of toluene, xylene and a 1,4-diene which is the product of the reaction.
13. The process of claim 1 in which the temperature is at least about 50°C . and less than 70°C .
14. The process of claim 13, in which said temperature is about 60°C .



* C L M S *

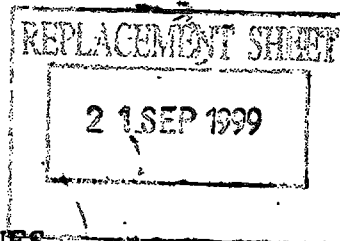
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15. The process of claim 1, in which said conjugated diolefin is butadiene and said alpha-olefin is propylene.
16. The process of claim 15, in which said cobalt catalyst system and said reaction conditions are effective to produce a rate of reaction, at the reaction temperature less than 70°C., of at least about 30 mols of 2-methyl-1,4-hexadiene per mol of cobalt per minute.
17. The process of claim 1, in which said conjugated diolefin is isoprene and said alpha-olefin is ethylene and in which said cobalt catalyst system and said reaction conditions are effective to produce a rate of reaction, at the reaction temperature less than 70°C., of at least about 30 mols of a mixture of 4-methyl-1,4-hexadiene and 5-methyl-1,4-hexadiene per mol of cobalt per minute.
18. The process of claim 1 in which said conjugated diolefin is isoprene and said alpha-olefin is propylene.
19. A process for preparing 1,4-hexadiene, which comprises: reacting butadiene with ethylene in the presence of a cobalt catalyst system consisting of (a) $\text{Co(II) - (acetylacetonate)}_2$ and 1,3-bis(diphenylphosphino)propane in a mol ratio of about 1:1.5, and (b) diethylaluminum chloride, at a mol ratio of Al/Co of at least 5:1, in a non-halogenated hydrocarbon solvent at reaction conditions controlled in a temperature range from about 50°C. to 69°C. and an ethylene partial pressure range from about 0.5 to about 100 atmospheres, effective to convert the butadiene to a 1,4-hexadiene with essentially 100% selectivity at a reaction rate of at least 500 mols of 1,4-hexadiene produced per mol of cobalt per minute.



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PROCESS FOR PRODUCING 1,4-DIENES

This invention relates to processes for the preparation of 1,4-dienes from the reaction of a conjugated diolefin with an alpha-monoolefin, and more particularly, to such processes involving a catalyst system including a salt of cobalt, a tertiary diphosphine, and an organoaluminum compound.

1,4-Dienes are useful as comonomers in polyolefin polymers since they allow the polymer to be cross linked.

US-A-3,405,194 teaches a method of producing hexadienes by the reaction of an alpha-monoolefin with a conjugated diolefin in the presence of a catalyst system of a salt of cobalt or iron, a tertiary diphosphine, and an organoaluminum compound. The tertiary diphosphines include 1,2-bis (diphenylphosphino) ethane ("dppe") and 1,3 -bis (diphenylphosphino) propane ("dppp").

The examples, and certain contemporaneous and subsequent publications, teach the importance of reacting a conjugated diolefin with an alpha-monoolefin at temperatures of 80°C or more when using a cobalt based catalyst system of the types described. Thus of the 88 examples in the patent, 68 examples (1-53 and 74-88) are directed to a catalyst system of a salt of cobalt, a tertiary diphosphine, and an organoaluminum compound, and 64 of these 68 examples employ a temperature of at least 80°C (example 2 is at 70°C and examples 39, 47 and 76 are at 50°C, all with a catalyst system including a cobalt complex with dppe).

In "A New Process for 1,4-Diene Synthesis", A. Miyake, G. Hata, M. Iwamoto, and S. Yuguchi, *Proceedings of the Seventh World Petroleum Congress*, 1967 volume 5, 317, the authors described the superiority of a cobalt diphosphine system of CoCl_2 -dppe in combination with an aluminum trialkyl, specifically, triethylaluminum, at 80°C (each also described in US-A-3,405,194).

The effects of reaction temperature on reaction rate for butadiene conversion are particularly described for the catalyst system of CoCl_2 -dppe- Et_3Al in "Reaction of Butadiene with Ethylene. IV. Synthesis of 1,4-Hexadiene by a Cobalt Chloride-Ditertiary Phosphine Complex and an Organolaluminum Compound Catalyst", M. Iwamoto and S. Yuguchi, *Bulletin of the Chemical Society of Japan*, 1968, 41, 150. Apparent optimum reaction temperatures are said to be in the range of 80 to 100°C. Two examples

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achieved 97% selectivity at 80°C. Below 80°C, rate of conversion is shown to fall precipitously, and at temperatures higher than 100°C a considerable loss of selectivity from isomerization of 1,4 hexadiene to conjugated dienes, mainly to 2,4-hexadiene, is reported.

Henrici-Oliv et al. in "Codimerization of Butadiene and Ethylene," *Journal of Organometallic Chemistry*, vol. 35, p. 381 (1972), a study of the catalytic system described in the above cited articles by Iwamoto et al. report that temperature of reaction appears critical for high selectivity using $\text{CoCl}_2\text{-dppe-Et}_3\text{Al}$ in dichloroethane. Page 381 expressly states that "between 80°C and 110°C *cis*-1,4-hexadiene is formed in high yield, whereas below 80°C more ethylene than butadiene is consumed with the result that C₈ compounds are produced. Above 110°C 1,4-hexadiene is isomerized to 2,4-hexadiene." Teaching the same is US-A-3,647,902, to Henrici-Oliv et al. (where the catalyst system is $\text{CoCl}_2\text{-dppe-Et}_3\text{Al}$ in a halogenated hydrocarbon solvent), stating that the temperature must be not less than 80°C when ethylene is reacted with 1,3-butadiene, or poor selectivity results (col. 2, lines 13-24).

The foregoing teachings in the prior art on conducting the reaction at temperatures of at least 80°C encompass specific described cobalt catalyst systems where the diphosphine ligand is dppp. In US-A-3,405,194, examples 18-27, 43 and 88 employ dppp as a cobalt catalyst ligand. In examples 18-27, the cobalt complex is CoCl_2 and dppp; in examples 43 and 48, the cobalt complex is the acetyl acetonate of trivalent cobalt, i.e., $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_3$, with the dppp ligand. (Acetylacetonate is sometimes referred to as "acac"; for example, the acetylacetonate of trivalent cobalt is $\text{Co}(\text{acac})_3$). The organoaluminum compound used in examples 18-27, 43 and 88 is trimethylaluminum ("TMAL") or triethylaluminum ("TEAL") when the cobalt salt is CoCl_2 and is sometimes diethylaluminum chloride ("DEAC") when the cobalt salt is $\text{Co}(\text{acac})_3$. In all these examples employing the dppp ligand, the temperatures are in the range 80° - 102° C.

