

π -Allylmetal Derivatives in Organic Synthesis

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I. Introduction

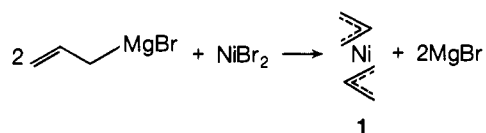
Few subjects have made greater progress within the space of a decade than organic synthesis involving organometallic reagents. Although organometallic chemistry is a monumental field, one part of it, that involving π -allylmetal intermediates, is proving of major interest to organic chemists. New synthetic methods are being reported, providing linkage of molecules into larger units in single-stage reaction of considerable economic importance. Of a number of groups of workers who have made great contributions to this field, those of Corey, Wilke, and Chiusoli must be mentioned. This review concentrates on organic synthesis involving π -allyl intermediates with emphasis on the nature of reactions and types of products which can be obtained. The mechanism of the reactions will be indicated wherever possible, but the bonding in the metal intermediates will not be examined in detail. In some cases, reactions will be included for which, although probably involving π -allyl intermediates, mechanisms have not been unambiguously confirmed.

Attempts have been made to avoid duplication of previous reviews¹⁻⁹ except where necessary to give per-

spective in the present manuscript. No attempt has been made to cover all conceivable reactions which pass through π -allylmetal derivatives. Polymerization reactions and olefin isomerizations have been excluded since both these fields would benefit only from a more detailed and extensive discussion than could be devoted in this review. No attempt has been made to comprehensively cover the extensive patent literature of many reactions which frequently involve changes in reaction conditions and ligands.

II. Bis- π -allylmetal Derivatives

A wide range of pure allylmetal compounds have been prepared by the general method first used for bis- π -allylnickel (1).¹⁰ Although the nickel derivative is extremely



volatile and can be easily obtained from the reaction solution by distillation or sublimation, allyl derivatives are normally obtained by extraction with hydrocarbon solvent followed by crystallization at low temperatures. In this way allyl derivatives of Ti, Zr, Th, V, Nb, Ta, Cr, Mo, W, Fe, Co, Ni, Pd, Pt, and Zn have been prepared; strict absence of air and moisture is required.² Ignition is found in air and propylene is readily formed in the presence of acids, water, and alcohol except with allyl compounds of nickel, palladium, and platinum which are stable to both water and alcohols in ether solution. It was found that within a given group of the periodic system, the stabilities of the allylmetal compounds increased with atomic number of metal: Ni < Pd < Pt, Cr < Mo < W, and Ti \ll Zr < Th.

The symmetrical structure of a π -allyl system is characterized by the ¹H nmr spectrum consisting of three sig-

(1) P. Heimbach, P. W. Jolly, and G. Wilke, *Advan. Organometal. Chem.*, **8**, 29 (1970).

(2) G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kroner, W. Oberkirch, K. Tanaka, E. Steinrucke, D. Walter, and H. Zimmerman, *Angew. Chem., Int. Ed. Engl.*, **5**, 151 (1966).

(3) G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **2**, 105 (1963).

(4) C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Lagos, London, 1967.

(5) G. N. Schrauzer, Ed., "Transition Metals in Homogeneous Catalysis," Marcel Dekker, New York, N. Y., 1971.

(6) J. M. Davidson, *MTP Int. Rev. Sci., Inorg. Chem., Ser. One*, **6** 347 (1972).

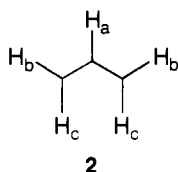
(7) G. Henrici-Olivé and S. Olivé, *Angew. Chem., Int. Ed. Engl.*, **10**, 105 (1971).

(8) B. Bogdanovic, B. Henc, H. G. Karmann, H. G. Nüssel, D. Walter, and G. Wilke, *Ind. Eng. Chem.*, **62**, 34 (1970).

(9) H. Bonnemant, C. Gard, W. Kopp, and G. Wilke, XXIIIrd International Congress of Pure and Applied Chemistry, Boston, 1971, Vol. 6.

(10) G. Wilke and B. Bogdanovic, *Angew. Chem.*, **73**, 756 (1961).

nals with intensity ratio 1:2:2. The protons of the CH₂ group appear as pairs, with the H_c protons being more shielded under the influence of the transition metal; both these pairs of protons appear as doublets and H_a is at least a septet (2).¹¹ This spectrum differs from that ex-



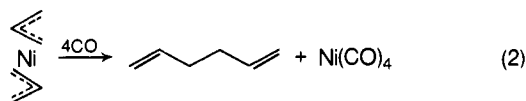
hibited by dynamic allylmetal derivatives such as allyl-magnesium halides in which the methylene protons are indistinguishable owing to the rapid equilibrium (eq 1).¹² A



third type of allylmetal compound can also be obtained which are static σ -allyl species. For σ -allylmanganese pentacarbonyl the nmr pattern is similar to allyl bromide and also displays an absorption at 1620 cm⁻¹ in the infrared spectrum due to an unperturbed vinyl group.¹³

X-Ray analysis has been reported of bis- π -methallylnickel which is more stable than bis- π -allylnickel.¹⁴ The sandwich structure is confirmed in which the three carbon atoms in each methallyl groups are in the same plane and situated about the same distance from the central nickel atom; the methyl groups are trans to each other. For the π -allylmetal derivatives a p orbital from each of the carbon atoms forms a delocalized molecular orbital which interacts with the metal via π -bonding. While the oxidation state of the metal can be considered, it need not be the source of controversy. The π -allylic system can be considered to supply four, three, or two electrons for coordination to the metal depending on whether this system is regarded as an anion, a radical, or a cation. This can be compensated by a formal change of valency of the metal atom. It is valuable to keep an account of the number of electrons donated by ligands since inert gas rule considerations indicate the maximum number of valence electrons which can be accommodated by a metal. For zerovalent nickel complexes the maximum is 8 electrons since, together with 10 electrons from the metal, this makes a total of 18 which is the maximum allowed. For 1, counting the allyl ligands as supplying 3 electrons each, a total of 16 is found. This is in line with the generalization that complexes with a pseudo-square-planar geometry display a most favorable electronic configuration involving 16 electrons, in agreement with ligand field theory.

Bis- π -allylnickel takes up 4 equiv of carbon monoxide to form 1,5-hexadiene and nickel tetracarbonyl (eq 2),



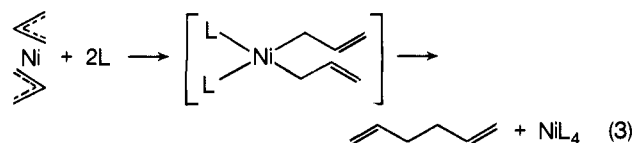
The mechanism of this coupling reaction is unclear, but intervention of a σ -bonded allyl derivative is strongly suggested (eq 3). Evidence for this is found in that in the

(11) R. F. Heck, and D. S. Breslow, *J. Amer. Chem. Soc.*, **82**, 750 (1960); G. E. Coates, M. L. H. Green, P. Powell, and K. Wade, "Principles of Organometallic Chemistry," Methuen, London, 1968.

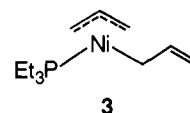
(12) J. E. Nordlander and J. D. Roberts, *J. Amer. Chem. Soc.*, **81**, 1769 (1959).

(13) H. D. Kaesz, R. B. King, and F. G. A. Stone, *Z. Naturforsch. B*, **15**, 682 (1960).

(14) H. Dietrich and R. Uttech, *Naturwissenschaften*, **50**, 613 (1963); *Z. Kristallogr.*, **122**, 60 (1965).

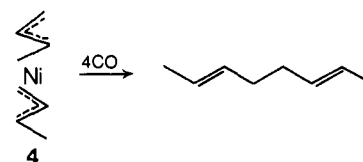


presence of good electron donors such as triphenylphosphine, or in good coordinating solvents such as dimethylformamide, π -allylnickel complexes have been shown by nmr spectroscopy to be converted into σ -bonded allyl systems (3).¹⁵ Carbonylation of other metal allyls has



also been examined; at -35°, tris- π -allylcobalt yields 1,5-hexadiene and π -allylcobalt tricarbonyl while tris- π -allylchromium requires carbon monoxide under pressure to proceed to hexadiene and chromium hexacarbonyl. Similarly, 2,5-dimethyl-1,5-hexadiene is obtained from carbon monoxide and bis- π -methallylnickel together with a small amount of 2,6-dimethyl-2,5-heptadien-4-one from insertion of carbon monoxide.²

With reaction of bis- π -crotylnickel, a number of stereochemical possibilities must be considered. In fact, at -40° and normal pressure, *trans,trans*-2,6-octadiene (98%) is formed together with 3-methyl-1,5-heptadiene (2%). It appears that the allyl derivative is almost totally in the *syn, syn* form (4) (the *syn* configuration referring to the



relationship of the central hydrogen atom and the methyl group). This highly specific reaction course is lost at room temperature when 2,6-octadiene (58%), 3-methyl-1,5-heptadiene (38%), and 3,4-dimethyl-1,5-hexadiene (4%) are formed;² coupling at the unsubstituted ends still appears to have the lowest activation energy.

A number of cyclic bis- π -allylnickel compounds have been prepared with bis- π -cyclooctenylnickel exhibiting greater stability than bis- π -cycloheptenylnickel and bis- π -cyclohexenylnickel. With the first of these, carbon monoxide in dimethylformamide yields a 1:1 mixture of di(2-cyclooctenyl) ketone and dicyclooctenyl.¹

Insertion of carbon monoxide in the coupling of π -allyl derivatives is discussed in more detail later, but the factors which determine either direct coupling of the allyl groups or insertion of carbon monoxide are not clear at this stage.

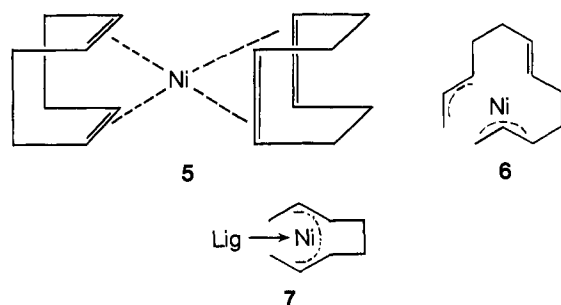
Wilke, *et al.*,¹⁶ have demonstrated that zerovalent nickel complexes can be prepared when a nickel salt (e.g., acetylacetonate) is reduced with an organoaluminum compound (e.g., triisobutylaluminum) in the presence of electron donors such as olefins. The real state of the reduced nickel species is not known with certainty, but in the absence of coordinating groups decomposition to nickel metal occurs; because of its ability to associate with weak ligands, it has been called "naked nickel." Reactions of 1,3-butadiene and other dienes with zerovalent nickel species have been studied and a number of elegant methods for formation of both cyclic and acyclic

(15) D. Walter and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **5**, 897 (1966).

(16) G. Wilke, *Angew. Chem.*, **72**, 581 (1960).

derivatives described. These processes exemplify the potential of syntheses involving organometallic complexes in which the metal activates and orientates a number of molecules for reaction. The blocking of coordination sites by added ligands which can control reaction pathways has also been demonstrated. Striking control of reaction pathways by ligands which operate by blocking coordination sites is also found.

Bis(1,5-cyclooctadiene)nickel (5) is a valuable zero-valent complex since this yellow crystalline material can be stored for fairly long periods in a refrigerator if kept under nitrogen. Frequent use of alkylaluminums can be avoided by preparation of a large batch of this material by reduction of a nickel salt in the presence of cyclooctadiene. On reaction of 5 with butadiene at temperatures below 0°, the complex 6 is formed which can be crystallized from solution at low temperatures.¹⁷ Similarly, in the presence of other ligands such as phosphines and phosphites, the cyclodimerization of butadiene has been suggested to involve the intermediate 7.¹⁸ Isolation of 7 has



not proved possible except when the ligand is tris(2-biphenyl) phosphite when a crystalline species has been isolated at low temperature.¹⁹ The outer shell of the nickel atom contains 18 electrons in 6 and 16 electrons in 7. A number of reactions will be discussed in the following sections which have been considered to involve these complexes and similar species formed with other metals, although in most cases the intermediates have not been isolated.

III. Oligomerization of 1,3-Dienes

A. Cyclodimerization

Following a brief report by Foster²⁰ on the dimerization of butadiene to cyclooctadiene in the presence of nickel catalysts, Reed²¹ obtained 1,5-cyclooctadiene in 30–40% yield when nickel carbonyl phosphine and phosphite complexes were used. Muller, *et al.*,²² subsequently found a procedure for removing the carbon monoxide liberated from the catalyst which was responsible for the low rate of reaction under Reed's condition.

In the presence of electron donors such as phosphines and phosphites, nickel(0) catalysts have been shown to be effective in the cyclodimerization of butadiene.^{1,3} Vinylcyclohexene and cyclooctadiene are formed predominantly but, depending upon reaction conditions, 1,2-divinylcyclobutane can also be formed.²³ The amount of

(17) B. Bogdanovic, P. Heimbach, M. Kroner, G. Wilke, E. G. Hoffman, and J. Brandt, *Justus Liebigs Ann. Chem.*, **727**, 143 (1969).

(18) W. Brenner, P. Heimbach, H. Hey, E. Muller, and G. Wilke, *Justus Liebigs Ann. Chem.*, **727**, 161 (1969).

(19) P. Heimbach and G. Wilke, *Justus Liebigs Ann. Chem.*, **727**, 183 (1969).

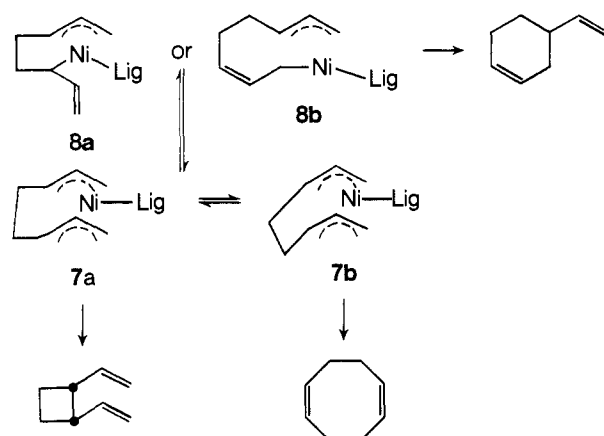
(20) R. E. Foster, Du Pont, U. S. Patent 2,504,016 (1947/50).

(21) H. W. B. Reed, *J. Chem. Soc.*, 1931 (1954).

(22) H. Muller, D. Wittenberg, H. Seibt, and E. Scharf, *Angew. Chem., Int. Ed. Engl.*, **4**, 327 (1965).

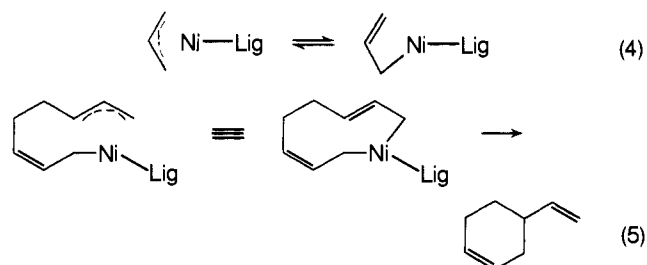
(23) See ref 4, pp 38–42, which lists a large number of nickel complex systems.

SCHEME I



this product has been shown to be dependent upon the extent of conversion of butadiene; in the presence of tris(2-biphenyl) phosphite, a 40% yield of divinylcyclobutane is obtained at 85% conversion of butadiene.^{1,18} Cyclooctadiene can be formed either directly from butadiene or by Cope rearrangement from divinylcyclobutane.¹

The ratio of cyclooctadiene to vinylcyclohexene is dependent upon the ligand attached to the nickel atom, being greater with phosphites than with phosphines.^{1,18} Scheme I has been postulated to account for product formation with 7 existing in two configurations. Cyclooctadiene and divinylcyclobutane can be formed by carbon-carbon coupling *via* electron shifts as indicated (eq 3). Since formation of vinylcyclohexene is very dependent upon the donor-acceptor character of the ligand, reaction through the σ -allyl form 8 was suggested. Because of their good electron donor character, phosphines favor the σ -allyl form, whereas phosphites, which are good electron acceptors, favor the π -allyl structure (eq 4 and 5). It



is, therefore, possible to exert some control over the reaction course by choice of ligand. In the presence of tris(cyclohexyl)phosphine, the reaction mixture contains 40% vinylcyclohexene, whereas 97% 1,5-cyclooctadiene is produced on addition of tris(2-biphenyl) phosphite. Similarly, formation of vinylcyclohexene is favored if the reaction solution is treated with excess carbon monoxide at low temperature; in this case the carbon monoxide probably converts one of the π -allyl groups into a σ -allyl derivative (8b) followed by carbon-carbon bond formation.

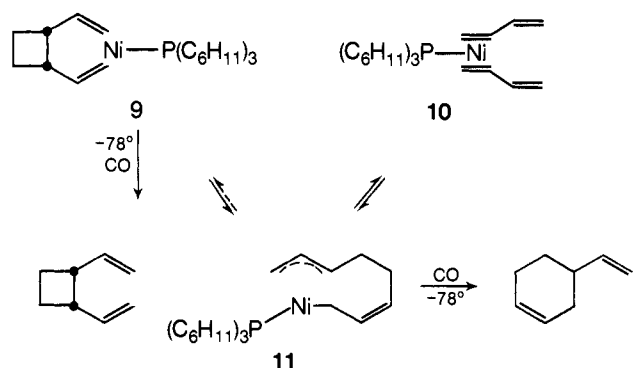
Following the preparation of 9 and 10 the mechanism of cyclodimerization of butadiene has been studied in more detail and shown to be a multistep process.^{25,26} At -78° , reaction of 9 with carbon monoxide takes place to produce divinylcyclobutane, but if this same reaction is carried out on a solution which has been left at room

(24) See ref 1, p 54.

(25) P. W. Jolly, I. Tkatchenko, and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **10**, 329 (1971).

(26) P. W. Jolly, I. Tkatchenko, and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **10**, 328 (1971).

temperature for 1 hr, vinylcyclohexene is obtained. It was concluded that **9** and **10** rearrange to a common intermediate **11** in solution with the ^1H nmr spectrum conforming



to a π -allyl- σ -allyl structure; under the influence of carbon monoxide at -78° , **11** yields vinylcyclohexene. It was reported that, at room temperature in the solid state, **9** rearranged to **10**.²⁵ Other workers²⁷ have also studied the ^1H nmr spectrum of **11** and report the π -allyl- σ -allyl structure in both solution and solid. Carbon-carbon bond formation in these processes has been discussed in terms of a hetero-ring-closure reaction in which each step is symmetry controlled. Each of the individual steps was viewed as an intramolecular redox process involving nickel(0) and nickel(II).²⁸

Cyclodimerization of butadiene to cyclooctadiene and vinylcyclohexene has been accomplished with other metal complexes such as zerovalent iron complexes, diethylbis(dipyridyl)iron, bis(dipyridyl)iron, and tris(dipyridyl)iron in 90, 21, and 63% conversions, respectively.^{29,30} A 3:1 ratio of cyclooctadiene:vinylcyclohexene was obtained, and the dimerization was inhibited by addition of electron donor ligands. No conversion was found on addition of triphenylphosphine which is consistent with coordination of the ligand to the iron complex, thus preventing coordination of butadiene. Using butadiene-1,1,4,4- d_4 , cyclooctadiene-3,3,4,4,7,7,8,8- d_8 and 4-vinyl- β,β - d_2 -cyclohexene-3,3,5,5,6,6- d_6 were formed. On the basis of these studies a mechanism similar to that proposed for the nickel system was suggested. Isoprene was also dimerized to a mixture of dimethylcyclooctadiene, isopropenylmethylcyclohexene, and dimethylvinylcyclohexene although no percentage conversion was reported.³⁰ Other systems for cyclodimerization include an iron-Schiff's base complex,³¹ dicarbonyldinitrosyliron and dicarbonyldinitrosyl- π -allyliron,³² and a mixture of cobalt trisacetylacetonate, triethylaluminum, methyl acrylate, and acetonitrile.³³

Butadiene is dimerized to a mixture of vinylcyclohexene and 1,5-cyclooctadiene by a catalyst generated by controlled potential electrolysis of solutions of nickel compounds such as nickel chloride, dimethoxyethane, triphenylphosphine, tetrabutylammonium perchlorate, and dimethylformamide. An almost equal amount of these two products is formed in about 60% yield, together with cyclododecatriene (5%) and polymeric material (11%).

(27) J. M. Brown, B. T. Golding, and M. J. Smith, *Chem. Commun.*, 1240 (1971).

(28) H. Buchholz, P. Heimbach, H. J. Hey, H. Selbeck, and W. Weise, *Coord. Chem. Rev.*, **8**, 129 (1972).

(29) A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito, Y. Uchida, and A. Misono, *J. Amer. Chem. Soc.*, **87**, 4652 (1965).

(30) A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito, Y. Uchida, and A. Misono, *J. Amer. Chem. Soc.*, **90**, 1878 (1968).

(31) C.-Y. Wu and H. E. Swift, *J. Catal.*, **24**, 510 (1972).

(32) J. P. Candlin and W. H. Janes, *J. Chem. Soc. C*, 1856 (1968).

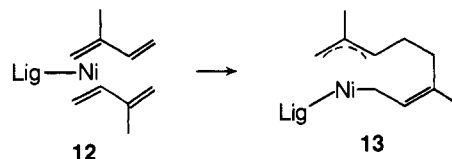
(33) T. G. Hyde, British Patent 1,149,927; *Chem. Abstr.*, **71**, 70071 (1969).

Only low conversions were found in the absence of triphenylphosphine, and acetonitrile or dimethylformamide as the most suitable solvent. The effects of other added ligands and electrolytes were also examined. Changing from triphenylphosphine to tributylphosphine enhances the selectivity to cyclooctadiene formation; the activity of the catalyst is affected by reduction potential.³⁴ In the presence of triphenylphosphine, cyclopentadienylnickel complexes have been employed for butadiene cyclodimerization.³⁵

Chepaikin and Khidekel have found butadiene is converted to a mixture of divinylcyclobutanes by palladium salts containing noncomplexing anions such as perchlorate and boron tetrafluoride. Palladium salts absorbed on a cationic exchange resin gave the same products.³⁶ The observations were discussed in terms of a matrix system containing allyl groups and charged species. Phosphines, phosphites, and amines directed the reaction toward formation of 1,3,7-octatriene which was considered to be due to prevention of matrix formation.

Cyclodimerization of other methyl-substituted 1,3-dienes has been studied using the nickel(0)-ligand catalyst system. In the series piperylene, isoprene, and 2,3-dimethylbutadiene, increasing methyl substitution is accompanied by a decrease in amount of cyclooctadiene product with an increasing amount of the C_6 cycloproduct.¹ It was considered that the intermediate complexes were stabilized by additional methyl substitution and also that an increased electron density at the nickel atom facilitated isomerization of the π -allyl to the σ -allyl group (Scheme I).

In the presence of tris(2-biphenyl) phosphite and zerovalent nickel, which converts 1,3-butadiene to a 97:3 ratio of 1,5-cyclooctadiene and 4-vinylcyclohexene, the amount of C_6 cycloproduct in the reaction of piperylene, isoprene, and 2,3-dimethylbutadiene increased to 5.3, 34.8, and 86.3%, respectively.¹ From *cis*-piperylene all four possible isomers of dimethyloctadiene were isolated, but *trans*-piperylene gave predominantly *trans*-3,7-dimethyl-1,5-cyclooctadiene and *trans*-3,4-dimethyl-1,5-cyclooctadiene. Heimbach and Hey³⁷ have shown that formation of cyclobutane derivatives from piperylene, in the presence of nickel-ligand catalysts, is not in agreement with a suprafacial concerted process.³⁸ Further evidence that catalytic dimerization of 1,3-dienes is a multistep process has been obtained from reaction of isoprene with cyclododecatriene-nickel trialkylphosphine (alkyl = $c\text{-}C_6H_{11}$).³⁹ The structure of the bis-isoprene complex formed was determined by X-ray diffraction and nmr spectroscopy as **13**. It was suggested that initial unsymmetrical coupling of isoprene to the nickel atom must have occurred (**12**). Treatment of **13** with carbon monoxide at -30° gave *dl*-limonene in over 90% yield, and reaction with a triphenylphosphine melt gave isoprene.