"Effects of Ditertiary Phosphine Ligands in Co-dimerization of Butadiene and Ethylene Catalyzed by cobalt Chloride-Ditertiary Phosphine-Triethylaluminum" T. Kagawa, Y. Inoue, and H. Hashimoto, *Bulletin of the Chemical Society of Japan*, 1970, 43, 1250, reports results for testing a $\text{CoCl}_2\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\text{-Et}_3\text{Al}$ catalyst system (Ph=phenyl, n=1,2,3,4 etc.) for effect of length of the methylene chain between the two phosphorus atoms on

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cis-1,4-hexadiene formation at 80-90°C. The data presented for the system CoCl₂-dppp-Et₃Al indicate a relatively low yield to 1,4-hexadiene on butadiene.

The temperature teachings in the art have applied whether the conjugated diolefin is butadiene or isoprene. Examples 74-75 and 77-82 of US-A-3,405,194 employ CoCl₂-dppe-Et₃Al at 80°C or 100°C to react isoprene with ethylene. In "Preparation of 3-Methyl-1,4-heptadiene, 3-Ethyl-1,4-hexadiene, and Methyl-1,4-hexadienes" by M. Iwamoto, K. Tani, H. Igaki, and S. Yuguchi, *Journal of Organic Chemistry* 1967, 32, 4148, reaction of isoprene with ethylene is reported rapid and selective (97.2 - 99%) at 80-98°C with the CoCl₂-dppe-Et₃Al catalyst system.

Even variants of the cobalt catalyst systems teach reaction conversion of conjugated diolefins to 1,4-dienes at a 80°C minimum. US-A-3,445,540 uses a triphosphine instead of a diphosphine, and US-A-3,574,139 uses cobalt complexed with two diphosphines, i.e., bis [ethylene bis (diphenylphosphine)] cobalt (0) or bis [ethylene bis (diphenylphosphine)] cobalt (I) hydride. Both of these two patents state that "temperatures below 80°C may be too slow for operating convenience. The preferred temperature range lies between 80 and 120°C..." (US-A-3,574,139, col. 3, lines 70-74; US-A-3,445,540, col. 5, lines 35-39.)

In US-A-3,405,194, toluene is the solvent in examples 18-23 and 43; halogenated hydrocarbon solvents are used in examples 24-27 and 88. Halogenated hydrocarbon solvents are instructed to be used to improve selectivity when the intended hexadiene is 1,4-hexadiene, and to provide the further advantage of easier cobalt catalyst handling, since these solvents dissolve the cobalt complex completely (col. 4, lines 60-67). In the article by Henrici-Oliv et al. cited above, halogenated hydrocarbon solvents are said to be favored, because CoCl₂-dppe is insoluble in toluene and alkylation reactions of transition metal salts with aluminum alkyls are faster and more complete in halogenated solvents than in aromatics. US-A-3,647-902 contain a similar teaching

According to the present invention there is provided a process for producing substantially pure 1,4 dienes, which comprises reacting a conjugated diolefin with an alpha-olefin in a hydrocarbon solvent reaction medium and in the presence of a catalyst system consisting essentially a cobalt compound, a tertiary diphosphine and an organo aluminum

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compound, characterized in that the catalyst system comprises: $\text{Co}(\text{acac})_n$ combined with dppp or a preformed complex of $\text{CoCl}_2(\text{dppp})$, where acac is acetylacetonate, dppp is 1,3-bis (diphenylphosphino) propane, and n is the valence of cobalt; and a dialkylaluminum halide, and in that the reaction is performed at a temperature of less than 70°C to convert the conjugated diolefin to the 1,4-diene with substantially 100% selectivity. It is preferred to perform the process at a temperature of about 60°C . It is also preferred to perform the process at an alpha-olefin partial pressure of from 50 to 10,000 kPa (0.5 to 100 atmospheres). By "pure" is generally meant more than about 99% 1,4-diene, preferably approaching or equaling 100% 1,4-diene.

The highest selectivity, essentially 100 percent selectivity, is desired, in order to maximize production of pure 1,4-dienes, thereby eliminating the difficult separation of 2,4-diene and other by-products to satisfy the commercial need for pure 1,4-dienes. It has been found that substantially 100% selectivity from reaction of conjugated diolefins with an alpha-olefin is possible using the process according to the invention. Preferably the selectivity is greater than 98.5%, more preferably greater than 99%, most preferably 99.5% and ideally 100%. It is also possible by selection of reaction conditions within the specified ranges to provide essentially pure 1,4-dienes from conjugated diolefins at high rates of reaction and/or high catalyst productivity.

In order to obtain highest reaction rates per unit of catalyst, the prior art has employed halogenated hydrocarbon solvents for preformed catalysts, particularly the favored $\text{CoCl}_2\text{-dppe/TEAL}$ catalyst system of the above referenced prior art. However, halogenated solvents are environmentally disfavored, are corrosive to equipment, and consequently are commercially unattractive as a means of improving catalytic reaction rates and product yields. With the process of this invention it is possible to promote reaction of conjugated diolefins and alpha-olefins at high rates of reaction without the use of halogenated hydrocarbon solvents.

Surprisingly, contrary to the teachings of the prior art, such results are achievable at temperatures less than 80°C . Further, exceptional selectivity at these reaction temperatures in this particular catalyst system may be accompanied by vastly increased rates of reaction and catalyst productivity, indicative of a very reactive species of catalyst. Still more surprisingly, these results may be accomplished without use of the corrosive and

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environmentally disfavored halogenated hydrocarbon solvents that the prior art teaches should be used to improve yields.

The catalysts employed in the process of this invention are $\text{Co}(\text{acac})_n$ combined with dppp and preformed $\text{CoCl}_2(\text{dppp})$, and the cocatalysts are selected from dialkylaluminum halides of the general formula $\text{R}'\text{R}''\text{AlX}$, where R is an alkyl, suitably in the $\text{C}_1 - \text{C}_4$ range, Al is aluminum, and X signifies a halide, for example, dimethylaluminum chloride, diethylaluminum chloride, di-n-propylaluminum halides, di-isopropylaluminum halides, and di-isobutylaluminum halides. Conjugated diolefins employed suitably are 1,3-butadiene (sometimes referred to herein simply as butadiene or "BD") or isoprene, and the alpha monoolefins suitably are ethylene or propylene. Where the reactants are butadiene and ethylene, pure 1,4-hexadiene is produced.