(34) W. B. Hughes, *J. Org. Chem.*, **36**, 4073 (1971).

(35) Y. Tajima and E. Kunioka, *J. Polym. Sci., Part B*, **5**, 221 (1967).

(36) E. G. Chepaikin and M. L. Khidekel, *Bull. Acad. Sci. USSR*, **20**, 1052 (1971).

(37) P. Heimbach and H. Hey, *Angew. Chem., Int. Ed. Engl.*, **9**, 528 (1970).

(38) F. D. Mango, *Tetrahedron Lett.*, 4813 (1969).

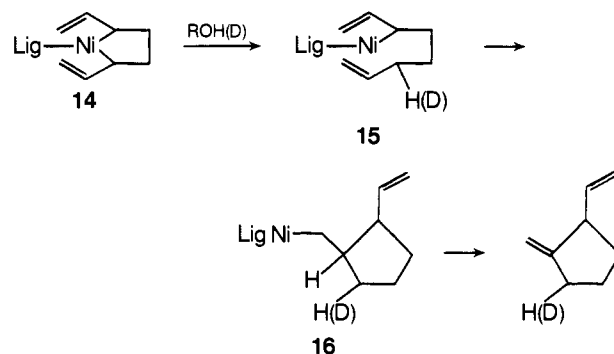
(39) B. Barnett, B. Busseimeier, P. Heimbach, P. W. Jolly, C. Kruger, I. Tkatchenko, and G. Wilke, *Tetrahedron Lett.*, 1457 (1972).

In the presence of a catalyst system, iron trisacetylacetonate, dipyriddy, and a Grignard reagent in tetrahydrofuran, a mixture of 1,5- and 1,6-dimethylcycloocta-1,5-dienes is favored in the cyclodimerization of isoprene, although the yields are only ca. 30%. A linear dimer, 2,6-dimethylocta-1,3,6-triene, is formed when the catalyst is changed to a mixture of bis(triphenylphosphine)-nickel dihalide and a Grignard reagent although the yield again is of the order of 30%. Electron donors also change the nature of the products in the presence of Grignard reagents and derivatives of iron, cobalt, chromium, and magnesium, but the yields of most of these reactions are extremely low.⁴⁰ Much higher conversions of isoprene into mixtures of dimethylcyclooctadienes have been found in the presence of iron or cobalt(III) acetylacetonates, electron donors, and triethylaluminum.⁴¹

Codimerization of butadiene with other 1,3-dienes in the presence of nickel-ligand catalysts has been shown to be an effective way of preparing cyclooctadiene derivatives. Preparation of the codimers is favored by low butadiene concentration; in almost all cases the best yields were obtained when nickel-tri(2-biphenyl) phosphite catalyst was used. Yields of from 86 to 92% of the substituted cyclooctadiene were obtained by codimerization of 1,3-butadiene with piperylene, isoprene, and 2,3-dimethylbutadiene.¹ A 45% yield of a cyclooctadiene derivative and substituted vinylcyclohexene (5%) has also been obtained by codimerization of 1,3-butadiene and ethyl penta-2,4-dienoate in the presence of zerovalent nickel and triphenylphosphine.¹ Cyclodimerization of butadiene and isoprene⁴² and 2,3-dimethylbutadiene⁴³ by catalysis with nickel acetylacetonate, lithium borohydride, and triphenyl phosphite in tetrahydrofuran has been reported.

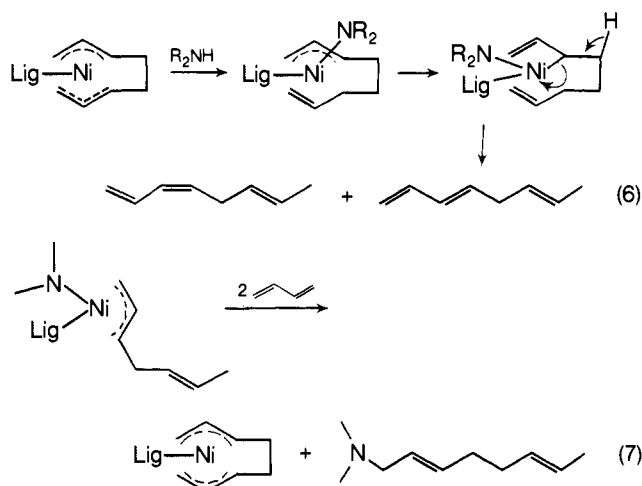
Changes in the nature of the cyclo product with different ligands is further illustrated by selective formation of 1-vinyl-2-methylenecyclopentane from butadiene in the presence of some nickel catalysts and moderate amounts of alcohols.⁴⁴ On heating bis(tri-*n*-butylphosphine)nickel dichloride, *o*-lithio-*N,N*-dimethylbenzylamine, butadiene, and methanol in benzene for 50 hr at 60°, 1-vinyl-2-methylenecyclopentane is formed in yields of between 50 and 90% together with minor amounts of 4-vinylcyclohexene and 1,5-cyclooctadiene. Butyllithium is also effective as the organolithium compound, but too large a quantity of alcohol cannot be used or high-boiling products (which are probably ether derivatives) are formed. Alternatively, in the presence of only traces of alcohol, cyclooctadiene and vinylcyclohexene are the only products. The reaction was suggested to proceed through intermediates **14**–**16** with formation of the σ complex (**14**) due to the presence of strong donor molecules such as tributylphosphine. Following alcoholysis, insertion of the double bond into the carbon-nickel bond could yield the cyclopentane derivative (**16**). Using deuterated solvent (CH₃OD), deuterium labeling was demonstrated at the 3 position with 50% isotopic purity. Although the detailed mechanism was not elucidated, the ability of ligands to direct the course of nickel-catalyst reactions was emphasized. Formation of small amounts of 1-vinyl-3-

methylenecyclopentane from nickel-catalyzed dimerization of butadiene has also been reported.²²



B. Linear Dimerization

In the presence of alcohols, 1,3-dienes are oligomerized by nickel-ligand catalysts into linear dimers with the product dependent upon the nature of the ligand; 1,3,6-octatriene and 2,4,6-octatriene are formed in the presence of triethyl phosphite, tributylphosphine, and phosphoric acid trimorpholide, respectively.²² A similar effect is also observed in the presence of amines, but the product, consisting of *trans,trans*, and *cis,trans* 1,3,6-octatriene in a yield of 90% at 50% conversion, is independent of the nature of the ligand.⁴⁵ The probable mechanism, again involving the bis- π -allylnickel intermediate, is indicated (eq 6) and supported by the formation of octadienylated amine (eq 7) under certain conditions (see later).



Dimerization of butadiene has also been accomplished using a variety of other metal systems; the nature of the dimer depends to some extent upon the metal (Table I). With cobalt catalysts the major product is *trans*-3-methyl-1,4,6-heptatriene. A complex (**17**) has been isolated during work on the polymerization of butadiene with cobal-

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(45) P. Heimbach, *Angew. Chem., Int. Ed. Engl.*, **7**, 882 (1968).

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TABLE I. Linear Dimerization of 1,3-Dienes

Olefin	Catalyst	Products	Yield	Ref	
1,3-Butadiene	Co(allyl) ₃	<i>trans</i> -3-Methyl-1,4,6-heptatriene	93	46	
	Co ₂ (CO) ₈ + Et ₃ Al	<i>trans</i> -3-Methyl-1,4,6-heptatriene	90	47	
	CoCl ₂ + NaBH ₄	3-Methyl-1,4,6-heptatriene		48	
	CoCl ₂ + Et ₃ Al	<i>trans</i> -3-Methyl-1,4,6-heptatriene (45.3%) + 1,3,6-octatriene (8.9%) + trimers (14.7%) + higher oligomers and polymers (30.5%)	20 ^a	49, 50	
	Co(acac) ₃ + Et ₃ Al	3-Methyl-1,4,6-heptatriene		51, 52	
	Co(acac) ₃ + BuLi	3-Methyl-1,4,6-heptatriene (65%) + trimers (35%)	77	53	
	Fe(acac) ₃ + Et ₃ Al	3-Methyl-1,4,6-heptatriene + other dimers (6%), 1,3,6,10-dodecatetraene (24%), branched trimer (7%), polymer (62%)	82 ^a	54	
	Fe(acac) ₃ + Et ₃ Al + PPh ₃	3-Methyl-1,4,6-heptatriene (37%), 1,3,6-octatriene (7%) + polymer	60 ^a	55	
	FeCl ₃ + Ph ₃ P + Et ₃ Al	1, <i>cis</i> -3,6-Octatriene (65%), 3-methyl-1,4,6-heptatriene (30%) + trimers (5%)	85	56	
	RhCl ₃	Isomers of 2,4,6-octatriene + vinylcyclohexene (70%) + higher oligomers (30%)	54 ^a	57	
	NiCl ₂ -electrolysis-pyridine-MeOH	Octadienes (60%) + dodecatrienes (27%) + hexadecatetraenes (13%)	25	58	
	NiCl ₂ -electrolysis-PPh ₃ -MeOH	1,3,7-Octatriene + methoxyoctadienes	46	58	
	NiCl ₂ -electron donors-LiAlH ₄ or NaBH ₄	Dihydrogenated dimers, trimers, tetramers	60 ^a	59	
	(Ph ₃ P) ₂ Pd(maleic anhydride) ₂	1,3,7-Octatriene	85	60	
	π -Allylpalladium chloride-phenol (NaOPh and Ph ₃ P added before distillation)	1,3,7-Octatriene	85	61	
	Isoprene	(Ph ₃ P) ₂ Pd(maleic anhydride) ₂	2,7-Dimethyl-1,3,7-octatriene		62
		(Ph ₃ P)NiCl ₂ or (Ph ₃ P)NiBr ₂ -EtMgCl	2,6-Dimethyl-1,3,6-octatriene	38	40
Ziegler-type TiCl ₄ -R ₃ Al		2,6-Dimethyl-1,3,6-octatriene + cyclodimers (39%), tetramers (9%), polymer (9%)	70-80	63, 64	
Zr(allyl) ₄ ethylaluminum sesquichloride		2,6-Dimethyl-1, <i>trans</i> -3,6-octatriene (selectivity 78%)	66	65	
Zr(IV) butoxide-Et ₂ AlCl-PPh ₃ (or tetrahydrofuran)		2,6-Dimethyl-1, <i>trans</i> -3,6-octatriene	50	66	
VO(OEt) ₃ -Et ₂ AlCl (1:12 mole ratio)		2,6-Dimethyl-1, <i>trans</i> -3,6-octatriene (50%) + trimers and higher oligomers (15%)	90	67	
Hf(IV) butoxide-Et ₂ AlCl		2,6-Dimethyl-1, <i>trans</i> -3,6-octatriene	20	68	

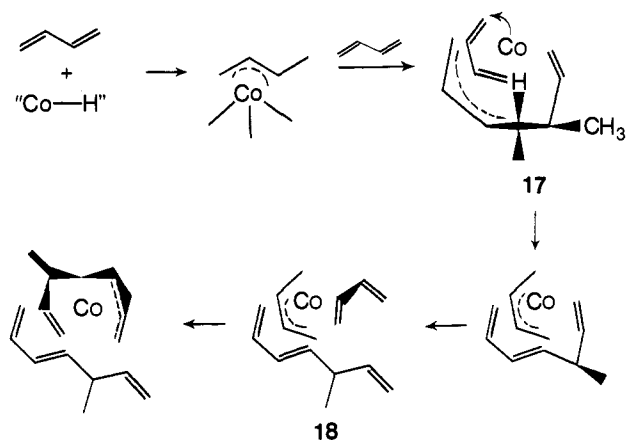
^a Conversions.

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 (53) E. A. Zuech, U. S. Patent 3,393,245; *Chem. Abstr.*, **69**, 51519 (1968).
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 (61) E. J. Smutny, *J. Amer. Chem. Soc.*, **89**, 6793 (1967).
 (62) S. Takahashi, T. Shibano, and N. Hagihara, *Shokubai*, **11**, 4 (1969).
 (63) G. Wilke, *J. Polym. Sci.*, **38**, 45 (1959).
 (64) L. I. Zakharkin, *Dokl. Akad. Nauk SSSR*, **131**, 1069 (1960); *Izv. Akad. Nauk SSSR*, 168 (1964); H. Takahashi and M. Yamaguchi, *Osaka Kogyo Gijutsu Shikensho Kiho*, **15**, 271 (1964); L. I. Zakharkin and V. M. Akhmedev, *Azerb. Khim. Zh.*, **58** (1969).

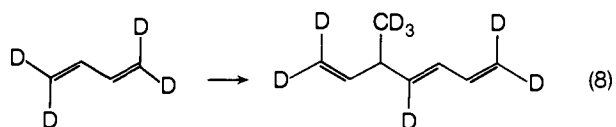
tous chloride and sodium borohydride.^{48,69} This probably arises by initial formation of a π -allylcobalt derivative from butadiene and a cobalt-hydrido species produced on reduction of the cobalt salt. Reaction of this π -allyl derivative with another molecule of butadiene yields **17**, but attachment occurs at the 3 position of the allyl group rather than at the 1 position with zerovalent nickel complexes. Considering the allylic group as a bidentate ligand, the fivefold coordination around the cobalt atom was roughly described as a distorted square pyramid with the apex in the middle of the vinyl group. In the step **17** →

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 (68) A. Misono, Y. Uchida, K. Furuhashi, and S. Yoshida, *Bull. Chem. Soc. Jap.*, **42**, 1383 (1969).
 (69) G. Allegra, F. L. Giudice, G. Natta, U. Giannini, G. Fagherazzi, and P. Pino, *Chem. Commun.*, 1263 (1967).

SCHEME II



18 (Scheme II) a hydrogen atom migrates from C-4 to C-8 with the possible intermediate formation of a cobalt hydride. Metal coordination in **18** is very similar to that in **17**, the butadiene and allylic groups being nearly parallel. The final stage involves displacement of the C-6-C-7 vinyl end of the molecule by a butadiene moiety, possibly promoted by the coordinating ability of this molecule compared to an isolated vinyl group. Using 1,1,4,4-tetra-deuteriobutadiene and a cobalt catalyst, hydrogen transfer in the linear dimerization occurs at the 1 and 4 position (eq 8).⁷⁰



The origin of the different mode of dimerization must depend on the steric requirements of the metal atom and also that of the accompanying ligands. The ability of ligands to change the course of cyclodimerization of butadiene and to change cyclodimerization to linear dimerization has previously been mentioned.

A surprising effect has also been observed in catalysis by tetrakis(triphenylphosphine)platinum and tetrakis(triphenylphosphine)palladium which yield mainly vinylcyclohexene from dimerization of butadiene in benzene solution.⁷¹ In the presence of carbon dioxide, however, linear dimerization also takes place, and a 70:30 ratio of 1,trans-3,7-octatriene and 4-vinylcyclohexene is formed. No mechanism was proposed, but all attempts at isolating metal-carbon dioxide complexes were unsuccessful. Catalytic activity was enhanced in the presence of carbon dioxide since a 30% conversion of butadiene was found compared to only 18% in the absence of this ligand. In the reaction of butadiene catalyzed by $[(\text{PhO})_3\text{P}]_4\text{Ni}$, an 87% conversion to mainly 1,5-cyclooctadiene (82%) and 4-vinylcyclohexene (14%) was found, but the addition of carbon dioxide had an inhibiting effect on this catalytic system. Butadiene gave mainly 4-vinylcyclohexene in a conversion of only 42% in the presence of $[(\text{PhO})_3\text{P}]_4\text{Ni}$ and carbon dioxide; much of this product might arise from a purely thermal reaction. It is clear that the effect of added ligands to these reactions is very subtle but conversion of π -allyl to σ -allyl derivatives might be involved which is dependent both on metal and ligand.

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(71) J. F. Kohnle, L. H. Slaugh, and K. L. Nakamaye, *J. Amer. Chem. Soc.*, **91**, 5904 (1969).

It has also been found that addition of nickel tetracarbonyl during oligomerization of 1,3-butadiene in the presence of bis- π -allylnickel suppresses formation of higher oligomerized products. Treatment of the solution with nickel carbonyl followed by sodium methoxide gave 1,8-dimethoxy-2,6-octadiene.⁷² Cationic palladium hydride complexes have been shown to be efficient catalysts for formation of 1,3,7-octatriene and methoxyoctadienes from butadiene in methanol.⁷³

The main product from dimerization of isoprene in the presence of a number of metal-catalyst systems is 2,6-dimethyl-1,trans-3,6-octatriene (Table I) which is the result of head-tail addition. With palladium, however, tail-tail addition takes place and 2,7-dimethyl-1,3,7-octatriene is produced. Selectivity varies from reaction to reaction but, in the dimerization of isoprene over a catalyst composed of zirconium(IV) *n*-butoxide and diethylaluminum chloride, selectivity can be improved to 79% by addition of triphenylphosphine or tetrahydrofuran. An increased selectivity for dimers rather than trimers is found in reaction over $\text{VO}(\text{OEt})_3$ and diethylaluminum chloride on addition of low concentration of electron donors such as dioxane, tetrahydrofuran, triphenylphosphine, triethylamine, and 1,2-bis(diphenylphosphine)ethane.⁶⁷

Dimerization of a cis,trans mixture of 1,3,7-octatriene by catalytic amounts of bis- π -allylpalladium has been shown to yield four linear hexadecapentaenes in about 50% conversion with 1,5,7,10,15-hexadecapentaene (**19**) in >70% selectivity.⁷⁴ The cis isomer of octatriene did not take part in the dimerization and could be separated from the reaction mixture. π -Allylpalladium acetate was also active for the dimerization, but addition of 1 mol of triphenylphosphine to bis- π -allylpalladium changed the mode of reaction to formation of 4-(butenyl-3)dodecatetraene-1,6,8,11 (**20**). The mechanism was proposed to involve hydrogen shifts as indicated in Scheme III, although none of the intermediates were positively identified. Codimerization of 1,3,7-octatriene with other conjugated dienes such as 1,3,6-octatriene, 1,3,7,11-dodecatetraene, and 1,5,7,10,15-hexadecapentaene was also studied. Hexadienes have been dimerized in the presence of cobalt and nickel catalysts.⁷⁵

It is apparent that dimerization of 1,3-dienes by metal complex catalysts has many possibilities, and, although a fair amount of control over the product nature is now apparent, a detailed rationale is not yet available. Formation of linear or cyclic products, and the nature of these products, is extremely sensitive to the metal, ligands, and the substituents on the dienes.

C. Cyclo- and Linear Trimerization

Although a cyclic trimer from 1,3-butadiene in the presence of bis(triphenylphosphine)nickel dicarbonyl was first mentioned by Reed,²¹ the first practical synthesis of cyclododecatriene was discovered by Wilke.⁷⁶

Three of the four possible isomeric 1,5,9-cyclododecatrienes (CDT) (**21-23**) have been obtained by catalytic cyclotrimerization of 1,3-butadiene, but the most readily available are the *trans,trans*-CDT (**21**) and the *cis,-trans,trans*-CDT (**22**). A large number of Ziegler-type catalysts consisting of a titanium(IV) halide and an alkyl-

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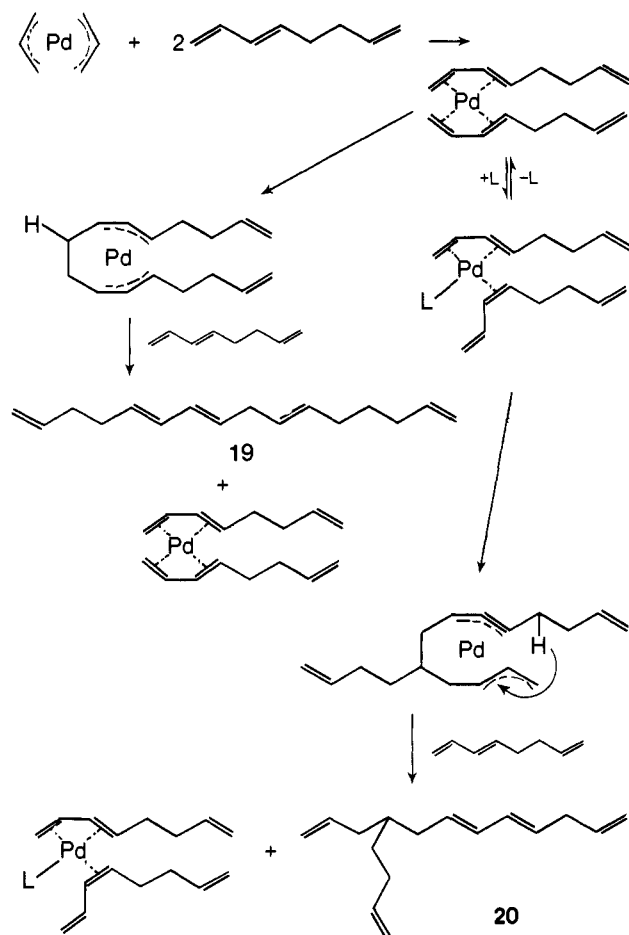
(73) M. L. H. Green and H. Munakata, *Chem. Commun.*, 549 (1971).

(74) W. Keim and H. Chung, *J. Org. Chem.*, **37**, 947 (1972).

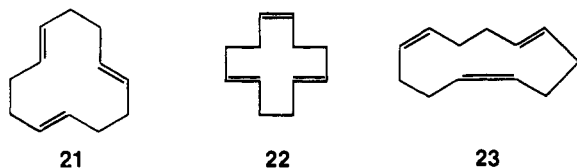
(75) E. N. Kropacheva, B. A. Dolgoplosk, I. I. Ermakova, I. G. Zhuchik-luna, and I. Y. Isereteli, *Dokl. Akad. Nauk SSSR*, **187**, 677 (1969).

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SCHEME III



aluminum compound have been developed;^{77,78} brief mention will be made to these systems although it is clear that π -allyl intermediates are probably not involved.



This type of catalytic system converts butadiene into mainly *cis,trans,trans*-CDT (**22**) accompanied by small amounts of the all-*trans* isomer **21**. Typically, yields of 80–90% can be obtained at 40° and atmospheric pressure with a titanium:aluminum ratio of between 1:3.4 and 1:10; benzene is a common solvent for reaction. The process probably involves successive addition of three butadiene molecules to the catalyst, and in one system an activation energy of 7.8 kcal/mol has been reported;⁷⁹ the rate of reaction is directly proportional to the titanium(IV) chloride concentration and independent of the aluminum chloride concentration. In this type of process reduction to the titanium(III) species is implicated.^{78,80,81} The activity and selectivity of these catalyst systems are improved by addition of substances such as sodium chloride and diphenyl sulfide which can complex with the

aluminum chloride present.⁸² The isomer ratio may also be changed by the addition of electron donors such as pyridine or triphenylphosphine when the *trans,trans,trans*-CDT isomer can be obtained up to 85% of the product mixture.⁸³ Aluminum hydrides can also replace the organoaluminum component of the titanium-based catalyst. Some typical titanium systems used are illustrated in Table II, and a review of the patent literature for further titanium and other metal systems can be found in ref 77.