When the cobalt catalyst is $\text{Co}(\text{acac})_n$, preferably from about 0.9 to less than 2 mols of dppp are combined with the $\text{Co}(\text{acac})_n$ in the reaction medium. Advantageously, the mol ratio of dppp to $\text{Co}(\text{acac})_n$ is effective to produce a rate of reaction, at a reaction temperature less than 70°C , preferably around 60°C , of at least about 120 mols of 1,4-hexadiene per mol of cobalt per minute, where the conjugated diene is butadiene or where isoprene or propylene are the reactants, of at least 30 mols of pure product per mol of cobalt per minute. Advantageously, the mol ratio of dppp to $\text{Co}(\text{acac})_n$ is effective for a catalyst productivity, at the reaction temperature less than 70°C , of at least about 1000 mols of 1,4-hexadiene per mol of cobalt.

In a preferred embodiment, the catalyst system is $\text{Co}(\text{acac})_2$ combined with dppp and diethylaluminum chloride or $\text{Co}(\text{acac})_3$ combined with dppp and diethylaluminum chloride.

In another preferred embodiment, the process catalyst system is $\text{CoCl}_2(\text{dppp})$ and diethylaluminum chloride. Using this system in the process, the rate of the reaction suitably exceeds 100 mols of 1,4-hexadiene produced per mol of cobalt per minute. The most preferred embodiment is a process for preparing pure 1,4-hexadiene, which comprises reacting butadiene with ethylene in the presence of a catalyst system consisting of (a) Co (II) (acetylacetonate) $_2$ and 1,3-bis (diphenylphosphino) propane in a preferred mol ratio of about 1:1.5, and (b) diethylaluminum chloride, at a mol ratio of Al/Co of at least 5:1, in a hydrocarbon solvent at reaction conditions controlled in a temperature range from about 50°C to 69°C and an

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alpha-olefin partial pressure range from 50 to 10,000 kPa (.5 to 100 atmospheres), effective to convert the butadiene to 1,4-hexadiene with essentially 100% selectivity at a reaction rate of at least 500 mols of 1,4-hexadiene produced per mol of cobalt per minute.

Optionally, the catalyst system employing the $\text{CoCl}_2(\text{dppp})$ preformed complex further includes triethylaluminum, preferably with no more than two molar equivalents of triethylaluminum pre mol of the preformed complex.

The improved catalyst preferably uses diethylaluminum chloride as the dialkylaluminum halide cocatalyst. This is used alone when the catalyst is formed in situ from $\text{Co}(\text{acac})_3$ or $\text{Co}(\text{acac})_2$. When the improved preformed complex $\text{CoCl}_2(\text{dppp})$ is used, triethylaluminum, preferably up to two equivalents ($\text{Et}_3\text{Al}:\text{Co}$ not more than 2), may be added with the diethylaluminum chloride.

The temperature of the reaction has a dramatic effect on the selectivity of the reaction to the desired 1,4-diene with the catalyst systems employed in the process of the present invention. The process temperature is less than 70°C , preferably from 50°C to less than 70°C , and most preferably from 55°C to 65°C , eg about 60°C . In examples 1 through 3 and 5 through 10 below of the present improved process, the temperature of reaction is 60°C . Selectivity to 1,4-hexadiene in these Examples approaches 100%. The reaction rate and catalyst productivity are very high with the improved catalyst despite the improvement in selectivity by use of a lower temperature.

The improved process may use a hydrocarbon solvent such as toluene or xylene or the 1,4-diene product of the reaction, e.g. 1,4-hexadiene from the reaction of butadiene with ethylene. No separation of a solvent from the product is needed when the product is used as the solvent for the reaction. Halogenated solvents are usable but unnecessary for adequate results.

The present invention is illustrated by the following Examples 1 through 3 and 5 through 10. In all of these examples except Example 5, data is given on (1) conversion of the charged conjugated diene by a catalyst system, i.e., the percent conversion of a conjugated diene charge to all products of reaction, (2) productivity of a catalyst system, i.e., yield of the desired 1,4-diene product per mol of cobalt catalyst, (3) selectivity of the catalyst system for the desired 1,4-diene, i.e., the percent of all the products which is the desired 1,4-diene, (4) the observed first order rate constant of the catalyst system, and (5) the overall reaction rate of the catalyst system.

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Thus, "conversion" of diene (expressed as a percentage) is mols of diene converted to all products divided by mols of diene charged (for 1,3-butadiene, percent conversion is the percent of mol 1,3-butadiene converted to all products/mol 1,3-butadiene charged). "Selectivity" (expressed as percentage) is the mols yield of a particular diene product divided by the mols of diene converted to all products. Thus, selectivity of the catalyst system for 1,4-hexadiene with a charge of ethylene and 1,3-butadiene is mols of 1,4-hexadiene yield/mols 1,3-butadiene converted to all products. "Yield" of a desired product results from multiplying the selectivity percentage of the catalyst system for that desired product under the conditions of the reaction times the aggregate mols of all the products into which the charge diene is converted.

The first order rate constant in the Examples is helpful for within system comparisons. As is shown, the first order reaction rate constant per mmole of cobalt can be about 15. Ethylene pressure in a 500 mL vessel was recorded vs. time during the reaction as the ethylene was fed to the reactor to keep the pressure constant. The reaction was permitted to proceed for a long enough time to determine the pressure of ethylene remaining after all butadiene had been consumed. The $P_{\text{time}} - P_{\text{final}}$ is then proportional to the amount of butadiene remaining in the autoclave. The reaction is first order for butadiene, and a plot of $\ln(P_{\text{time}} - P_{\text{final}})$ vs. time yields a straight line, the slope of which is the observed rate constant.

Example 1

In a nitrogen-filled glove box 6 mg (0.01 mmole) of a preformed complex of CoCl_2 (1,3-bis (diphenylphosphino) propane) was dissolved in 80 mL anhydrous toluene. To this was added with stirring a 25 wt% solution of diethylaluminum chloride in toluene (0.6 mL, 1.0 mmole). This solution was transferred under nitrogen to a 300 mL stirred autoclave and heated to 60°C. With the stirrer stopped, butadiene (20.8 g, dried and with *t*-butylcatechol inhibitor removed by passing through a column of 3A molecular sieve and a column of basic alumina) was pressured into the autoclave using ethylene and the total pressure brought to 2089 kPa with the ethylene. The stirrer was started, and the total pressure in the autoclave was kept constant at 1400 kPa (200 psig) by feeding ethylene through a pressure regulator from a 500 mL vessel containing ethylene at a higher pressure. The rate of the reaction was

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monitored by the drop in pressure in this vessel. After the consumption of ethylene had essentially stopped (71 minutes) the autoclave was cooled rapidly in an ice bath. The autoclave was vented, opened, and the contents removed and analyzed by gas chromatography. Conversion of butadiene was 97%. Selectivity to *cis*-1,4-hexadiene was 99.9%. The only other product of the reaction was 2,4-hexadiene. Vinylcyclohexene, which is an impurity in the butadiene, was also found. The observed first-order rate constant for the reaction was 0.106 min^{-1} . The rate constant per mmole Co is 10.6

Example 2

This example illustrates that the rate of the reaction doubles when the amount of starting cobalt complex is doubled. The reaction was carried out in a similar manner and at the same temperature and pressure as in Example 1.

11 mg (0.02 mmole) of the preformed complex of $\text{CoCl}_2(1,3\text{-bis (diphenylphosphino) propane})$ was dissolved in 80 mL anhydrous toluene. To this was added with stirring a 25 wt% solution of diethylaluminum chloride in toluene (0.6 mL, 1.0 mmole). Only 11.8 g of butadiene was added to the autoclave, and consumption of ethylene stopped after 37 minutes. Conversion of butadiene was 94%. Selectivity to *cis*-1,4-hexadiene was 100%. A trace of 2,4-hexadiene (less than 0.1%) was found. The observed first-order rate constant for the reaction was 0.206 min^{-1} . The rate constant per mmole Co is 10.3.

Example 3

This example illustrates the use of two equivalents of triethylaluminum per cobalt in addition to an excess of diethylaluminum chloride.

The reaction was carried out in a similar manner and at the same temperature and pressure as Example 1. The preformed complex $\text{CoCl}_2(1,3\text{-bis (diphenylphosphino) propane})$ (11 mg, 0.02 mmole) was dissolved in 80 mL anhydrous toluene. To this was added with stirring a 25 wt% solution of diethylaluminum chloride in toluene (0.5 mL, 0.96 mmole) and also a 2.5 wt% solution of triethylaluminum in toluene (0.2 mL, 0.04 mmole). Butadiene (22.7 g) was added to the autoclave, and consumption of ethylene stopped after 25 minutes. Conversion of butadiene was 98%. Selectivity to

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cis-1,4-hexadiene was 100%. A trace of 2,4-hexadiene (less than 0.1%) was found. The observed first-order rate constant for the reaction was 0.206 min⁻¹. The rate constant per mmole Co is 10.3.

Tables 1, 2 and 3

The data of Examples 1, 2 and 3 for *cis*-1,4-hexadiene production using a preformed cobalt chloride-dppp catalyst and DEAC cocatalyst at a temperature less than 70°C are set forth in Table 1, arranged in descending order of overall rate of reaction. The surprising difference between these results and those using the same catalyst but with a TEAL cocatalyst at temperatures above 70°C are seen by comparison of the data of Table 1 with the data of following Table 2, a tabulation of data from examples contained in US-A-3,405,194, also arranged in the same descending order. There is an order of magnitude greater rate of reaction when using a preformed cobalt chloride-dppp catalyst and DEAC cocatalyst at less than 70°C in accordance with the invention, compared to using a preformed cobalt chloride-dppp catalyst and TEAL cocatalyst at more than 70°C; further, the selectivity to 1,4-hexadiene is essentially 100% when using the preformed cobalt chloride-dppp catalyst and DEAC cocatalyst at less than 70°C, but is less than 90% with the prior art catalyst system at the higher temperatures. The same improvement exists whether the prior art process CoCl₂-dppp is preformed or not. Table 3 tabulates data calculated from examples in the US-A-3,405,194 patent in which the CoCl₂-dppp catalyst was formed *in situ* and used in the presence of TEAL at temperatures above 70°C. Reaction rates are on the same order as the preformed catalyst set out in Table 2. In Tables 1, 2 and 3, "Al" is aluminum, "Co" is cobalt, "Cmpd" is compound, "BD" is butadiene, "Di" is diene, and "1,4-HD" is 1,4-hexadiene. "Prod'ty" is catalyst productivity. "Conv" is conversion of butadiene to 1,4-hexadiene, and "Select'y" is selectivity of conversion of butadiene to 1,4-hexadiene. "TMAL" is Trimethyl Aluminum.

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Table 1

Preformed $\text{CoCl}_2(\text{dppp})$ Catalyst, DEAC Cocatalyst
Less Than 70° C

Ex	3	1	2
Co Compd	CoCl_2 (dppp)	CoCl_2 (dppp)	CoCl_2 (dppp)
Organo-Aluminum Compd	DEAC+ TEAL	DEAC	DEAC
Al (mmol)	1.00	1.00	1.00
Al/Co	50	100	50
Solvent	toluene	toluene	toluene
BD (gms)	22.70	20.80	11.80
BD (mmol)	420	385	219
Di/Co	21,019	38,519	10,926
Time (min)	25	71	37
Temp (°C)	60	60	60
1,4-HD Yield (gms)	33.78	30.61	16.84
1,4-HD Yield (mols)	0.41	0.37	0.21
Prod'ty (mol/mol)	20,563	37,262	10,253
Rate (mol/mol/min)	823	525	277
Observed 1st Order Rate K (min^{-1})	0.206	0.106	0.206
Rate per mmol Co	10.30	10.60	10.30
Conv (%)	98	97	94
Select'y (%)	100	99.9	100

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Table 2

U.S. Patent 3,405,194: Preformed $\text{CoCl}_2(\text{dppp})$ Catalyst
TEAL Cocatalyst, More Than 70° C