In the presence of nickel acetylacetonate and trialkylaluminum, *trans,trans,trans*-CDT gives a red, crystalline zerovalent nickel complex (**24**) which, although sensitive to air, is stable to water.^{16,105,106} This has also been employed as a catalyst for trimerization of butadiene in a similar way to bis(1,5-cyclooctadiene)nickel¹⁶ and bis- π -allylnickel.¹⁰⁶ Stable 1:1 complexes are formed with **24** and electron donors such as triphenylphosphine and carbon monoxide, **25** and **26**.¹⁰ Cyclododecatriene-nickel undergoes facile displacement reactions with other ligands which led Wilke to propose the term "bare nickel species" for this type of complex.³ In the formation of cyclododecatriene, for example, the triene is displaced by 3 molecules of butadiene at -40° to form a species which has been characterized as the open bis- π -allyl complex **6**. Reaction of both **24** and **6** with carbon monoxide at 20° leads to cyclododecatriene and nickel tetracarbonyl; the coupling found in reaction of **6** is analogous to that

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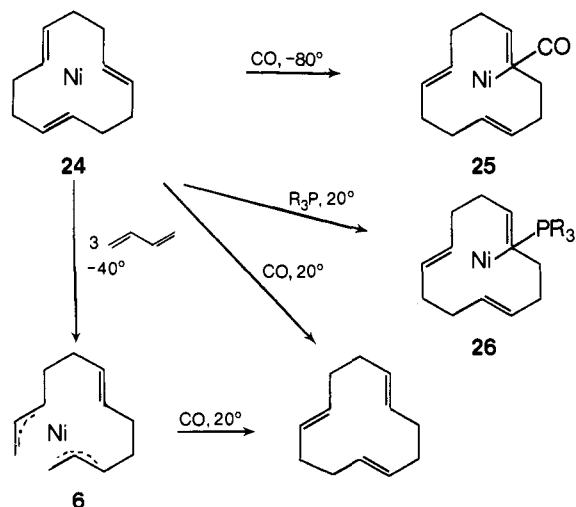
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TABLE II

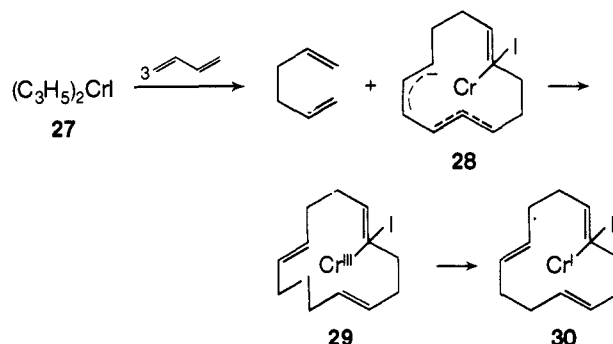
Catalyst	Cyclododecatriene yield, %	Ref
TiCl ₄ -Et ₃ Al-AlCl ₃	87.2	84
TiCl ₄ -Et ₂ AlCl	90	78
TiCl ₄ -Et ₂ AlCl	88.5 cis,trans,trans	
	3 trans,trans,trans	78
TiCl ₄ -Et ₃ Al ₂ Cl ₃	79 cis,trans,trans	85
TiCl ₄ -EtAlCl ₂ -Et ₂ AlH	86.6 cis,trans,trans	78
	2.5 trans,trans,trans	
TiCl ₄ -EtAlCl ₂ -Et ₂ AlH-PPh ₃	45.9 trans,trans,trans	78
	14.0 cis,trans,trans	
TiCl ₄ -AlCl ₃ -Al-C ₆ H ₆	70	86
Ti(OBz) ₄ -Et ₂ AlCl	72 cis,trans,trans	87
Poly(butyl titanate)-Et ₂ AlCl	42 trans,trans,trans	88
	20 cis,trans,trans	
TiCl ₄ -AlCl ₃ -CaH ₂	81.7	78
TiCl ₄ -Ph ₂ Zn	70 cis,trans,trans	89
Ni(acac) ₂ -Et ₃ Al		16
Ni(acac) ₂ -Et ₂ AlOEt	65.3 trans,trans,trans	10
	9.1 cis,trans,trans	
Bis- π -allylnickel		10
Bis(1,5-cyclooctadiene)nickel	71-80	90, 91
Ni(acac) ₂ -cyclododecene-Et ₂ AlOEt	72	91
Ni-ethyl hexanoate-Et ₃ Al	83	92
Ni-dimethylglyoxime-Et ₃ Al	66	93
Ni(OAc) ₂ -NaH	76	94
(Ph ₃ P) ₂ Ni(CO) ₂ -BuLi	54	95
(CH ₂ =CHCN) ₂ Ni-DMSO	75 trans,trans,trans	96
(CH ₂ =CHCN) ₂ Ni-Et ₃ Al	72	97
Bis- π -crotylnickel		98
CrO ₂ Cl ₂ -Et ₃ Al	46.7 trans,trans,trans	78, 99
	32.6 cis,trans,trans	
CrO ₂ Cl ₂ -AlH ₃	50 trans,trans,trans:cis,	100
	trans,trans, 7:3	
CrO ₃ -AcCl-Et ₃ Al	87	101
CrCl ₃ -Et ₃ Al	75	102
Cr(acac) ₃ -Et ₃ Al-Et ₂ AlCl	70 trans,trans,trans; cis,	103
	trans,trans;cis,cis,	
	trans	
Ph ₂ Mn-THF	40-70 cis,trans,trans	104

found for bis- π -allylnickel. Hydrogenation of **24** and **6** yields cyclododecane and *n*-dodecane, respectively. Other reactions of **6** are described later. Nickel catalyst systems for formation of *trans,trans,trans*-cyclododecatriene are summarized in Table II.



Bis- π -allylchromium iodide (**27**), prepared by reaction of iodine with tris- π -allylchromium, also catalyzes forma-

tion of cyclododecatriene.² Although intermediate complexes have not been isolated, reaction has been envisaged as proceeding *via* intermediates **28**-**30**. The cata-

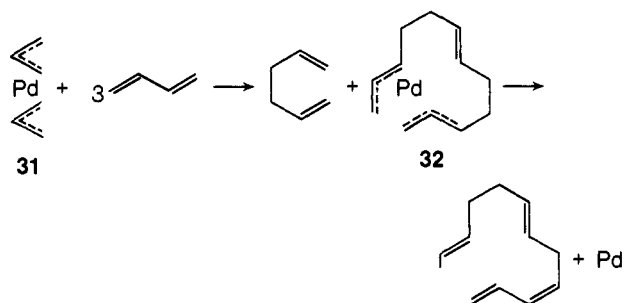


lytic process involves a formal change in oxidation state, Cr(I) \rightleftharpoons Cr(III), and the yield of cyclododecatriene is much higher in methylene chloride than in benzene, reflecting the greater dissociation of the bis- π -allylchromium iodide in the former solvent. Other chromium-containing catalysts (Table II) have been employed¹⁰⁷ and,

(107) F. T. Wadsworth, U. S. Patents 3,366,701, 3,429,940; *Chem. Abstr.*, **68**, 60057n (1968); 70, 87144s (1969); J. R. Olechowski, German Offen. 1,807,700, 1,801,723; *Chem. Abstr.*, **71**, 81539y, 90935b (1969).

in comparison to titanium-based systems, yield a larger amount of trans,trans,trans product compared to cis,trans,trans CDT. Although iron-containing catalysts normally lead to acyclic products, a mixture of trans,trans,trans and trans,trans,cis 1,5,9-cyclododecatrienes, together with other cyclic and open-chain oligomers of butadiene, have been formed with the catalyst system ferric chloride, aluminum, and aluminum chloride in benzene.²²

Other metals produce predominantly linear oligomers; bis- π -allylpalladium (**31**) yields *n*-dodecatetraenes together with higher oligomers.² A pathway similar to the reaction with bis- π -allylnickel has been suggested in which an analogous intermediate (**32**) is formed but does



not cyclize owing to the larger volume of a palladium atom. Reaction of butadiene with π -allylpalladium acetate in benzene at 50° yields 1,3,6,10-dodecatetraene with a selectivity of 77% in good conversions.¹⁰⁸ A small amount of 1,3,7-octatriene was also formed, and this became the main product when triphenylphosphine was added (Pd/PPh₃ = 1) to the reaction; this is a further example of a ligand acting in a coordination blocking role and directing the reaction to dimerization rather than trimerization.

Although dimerization and polymerization were observed on reaction of butadiene with allyl compounds of cobalt,² linear trimers have been obtained with certain cobalt-containing systems. Formation of 3-methyl-1,5,7,9-undecatetraene was found from reaction of butadiene in the presence of cobalt tris(acetylacetonate) and triethylaluminum,¹⁰⁹ and a mixture of 3,6-dimethyldeca-1,4,7,9-tetraene, 3,8-dimethyldeca-1,4,7,9-tetraene, and 3-methylundeca-1,5,8,10-tetraene has been isolated from reaction of butadiene in the presence of cobalt chloride and triethylaluminum although the major reaction was dimer formation and the trimer fraction constituted only 15% of the total product.⁵⁰ In the presence of bis(cyclooctatetraene)iron, butadiene has been oligomerized selectively to 1,3,6,10-dodecatetraene together with a small amount of 1,5-cyclooctadiene.¹¹⁰ Bis(butadiene)iron carbonyl and butadienecyclooctatetraeneiron carbonyl have proved catalysts of low activity for oligomerization of butadiene into a mixture of cyclic and linear dimers.^{111,112} A small amount of 3-methyl-5-vinyl-1,6,8-nonatriene has been formed in the oligomerization of butadiene in the presence of ferric chloride, triethylaluminum, and phosphines, but, although conversions were almost quantitative, most of the product consisted of dimers.¹¹³

(108) D. Medema and R. Van Helden, *Recl. Trav. Chim. Pays-Bas*, **90**, 324 (1971).

(109) J. Beger and C. Duschek, *Z. Chem.*, **12**, 18 (1972).

(110) A. Carbonaro and A. Greco, *J. Organometal. Chem.*, **25**, 477 (1970).

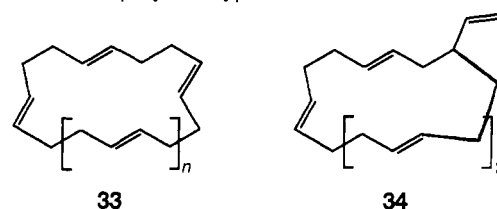
(111) A. Carbonaro, A. Greco, and G. Dall'Astra, *Tetrahedron Lett.*, 2037 (1967).

(112) A. Carbonaro and F. Cambisi, *J. Organometal. Chem.*, **44**, 171 (1972).

(113) J. Beger and C. Duschek, *Z. Chem.*, **12**, 134 (1972).

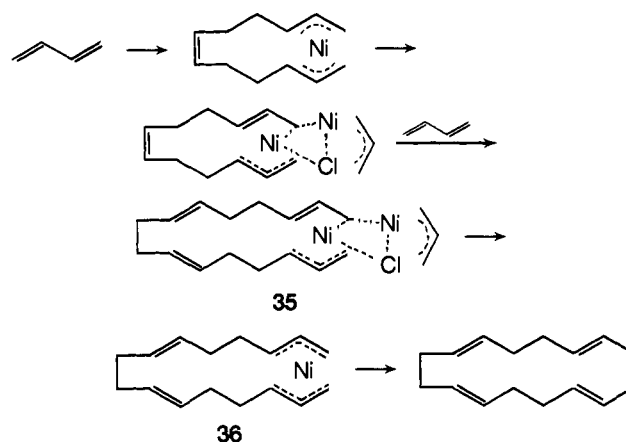
D. Higher Oligomers

Variable amounts of higher oligomers of butadiene are also formed under some of the conditions previously described. In Reed's earlier work, a small amount of a cyclic tetramer of butadiene, cyclohexadecatetraene, was formed.²¹ Miyake, Kondo, and Nishino have shown that a catalyst system of bis- π -allylnickel chloride converts butadiene to a mixture of cyclic polyenes **33**;^{114,115} smaller amounts of the polyene type **34** are also formed. It was



suggested that the specific activity is due to interaction of the two components, growth taking place on an associated system (**35**) and ring closure occurring on dissociated "naked" nickel species **36** (Scheme IV). This latter process is, of course, analogous to the ring closure of the bis- π -allylnickel derivative from trimerization of butadiene to form cyclododecatriene. In the mechanism for cyclic polyene formation, association of the π -allylnickel chloride with a nickel(0) species occurs through a carbon and a chlorine bridge. This latter bridging atom can be replaced by other halides. Organic acids such as trifluoroacetic acid and other Lewis acids can also be employed in place of π -allylnickel halides (Table III), and systems based on other metals are also effective.

SCHEME IV



Hexadecatetraene, a partially reduced linear tetramer of butadiene, has been obtained in a yield of 59% by electrolysis of nickel salts.¹¹⁶ This product is obtained by acid treatment of a complex formed by electrolytic reduction at a platinum cathode of a solution containing butadiene, (tetrakispyridine)nickel diperchlorate or nickel chloride, and tetrabutylammonium perchlorate as electrolyte in ethanol or dimethoxyethane. Performing the electrolysis with bis(triphenylphosphine)nickel dichloride led to formation of 1,3,7-octatriene.

IV. Reactions of 1,3-Dienes with Other Reagents

From the previous discussions it should now be clear that π -allyl derivatives can be formed involving a different

(114) A. Miyake, H. Kondo, and M. Nishino, *Angew. Chem., Int. Ed. Engl.*, **10**, 802 (1971).

(115) A. Miyake, H. Kondo, M. Nishino, and S. Tokizane, XXIIIrd International Congress of Pure and Applied Chemistry, Boston, 1971, Vol. 6.

(116) N. Yamazaki and S. Murai, *Chem. Commun.*, 147 (1968).

TABLE III. Formation of Macrocyclic Polyenes from Butadiene and a Two-Component Catalyst System¹¹⁵

Catalyst system ^a	%			
	C ₈	C ₁₂	C ₆ -C ₃₂	>C ₃₂
A ₂ Ni + C ₃ H ₅ NiCl	5	20	35	40
A ₂ Ni + C ₃ H ₅ NiBr	3	13	37	43
A ₂ Ni + C ₃ H ₅ NiI	3	10	38	49
A ₂ Ni + CF ₃ COOH	0.3	11	28	61
A ₂ Ni + CH ₃ SO ₃ H	tr	2	11	87
A ₂ Ni + APdBr	7	37	31	25
A ₂ Pd + ANiBr	12	29	28	31
A ₂ Ni + Cp ₂ TiBr	4	69	13	14
ANiBr + Cp ₂ Ti	8	18	33	40

^a A = allyl; Cp = cyclopentadienyl.

Product structures were discussed in terms of a reaction path initially involving the addition of a nickel hydride to the conjugated diene to form a substituted allylnickel species. A hydrido species was suggested to arise from a nickel-hydrido β -elimination from an allylnickel precursor. Insertion of ethylene into position a or b of π -allylnickel complex **37** would yield allylnickel complexes which on Ni-H elimination leads to 1,4-diene formation. A mechanism involving a σ -methylallylnickel could not, however, be excluded. All the observed products could be explained on the basis of an initial 1,2 addition to the least substituted double bond of the 1,3-dienes. Only one product was obtained from reaction of 1,3-pentadiene, consistent with intervention of the symmetrical π -allylnickel complex **38**; again σ -methylallyl complexes could not be excluded.

A detailed kinetic investigation has been made into a

TABLE IV. Codimerization of α -Olefin with Conjugated Dienes Catalyzed by Nickel Complexes¹¹⁷

Olefin	1,3-Diene	Solvent	Major 1:1 adduct	% ^a conversion	% ^b yield
Ethylene	Butadiene	Toluene	1,4-Hexadiene	33	65
Ethylene	1,3-Pentadiene	Perchloro-ethylene	3-Methyl-1,4-hexadiene	30	79
Ethylene	2-Methyl-1,3-butadiene	Perchloro-ethylene	4-Methyl-1,4-hexadiene	31	33
Ethylene	2-Chloro-1,3-butadiene	<i>n</i> -Hexane	4-Chloro-1,4-hexadiene	37	75
Ethylene	Cyclo-1,3-hexadiene	Decalin	3-Vinylcyclohexene	70	83
Ethylene	Cyclo-1,3-octadiene	<i>n</i> -Hexane	3-Vinylcyclooctene	19	45
Propylene	Butadiene	Perchloro-ethylene	2-Methyl-1,4-hexadiene	31	25

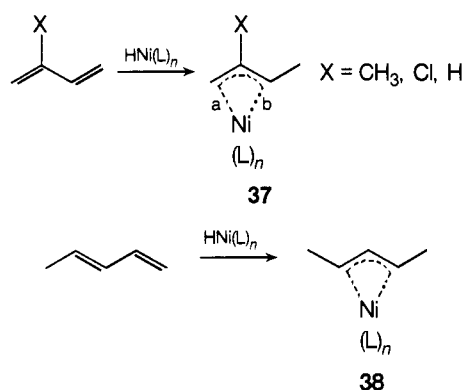
^a Based on moles of conjugated diene introduced. ^b Based on moles of conjugated diene reacted.

number of butadiene molecules. Thus the bis- π -allylnickel intermediates **6** and **7** involve three and two molecules, respectively. In this way reactions can be directed through **7** by addition of donor ligands which effectively block incorporation of the third butadiene unit. Conditions can also be utilized which bring about reaction of only one molecule of butadiene with other reagents. In this way, products can be formed with different skeletal structures, and, although some overlap is essential, reactions will be discussed with this in mind. Definitive evidence is not available in all cases to identify the importance of π -allylmetal intermediates, but these reactions have been included to obtain as wide a view as possible.

A. Products with One Diene Unit

Because of its commercial importance, formation of hexadiene from butadiene and ethylene has been extensively investigated with a wide variety of metal catalysts. Nickel-containing catalysts lead to either 1:1 or 2:1 adducts of butadiene and ethylene, but a mixture of *trans*- and *cis*-1,4-hexadiene and 3-methyl-1,4-pentadiene has been obtained in the presence of bis(tri-*n*-butylphosphine)-nickel(II) chloride and diisobutylaluminum chloride.¹¹⁷ A similar reaction was obtained with other nickel(II) complexes such as (R₃P)₂Ni(NO₃)₂ and zerovalent nickel complexes (Ph₃P)₂Ni(CO)₂ and [(PhO)₃P]₂Ni(CO)₂; reaction between ethylene and other 1,3-dienes has also been studied (Table IV).

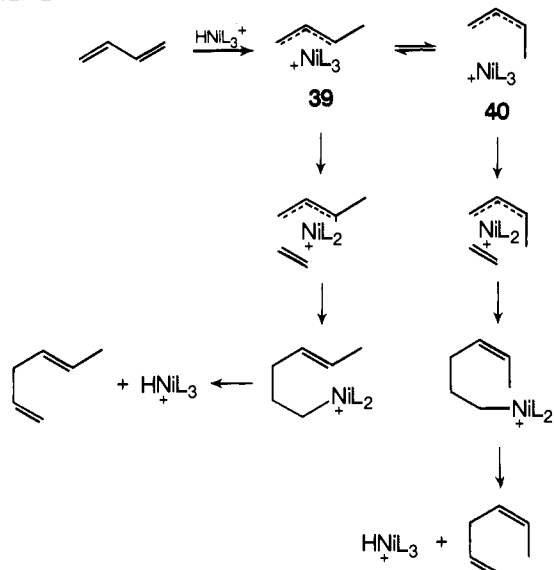
(117) R. G. Miller, T. J. Kealy, and A. L. Barney, *J. Amer. Chem. Soc.*, **89**, 3756 (1967).



similar reaction with the nickel hydride complex, HNi-[P(OEt)₃]₄⁺, as catalyst.¹¹⁸ The rate-limiting step for reaction of hydride with butadiene was found to be ligand dissociation of HNiL₄⁺ to HNiL₃⁺, followed by formation of *syn*- and *anti*- π -crotylnickel-phosphite complexes **39** and **40** (Scheme V) with an equilibrium ratio of *anti*:*syn* of 1:19. Nmr experiments indicated that initial formation of the *anti* isomer is kinetically preferred over the *syn* isomer by a ratio of 7.5:1 but that isomerization occurs to the thermodynamically preferred *syn* isomer. Predominant formation of 1,trans-4-hexadiene was attributed to rate-determining ethylene insertion reaction with the *syn*-crotyl complex which is slow compared to the *anti*-*syn* equilibration.

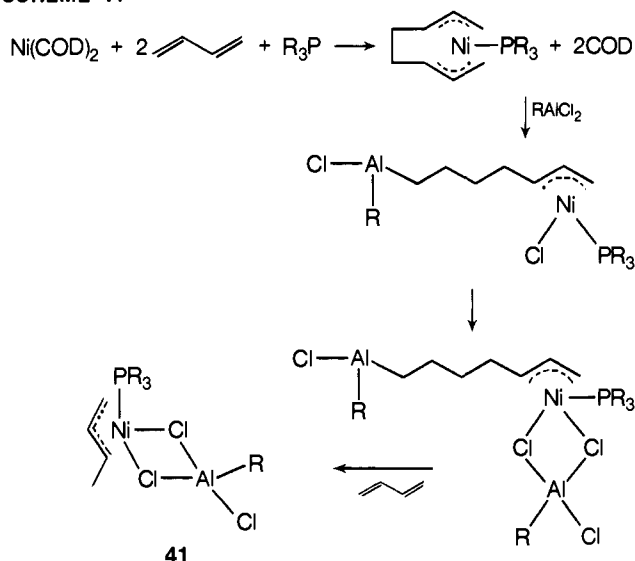
(118) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 6777 (1970).

SCHEME V



Following the work of Miller, Kealy, and Barney a detailed examination has been made into the role of phosphorus ligands and aluminum cocatalyst in a nickel-based catalyst system in the reaction of butadiene and ethylene.¹¹⁹ The system employed is generally represented as $\text{Ni}(\text{COD})_2\text{-R}_3\text{P-R}_x\text{AlCl}_3 - x$ ($\text{Ni}:\text{P}:\text{Al} = 1:1:3-6$) and led to formation of mainly 1,4-hexadiene (67%), 3-methyl-1,4-pentadiene (7%), and 2,4-hexadiene (9%) together with higher boiling olefins (16%); conversions were of the order 70%. Only one phosphorus ligand per nickel was required for maximum catalytic activity, and **41** was suggested as the active form of the catalytic species (Scheme VI). The ratio of *trans* and *cis* isomers was again discussed in terms of *syn*- and *anti*- π -crotyl intermediates. It was shown that steric and electronic factors which cause butadiene to coordinate as a monodentate ligand rather than a bidentate ligand leads to higher proportions of *syn*- π -crotyl species and subsequently to a higher ratio of 1,*trans*-4-hexadiene.

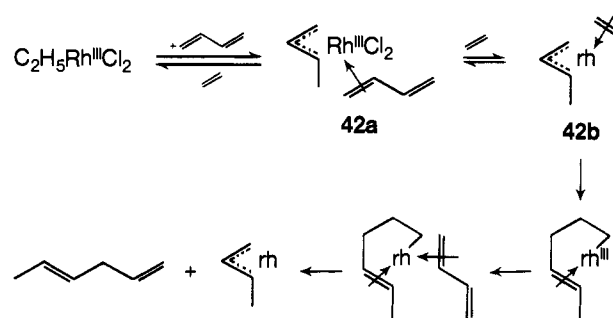
SCHEME VI



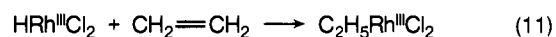
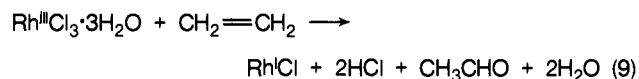
π -Crotylrhodium complexes are also intermediates in the rhodium chloride catalyzed reaction of butadiene and ethylene, yielding 1,4-hexadiene in 90% yield and high

(119) A. C. L. Su and J. W. Collette, *J. Organometal. Chem.*, **36**, 177 (1972).