Ex.	23	24	21	22	20	19	18
Co Cmpd	CoCl_2 (dppp)	CoCl_2 (dppp)	CoCl_2 (dppp)	CoCl_2 (dppp)	CoCl_2 (dppp)	CoCl_2 (dppp)	CoCl_2 (dppp)
Co (mmol)	0.25	0.18	0.25	0.13	0.50	0.50	0.50
Organo-Aluminum Cmpd	TMAL	TEAL	TEAL	TEAL	TEAL	TEAL	TEAL
Al (mmol)	15.65	8.47	10.95	10.95	1.46	5.11	5.11
Al/Co	63	46	44	88	3	10	10
Solvent	toluene	ethylene chloride	toluene	toluene	toluene	toluene	toluene
BD (gms)	114	85.7	100	100	100	20.5	20.5
BD (mmol)	2,111	1,587	1,852	1,852	1,852	380	380
Di/Co	8,444	8,625	7,4017	14,815	3,704	759	759
Time (min)	180	120	180	180	156	60	1140
Temp (°C)	80-90	98-102	80-90	80-90	80-90	80-90	80-90
1,4-HD Yield (g)	161.80	67.20	116.70	51.80	105.80	24.40	13.40
1,4-HD Yield (mols)	1.97	0.82	1.42	0.63	1.29	0.30	0.16
Prod'y (mol/mol)	7,879	4,446	5,683	5,045	2,576	594	326
Rate (mol/mol/ min)	43.77	37.05	31.57	28.03	16.51	9.90	0.29
Conv (%)	107.41	65.05	89.25	40.41	93.87	112.59	149.37
Select'y (%)	87.01	79.37	86.11	84.41	74.22	69.61	28.82

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Table 3

U.S. Patent 3,405,194: In Situ $\text{CoCl}_2(\text{dppp})$ Catalyst
TEAL Cocatalyst, More Than 70° C

Ex.	27	26	25
Co Compd	$\text{CoCl}_2 + \text{dppp}$	$\text{CoCl}_2 + 0.5 \text{ dppp}$	$\text{CoCl}_2 + \text{dppp}$
Co (mmol)	0.13	0.25	0.50
Organo-Aluminum Compd	TEAL	TEAL	TEAL
Al (mmol)	7.27	7.30	7.30
Al/Co	58	29	15
Solvent	ethylene chloride	chloro-benzene	chloro-benzene
BD (gms)	67	67	67
BD (mmol)	1,241	1,241	1,241
Di/Co	9,926	4,963	2,481
Time (min)	180	180	180
Temp (°C)	80-90	80-90	80
1,4-HD Yield (g)	83.70	78.50	85.00
1,4-HD Yield (mols)	1.02	0.96	1.04
Prod't'y (mol/mol)	8,151	3,822	2,069
Rate (mol/mol/min)	45.28	21.23	17.24
Conv (%)	85.75	92.72	96.80
Select'y (%)	95.93	83.21	86.30

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Comparative Example 4 and Example 5 which follow demonstrate that use of excess triethylaluminum (TEAL) as cocatalyst at less than 70°C yields unsatisfactory results with the preformed cobalt chloride-dppp catalyst system of the present invention compared to the use of excess diethylaluminum chloride (DEAC) as cocatalyst. In these two examples the preformed complex $\text{CoCl}_2(\text{dppp})$ is initially dissolved in a small amount of chlorobenzene in order to assure it is completely dissolved before addition of the cocatalyst.

Comparative Example 4

The reaction was carried out in a similar manner and at the same temperature and pressure as in Example 1. The preformed complex $\text{CoCl}_2(\text{dppp})$ (27 mg, 0.05 mmole) was dissolved in 10 mL anhydrous chlorobenzene. To this was added with stirring a 25 wt% solution of triethylaluminum (TEAL) in toluene (0.8 mL, 1.5 mmole). Anhydrous toluene (70 mL) was then added to this solution. Butadiene (21.6 g) was added to the autoclave at 60°C, which was pressured with ethylene, and the reaction was allowed to proceed for 14 minutes. No significant uptake of ethylene was observed during this time. Conversion of butadiene to *cis*-1,4-hexadiene was less than 1%. No other product of the reaction was observed.

Example 5

The reaction was carried out in a similar manner and at the same temperature and pressure as in Example 1. The preformed complex $\text{CoCl}_2(\text{dppp})$ (27 mg, 0.05 mmole) was dissolved in 10 mL anhydrous chlorobenzene. To this was added with stirring a 25 wt% solution of diethylaluminum chloride (DEAC) in toluene (0.8 mL, 1.5 mmole). Anhydrous toluene (70 mL) was then added to this solution. Butadiene (21.1 g) was added to the autoclave at 60°C, which was pressured with ethylene, and the reaction was allowed to proceed for 30 minutes. During the first few minutes the reaction rate was so fast that the temperature could not be controlled. Consumption of ethylene had essentially ceased after 6 minutes. Conversion of butadiene was greater than 99%. Selectivity to *cis*-1,4-hexadiene was 99.9%; the only other product of the reaction was 2,4-hexadiene.

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Example 6

This Example illustrates the use of $\text{Co}(\text{acac})_3$ as the starting cobalt compound component of the complex. Twice as much of this cobalt compound is needed to achieve essentially the same observed first-order rate constant as with the preformed complex.

The reaction was carried out in a similar manner and at the same temperature and pressure as Example 1. Cobalt(III) acetylacetonate (14 mg, 0.04 mmole), and 1,3-bis (diphenylphosphino) propane (19 mg, 0.045 mmole) were dissolved in 80 mL anhydrous toluene. To this was added with stirring a 25 wt% solution of diethylaluminum chloride in toluene (0.6 mL, 1.0 mmole). Butadiene (24.0 g) was added to the autoclave, which was pressured with ethylene, and consumption of ethylene stopped after 27 minutes. Conversion of butadiene was 99%. Selectivity to *cis*-1,4-hexadiene was 99.9%. The only other product of the reaction was 2,4-hexadiene. The observed first-order rate constant for the reaction was 0.195 min^{-1} . The rate constant per mmole Co is 4.9.

Example 7

This Example illustrates the use of $\text{Co}(\text{acac})_2$ as the starting cobalt compound component of the complex. Use of this cobalt compound in the same relative molar amounts results in a rate of reaction about one and a half times that found when the preformed complex $\text{CoCl}_2\text{-dppp}$ is used (as in Example 1).

The reaction was carried out in a similar manner and at the same temperature and pressure as in Example 1. Cobalt(II) acetylacetonate (2.6 mg, 0.01 mmole) and dppp (6.2 mg, 0.015 mmole, dppp = 1,3-bis (diphenylphosphino) propane) were dissolved in 80 mL anhydrous toluene. This was accomplished by using 2 mL of a stock solution made by dissolving $\text{Co}(\text{acac})_2$ (26 mg, 0.10 mmole) and dppp (62 mg, 0.15 mmole) in 20 mL of anhydrous toluene. To the 80 mL catalyst solution was added with stirring a 25 wt% solution of DEAC in toluene (0.6 mL, 1.0 mmole). Butadiene (22.5 g) was added to the autoclave at 60°C , which was pressured with ethylene, and consumption of ethylene stopped after 32 minutes. Conversion of butadiene was 98%. Selectivity to *cis*-1,4-hexadiene was 100%; a trace of 2,4-hexadiene (less than 0.1%) was found. The observed first-order rate constant for the reaction was 0.150 min^{-1} . The rate constant per mmole Co is 15.00.