SCHEME VII



conversions.^{57,120} Activation of rhodium trichloride had been shown earlier to involve reduction of rhodium(III) to rhodium(I) (eq 9), oxidation of rhodium(I) by hydrochloric acid (eq 10), and reaction of this hydride with coordinated olefin to give a rhodium(III) alkyl (eq 11).¹²¹ For-



formation of the π -crotyl species **42a** is then postulated from the reaction of the hydridorhodium(III) complex with butadiene (Scheme VII). Ligand insertion of ethylene with the π -crotyl group, followed by hydrogen abstraction, subsequently leads to hexadiene.¹²² The stability of **42b** was suggested as the reason for formation of hexadienes rather than dimerization of ethylene. Products obtained with 1,3-pentadiene and isoprene were consistent with those expected on the basis of the most stable π -allyl complexes **43** and **44**.



Following early work on the formation of mixtures of 1,3-hexadiene, 1,4-hexadiene, and butadiene dimers from butadiene and ethylene catalyzed by cobalt compounds and metal alkyls,^{52,123} a number of reports have appeared of 1,4-hexadiene formation with catalysts comprising cobalt salts, di(tertiary phosphines), and organoaluminum compounds with a selectivity of 90% and conversions up to 100%.¹²³⁻¹²⁷ Since the cobalt-hydride complex, bis(diphosphinoethane)cobalt hydride and a system formed from cobalt tris(acetylacetonate) with diethylaluminum ethoxide in the presence of di(tertiary phosphine) was inactive, it was suggested that the organoaluminum reagent had a twofold role.^{123,124} A hydride cobalt species is initially formed which must be activated

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

(121) R. Cramer, *J. Amer. Chem. Soc.*, **87**, 4717 (1965).

(122) The product has been written as 1,*trans*-4-hexadiene, but 1,*cis*-4-hexadiene is also formed⁵⁷ presumably via the *trans*- π -crotyl species. Following Cramer, the symbol "rh" is used when ligands are omitted from a formula.

(123) M. Iwamoto and S. Yuguchi, *Bull. Chem. Soc. Jap.*, **4**, 150 (1968).

(124) M. Iwamoto and S. Yuguchi, *Chem. Commun.*, 28 (1968).

(125) M. Iwamoto and S. Yuguchi, *Kogyo Kagaku Zasshi*, **70**, 1505 (1967).

(126) M. Iwamoto and S. Yuguchi, *Kogyo Kagaku Zasshi*, **71**, 234 and 237 (1968); *Chem. Abstr.*, **69**, 35304 (1968).

(127) T. Kagawa, Y. Inoue, and H. Hashimoto, *Bull. Chem. Soc. Jap.*, **43**, 1250 (1970).

to a coordinately unsaturated state by the action of an organoaluminum compound or other Lewis acid. This could occur by attack on the basic phosphorus coordinated with the cobalt atom thus producing coordinative unsaturation. Subsequently, a reaction of butadiene on the activated complex yields a π -butenyl complex similar to that formed from butadiene and cobalt hydrocarbon-yl.¹²⁸ Coupling with a coordinated ethylene molecule finally yields 1,*cis*-4-hexadiene with release of a hydrido complex for further reaction. In a number of these reactions small amounts of other products are formed such as C₈ dienes from further reaction of 1,4-hexadiene and ethylene. It was also found with similar catalyst systems that reaction between these reagents leads to a mixture of 2,4-hexadiene and the C₈ dienes 3-methyl-1,4-heptadiene and 3-ethyl-1,4-hexadiene; the selectivity was temperature dependent.¹²⁹

Formation of 1,4-hexadiene by these reactions corresponds to 1,4-addition of a carbon-hydrogen bond of ethylene to butadiene. With unsymmetrical 1,3-dienes there are two possible modes of addition, and this has been investigated by Hata and Miyake¹³⁰ with a catalyst system, cobalt chloride-(RO)_nPCl_{3-n}-triethylaluminum. Isoprene reacts to give a 90% yield of 4-methyl-1,*cis*-4-hexadiene and 5-methyl-1,4-hexadiene (84:16), and 1,3-pentadiene gave 3-methyl-1,*cis*-4-hexadiene and 1,*cis*-4-heptadiene (91:9). These ratios indicate a preferential addition of the vinyl moiety of ethylene to the terminal carbon atom of a 1,3-diene system. Since the 1,4-hexadiene consisted of only the *cis* isomer, it was suggested that the intermediate π -allyl complex existed only in the anti form.

A catalyst system of cobalt thiocyanate, triphenylphosphine, and triethylaluminum has been found to be effective for reaction of butadiene and isoprene with ethylene.¹³¹ The use of a Grignard reagent as reducing agent rather than alkylaluminum has been employed together with cobaltous chloride and di(tertiary phosphine) complexes for dimerization of ethylene and butadiene.¹³² In these reactions, however, an appropriate amount of alcohol or acetone must be present. It was suggested that the complex produced by reduction of the cobalt salt with Grignard reagent can only act as a catalyst when activated by alkoxy magnesium chloride. Under these conditions, selective formation of 1,*cis*-4-hexadiene occurs with yields of between 50 and 70%, dependent upon the nature of the phosphine and alcohol present. This question of catalyst activation is extremely important and again illustrates that a coordinatively unsaturated species must be present for reaction to occur. The alkoxy magnesium chloride was suggested to promote ligand dissociation of the cobalt species and a similar activation of bis(di(tertiary phosphine)ethane)hydridocobalt by phenol has also been observed.¹²⁶

A mixture of 3-methyl-1,4-pentadiene, 1,4-hexadiene, and 1,3-hexadiene in a ratio of 2:1:2 was obtained from reaction of butadiene and ethylene in the presence of a catalyst consisting of ferric chloride, triethylaluminum, and triphenylphosphine.¹³³ Since the ratio of the total C₆

(128) H. B. Jonassen, R. I. Stearns, J. Kenttamaa, D. W. Moore, and A. G. Whittaker, *J. Amer. Chem. Soc.*, **80**, 2586 (1958).

(129) M. Iwamoto, K. Tani, H. Igaki, and S. Yuguchi, *J. Org. Chem.*, **32**, 4148 (1967).

(130) G. Hata and A. Miyake, *Bull. Chem. Soc. Jap.*, **41**, 2443 (1968).

(131) M. Iwamoto and S. Yuguchi, *Kogyo Kagaku Zasshi*, **71**, 133 (1968).

(132) T. Kagawa and H. Hashimoto, *Bull. Chem. Soc. Jap.*, **45**, 2586 (1972).

(133) M. Iwamoto and S. Yuguchi, *Bull. Chem. Soc. Jap.*, **39**, 2001 (1966).

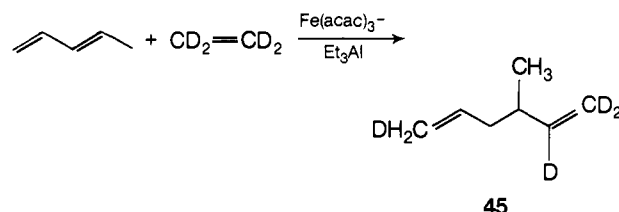
TABLE V: Reaction of 1,3-Dienes with Ethylene Catalyzed by Fe(acac)₃-Et₃Al¹³⁶

1,3-Diene	Conversion, %	Product	Yield ^a
Isoprene	77	4-Methyl-1, <i>cis</i> -4-hexadiene	69
		5-Methyl-1,4-hexadiene	
		Conjugated methylhexadienes	9
1,3-Pentadiene	43	3-Methyl-1, <i>cis</i> -4-hexadiene	46
		1, <i>cis</i> -4-Heptadiene	14
		2,4-Heptadiene	4
2,3-Dimethyl-1,3-butadiene	99	4,5-Dimethyl-1,4-hexadiene	71
		2,3-Dimethyl-2,4-hexadiene	9
2-Methyl-1,3-pentadiene	97	3,5-Dimethyl-1,4-hexadiene	65
		4-Methyl-1, <i>cis</i> -4-hexadiene	21
2-Phenyl-1,3-butadiene	80	4-Phenyl-1,4-hexadiene	52

^a Based on converted 1,3-diene.

dienes to butadiene dimer formed was about 4.5:1, the average yield of 3-methyl-1,4-pentadiene was about 25–30%. A much more selective catalyst for 1,4-hexadiene formation was found by use of di(tertiary phosphines).^{134,135} With bis(diphenylphosphino)propane, ferric chloride, and triethylaluminum, a 100% conversion of butadiene and ethylene to 1,4-hexadiene is found with a selectivity of 96%;¹³⁴ reaction mechanisms appear to be similar to those described with the cobalt systems. In reactions of a number of 1,3-dienes with ethylene, catalyzed by iron trisacetylacetonate and triethylaluminum, stereospecific 1,*cis*-4-diene formation was found (Table V). Again it is apparent that addition of ethylene takes place preferentially at the terminal position of the substituted double bond. No reaction was found with 1,3-dienes which have an unfavorable *cisoid* configuration such as 1,*cis*-3-pentadiene and 4-methyl-1,3-pentadiene. Two types of hydrogen transfer were found with reaction of propylene and 1,3-butadiene leading to formation of 2-methyl-1,*cis*-4-hexadiene and 1,*cis*-5-heptadiene. The selectivity of the 1,3-butadiene-ethylene reaction has been examined with the system Et₃Al-Fe(OAc)_n(OR)_{3-n} and varying R groups.¹³⁷

Although a π -allyl mechanism can account for formation of some products in the reactions discussed, it has been positively excluded in the codimerization of 1,*trans*-3-pentadiene and perdeuterated ethylene catalyzed by iron trisacetylacetonate and triethylaluminum. This gave a 3-methyl-1,*cis*-4-hexadiene component consisting only of **45** rather than an equimolar mixture of two isomers re-



quired by a π -allyl mechanism.¹³⁸ It was suggested that in the codimerization of butadiene and ethylene catalyzed

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

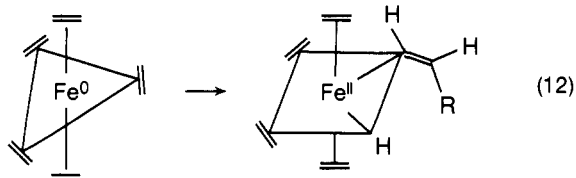
(135) G. Hata and A. Miyake, *Bull. Chem. Soc. Jap.*, **41**, 2762 (1968).

(136) G. Hata, *J. Amer. Chem. Soc.*, **86**, 3903 (1964); G. Hata and D. Aoki, *J. Org. Chem.*, **32**, 3754 (1967).

(137) M. Iwamoto and S. Yuguchi, *Kogyo Kagaku Zasshi*, **70**, 1221 (1967).

(138) A. Carbonaro, A. Greco, and G. Dall'Astra, *J. Organometal. Chem.*, **20**, 177 (1969).

by iron complex catalysts simultaneous formation of 1,*cis*-4-hexadiene and 1,*trans*-3-hexadiene¹³³ cannot be explained through a π -crotyliron intermediate. A mechanism involving oxidative addition (eq 12), followed by re-



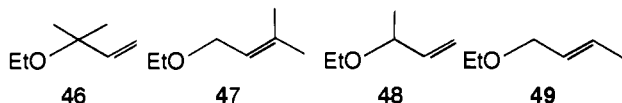
ductive elimination, was suggested. This latter process involves simultaneous rupture of two bonds and the addition of hydrogen and vinyl to a coordinated butadiene molecule. Simultaneous formation of 1,*trans*-3-hexadiene, 1,5-hexadiene, 3-methyl-1,4-pentadiene, and 1,*cis*-4-hexadiene was suggested to arise from different complexation of the butadiene to the iron. It is evident that the mode of hydrogen transfer must be considered in each catalytic system. Insertion of ethylene into a σ - or π -allyliron bond formed in a previous step, or an oxidative addition mechanism, might operate without involving a hydrogen or alkyl carrier from outside the complexed molecules.

Codimerization of propylene and butadiene has been achieved using a catalyst system of π -allylpalladium chloride, aluminum chloride, and triphenylphosphine in nitrobenzene at 100°. ¹³⁹ A mixture of straight-chain heptadienes and 2-methylhexadienes was obtained in yields of about 30% together with a smaller amount of butadiene dimers. The ratio of straight-chain C₇ dienes to total C₇ dienes varied with the phosphine and changed from tricyclohexylphosphine (0.22) to triphenyl phosphite (0.80); the catalytic activity was also influenced by the aluminum:palladium and phosphine:palladium ratios.

Reaction of butadiene and isoprene with acrylates catalyzed by cobalt or iron tris(acetylacetonate) has been reported to yield hepta-2,5-dienoates and 5- and 6-methylhepta-2,5-dienoates in yields of 30 and 45%, respectively. ¹⁴⁰ A larger amount of triethylaluminum was required in the iron compared to the cobalt-catalyzed system; the results also indicated the importance of the triethylaluminum:metal salt ratio in these reactions.

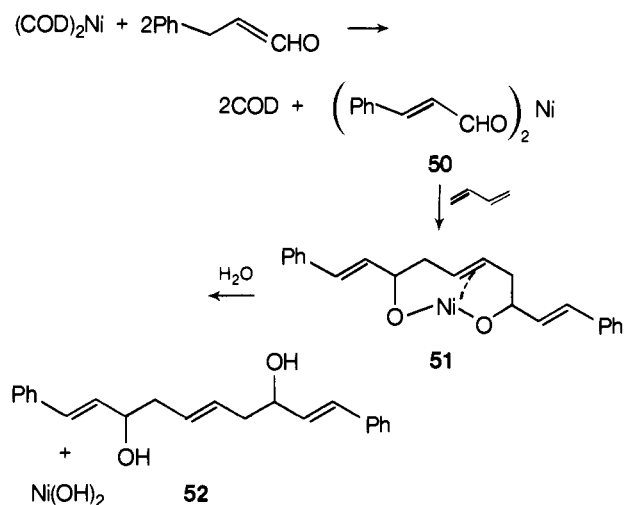
Although it is clear that the reaction does not involve a π -allyl intermediate, codimerization of ethylene and 1,3-butadiene to vinylcyclobutane has been found in the presence of a homogenous titanium catalyst. ¹⁴¹

In rhodium trichloride catalyzed reactions of ethanol and isoprene, **46** and **47** were obtained in 58 and 21% yields, respectively, at room temperature, while the dominant product was **47** at 60°. ¹⁴² Reaction with butadiene at room temperature gave 33 and 6% yields of **48** and **49**; this type of reaction is discussed in greater detail later in this review.

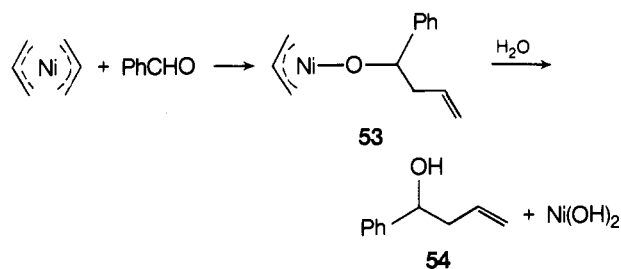


A 51% yield of **52** was obtained from reaction of cinnamaldehyde and butadiene in the presence of bis(cyclooctadiene)nickel. ¹⁴³ It is apparent that a π -allylnickel de-

rivative is not involved, but the reaction was suggested to involve formation of **50** and **51**; treatment with water leads to **52**. Similar reactions were studied with acetone,



cyclohexanone, acetophenone, and other aldehydes. In contrast, bis- π -allylnickel has been shown to yield **53** with benzaldehyde which, on hydrolysis, gave 4-phenylbut-1-en-4-ol (**54**). ¹⁴³



B. Products with Two Diene Units

Although no direct evidence is available, it is apparent that these reactions involve an intermediate analogous to **7**. It is again evident that, as in oligomerization reactions, either cyclic or open-chain products can be formed with the latter involving hydrogen transfer, and changes in reaction pathways by variation in added ligands have been strikingly demonstrated. Since this control is possible, these reactions provide an excellent method for synthesis of unsubstituted or substituted medium-sized rings and also acyclic derivatives.

1. Olefins

A mixture of *cis,trans*-1,5-cyclodecadiene (**58**) and 1,*trans*-4,9-decatriene (**59**) is formed on reaction of butadiene and ethylene, catalyzed by bis(cyclooctadiene)-nickel. ¹⁹ Formation of cyclodecadiene can be optimized by use of as low a temperature as possible; at room temperature 88% of **58** and 12% of **59** are formed in 3–4 weeks, but at 60° equal amounts of the two products are formed. Production of cyclic product **58** is favored by addition of ligands such as phosphines and phosphites, but the yield falls to ca. 40% owing to formation of substantial amounts of vinylcyclohexene and cyclooctadiene. The proposed mechanism involves reaction of ethylene with the bis- π -allyl intermediate **55a** to yield **55b** (Scheme VIII) followed by coupling with the terminal atom of an anti- π -allyl group or the terminal atom of an anti- σ -allyl group (**56**) leading to cyclodecadiene. Alternatively, initial reaction with an anti- π group might occur, followed by involvement of a syn- π -allyl group. ¹⁴⁴ Formation of

(139) T. Ito, T. Kawai, and Y. Takami, *Tetrahedron Lett.*, 4775 (1972).

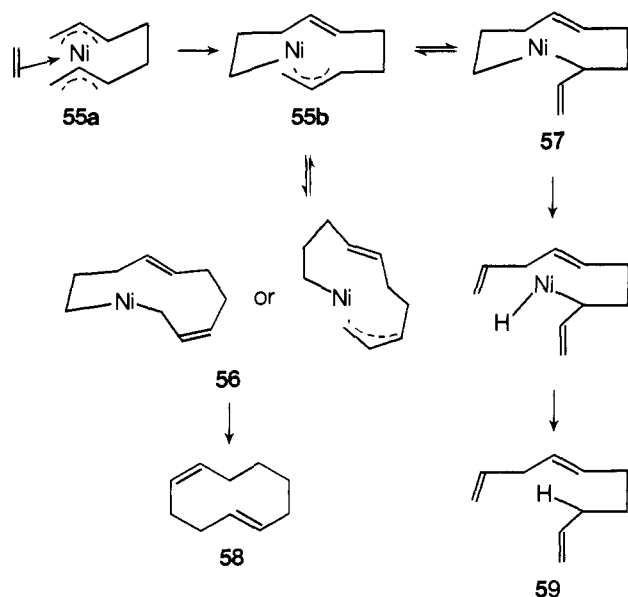
(140) A. Misono, Y. Uchida, T. Saito, and K. Uchida, *Bull. Chem. Soc. Jap.*, 40, 1889 (1967).

(141) L. G. Cannell, *J. Amer. Chem. Soc.*, 94, 6867 (1972).

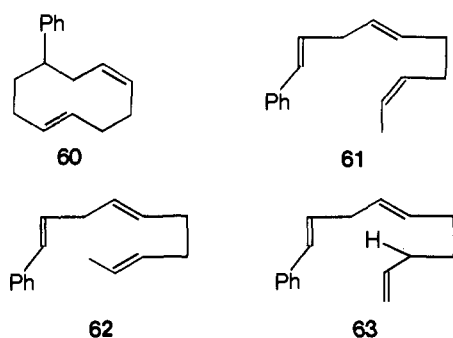
(142) K. C. Dewhirst, *J. Org. Chem.*, 32, 1297 (1967).

(143) Reference 1, p 39.

SCHEME VIII



1,*trans*-4,9-decatriene was envisaged through the σ -allyl intermediate **57** followed by elimination of hydridonickel and addition of hydrogen with cleavage of the carbon-nickel bond. Good acceptor ligands such as triphenyl phosphite appeared to favor intermediacy of **56** with consequent formation of cyclodecatriene. Formation of *cis*,*trans*-1,5-cyclodecadiene has also been found from reaction of butadiene with the catalyst system comprised of nickel acetylacetonate, triphenylphosphine, and triethylaluminum,¹⁴⁵ and 2,6-dimethyl-*cis*,*trans*-1,5-cyclodecadiene from isoprene and ethylene.³⁹ A similar reaction occurs with butadiene and styrene although a mixture of isomers is formed (**60–63**).¹ Using tris(2-biphenyl) phosphite as ligand, 75% of the styrene can be converted into phenylcyclodecadiene, but, in the absence of a ligand, the main product consists of isomers of 1-phenyl-1,4,8-decatrienes. This again illustrates the dramatic way in which ligands can affect the course of reaction pathways.

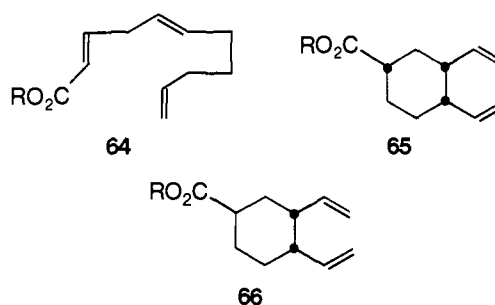


In reactions of methyl acrylate with butadiene, added ligands such as triphenyl phosphite must be used with the nickel catalyst system for effective reaction.^{1,146} The formation of 1,*trans*-4,9-decatriene-1-carboxylic acid ester (**64**) together with two divinylcyclohexane derivatives **65** and **66** from thermal Cope rearrangement from the cyclodecadiene derivatives was found. Although the Diels-Alder reaction between diene and olefin can be avoided by dropwise addition of the reactants to the catalyst, the

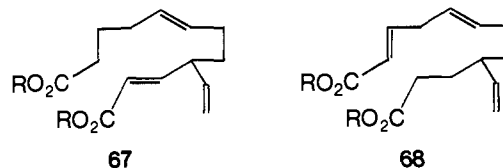
(144) An alternative and valuable nomenclature for considering the stereochemistry of allyl groups has been discussed in ref 1.

(145) Y. M. Akhmedov, M. A. Mardanov, and A. V. Khanmetov, *Zh. Org. Khim.*, 7, 2511 (1971).

(146) Rhone-Poulenc, French Patent 1,433,409 (1965).

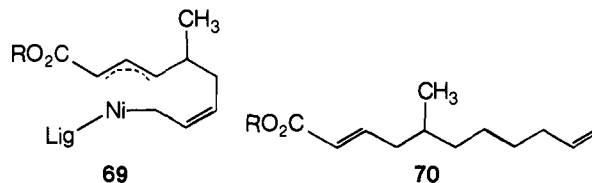


reaction is complicated by addition of a second molecule of methyl acrylate to yield dicarboxylic ester derivatives **67** and **68**. Both a decrease in concentration of acrylic



ester and choice of a large ligand suppresses formation of these diesters. The process has been operated continuously, and good conversions have been found. Detailed aspects of the stereochemistry of this reaction and the configuration of intermediates involved were discussed in the review by Heimbach, Jolly, and Wilke.¹ Reaction between methacrylic ester and butadiene has also given evidence for involvement of the nickel atom in the hydrogen-transfer process in that 1,*trans*-5,10-undecatriene-2-carboxylic ester is formed rather than the 2,5,10-triene.¹ Further reaction of the product with the C_3 nickel intermediate (**7**) also occurs to yield a nonadecapentaene derivative.