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Example 8

This Example illustrates the use of the product *cis*-1,4-hexadiene as solvent for the reaction.

The reaction was carried out in a similar manner and at the same temperature and pressure as in Example 1. Cobalt(II) acetylacetonate (10 mg, 0.04 mmole) and dppp (19 mg, 0.045 mmole) were dissolved in 80 mL *cis*-1,4-hexadiene (dried by passing through a column of 3A molecular sieve and alumina under nitrogen). To this was added with stirring a 25 wt% solution of DEAC in toluene (0.6 mL, 1.0 mmole). Butadiene (22.9 g) was added to the autoclave at 60°C, which was pressured with ethylene, and consumption of ethylene stopped after 23 minutes. Conversion of butadiene was 99%. Selectivity to *cis*-1,4-hexadiene (based on product formed in the reaction) was 99.9%; the only other product of the reaction was 2,4-hexadiene. The observed first-order rate constant for the reaction was 0.095 min⁻¹. The rate constant per mmole Co is 2.38.

Example 9

This example illustrates the use of isoprene as the conjugated diene reactant. In the reaction of isoprene with ethylene, the product is a mixture of 4-methyl-1,4-hexadiene and 5-methyl-1,4-hexadiene.

The reaction was carried out in a similar manner and at the same temperature and pressure as in Example 1. Cobalt(II) acetylacetonate (31 mg, 0.12 mmole) and dppp (52 mg, 0.125 mmole) were dissolved in 80 mL anhydrous ortho-xylene. To this was added with stirring at 25 wt% solution of DEAC in toluene (3.3 mL, 6 mmole). Isoprene (23.6 g, dried by passing through a column of 3A molecular sieve and alumina) was added to the autoclave at 60°C, which was pressured with ethylene, and consumption of ethylene stopped after 33 minutes. Conversion of isoprene was 99%. Selectivity to 4-methyl-1,4-hexadiene (88%) and 5-methyl-1,4-hexadiene (12%) was essentially 100%. The observed first-order rate constant for the reaction was 0.218 min⁻¹. The rate constant per mmole Co is 1.82.

Example 10

The Example shows that using a molar ratio of dppp ligand to Co(acac)₃ that is less than two is preferred. In this example, even though the

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amount of the cobalt salt of highest activity was quadrupled and a 2:1 ratio of dppp ligand to $\text{Co}(\text{acac})_2$ was used, a much slower rate of reaction resulted. A molar ratio of dppp ligand of from a little less than unity to less than 2 is preferred, as in Example 7, which uses a dppp:Co ratio of 1.5:1, yet achieves significantly greater activity with one-fourth the amount of cobalt.

The reaction was carried out in a similar manner and at the same temperature and pressure as in Example 7 but with a 2:1 dppp:Co mol ratio. Cobalt(II) acetylacetonate (10 mg, 0.04 mmole) and dppp (33 mg, 0.08 mmole) were dissolved in 80 mL anhydrous toluene. To this was added with stirring a 25 wt% solution of DEAC in toluene (0.6 mL, 1.0 mmole). Butadiene (20.3 g) was added to the autoclave at 60°C, which was pressured with ethylene, and the reaction was allowed to proceed for 60 minutes. At this time conversion of butadiene was only 76%. Selectivity to *cis*-1,4-hexadiene was 99.9%; the only other product of the reaction was 2,4-hexadiene. The observed first-order rate constant for the reaction was 0.040 min^{-1} . The rate constant per mmole Co is 1.00.

Tables 4 and 5.

Table 4 sets forth the data of Examples 6 - 10, in descending order of rate of reaction. The rate of reaction for butadiene to 1,4-hexadiene is at least about 120 (119) mols of 1,4-hexadiene per mol of cobalt catalyst per minute. When less than 2 mols of dppp are used per mol of $\text{Co}(\text{acac})_2$ or $\text{Co}(\text{acac})_3$, rates of reaction are from about 4 (Examples 6,8) to about 11 (Example 7) times higher than with 2 mols of dppp per mol of $\text{Co}(\text{acac})_2$ or $\text{Co}(\text{acac})_3$. In all instances, selectivity to 1,4-hexadiene is essentially 100%.

Table 5 tabulates data from the comparable examples of US-A-3,405,194 (these use a $\text{Co}(\text{acac})_3$ combined with dppp catalyst). In Example 43 of the patent, a DEAC cocatalyst is used at a temperature above 70°C. Rate of reaction was very slow, about one fifth that of the minimum preferred rate for the $\text{Co}(\text{acac})_n$ combined with dppp system at less than 70°C. In patent Example 88, the monoolefin is propylene and the rate is about a third that of Example 43 of the patent.

In the tables, "IP" is isoprene, "C2" is ethylene, "C3" is propylene, and other abbreviations are the same as in Tables 1, 2 and 3.

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Table 4

Co(acac)₃ Combined With dppp Catalyst, DEAC Cocatalyst
Less Than 70° C

Ex.	7	8	6	10	9
Co Cmpd	Co(acac) ₂ + 1.5 dppp	Co(acac) ₂ + dppp	Co(acac) ₃ + dppp	Co(acac) ₂ + 2 dppp	Co(acac) ₂ + dppp
Co (mmol)	0.01	0.04	0.04	0.04	0.12
Organo-Aluminum Cmpd	DEAC	DEAC	DEAC	DEAC	DEAC
Al (mmol)	1.00	1.00	1.00	1.00	6.00
Al/Co	100	25	25	25	50
Solvent	toluene	1,4-HD	toluene	toluene	o-xylene
Di	BD	BD	BD	BD	IP
Di (gms)	22.5	22.9	24.00	20.3	23.6
Di (mmol)	417	424	444	376	350
Di/Co	41,667	10,602	11,111	9,398	2,917
C=	C2	C2	C2	C2	C2
Time (min)	32	23	27	60	33
Temp (°C)	60	60	60	60	60
1,4-HD Yield (g)	33.48	34.39	36.04	23.40	32.99
1,4-HD Yield (mols)	0.41	0.42	0.44	0.29	0.34
Prodt'y (mol/mol)	40,764	10,468	10,970	7,123	2,858
Rate (mol/mol/min)	1,274	455	406	119	87
Observed 1st Order Rate K (min ⁻¹)	0.15	0.095	0.195	0.04	0.218
Rate/mmol	15.00	2.38	4.90	1.00	1.82
Conv (%)	98	99	99	76	99
Select'y (%)	100	99.9	99.9	99.9	100

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Table 5

U.S. Patent 3,405,194: Co(acac)₃ Combined With dppp Catalyst
Organoaluminum Cocatalyst, More Than 70° C

Ex.	43	88
Co Cmpd	Co(acac) ₃ + dppp	Co(acac) ₃ + 2 dppp
Co (mmol)	0.50	0.10
Organo- Aluminum Cmpd	DEAC	TEAL
Al (mmol)	8.0	7.3
Al/Co	16	73
Solvent	toluene	ethylene chloride
Di	BD	BD
BD (gms)	16.2	21.1
BD (mmol)	0.31	0.39
Di/Co	620	3900
C=	C2	C3
Time (min)	25	300
Temp (°C)	80	90-100
1,4-HD Yield (g)	23.70	22.10
1,4-HD Yield (mols)	0.29	0.23
Prodr'y (mol/mol)	577	2298
Rate (mol/mol/min)	23.08	7.66
Conv (%)	97.96	79.33
Select'y (%)	98.34	74.26

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In the following Examples 11 through 14, results of using a catalyst system having a 1,2-bis (diphenylphosphino)ethane (dppe) catalyst ligand at a temperature less than 70°C are shown.

Comparative Examples 11 and 12 show that a substantially slower rate of reaction results when dppe is combined with Co(acac)₂ and DEAC at a temperature of 60°C. This is the case with a molar ratio of dppe:Co of either 1:1 or 2:1.

Comparative Example 11

The reaction was carried out in a similar manner and at the same temperature and pressure as in Example 1. Cobalt(II) acetylacetonate (10 mg, 0.04 mmole) and dppe (16 mg, 0.04 mmole) were dissolved in 80 mL anhydrous toluene. To this was added with stirring a 25 wt% solution of diethylaluminum chloride in toluene (0.6 mL, 1.0 mmole). Butadiene (22.3 g) was added to the autoclave at 60°C, which was pressured with ethylene, and the reaction was allowed to proceed for 60 minutes. Conversion of butadiene was 99%. Selectivity to *cis*-1,4-hexadiene was 99.4%; the only other product of the reaction was 2,4-hexadiene. The observed first order rate constant for the reaction was 0.073 min⁻¹. (Rate constant) / (mmole Co) = 1.83.

Comparative Example 12

The reaction was carried out in a similar manner and at the same temperature and pressure as in Example 1. (Cobalt(II) acetylacetonate (10 mg, 0.04 mmole) and dppe (32 mg, 0.08 mmole) were dissolved in 80 mL anhydrous toluene. To this was added with stirring a 25 wt% solution of diethylaluminum chloride in toluene (0.6 mL, 1.0 mmole). Butadiene (20.6 g) was added to the autoclave at 60°C, which was pressured with ethylene, and the reaction was allowed to proceed for 60 minutes. Conversion of butadiene was 99%. Selectivity to *cis*-1,4-hexadiene was 99.6%; the only other product of the reaction was 2,4-hexadiene. The observed first-order rate constant for the reaction was 0.116 min⁻¹. (Rate constant) / (mmole Co) = 2.90.

Comparative Examples 13 and 14 which follow show that a substantially slower rate of reaction results when dppe is combined with

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Co(acac)₃ and DEAC at a temperature less than 70°C. This is the case with a dppe:Co molar ratio of either 1:1 or 2:1.

Comparative Example 13

The reaction was carried out in a similar manner and at the same temperature and pressure as in Example 1. Cobalt(III) acetylacetonate (14 mg, 0.04 mmole) and dppe (16 mg, 0.04 mmole) were dissolved in 80 mL anhydrous toluene. To this was added with stirring a 25 wt% solution of DEAC in toluene (0.6 mL, 1.0 mmole). Butadiene (20.1 g) was added to the autoclave at 60°C, which was pressured with ethylene, and the reaction was allowed to proceed for 60 minutes. Conversion of butadiene was 99%. Selectivity to *cis*-1,4-hexadiene was 99.6%; the only other product of the reaction was 2,4-hexadiene. The observed first order rate constant for the reaction was 0.114 min⁻¹. (Rate constant) / (mmole Co) = 2.85.

Comparative Example 14

The reaction was carried out in a similar manner and at the same temperature and pressure as in Example 1. Cobalt(III) acetylacetonate (14 mg, 0.04 mmole) and dppe (32 mg, 0.08 mmole) were dissolved in 80 mL anhydrous toluene. To this was added with stirring a 25 wt% solution of DEAC in toluene (0.6 mL, 1.0 mmole). Butadiene (23.6 g) was added to the autoclave at 60°C, which was pressured with ethylene, and the reaction was allowed to proceed for 49 minutes. Conversion of butadiene was 76%. Selectivity to *cis*-1,4-hexadiene was 99.75; the only other product of the reaction was 2,4-hexadiene. The observed first order rate constant for the reaction was 0.020 min⁻¹. (Rate constant) / (mmole Co) = 0.50.

Tables 6 and 7

The data of Examples 11, 12 13 and 14, all obtained at a reaction temperature less than 70°C, are set forth in Table 6, in descending order of rate of reaction. The following Table 7 sets forth tabulations of data calculated from the patent examples of US-A-3,405,194 obtained at a reaction temperature less than 70°C. The quantities of Co(acac)_n employed in Examples 11 through 14 are the same as the quantities employed in Example 6 for Co(acac)₃ combined with dppp (toluene solvent) and Example 8 for Co(acac)₂ combined with dppp (1,4-hexadiene solvent). As seen from

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Table 6, a catalyst system employing the ligand 1,2-bis (diphenylphosphino) ethane, or "dppe" as abbreviated herein, in combination with $\text{Co}(\text{acac})_2$ or $\text{Co}(\text{acac})_3$, even in the presence of a dialkylaluminum halide, and even at the same temperatures as used in Examples 6 and 8, is less than half as catalytically active as Examples 6 and 8. The reaction rates for the comparable patent examples shown in table 7 show an extremely slow reaction rate, more than 30 times slower than the rates of Examples 11 through 14. In Table 7, "EASC" is ethyl aluminum sesquichloride.