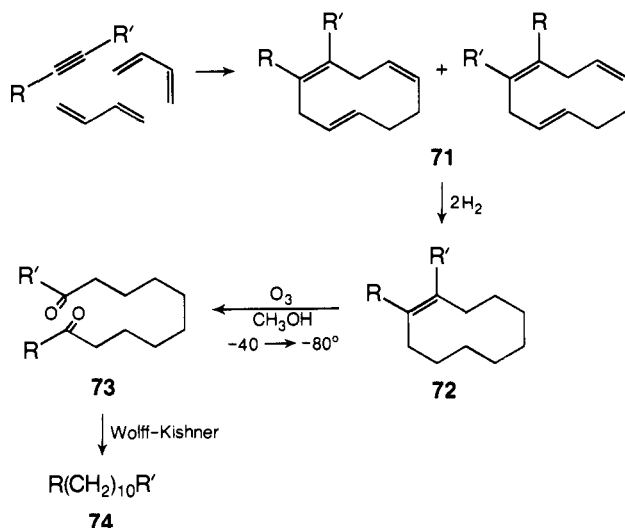
Codimerization of other substituted 1,3-dienes and 1,3-butadiene has also been shown to lead to acyclic derivatives if ethylene is added to the reaction. Formation of **70** in a yield of over 80% from 1-carbomethoxy-1,3-pentadiene, 1,3-butadiene, and ethylene in the presence of zerovalent nickel has been suggested to implicate the intermediate **69**.¹



Cooligomerization of ethylene and butadiene catalyzed by a mixture of nickel chloride, triethylaluminum, and di(tertiary phosphine) has been found to be extremely sensitive to the structure and concentration of the di(tertiary phosphine).^{147,148} With 1,2-bis(diphenylphosphino)ethane in toluene at 110° the main product was 1,4,9-decatriene in ca. 30% yield when the mole ratio of phosphine to nickel chloride was less than unity. Above unity, 1,4-hexadiene was produced almost exclusively in similar yields, but the reaction was almost completely stopped at a mole ratio of 3. While 1,2-bis(diphenylphosphino)ethane showed a similar behavior, bis(diphenylphosphino)methane showed different characteristics. With a phosphine:nickel chloride mole ratio of less than 2, the main product was 1,4,9-decatriene with some 1,4,8-decatriene; no selectivity was found with triphenylphosphine. In the series of ligands $Ph_2P(CH_2)_nPPh_2$, selectivity for 1,4,9-decatriene was high when $n = 1$ or 3.

(147) Y. Inoue, T. Kagawa, and H. Hashimoto, *Tetrahedron Lett.*, 1099 (1970).

SCHEME IX



This work illustrates that operation of a bisphosphine as a bidentate ligand is controlled by the size of ring formed when both phosphines donate electrons to the metal atom.

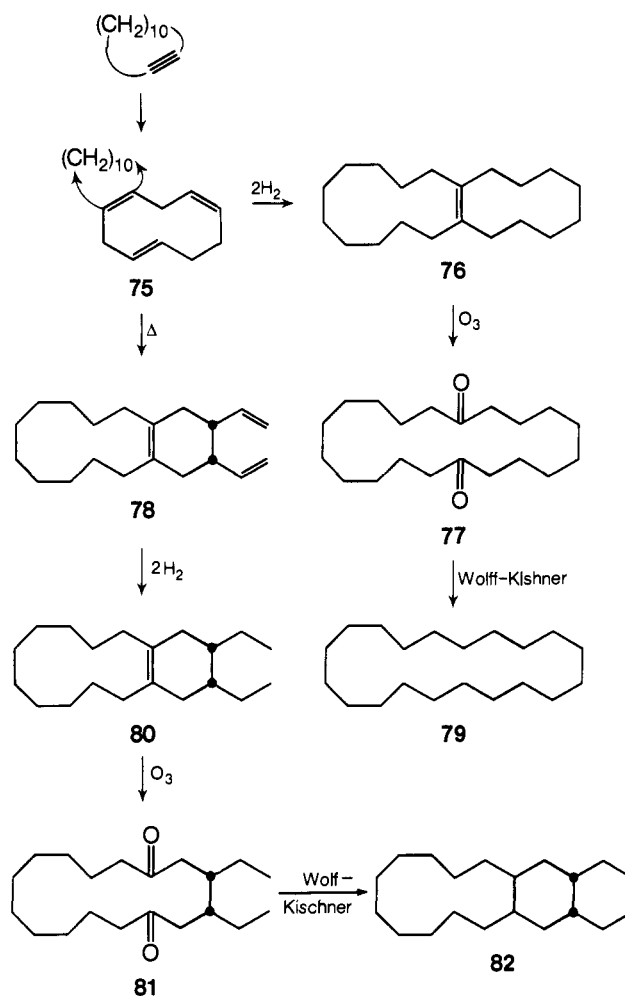
2. Acetylenes

These reactions have been developed to provide probably the best route to 1,2-disubstituted cyclodecatrienes. Butadiene and 2-butyne (10:1 ratio) undergo reaction in presence of a zerovalent nickel-ligand catalyst to form 4,5-dimethyl-*cis,cis,trans*-1,4,7-cyclodecatriene (**71**, $R = R' = CH_3$) in $>90\%$ yield; only a low conversion is found if a phosphorus ligand is absent.^{17,149,150} The reaction was favored by a good electron-donating ligand such as triphenylphosphine; this observation has been contrasted with formation of a ten-membered ring from butadiene and ethylene which is favored by good acceptor ligands such as triphenyl phosphite. Since ethylene is a better donor relative to butyne, it has been suggested that optimal conditions for both reactions require a similar electronic density around the nickel atom.¹ A step-wise mechanism rather than simultaneous formation of carbon-carbon bonds has been suggested. Heimbach has demonstrated that the products from reaction of butadiene with mono- and disubstituted acetylenes can be employed as valuable starting materials, **72-74**¹⁵⁰ (Scheme IX). In a similar way cyclodecyne reacts with butadiene in the presence of catalysts containing zerovalent nickel to give **75** in 95% yield, and similar conversions to those described above lead to products with large rings, **76-82**¹⁵¹ (Scheme X). With cyclotetradecadiyne a bicyclic hydrocarbon **83** (55%) and tricyclic hydrocarbons **84** and **85** (40% combined) were formed¹⁵¹ (Scheme XI).

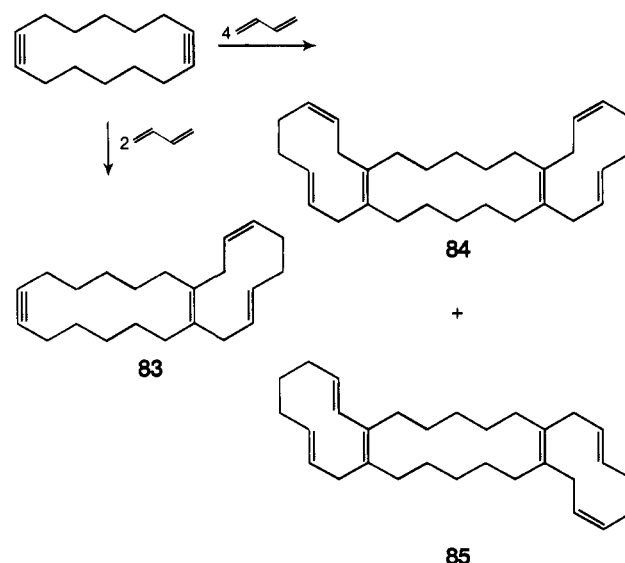
Reactions with other substituted alkynes have been studied and ten-membered rings (**86**) together with the mixed oligomers **87** and **88** formed¹⁵² (Scheme XII). At higher alkyne concentration the 12-membered rings **88** and aromatic compound **89** can be obtained in larger

(148) Y. Inoue, T. Kagawa, Y. Uchida, and H. Hashimoto, *Bull. Chem. Soc. Jap.*, **45**, 1996 (1972).
 (149) W. Brenner, P. Heimbach, and G. Wilke, *Justus Liebigs Ann. Chem.*, **727**, 194 (1969).
 (150) P. Heimbach, *Angew. Chem., Int. Ed. Engl.*, **5**, 961 (1966).
 (151) P. Heimbach and W. Brenner, *Angew. Chem., Int. Ed. Engl.*, **5**, 961 (1966).
 (152) W. Brenner, P. Heimbach, K.-J. Ploner, and F. Thomel, *Angew. Chem., Int. Ed. Engl.*, **8**, 753 (1969).

SCHEME X

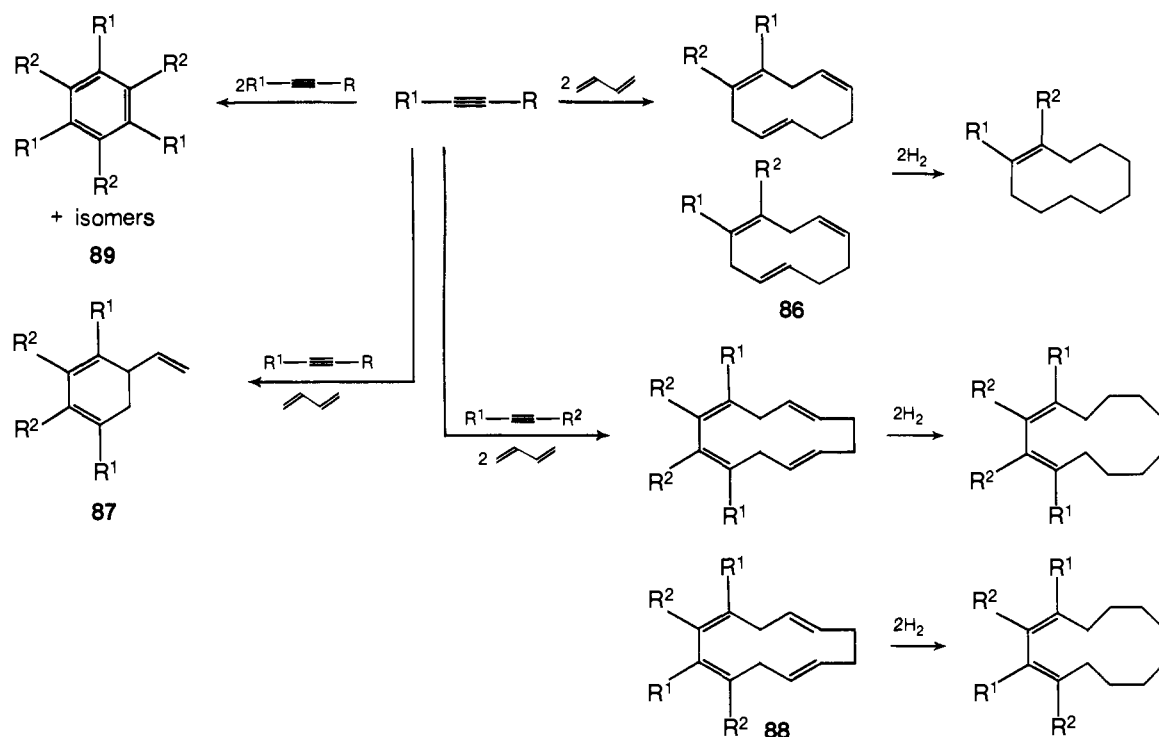


SCHEME XI



yields. The nature of the products is affected by the substituents on the triple bond (Table VI) and also by the ligand used. With 2-butyne, a larger amount of the 12-membered ring is formed if triphenyl phosphite is added rather than triphenylphosphine. Two of the three isomeric 12-membered ring compounds were formed on reaction with 1-methoxy-2-pentene, and reaction with phenylacetylene leads to a 1,3-cyclohexadiene derivative in about 25% yield.

SCHEME XII



Butadiene reacts with alkyl- or aryl-substituted acetylenecarboxylic esters in the presence of a nickel-ligand catalyst to give substituted 5-vinylcyclohexa-1,3-dienes in yields between 75 and 90%.¹⁵³ Tri- and tetra-substituted aromatic compounds have been prepared in high yields from the products of reaction of substituted alkynes and butadiene¹⁵⁴ by conversion to 1,2-disubstituted *cis*-4,5-divinylcyclohexenes followed by isomerization by potassium *tert*-butoxide in dimethyl sulfoxide.

5-Vinylcyclohexa-1,3-diene was found to be the major product (60% yield) on cooligomerization of acetylene and butadiene in the presence of nickel(0)-tri-*n*-alkylphosphine complexes.¹⁵⁵ The major by-product was benzene in about 20% yield with small amounts of 1,3,6-cyclooctatriene, styrene, 4-vinylcyclohexene, and 1,5-cyclooctadiene. The highest selectivity for 5-vinylcyclohexa-1,3-diene formation was found with phosphine:nickel ratios of between 1:1 and 4:1.

3. Active Hydrogen Compounds

Reactions of active hydrogen compounds with 1,3-butadiene have been reported with catalysis by both nickel and palladium complexes. Palladium(0) complexes have been shown to catalyze the reaction of butadiene with alcohols,^{60,61,156-158} amines,^{157,158} carboxylic acids,^{60,157-161} and active methylene and methyne compounds.¹⁶²⁻¹⁶⁶

(153) P. Heimbach, K.-J. Ploner, and F. Thomel, *Angew. Chem., Int. Ed. Engl.*, **10**, 276 (1971).

(154) P. Heimbach and R. Schimpf, *Angew. Chem., Int. Ed. Engl.*, **7**, 727 (1968).

(155) D. R. Fahey, *J. Org. Chem.*, **37**, 4471 (1972).

(156) E. J. Smutny, U. S. Patent 3,499,402.

(157) S. Takahashi, T. Shibano, and N. Hagihara, *Bull. Chem. Soc. Jap.*, **41**, 454 (1968).

(158) Japan Synthetic Rubber Co., Ltd., British Patent 1,178,812.

(159) W. E. Walker, R. M. Manyik, K. E. Atkins, and M. L. Farmer, *Tetrahedron Lett.*, 3817 (1970).

(160) E. J. Smutny, U. S. Patent 3,407,224.

(161) T. M. Shryne, U. S. Patent 3,562,314.

TABLE VI. Reaction of Alkynes with Butadiene Catalyzed by Nickel(0)-Triphenylphosphine¹⁵²

Alkyne	Product	Yield, %
1-4-Dimethoxy-2-butyne	77, $R_1 = R_2 = CH_2OCH_3$	30
	78	38
1-Methoxy-2-pentyne	77, $R_1 = CH_2OCH_3$; $R_2 = CH_2CH_3$	60
	78	29
2-Butyne	76, $R_1 = R_2 = CH_3$	>90
	78	≈ 2

Treatment of phenol with butadiene at 100° in the presence of a catalyst comprising palladium dichloride and sodium phenoxide gave 96% conversion of phenol to 1-phenoxy-2,7-octadiene (90) (95%) and 3-phenoxy-1,7-octadiene (91) (5%)^{60,166,167} (Scheme XIII). The reaction can be extended to other palladium catalysts (e.g., π -allylpalladium chloride or bis(benzonitrile)palladium chloride with sodium phenoxide) and phenols (*p*-chloro-, *p*-methoxy-, 2,6-dimethyl-, 2,4-dichloro-, etc.) with yields between 50 and 100% and achieving greatest success with butadiene in excess (phenol:butadiene, 1:4). It was noted that addition of triphenylphosphine to the reaction mixture, prior to distillation at reduced pressure, caused the conversion of phenoxyoctadiene to 1,3,7-octatriene

(162) G. Hata, K. Takahashi, and A. Miyake, *Chem. Ind. (London)*, 1836 (1969).

(163) G. Hata, K. Takahashi, and A. Miyake, *J. Org. Chem.*, **36**, 2116 (1971).

(164) G. Hata, K. Takahashi, and A. Miyake, French Patent 1,583,249.

(165) S. Hattori, H. Munakata, T. Suzuki, and N. Imaki, Netherlands Patent 6,816,008.

(166) E. J. Smutny, H. Chung, K. C. Dewhirst, W. Keim, T. M. Shryne, and H. E. Thyret, Preprints of the Symposium on Homogenous Catalytic Reactions Involving Palladium, 1969, No. B-100.

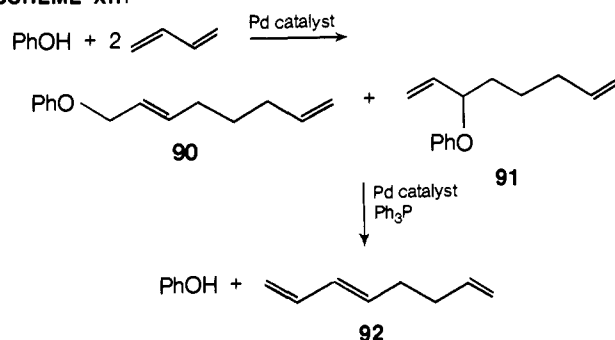
(167) E. J. Smutny, H. Chung, K. C. Dewhirst, W. Keim, T. M. Shryne, and H. E. Thyret, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **14**, B100 (1969).

TABLE VII. Reaction of Butadiene with Alcohols¹⁵⁷

Catalyst ^a	Solvent	Temp, °C	Time, hr	Yield, % ^d		
				1-RO-OD	3-RO-OD	OT
(Ph ₃ P) ₂ Pd(C ₄ H ₂ O ₃)	MeOH	40	2	62	1	0
	MeOH	70	1	85	5	3
	MeOH	90	1	73	6	4
	EtOH	110–115	1	33		50
	EtOH	110–115	6	35		49
	EtOH ^b	110	3	68		25
(Ph ₃ P) ₄ Pd	Pr ⁱ OH ^c	110	4			75
	MeOH	40	2	87	7	1
	MeOH	70	1	90	8	1
	MeOH	90	1	86	9	2
	EtOH	110–115	6	62		27
(Ph ₃ P) ₂ Pd(C ₆ H ₄ O ₂)	Pr ⁱ OH	112–116	7.5			11
	MeOH	70	1	85	2	1
	EtOH	110	1.5	39		48
	Pr ⁱ OH	110–114 ^c	4.5			77

^a Catalyst, 0.1 mmol; MeOH, 20 ml; butadiene, 13 g. ^b EtOH, 50 ml; butadiene, 6.5 g. ^c A small amount of a butadiene dimer-isopropyl alcohol adduct was detected by gas chromatography. ^d 1-RO-OD, 1-alkoxy-2,7-octadiene; 3-RO-OD, 3-alkoxy-2,7-octadiene; OT, 1,3,7-octatriene.

SCHEME XIII



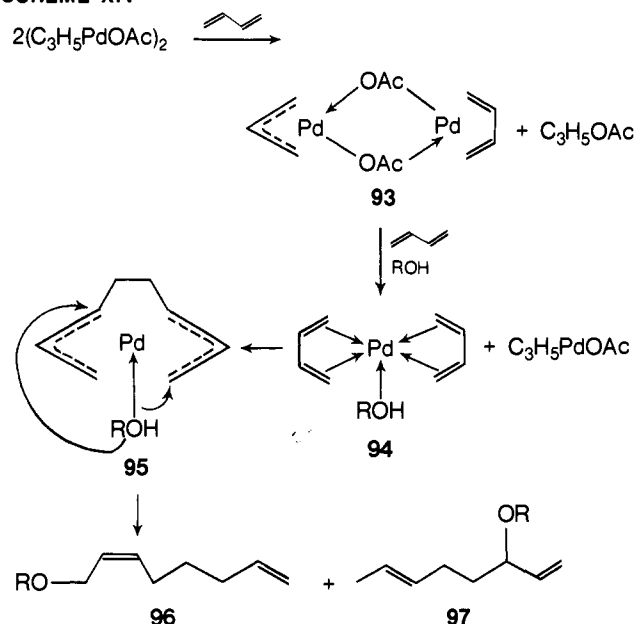
(92) and phenol. This phenomenon was also noted with the corresponding methoxy adducts.¹⁶⁸

Octadienyl, dodecatrienyl, hexadecatrienyl, and higher methyl ethers were obtained catalytically on interacting butadiene at atmospheric or super atmospheric pressure and room temperature with a methanolic solution of π -allylpalladium acetate.¹⁶⁸ The octadienyl methyl ether fraction consisted of two components, *viz.*, 1-methoxy-2,7-octadiene (96) (90%) and 3-methoxy-1,6-octadiene (97) (10%). A mechanism involving the orange complex 93 was considered to be involved (Scheme XIV). The complex of empirical formula C₉H₁₄Pd₂O₂ was too unstable in solution for molecular weight determination and nmr analysis, its structure being assigned on the basis of its infrared spectrum and chemical reactions. Nucleophilic attack of the alkoxy group at the 1 or 3 position of one of the π -allyl groups coordinated to palladium (95) could lead to the observed products 96 and 97.

It has been previously mentioned that palladium-phosphine complexes catalyze the linear dimerization of butadiene.⁶⁰ Dimerization of butadiene with bis(triphenylphosphine) (maleic anhydride)palladium in aprotic solvents such as benzene, tetrahydrofuran, and acetone (100–120°) gave 1,3,7-octatriene selectively in good yields, accompanied by small amounts of vinylcyclohexene formed probably by thermal dimerization. In contrast, the dimerization in alcohols proceeds smoothly even at lower temperatures (40–100°C) to give 1-alkoxy-2,7-octadiene and/or 1,3,7-octatriene, depending on the nature of the

(168) D. Medema and R. Van Helden, *Recl. Trav. Chim. Pays-Bas*, 90, 330 (1971).

SCHEME XIV



alcohols employed¹⁵⁷ (Table VII). The alkoxyoctadienes are not derived from reaction of octatriene with alcohol, as the latter two compounds were found not to react under the same conditions employed in the dimerization reaction of butadiene. The ratio of ethoxyoctadiene to octatriene was independent of reaction time during the bis-(triphenylphosphine)(maleic anhydride)palladium catalyzed dimerization of butadiene in absolute ethanol.

The more acidic phenol reacts smoothly with butadiene at 80° in a benzene solution of bis(triphenylphosphine)-(maleic anhydride)palladium catalyst to give a 57% conversion to 1-phenoxy-2,7-octadiene (90) (78%) and 3-phenoxy-1,7-octadiene (91) (22%). Additional low-boiling butadiene dimers were not completely characterized. This ratio of phenoxyoctadienes differs markedly from that previously mentioned involving a palladium chloride and sodium phenoxide catalyst system.^{61,166}

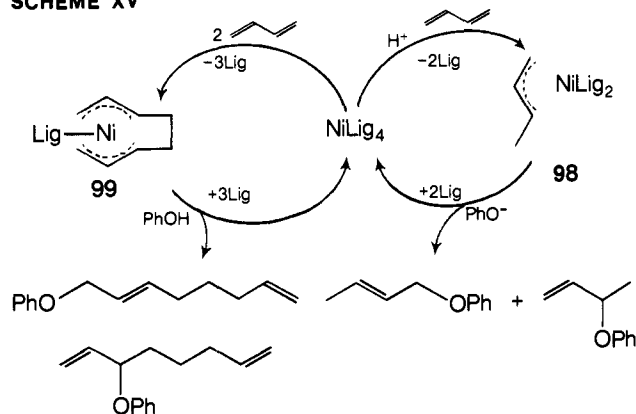
A mixture of 3-phenoxy-1-butene, 1-phenoxy-2-butene, 3-phenoxy-1,7-octadiene, and 1-phenoxy-2,7-octadiene has been obtained from a nickel(0) and organophosphorus catalyzed reaction of phenol and butadiene.¹⁶⁹ For-

TABLE VIII. Synthesis of Octadienols from Butadiene and Water^a

Solvent (mol)	Temp, °C	Time, hr	Products, % yield			
			100	101	102	103
Bu ^t OH (2.0)	85	4	65	19	4	4
CH ₃ COCH ₃ (1.8)	90	2	69	7	13	10
CH ₃ CN (3.5)	82	3	56	4	6	6

^a 1.0 mol of butadiene, 0.5 mol of CO₂, 2.0 mol of H₂O, 2 mmol of Pd(acac)₂, and 6 mmol of PPh₃.

SCHEME XV



mation of phenoxybutenes was favored by electron-donating ligands, excess ligand, high phenol concentration, and low conversions. It was suggested that phenoxybutenes and phenoxyoctadienes were formed in separate but interrelated pathways (Scheme XV) involving the π -allyl intermediate **99**. Reaction of **98** with phenoxide anion leads to phenoxybutene regenerating the nickel(0) catalyst for further protonation and reaction with butadiene. The alternative catalytic cycle leads to phenoxyoctadiene formation.

Reaction between isoprene and phenol in the presence of nickelocene and phenylmagnesium bromide has also been studied; a mixture of 2-(3-methyl-2-buten-1-yl)phenol, 4-(3-methyl-2-buten-1-yl)phenol, 2,2-dimethylchroman, and 2,2-dimethyl-6-(3-methyl-2-buten-1-yl)chroman was formed.¹⁷⁰

Water has also been shown to react catalytically with butadiene, yielding 2,7-octadien-1-ol (**100**) as the major product, when an *in situ* palladium complex system was employed in the presence of carbon dioxide¹⁷¹ (Scheme XVI). In the absence of carbon dioxide the reaction was very slow and yielded only octatrienes, although a small amount of octadienols may be obtained by inclusion of solvents such as *tert*-butyl alcohol, acetone, or acetonitrile. Table VIII shows the high yields of octadienols obtained in the carbon dioxide assisted reaction in various solvents using catalysts formed *in situ*.

Preformed palladium complexes such as tetrakis(triphenylphosphine)palladium and bis(triphenylphosphine)palladium carbonate are also effective catalysts for this reaction. Reactions in *tert*-butyl alcohol, acetone, and acetonitrile differed markedly when higher triphenylphosphine:palladium acetylacetonate ratios were used for the *in situ* formation of the catalyst (Table IX). This was attributed to the ligand properties of the solvents. They are

(169) F. J. Weigert and W. C. Drinkard, personal communication.

(170) K. Suga, S. Watanabe, M. Kikuchi, and K. Hijikata, *J. Appl. Chem.*, **20**, 175 (1970).

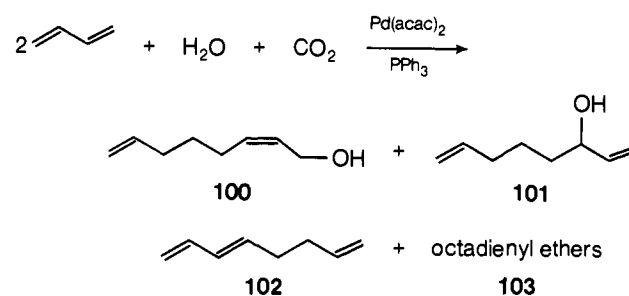
(171) K. E. Atkins, W. E. Walker, and R. M. Manyik, *Chem. Commun.*, 330 (1971).

TABLE IX. Octadienols: Effects of High P:Pd Ratios in Various Solvents

Solvent ^a	Products, % yield		
	100	101	102
Bu ^t OH		Traces	
CH ₃ COCH ₃	18	16	13
CH ₃ CN	45	6	2

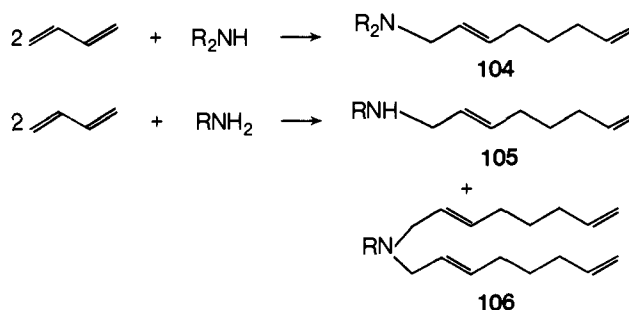
^a Solvent, 180 ml, 1.1 mol; CO₂, 0.16 mol; H₂O, 0.9 mol; Pd(acac)₂, 2.3 mmol; PPh₃, 13.0 mmol, 75° for 4 hr.

SCHEME XVI



all weak ligands compared to triphenylphosphine, but the stronger ones, acetonitrile and acetone, can by means of mass action compete with triphenylphosphine for the palladium. In effect, this lowers the "effective concentration" of triphenylphosphine. Of the three solvents, *tert*-butyl alcohol is the weakest ligand, and hence the reaction rate is slowest, as triphenylphosphine exerts its maximum effective concentration. The role of carbon dioxide is not clear, but a recent report⁷¹ regarding a novel effect of carbon dioxide on transition metal catalyzed dimerizations of butadiene suggests that the effect could be directly on the catalyst. The fact that even much lower levels of carbon dioxide enhance the reaction rate supports this possibility rather than the intermediacy of carbonate esters.

Tertiary phosphine complexes of palladium(0) also catalyze formation of butadiene dimer adducts with amines.¹⁵⁷ The reactions of butadiene with secondary amines such as morpholine, piperidine, and diisopropylamine in the presence or absence of solvent afforded **104** while reactions with primary amines such as aniline and *n*-butylamine afforded a mixture of **105** and **106**. The



use of amines such as morpholine and aniline gave high conversions to amine adducts under mild reaction conditions, whereas a weak base such as carbazole gave a low rate of conversion under more vigorous conditions. 2-Pyrrolidone and acetamide gave no amine adducts yielding only 1,3,7-octatriene (Table X). Tetrakis(triphenylphosphine)palladium was less effective as a catalyst for this reaction than was bis(triphenylphosphine)(maleic anhydride)palladium. The reactivities of aniline deriv-

TABLE X. Palladium Catalyzed Alkylation of Amines with Butadiene

Amine (mmol)	Solvent ^a	Temp, °C	Time, hr	Yield, %		
				1,3,7-Octatriene	R ₂ N(C ₈ H ₁₃)	RN(C ₈ H ₁₃) ₂
Morpholine (230)	None ^b	80	1	0	90	
Piperidine (200)	None ^b	110	5	0	60	
Diisopropylamine (140)	None	100–100	5	34	51	
Morpholine (160)	Acetone	80–90	1	0	97	
Diisopropylamine (160)	Acetone	100–104	3	Trace	69	
Carbazole (120)	Acetone	120–125	5	Trace	57	
2-Pyrrolidone (210)	None ^b	110–115	6	64	0	
Acetamide (160)	Acetone	114–116	5	64	0	
Aniline (160)	Acetone	100–104	0.5	0	60	25
Aniline ^c (160)	Acetone	113–115	2	8	44	23
<i>n</i> -Butylamine (200)	None ^b	90–98	8	Trace	29	42

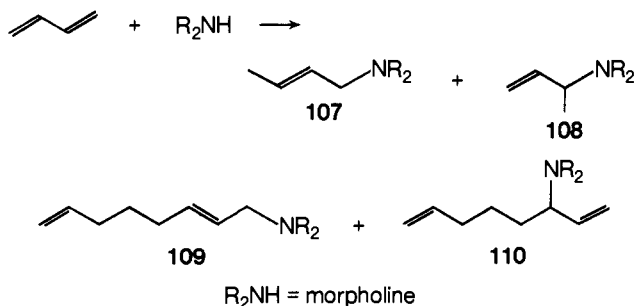
^a 20 ml. ^b Catalyst, 0.3 mmol. ^c Pd(PH₃P)₄ catalyst. Catalyst Pd(PH₃P)₂(C₄H₂O₃), 0.2 mmol; butadiene, 13 g, 240 mmol.

TABLE XI. Alkylation of Substituted Anilines

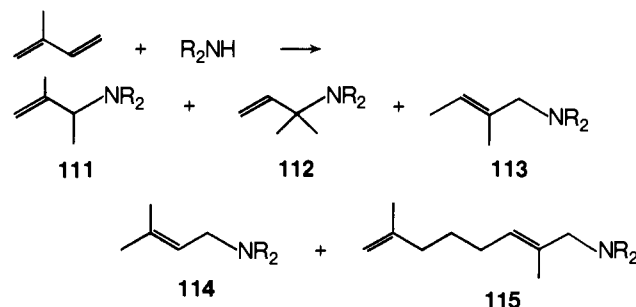
Amine	pK _a	Temp, °C	Time, hr	% yield	
				(RNH-C ₈ H ₁₃)	RN-C ₈ H ₁₃) ₂
<i>p</i> -Methoxyaniline	5.29	90	0.5	54	33
<i>p</i> -Methylaniline	5.07	90–95	0.5	48	36
	4.58	90–95	0.5	46	24
<i>p</i> -Chloroaniline	3.81	90–95	0.5	58	0
<i>p</i> -Acetoxyaniline	2.47	101–104	2.0	48	0

atives in terms of the dimerization rate of butadiene were found to increase in the order *p*-acetoxyaniline < *p*-chloroaniline < *p*-methylaniline < *p*-methoxyaniline (Table XI). This suggests a possible relationship between reactivity and basicity of the amine in these reactions.

Octadienyl- and butenyl-substituted amines have also been prepared by reaction of primary and secondary amines with butadiene catalyzed by nickel(0) complexes.¹⁷² A catalyst system of nickel acetylacetonate, phenyldiisopropoxyphosphine, and a trace of borohydride was employed; similar conditions have been used to catalyze reaction between methanol and butadiene.¹⁷³ Reaction of morpholine with butadiene gives total conversion to a mixture: **107** (32%), **108** (15%), **109** (51%), and **110** (2%). Other reactions with secondary and primary



amines and substituted 1,3-dienes have been studied. With isoprene and morpholine, a 47% conversion was found to a mixture comprising **111** (10%), **112** (14%), **113** (54%), **114** (5%), and **115** (17%). These reactions can again be interpreted as involving π -allyl and bis- π -allyl intermediates and were considered to depend upon the ability of the alkoxyphosphine to reduce the nickel(II)



salt to a nickel(0) species.¹⁷⁴ Since borohydride is only required for reactions with primary amines and secondary amines similar to morpholine, its role appears to be either the breakdown or prevention of complex formation between certain amines and the nickel atom.¹⁷⁵ Other nickel salts such as the bromide, chloride, and acetate do not require the presence of borohydride, and it was suggested that this was attributable to a decreased tendency for amine-complex formation with these salts. A detailed study of the reaction of diethylamine and butadiene, catalyzed by nickel salts and a range of phosphines, has been made.¹⁷⁶ Other phenyldialkoxyphosphines also exhibit catalytic activity in these reactions, but it was suggested that the particular reactivity associated with these complexes involving secondary alcohols is the result of an interaction between the metal and the secondary hydrogen atom of the alkoxy group.

Similar reactions between amines and butadienes have been reported with rhodium trichloride as catalyst and striking effects of added ligands observed.¹⁷⁷ In the presence of rhodium trichloride trihydrate in ethanol at 75% for 15 hr, morpholine and butadiene are converted (85%) to a mixture of **108** (70%) and **107** (30%). Inclusion of triphenylphosphine in the reaction (1:1 with respect to rhodium trichloride trihydrate) gave an 83% conversion to a mixture containing not only **108** (26%) and **107** (11.5%) but also **109** (57.6%) and **110** (5%), and a similar effect was observed with other amines. Inclusion of phosphine appears to encourage formation of octadienyl adducts while also increasing the efficiency of the process. A further increase in triphenylphosphine concentration relative to rhodium trichloride produced a decrease in amount of octadienyl adduct obtained. Formation of

(174) A. A. Orio, B. B. Chastain, and H. B. Gray, *Inorg. Chem. Acta*, **3**, 8 (1969).

(175) R. Baker, A. H. Cook, and T. N. Smith, *Tetrahedron Lett.*, 503 (1973).

(176) D. Rose, *Tetrahedron Lett.*, 4197 (1972).

(177) R. Baker and D. E. Halliday, *Tetrahedron Lett.*, 2773 (1972).

(172) R. Baker, D. E. Halliday, and T. N. Smith, *Chem. Commun.*, 1583 (1971).

(173) T. C. Shields and W. E. Walker, *Chem. Commun.*, 193 (1971).

this adduct is favored by use of preformed rhodium(I) complexes such as $(\text{Ph}_3\text{P})_3\text{RhCl}$ and $(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{Cl}$. Intermediates **116** and **117** were suggested to be involved in the production of the two types of products. Formation of **117** requires the presence of a stabilizing ligand, but a large increase in amount of phosphine ligand present makes formation of **117** less likely owing to competition between phosphine and butadiene for the available coordination sites. Reaction of morpholine with other 1,3-dienes decreased in the order butadiene > piperylene > isoprene.



A novel synthesis of long chain amines by the palladium catalyzed telomerization of butadiene with aqueous ammonia, yielding tri-2,7-octadienylamine as major product in high yield, has also been reported. A small amount of diocta-2,7-dienylamine was also formed.¹⁷⁸

The reaction of butadiene with carboxylic acids does not generally give high yields of octadienyl esters in the presence of either tertiary phosphine complexes of palladium(0)¹⁵⁷ or a palladium dichloride-sodium phenoxide catalyst system.^{157,160} Isoprene reacts with acetic acid in the presence of sodium acetate with a catalyst system of palladium dichloride and triphenylphosphine to give a mixture of isoprene monomer acetates and isoprene dimer acetates in low yield.¹⁷⁹ Use of polar solvents favors formation of isoprene dimer acetates over that of isoprene monomer adducts.

Formation of octadienyl acetates has also been reported from reaction of butadiene and palladium(II) salts in acetic acid; substantial amounts of butadiene dimer are also formed.¹⁸⁰ A 21% yield of a mixture of C_{10} terpene acetates has been obtained by reaction of myrcene (50% conversion) with acetic acid in the presence of sodium acetate, triphenylphosphine, and palladium dichloride in benzene solution.¹⁸¹

The C_{10} acetates consisted of a mixture of linalyl acetate (5%), 2-acetoxy-3-methylene-7-methyloct-6-ene (11%), 3-acetoxy-3,7-dimethyl-2,6-octadiene (5%), neryl acetate (31%), geranyl acetate (36%), and other unidentified acetates (12%).

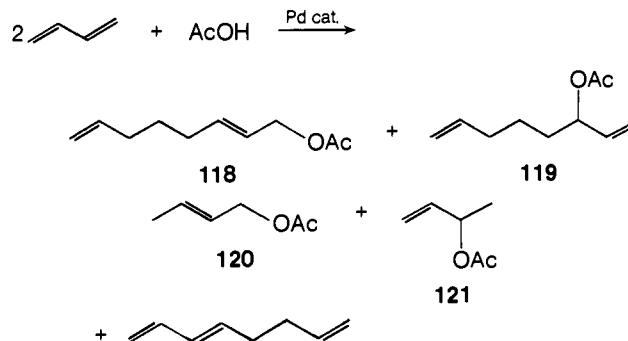
A facile synthesis of octadienyl esters resulted from a recent study of ligand effects on the palladium-catalyzed telomerization of butadiene with acetic acid.¹⁵⁹ In the presence of molar quantities of tertiary amines, a palladium acetylacetonate and triphenylphosphine (1:1) catalyst afforded complete conversion of butadiene and acetic acid to a mixture of 1-acetoxy-2,7-octadiene (**118**, 71%), 3-acetoxy-1,7-octadiene (**119**, 28%), and 1,3,7-octatriene (8%) after 2 hr at 90°. A poorer conversion of acetic acid and a substantial amount of butenyl adducts **120** and **121** resulted from omission of tertiary amine. The effect of the triphenylphosphine:palladium ratio on the reaction was investigated using 2-(*N,N*-diethylamino)ethanol as solvent. Varying the triphenylphosphine:palladium ratio from 0.5:1 to 4:1 had little influence on the rate of reaction,

(178) T. Mitsuyasu, M. Hara, and T. Tsuji, *Chem. Commun.*, 345 (1971).

(179) K. Suga, S. Watanabe, and K. Hijikata, *Aust. J. Chem.*, **24**, 197 (1971).

(180) T. Arakawa and H. Miyake, *Kogyo Kagaku Zasshi*, **74**, 1143 (1971).

(181) K. Suga, S. Watanabe, and K. Hijikata, *Chem. Ind. (London)*, 33 (1971).



but the ratio of **118**:**119** in the reaction mixture changed from 83:17 to 68:32. This variation was shown to be due to the formation of **118** in a kinetically controlled reaction followed by isomerization of **118** to **119**. Analysis of the reaction mixture with the triphenylphosphine and palladium complex as catalyst in tertiary amine solvent showed that the ratio of **118** to **119** fell as the reaction progressed. In addition, the equilibrium value of 70% of **118** at 100° was achieved in 0.5 hr starting from either pure **118** or pure **119**. Triphenyl phosphite containing catalysts took 24 hr to reach the equilibrium value, and hence a higher **118**:**119** ratio was observed after 0.5 hr at 50°, using equimolar quantities of triphenyl phosphite and palladium acetylacetonate as the catalyst system. When the reaction was carried out in a primary or secondary amine, only traces of octadienyl acetates were observed, and the corresponding octadienyl amines were obtained in high yield. This was attributed to a rapid reaction of amine with octadienyl acetate as it was formed, rather than to direct telomerization of butadiene with amine. The relatively low conversion of primary and secondary amines to the corresponding octadienylamine adducts in the absence of acetic acid lends some support to such an explanation.

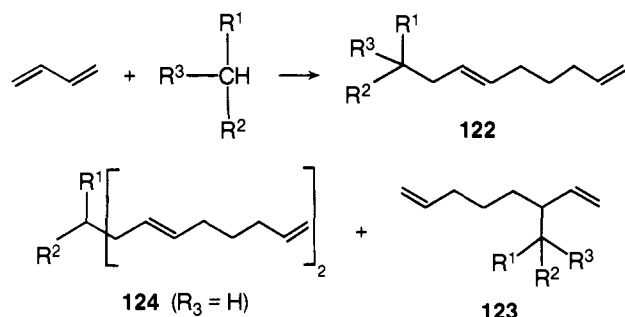
A different reaction course is found in reaction of butadiene in the presence of formic acid.¹⁸² 1,6-Octadiene was formed in 79% yield when a mixture of butadiene, formic acid, triethylamine, and diacetatopalladium(II) was heated in an autoclave at 50°. Metal-hydrido species were considered to be responsible for the reduction step. Use of platinum salts gave both 1,7-octadiene and 1,6-octadiene, and the ratio of these olefins varied with the phosphine when palladium salts and phosphines were employed.

In the presence of palladium and platinum catalysts, 1,3-dienes react with active methylene and methyne compounds such as β -keto esters, β -diketones, dialkyl malonates, α -formyl ketones and esters, α -cyano and α -nitro esters, and ethyl phenylsulfonylacetate to form the corresponding 2,7-alkadienyl derivatives.^{162,163}

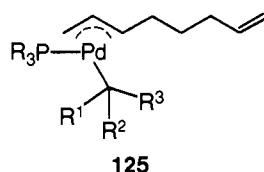
In the palladium-catalyzed reactions of active methylene compounds with 1,3-butadiene, the 1:2 adduct (**122**) was the major product and small amounts of the branched 1:2 adduct were also produced. When $\text{R}_3 = \text{H}$, small amounts of **124** were also formed. For example, with ethyl acetoacetate and 1,3-butadiene in the presence of bis(triphenylphosphine)palladium dichloride and sodium phenoxide, **122** and **124** were formed in yields of 61 and 7%, respectively, and with acetylacetone the corresponding yields were 62 and 18%. Addition of isoprene to ethyl acetoacetate gave 2,7-dimethyl-2,7-octadienyl derivatives derived from tail-to-tail dimerization of isoprene selectively and in a 95% yield; the product was a

(182) S. Gardner and D. Wright, *Tetrahedron Lett.*, 163 (1972).

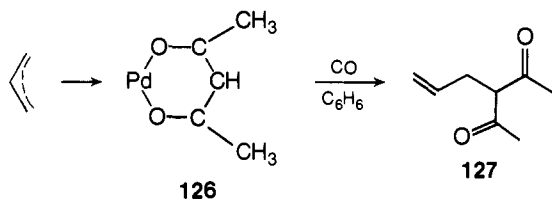
mixture of the analogs of **122** and **124** in a ratio of 70:30.



In contrast the reaction of 1,3-pentadiene afforded a head-to-tail adduct in a 32% yield, but the reactivity of 2,3-dimethyl-1,3-butadiene was extremely low. In the platinum-catalyzed reaction of butadiene with active methylene compounds, the ratio of branched 1:2 adduct **123** to all adducts was larger than that observed in the palladium catalyzed reaction, and 1:1 and 1:3 adducts were isolated as by-products together with **122**, **123**, and **124**. Although β -keto esters, β -diketones, α -formyl ketones, and α -formyl esters are in equilibrium between keto and enol forms, no products were observed resulting from reaction of the hydroxy groups of the enol forms with 1,3-butadiene. Addition of 1,3-butadiene to the carbon atom of the active methylene and methyne compounds occurred selectively. 1,3-Cyclohexadiene, dialkyl malonates, and malonitrile react smoothly with butadiene indicating that the chelation of the active methylene or methyne compounds to palladium atom is not requisite for the reaction. This lends support to the hypothesis in which active methylene and methyne compounds act as unidentate ligands rather than bidentate ligands in the palladium-catalyzed dimerization of butadiene. The fact that tertiary phosphine complexes of palladium(0) are active catalysts strongly suggests that the catalytic species must be derived from the complexes of palladium(0). A reaction intermediate **125**, involving a four-



coordinated palladium system derived from the tertiary phosphine complex of palladium(0) has been postulated. Coupling between the substituted allyl group and the other ligand would give the product and regenerate a tertiary phosphine complex of palladium(0). This possibility is enhanced by the reported ligand-ligand coupling in π -allylpalladium acetylacetonate (**126**) between the active methylene carbon of the acetylacetonate group and the π -allyl group in the presence of a donor molecule such as carbon monoxide; **127** is formed with subsequent precipitation of metallic palladium.¹⁸³

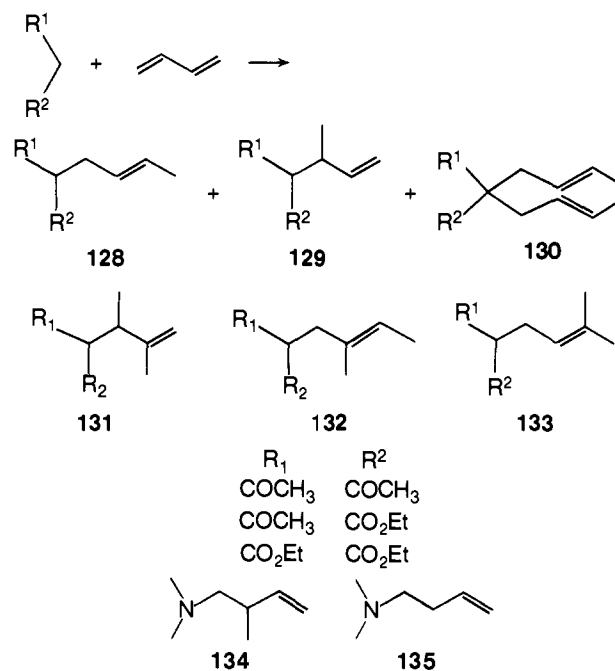


Adducts (1:1) are formed between 1,3-dienes and ac-

(183) Y. Takahashi, S. Sakai, and Y. Ishii, *Chem. Commun.*, 1092 (1967).

tive methylene compounds or primary and secondary amines when palladium-diphosphine complex catalysts are employed.¹⁸⁴

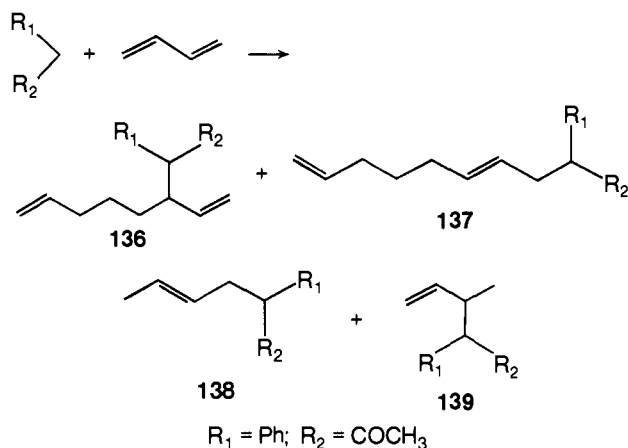
In the presence of $PdBr_2(Ph_2PCH_2CH_2PPh_2)_2$ and sodium phenoxide, acetylacetonate or ethyl acetoacetate and 1,3-butadiene gave yields of 70–80% of the adducts **128** and **129** with smaller amounts of the 1:2 adduct **130**. With phosphines $Ph_2P(CH_2)_n PPh_2$, 1:1 adducts were most favored when $n = 2$ or 3, but octadienyl derivatives were mainly formed when $n = 4$, and it is again observed that operation of the biphosphine as a bidentate ligand is dependent upon the size of ring formed on coordination with the metal atom. Isoprene reacts with acetylacetonate to give three kinds of 1:1 adduct (**131–133**) in a total yield of 70%, and reaction was also found with 1,3-pentadiene and 2,4-hexadiene. With amines and 1,3-butadiene, the 1:1 adducts **134** and **135** were found and the catalytic activity was remarkably enhanced by addition of a small amount of phenol. Again a correlation was found between amine basicity and reactivity. Reaction with morpholine ($pK = 9.61$) and aniline ($pK = 9.42$) gave 79 and 67% yields, respectively, whereas *n*-butylamine ($pK = 3.39$) and piperidine ($pK = 2.80$) gave 19 and 29% yields of 1:1 adducts.