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Table 6

Co(acac)₃ Combined With dppe Catalyst
DEAC Cocatalyst, Less Than 70° C

Ex.	11	14	12	13
Co Compd	Co(acac) ₂ + dppe	Co(acac) ₃ + dppe	Co(acac) ₂ + 2 dppe	Co(acac) ₃ + dppe
Co (mmol)	0.01	0.01	0.04	0.04
Organo-Aluminum Compd	DEAC	DEAC	DEAC	DEAC
Al (mmol)	1.00	1.00	1.00	1.00
Al/Co	25	25	25	25
Solvent	toluene	toluene	toluene	toluene
BD (gms)	22.3	23.6	20.6	20.1
BD (mmol)	413	437	381	372
Di/Co	10,324	10,926	9,537	9,306
Time (min)	60	49	60	60
Temp (°C)	60	60	60	60
C=	C2	C2	C2	C2
1,4-HD Yield (g)	33.32	27.15	30.84	30.10
1,4-HD Yield (mols)	0.41	0.33	0.38	0.37
Prod'ty (mol/mol)	10,142	8,265	9,388	9,160
Rate (mol/mol/min)	169	169	156	153
Observed 1st Order Rate K (min ⁻¹)	0.073	0.02	0.116	0.114
Rate/mmol	1.83	0.50	2.90	2.85
Conv (%)	99	76	99	99
Select'y (%)	99.4	99.7	99.6	99.6

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Table 7

U.S. Patent 3,405,194: Co(acac)₃ Combined With dppp Catalyst
Organoaluminum Cocatalyst, Less Than 70° C

Ex.	39	47
Co Cmpd	Co(acac) ₃ + 2.2 dppp	Co(acac) ₃ + 2.2 dppp
Co (mmol)	1.00	1.00
Organo-Aluminum Cmpd	DEAC	EASC
Al (mmol)	15.9	17.6
Al/Co	15.9	17.6
Solvent	ethane	toluene
BD (gms)	32.4	16.7
BD (mmol)	0.60	0.31
Di/Co	600	310
Time (min)	120	1380
Temp (°C)	50	50
C=	C2	C2
1,4-HD Yield (g)	42.50	11.30
1,4-HD Yield (mols)	0.52	0.14
Prodt'y (mol/mol)	517	138
Rate (mol/mol/min)	4.31	0.10
Conv (%)	91.31	47.71
Select'y (%)	94.60	93.39



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Claims:

1. A process for producing substantially pure 1,4 dienes, which comprises reacting a conjugated diolefin with an alpha-olefin in a hydrocarbon solvent reaction medium and in the presence of a catalyst system consisting essentially a cobalt compound, a tertiary diphosphine and an organo aluminum compound, characterized in that the catalyst system comprises:
 1. $\text{Co}(\text{acac})_n$ combined with dppp or a preformed complex of $\text{CoCl}_2(\text{dppp})$, where acac. is acetylacetonate, dppp is 1,3-bis (diphenylphosphino) propane, and n is the valence of cobalt; and
 2. a dialkylaluminum halide,wherein the reaction is performed at a temperature of less than 70°C to convert the conjugated diolefin to the 1,4-diene with substantially 100% selectivity.
2. The process of Claim 1, wherein the temperature is at least 50°C and less than 70°C , preferably about 60°C .
3. The process of Claim 1 or 2, wherein the halide is chloride.
4. The process of any preceding claim, when performed at an alpha-olefin partial pressure of from 50 to 10,000 kPa (0.5 to 100 atmospheres).
5. The process of any preceding claim, wherein the hydrocarbon solvent is non-halogenated.
6. The process of Claim 5, wherein the solvent is toluene, xylene, a 1,4-diene which is the product of the reaction, or a mixture of any two or more thereof.
7. The process of any preceding claim, wherein the conjugated diolefin is butadiene or isoprene, the alpha-olefin is ethylene or propylene and



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the 1,4-diene is 1,4-hexadiene, 2-methyl-1,4-hexadiene, or a mixture of 4-methyl-1,4-hexadiene and 5-methyl-1,4-hexadiene.

8. The process of any preceding claim, wherein the selectivity is greater than 99.5%.
9. The process of any preceding claim, in which the rate of reaction is at least 100 mols of 1,4-diene per mol of cobalt per minute.
10. The process of Claim 9, wherein conjugated diolefin is butadiene and the alpha-olefin is ethylene, and wherein the cobalt catalyst system and the reaction conditions are effective to produce a rate of reaction of at least 500 mols of 1,4-hexadiene produced per mol of cobalt per minute.
11. The process of any of Claims 1 to 8, wherein the conjugated diolefin is butadiene and the alpha-olefin is propylene and wherein the cobalt catalyst system and the reaction conditions are effective to produce a rate of reaction of at least 30 mols of 2-methyl-1,4 hexadiene per mol of cobalt per minute.
12. The process of any of Claims 1 to 8, wherein the conjugated diolefin is isoprene and the alpha-olefin is ethylene and wherein the cobalt catalyst system and the reaction conditions are effective to produce a rate of reaction of at least 30 mols of a mixture of 4-methyl-1,4-hexadiene and 5-methyl-1,4-hexadiene per mol of cobalt per minute.
13. The process of any preceding claim, wherein the dialkylaluminum halide is diethylaluminum chloride.
14. The process of any preceding claim, when performed at a catalyst productivity of at least 1000 mols of 1,4-diene per mol of cobalt.
15. The process of any preceding claim, wherein the cobalt catalyst system comprises $\text{Co}(\text{acac})_n$ and wherein from 0.9 to less than 2 mols of dppp are combined with the $\text{Co}(\text{acac})_n$.



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16. The process of any preceding claim, wherein the cobalt catalyst system comprises $\text{Co}(\text{acac})_2$ combined with dppp and wherein the first order reaction rate constant per mmole of cobalt is at least 15.
17. The process of any of Claims 1 to 14, wherein the catalyst system comprises $\text{CoCl}_2(\text{dppp})$ and further includes triethylaluminum with no more than two molar equivalents of triethylaluminum per mol $\text{CoCl}_2(\text{dppp})$.
18. The process of any preceding claim, wherein the catalyst system has an Al/Co molar ratio of at least 5:1.
19. The process in accordance with any one or more of the preceding claims, comprising the further step of using the produced 1,4-dienes in a polymerization process.
20. Polyolefin polymers manufactured with 1,4-dienes produced according to any one or more of the preceding claims.

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PROCESS FOR PRODUCING 1,4-DIENES

Abstract

Pure 1,4-dienes are produced at high rates of reaction by reacting a conjugated diene and an alpha monoolefin at a temperature below 70°C in the presence of a catalyst comprising a 1,3-bis-(diphenylphosphino) propane ligand of Co(II) (acetylacetonate)₂ or Co(II)(acetylacetonate)₃ or CoCl₂ in combination with a dialkylaluminum halide such as diethylaluminum chloride.