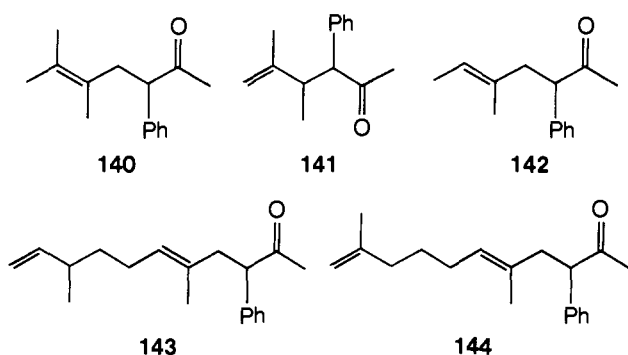
The nickel(II) salt and phenyldiisopropoxyphosphine system described previously has also been used to catalyze the reaction between active methylene compounds and butadiene.¹⁸⁵ At 75° for 16 hr, reaction between benzyl methyl ketone and butadiene gave a 93% conversion to a mixture of **136** (5%), **137** (81%), **138** (8%), and **139** (6%). Since a larger amount of catalyst was required for reaction with ethyl acetoacetate and diethyl malonate and no reaction was obtained with acetylacetonate, it was suggested that chelation effects were important in these reactions. Products were also obtained from benzyl methyl ketone and isoprene and 2,3-dimethylbutadiene, but the extent of reaction decreased in the order butadiene > isoprene > 2,3-dimethylbutadiene. The amount of butenyl derivatives increased with substitution on the

(184) K. Takahashi, A. Miyake, and G. Hata, *Bull. Chem. Soc. Jap.*, **45**, 1183 (1972); *Chem. Ind. (London)*, 488 (1971).

(185) R. Baker, D. E. Halliday, and T. N. Smith, *J. Organometal. Chem.*, **35**, C61 (1972).



diene; **140** was the major product obtained from 2,3-dimethylbutadiene and a mixture of **141** (21%), **142** (56%), **143** (4%), and **144** (19%) was obtained from isoprene.



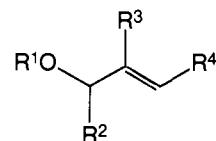
Hydrogens at the α carbon of nitroalkanes have also been reported to be replaced by 2,7-octadienyl groups on reaction with butadiene in the presence of a palladium acetylacetonate, triphenylphosphine, and sodium phenoxide catalyst system.¹⁷⁸

A good yield of an almost equal amount of 9-nitroun-deca-1,6-diene and 9-ethyl-9-nitro-1,6,11,16-heptadeca-tetraene was obtained from reaction of 1-nitropropane and 1,3-butadiene. The adducts can be readily reduced over Raney nickel catalyst to yield long-chain amines, which are important in that they have a primary amino group at the middle of the carbon chain, rather than at a terminal position.

An interesting feature of palladium-catalyzed reactions of butadiene with active hydrogen compounds is the possible interconversion of adducts. The octadienyl group of 2,7-octadienyl phenyl ether exchanges with a variety of active hydrogen compounds in the presence of palladium catalysts.¹⁸⁶

The reaction of methyl acetoacetate with octa-2,7-dienyl phenyl ether in the presence of bis(triphenylphosphine)-palladium dichloride and sodium phenoxide at 85° for 2 hr gave methyl 2-acetyldeca-4,9-dienoate and methyl 2-(octa-2,7-dienyl)-2-acetyldeca-4,9-dienoate in 84 and 7% yields, respectively. Further studies have shown that allylic compounds **145** react with active hydrogen compounds, such as phenols, alcohols, carboxylic acids, primary and secondary amines and active methylene compounds, to give allylic derivatives of the active hydrogen compounds by an intermolecular exchange of the allylic groups of **145**.¹⁸⁷ Allyl and substituted allyl ethers are

(186) G. Hata, K. Takahashi, and A. Miyake, *Chem. Commun.*, 1392 (1970).

**145**

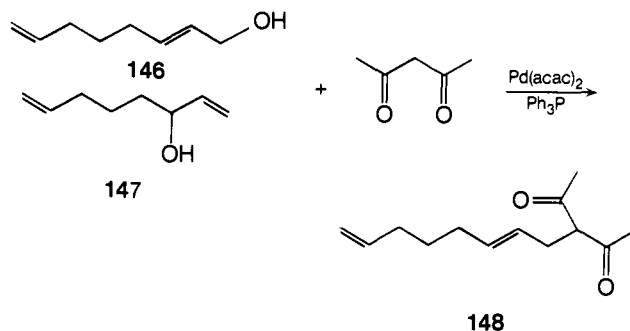
$R^1 = \text{Ph, Me, PhCH}_2, \text{MeCO}; R^3 = \text{H, Me}$

$R^2 = \text{H, Me, } \text{---}; R^4 = \text{H, Me, } \text{---}$

more reactive than the corresponding carboxylates. These exchange reactions are postulated to proceed via π -allylic intermediates, analogous to **125**, which would be derived from an oxidative addition of the allylic carbon-oxygen bonds to the palladium complexes. The existence of such an intermediate can also account for the degradation reaction of 1-phenoxy-2,7-octadiene to phenol and 1,3,7-octatriene.⁶¹

Independently it was found that allylic alcohols, esters, and amines react with active methylene compounds, such as acetylacetone, phenylacetone, and phenylacetonitrile, in the presence of catalytic amounts of a palladium-triphenylphosphine complex to give carbon-alkylated products in high yields.¹⁸⁸

Reaction of acetylacetone, allyl alcohol, palladium acetylacetonate, and triphenylphosphine at 85° for 3 hr gave 3-allylacetylacetone (70%) and 3,3-bisallylacetylacetone. 3-(2,7-Octadien-1-yl)acetylacetone (**148**) was obtained from reaction of acetylacetone with both 2,7-octadien-1-ol (**146**) and 1,7-octadien-3-ol (**147**). This



lends support to the possibility of a common intermediate, a palladium π -allyl complex, in the reaction of both alcohols with butadiene. Tertiary amines have a marked effect upon the reaction of allylic esters, which otherwise react more slowly than allylic alcohols with acetylacetone. This catalytic effect is not yet fully understood, but it is strongly suspected that the effect may be coupled with the ability of tertiary amines to act as ligands with palladium.

1-Trimethylsilyl-2,6-octadiene has been obtained by reaction of trimethylsilane and butadiene in the presence of bis(triphenylphosphine) (maleic anhydride)palladium in benzene.¹⁸⁹

4. Aldehydes and Isocyanates

Palladium complexes also catalyze the dimerization of butadiene in the presence of aldehydes yielding products which differ markedly from those previously discussed. Tetrakis(triphenylphosphine)palladium catalyzes the reaction of butadiene with formaldehyde under mild con-

(187) K. Takahashi, A. Miyake, and G. Hata, *Bull. Chem. Soc. Jap.*, **45**, 230 (1972).

(188) K. E. Atkins, W. E. Walker, and R. M. Manyik, *Tetrahedron Lett.*, 3821 (1970).

(189) S. Takahashi, T. Shibano, and N. Hagihara, *Chem. Commun.*, 161 (1969).

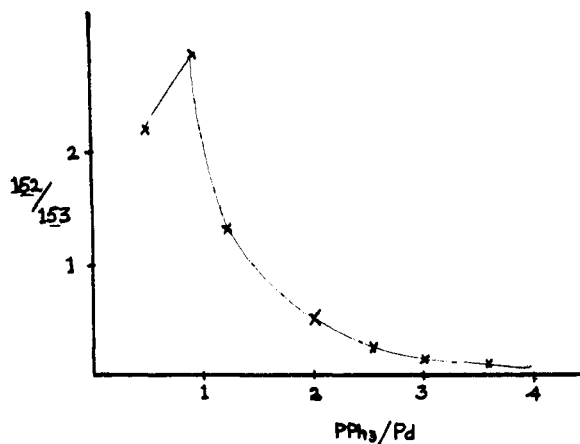
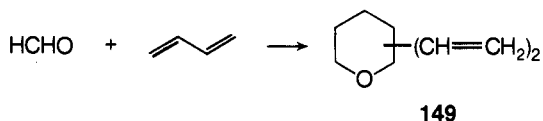
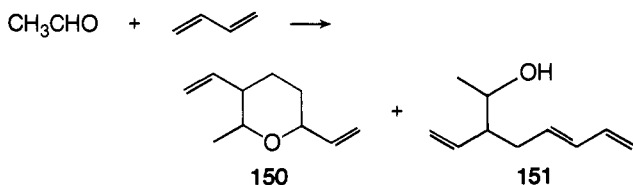


Figure 1.

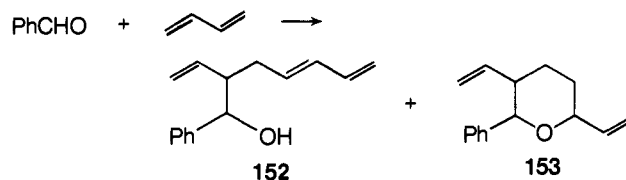
ditions (30–80°), producing a mixture of isomeric divinyl-tetrahydropyrans (**149**) in good yields (>65%) and selectivities (>95%) with traces of higher boiling compounds.¹⁹⁰



A similar reaction was obtained upon employing palladium acetylacetonate and triphenylphosphine as the catalyst system,¹⁹¹ although with acetaldehyde a mixture of **150** and **151** was obtained in the presence of butadiene. Increasing the phosphine:palladium ratio favored formation of **150** over **151**. At a 4:1 ratio of phosphine:palladium a 70% yield of **150** was obtained after 65 hr at 25°, whereas at a 1:1 ratio **151** was formed in 70% yield. The rates of reaction with formaldehyde and acetaldehyde were dramatically increased by the use of tertiary amines and alcohols, respectively, as solvents. The formation of branched octadienyl adducts **151** contrasts with that of the linear adducts which arise predominantly by terminal addition of the nucleophile, as previously mentioned.

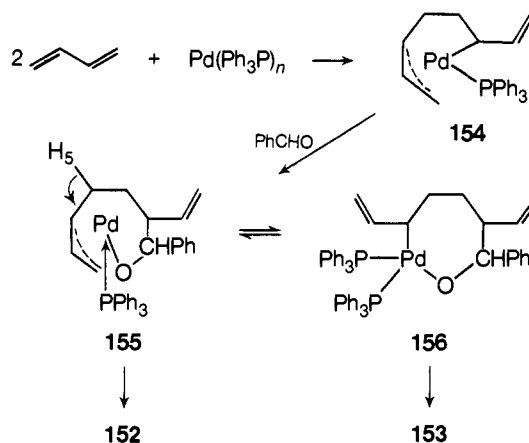


Similar results were obtained using benzaldehyde with a π -allylpalladium chloride catalyst.¹⁹² Thus reaction of butadiene with benzaldehyde in the presence of π -allylpalladium chloride, triphenylphosphine, and sodium phenoxide, yielded a mixture of **152** and **153**. Component **153**, assigned the 2-phenyl-3,6-divinyltetrahydropyran structure, comprised a mixture of four stereoisomers, isolable by repeated chromatography. Again the molar ratio of triphenylphosphine:palladium had a marked effect upon the product distribution, the unsaturated alcohol **152** predominating when triphenylphosphine:palladium ratio was nearly one. On the other hand, the pyran **153** was obtained as a main product when triphenylphosphine:palladium was larger than 2. The relationship is shown in Figure 1.

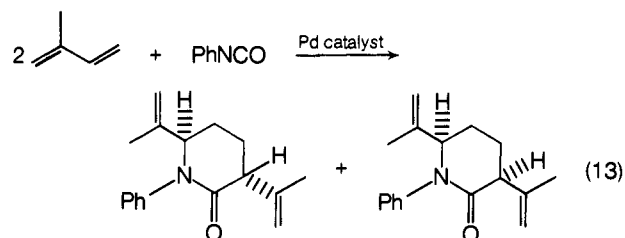
(190) P. Haynes, *Tetrahedron Lett.*, 3687 (1970).(191) R. M. Manyik, W. E. Walker, K. E. Atkins, and E. S. Hammack, *Tetrahedron Lett.*, 3813 (1970).(192) K. Ohno, T. Mitsuyasu, and J. Tsuji, *Tetrahedron Lett.*, 67 (1971).

A mechanism has been postulated to explain these facts in which butadiene dimerizes to give a π -allylpalladium complex **154**, which then undergoes reaction with aldehyde to give **155**. When 1 mol of phosphine is present the complex **155** collapses with transfer of hydrogen from C-5 to the oxygen to form the alcohol **152**. The cyclization takes place by ligand coupling to give **153** when 2 mol of phosphine coordinates to the palladium (Scheme XVII).

SCHEME XVII



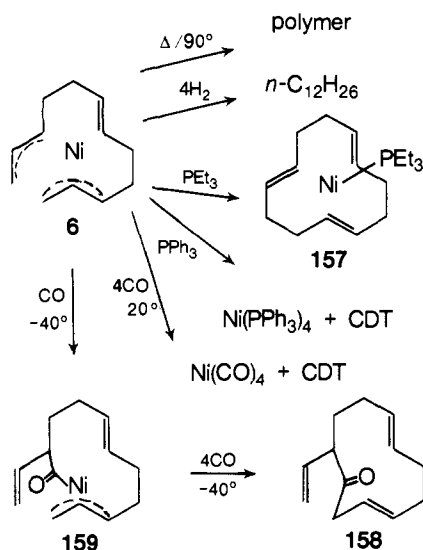
Similarly, isocyanates have been reported to undergo reaction with conjugated dienes in the presence of triphenylphosphine-palladium(0) complexes to give divinylpiperidones¹⁹³ (eq 13). Mechanistic considerations, along the lines discussed above, suggest that insertion of the $-\text{C}=\text{N}-$ grouping into the palladium-carbon bond of **155** must occur in preference to that of the $-\text{C}=\text{O}$ grouping, hence leading to the nitrogen heterocycle rather than to the pyran.

C. Reactions of the Bis- π -allyl Complex 6 Formed from Three Molecules of Butadiene

The crystalline complex **6** has previously been mentioned as an intermediate in the cyclotrimerization of butadiene catalyzed by nickel(0) complexes.¹⁷ In contrast to ligand displacement reactions at low temperature, no cyclododecatriene is obtained. If **6** is shaken in ether with hydrogen at atmospheric pressure, a very rapid absorption of 4 molecules of hydrogen occurs, nickel is liberated, and *n*-dodecane is formed. With excess triphenylphosphine at 20°, **6** yields cyclododecatriene (*trans*-, *trans*-, *trans*-, 94.4%; *cis*-, *trans*-, *trans*-, 5.0%; and *cis*-, *cis*-, *trans*-, 0.4%). Ring formation also occurs when only 1 mol of phosphine is added and complex **157** can be iso-

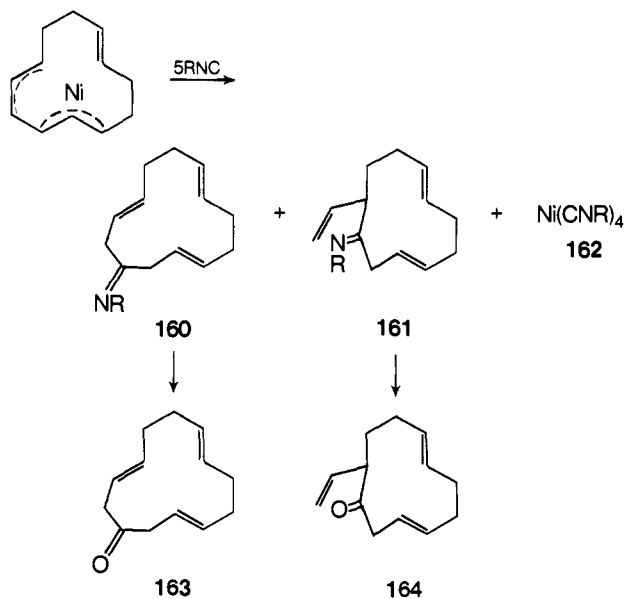
(193) K. Ohno and J. Tsuji, *Chem. Commun.*, 247 (1971).

SCHEME XVIII



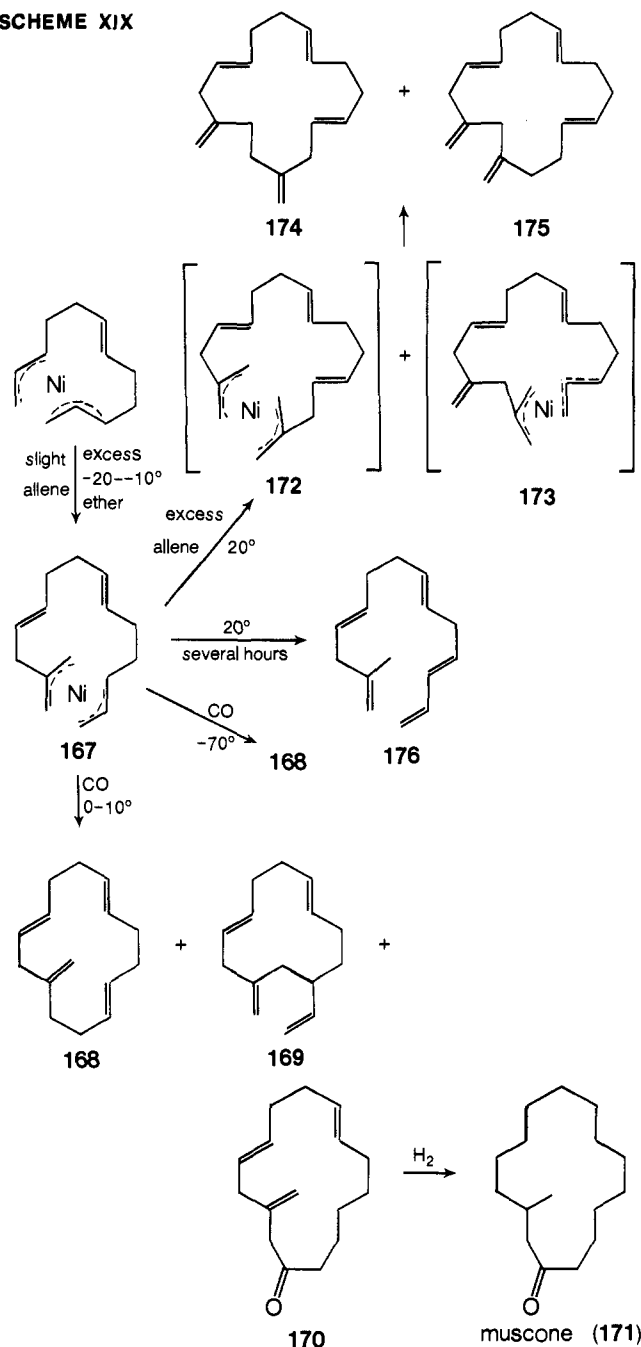
lated; this inducement to cause facile ring formation applies generally to all donor-acceptor molecules. With carbon monoxide at 20° , **6** reacts to give nickel carbonyl and cyclododecatriene, but at -40° **158** is obtained; carbon-carbon bond formation is induced in the first case, but insertion of carbon monoxide occurs in the second. These reactions must pass through a metal-acyl compound **159** which is not stable and readily yields **158** by carbon-carbon bond formation (see Scheme XVIII).

Although the major product from the previous reaction was the 11-membered ketone, a 13-membered ring has been obtained by reaction of **6** with isocyanides.¹⁹⁴ Insertion occurs at 0° to give imines **160** and **161**, accompanied by tetrakis(alkyl isocyanide)nickel(0) (**162**); yields lie between 40 and 70%. Hydrolysis by 30% CH_3COOH -3.5 N H_2SO_4 (1:1) gave the ketones **163** and **164** together with the isomeric 11-ethylidene-3,7-cycloundecadien-1-one (**165**) and an isomer of **163** having a cis double bond (**166**). The isomer distribution varied according to the isocyanide employed. With *tert*-butyl and cyclohexyl isocyanides, the ratio of products **164**:**165**:**163**:**166** was 2:1:90:7 and 42:41:13:4, respectively. It is apparent that



(194) H. Breil and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **9**, 367 (1970).

SCHEME XIX



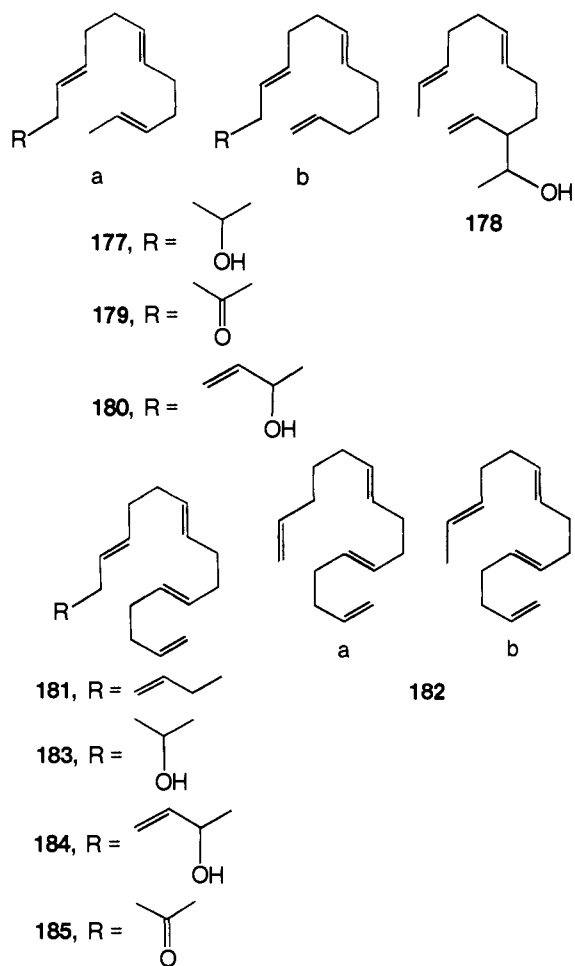
the large *tert*-butyl group favors linkage of the terminal carbon atoms.

Reaction of **6** with allene has led to formation of a number of cyclic products.¹⁹⁵ Carbonylation at -70° of an ether solution obtained by passing allene from a gas reservoir into **6** gave, after treatment with potassium cyanide, a 2:1 mixture of cyclododecatrienes and 1-methylenecyclotetradeca-3,7,11-triene (**168**). At 0 – 10° , however, carbonylation of the solution gave a 5:2 mixture of **168** and 1-methylene-11-vinylcyclododeca-3,7-diene (**169**) together with a small amount of **170** which on hydrogenation yielded muscone (**171**) (Scheme XIX). The reactions were suggested to proceed through the bis- π -allyl intermediate **167** which, under carbonylation conditions, either undergoes ring closure to give the cyclic hydrocarbons or carbonyl insertion to yield the muscone precursor. On reaction of **6** in ether with excess allene at -50° , allowing the solution to warm to room temperature

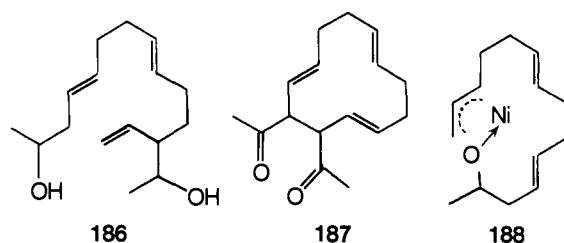
(195) R. Baker, B. N. Blackett, and R. C. Cookson, *Chem. Commun.*, 802 (1972).

and stirring with aqueous potassium cyanide, the hydrocarbons **174** and **175** were obtained. Although the intermediates were not isolated the reaction was suggested to involve the bis-allyl complexes **172** and **173**. Formation of **176**, after stirring the solution obtained by addition of 1 mol of allene to **6** at 20°, was proposed to arise as a result of a 1,11-hydrogen shift in **167**.

A series of compounds have been prepared by reaction of **6** with acetaldehyde, acetyl chloride, and allyl bromide.¹⁹⁶ Addition of acetaldehyde to an ethereal solution of **6** at -78°, warming to room temperature, and quenching with an aqueous solution of potassium cyanide led to a 30–40% conversion into a mixture of **177** (66% consisting of a 2:1 ratio of **177a**:**177b**), **178** (5%), and a mixture of diols (22%) together with a small amount of cyclododecatrienes. Similar products **179** and **180** were obtained from reaction with acetyl chloride and acrolein, and a 5:2 mixture of **181**:**182** was obtained from allyl bromide. Addition of a second molecule of acetaldehyde or acetyl chloride to yield **186** and **187** was facilitated in the presence of ligands such as cyanide or carbon monoxide; compounds **183–185** were obtained by reaction of **6** with acetaldehyde, acrolein, or acetyl chloride together with, or followed by, allyl bromide. It was suggested that a group of reagents do not display the same order of reactivity toward the second π -allyl group of **6** as to the first, and this is valuable in designing specific synthesis. The intermediate in the reaction with acetaldehyde was suggested to be **188**. The necessity for the presence of an activating ligand for further reaction was attributed to activation of the second π -allyl group by coordination of the



(196) R. Baker, B. N. Blackett, R. C. Cookson, R. C. Cross, and D. P. Madden, *Chem. Commun.*, 343 (1972).



ligand to the nickel atoms and conversions into a σ -allyl intermediate.

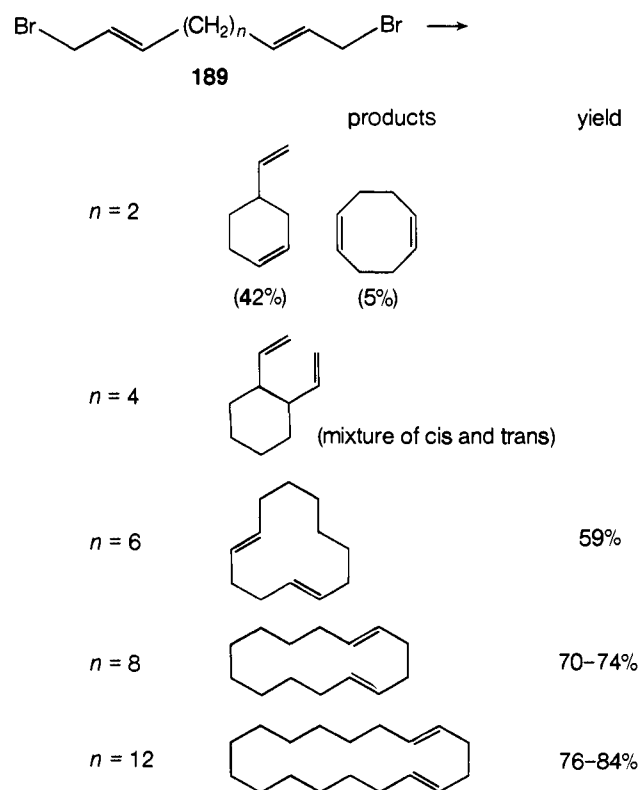
V. Synthesis from Allyl Derivatives

A. Allylic Coupling

Webb and Borchardt showed that reaction of 1-chloro-2-butene or 3-chloro-1-butene with nickel carbonyl in methanol led to a mixture of 2,6-octadiene (78%) and 3-methyl-1,5-heptadiene (22%) in 74 and 81% yield, respectively.¹⁹⁷ Subsequently, Corey and coworkers have used the basis of this reaction for a series of extremely elegant syntheses and demonstrated a number of new reactions.¹⁹⁸

A series of large-ring 1,5-dienes have been prepared by cyclization of allylic dibromides **189** with nickel carbonyl.¹⁹⁹ In each case the allylic dibromide was added to a solution of nickel carbonyl (1:5 molar ratio) in dimethylformamide under argon at 50° for 12 hr. The same cyclization product was obtained starting with either *cis*-, *cis*- or *trans*,*trans*-**189**. For $n = 6, 8$, and 12, the indicated *trans*,*trans* product was obtained as 95–98% of the product and only a trace of the *cis*,*trans* isomer was detected (Scheme XX). In the case of $n = 2$, some 1,5-

SCHEME XX



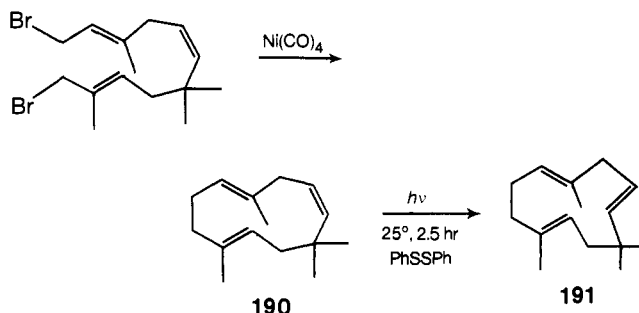
(197) I. D. Webb and G. T. Borchardt, *J. Amer. Chem. Soc.*, **73**, 2654 (1951).

(198) Since this review was first written, an excellent discussion of the synthetic values of these reactions has appeared; M. F. Semmelhack, *Org. React.*, **19**, 115 (1972).

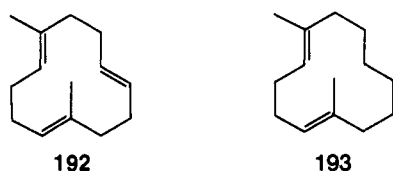
(199) E. J. Corey and E. K. W. Wat, *J. Amer. Chem. Soc.*, **89**, 2757 (1967).

cyclooctadiene was formed together with vinylcyclohexene. On using triphenylphosphinenickel tricarbonyl a larger amount of 1,5-cyclooctadiene (ca. 20% of the mixture) was obtained. A mixture of *cis*- and *trans*-divinylcyclohexane was formed when $n = 4$ and again a change in product ratio was observed when triphenylphosphinenickel tricarbonyl was employed. This ratio changed from 1:1 in the presence of nickel carbonyl to 1:2 in favor of the *trans* isomer. Formation of the six-membered ring indicates that coupling is sufficiently favorable here to overcome the preference for coupling at the primary carbon atoms. Dimethylformamide and *N*-methylpyrrolidone were found to be the best solvents, and high dilutions favor intramolecular compared to intermolecular coupling. This method can probably be adapted to larger sized cyclic structures.

Hydrocarbon **190**, which on irradiation leads to humulene (**191**), and 1,6-dimethylcyclododeca-1,5,9-triene (**192**) have been prepared by a similar procedure.^{200,201} In the latter case two isomers in a ratio of ca. 2:1 were formed; the major isomer had the all-*trans* structure and the minor isomer was considered to be *cis,trans*.

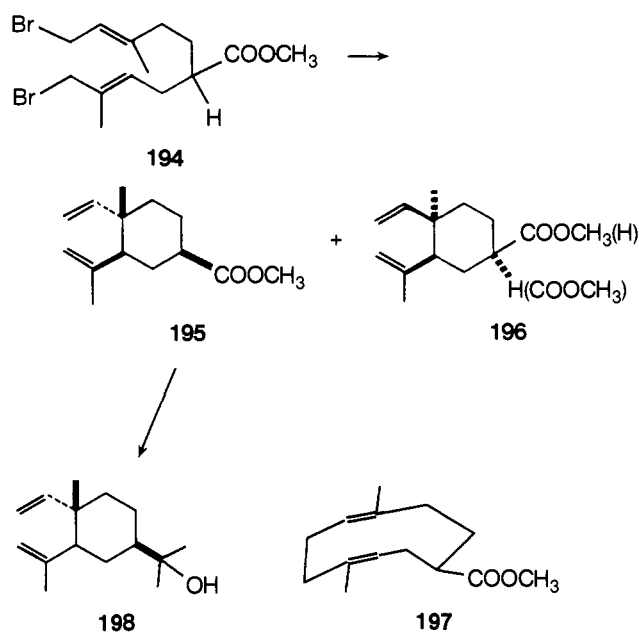


Three other cyclic products are also formed accompanying **190**, but humulene is still produced in 10% overall yield after irradiation. An alternative pathway to humulene, beginning with the isomeric allylic dibromide with a *trans* double bond, is less efficient and only a 5% overall yield is obtained. The importance of the presence and stereochemistry of the internal double bond is demonstrated in that, although **192** is obtained, together with the *cis,trans* isomer, in a 68% yield, the analogous cyclic diene **193** is only formed in 4% yield from the corresponding allylic dibromide. A template effect of the disubstituted double bond appears to be operating in the formation of both **190** and **192** which assists coupling by some control of the stereochemistry of the nickel complex intermediate.

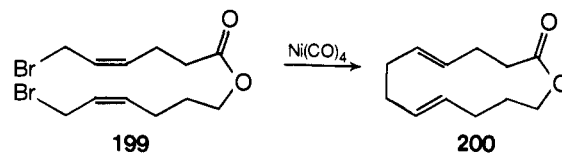


Slow addition of the dibromo ester **194** to 7 equiv of nickel carbonyl in *N*-methylpyrrolidone at 47 – 50° under an atmosphere of carbon monoxide led to a mixture of products **195**–**197** in 83% yield.²⁰² Separation by column chromatography gave the most polar fraction (**195**) in 32% yield contaminated by ca. 10% of the diastereoisomer with the different orientation of ester group. Other fractions gave an 8:1 mixture of **196** in 27% yield

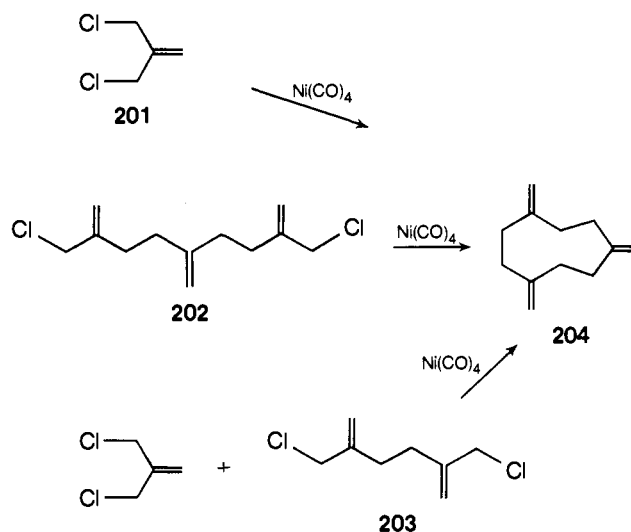
and an 11% yield of **197** which was identified as the *cis*-, *cis*-*cis* or *cis,trans* isomer by spectroscopic studies. Further reaction of **195** with excess methylmagnesium bromide gave an 85% yield of *dl*-elemol (**198**).



The same method has been shown to be applicable to formation of macrocyclic lactones, and reaction of **199** with nickel carbonyl has been shown to yield **200**.²⁰³ The application of the method to reaction in the presence of ester groups was also demonstrated.²⁰⁴



An interesting study has been made of both intramolecular and intermolecular coupling processes. Reaction of 1,1-bis(chloromethyl)ethylene (**201**) with excess nickel carbonyl in tetrahydrofuran at 50° for 51 hr led to 54% of 1,4,7-trimethylenecyclononane (**204**).²⁰⁵ This product



was also prepared by cyclization of 1,9-dichloro-2,5,8-trimethylenenonane (**202**) and also from reaction of 1,1-

(200) E. J. Corey and E. Hamanaka, *J. Amer. Chem. Soc.*, **89**, 2758 (1967).

(201) E. J. Corey and E. Hamanaka, *J. Amer. Chem. Soc.*, **86**, 1641 (1964).

(202) E. J. Corey and E. A. Broger, *Tetrahedron Lett.*, 1779 (1969).

(203) E. J. Corey and H. A. Kirst, *J. Amer. Chem. Soc.*, **94**, 667 (1972).

(204) G. P. Chiusoli and G. Cometti, *Chim. Ind. (Milan)*, **45**, 401 (1963).

(205) E. J. Corey and M. F. Semmelhack, *Tetrahedron Lett.*, 6237 (1966).

bischloromethylethylene and 1,6-dichloro-2,5-dimethylenecyclohexane (**203**). When 1,6-dichloro-2,5-dimethylenecyclohexane-1,1,6,6-*d*₄ and 1,1-bischloromethylethylene were treated with nickel carbonyl in tetrahydrofuran, 88% of the cyclononane formed originated from the C₈ dichloride. In the reaction of **201** in tetraglyme, 11% of 1,4-dimethylenecyclohexane was detected. Use of triphenylphosphinenickel tricarbonyl in tetraglyme appeared to favor ring closure at the C₈ stage rather than intermolecular coupling since 1,4-dimethylenecyclohexane was produced from reaction of **201**. This product was also formed in good yield on reaction of **202** with the phosphine complex. A small amount of 3,6-dimethylenecycloheptanone was also formed from reaction of **203** with nickel carbonyl.

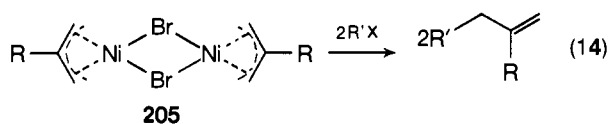
Allylic iodides and *p*-toluenesulfonates²⁰⁶ also couple efficiently with nickel carbonyl in polar media, and coupling of allylic acetates by nickel carbonyl has been reported; allyl and cinnamyl acetates gave 50 and 31% conversions to biallyl and bicinnamyl in tetrahydrofuran at 45–65° in 3 hr.²⁰⁷ The rates of coupling are in the order I > Br > Cl and OTs > OAc.

Since addition of allyl bromide to nickel carbonyl at ca. 60° in ether or polar solvents such as dimethylformamide, hexamethylphosphoramide, or dimethyl sulfoxide forms π -allylnickel bromide, it is clear that allylic coupling reactions proceed through this intermediate. Before discussing the mechanism of this in detail, a number of reactions will be discussed in the next section where π -allylnickel halides are used as reagents.

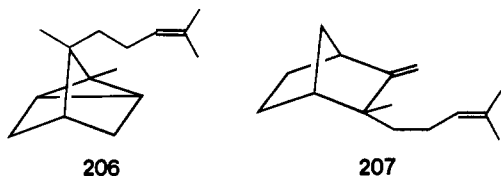
B. Reactions of π -Allylnickel Halides

These are valuable reagents since they can be prepared by a number of methods, easily purified, and stored in the absence of oxygen for periods of weeks. Yields of 75–90% can be obtained, after crystallization, by heating allyl halides with nickel carbonyl in benzene. Reaction of bis(1,5-cyclooctadiene)nickel with allyl halides at –10° also yields π -allylnickel complexes, and an alternative method, although of less value, is reaction of bis- π -allylnickel with hydrogen halides.

Corey and Semmelhack have shown that in polar, coordinating solvents π -allylnickel halides (**205**) react with a range of halides (eq 14, Table XII).²⁰⁸ This proce-



dure has been employed to prepare α -santalene (**206**) and epi- β -santalene (**207**) in 88 and 90% yields. Dihal-



ides also undergo reaction; with π -methallylnickel bromide, 1,6-diiodohexane and 1,4-dibromobenzene yield 95 and 97% of 2,11-dimethyl-1,11-dodecadiene and 1,4-dimethylallylbenzene, respectively. Since these reactions of organic halides proceed equally readily with aryl, vinyl,

(206) E. J. Corey, M. F. Semmelhack, and L. S. Hegedus, *J. Amer. Chem. Soc.*, **90**, 2416 (1968).

(207) N. L. Bauld, *Tetrahedron Lett.*, 859 (1962).

(208) E. J. Corey and M. F. Semmelhack, *J. Amer. Chem. Soc.*, **89**, 2755 (1967).

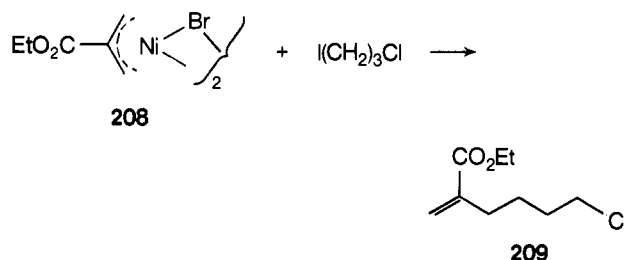
TABLE XII. Coupling of π -Methallylnickel Bromide with Halides in Dimethylformamide (Eq 14)²⁰⁸

Halide	React time, hr (temp, °C)	Yield, %
Methyl iodide	10 (22)	90
Methyl bromide	19 (22)	90
Cyclohexyl iodide	3 (22)	91
<i>trans</i> -4-Hydroxycyclohexyl iodide	10 (22)	88 ^a
<i>tert</i> -Butyl iodide	24 (22)	25
Iodobenzene	1 (22)	98
Vinyl bromide	13 (22)	70
Benzyl bromide	6 (60)	91
3-Phenylpropyl bromide	46 (65)	92
Phenyl α -chloromethyl ester	18 (60)	50
<i>p</i> -Bromophenacyl bromide	0.5 (22)	75
Chloroacetone	2 (22)	46

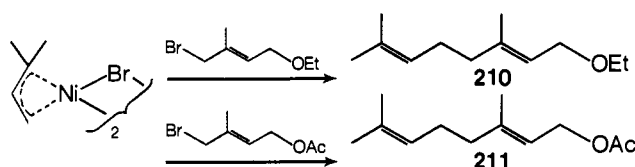
^a Mixture of *cis* and *trans* isomers.

and alkyl halides, an S_N2 displacement is not in operation. Further evidence against this mechanism is also found in the mixture of epimers (38:62) found in the reaction of *trans*-4-hydroxycyclohexyl iodide with π -methallylnickel bromide (Table XII).

The reactions also proceed smoothly in the presence of hydroxy, ester, and other common functional groups. For example, reaction of **208** with 1-iodo-3-chloropropane yields **209** which can be used for further synthetic appli-



cation, and 1-bromo-4-ethoxy-2-methyl-2-butene and 4-acetoxy-1-bromo-2-methyl-2-butene have been shown to react with 1,1-dimethyl- π -allylnickel bromide to give geranyl ethyl ether (**210**) and geranyl acetate (**211**); ethyl



geranate was formed in a similar manner from ethyl γ -bromosenecioate.²⁰⁹ Geranyl acetate (85%) together with the *cis* isomer (15%) (eq 15)²¹⁰ and the farnesic esters (eq 16) have been prepared with the ratio of *cis*:-*trans*:*trans*:*trans*:*trans*:*cis*, 2,1:0.3:0.3.²¹¹

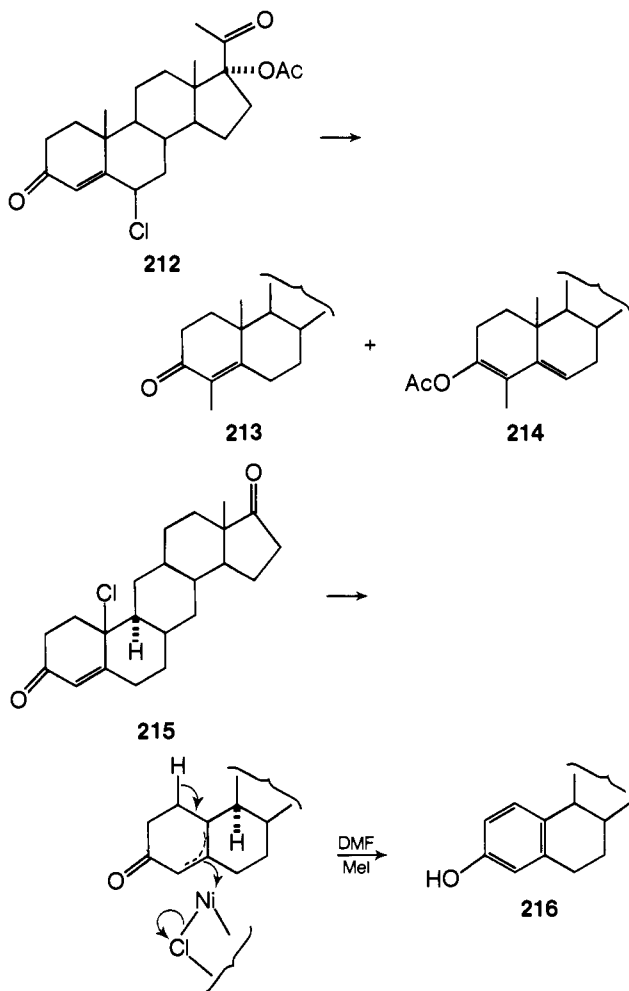
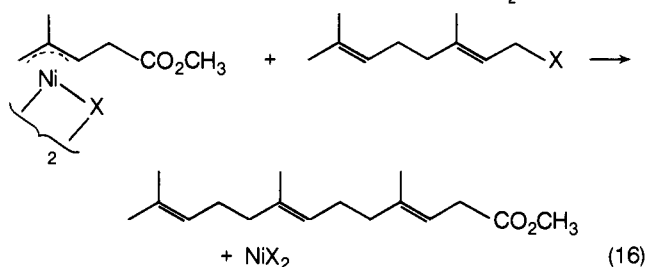
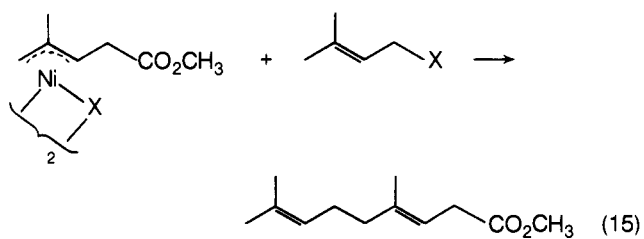
A red complex has been obtained by reaction of **212** with nickel carbonyl in benzene; treatment with methyl iodide in dimethylformamide gave **213** and **214** in 24% combined yield. This latter compound was considered to arise *via* acetylation with acetyl iodide obtained by carbonylation of methyl iodide.²¹² Attempted alkylation of **215** led to formation of estrone **216**.

(209) K. Sato, S. Inoue, S. Ota, and Y. Y. Fujita, *J. Org. Chem.*, **37**, 462 (1972).

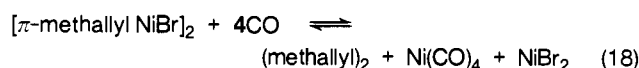
(210) F. Guerrieri and G. P. Chiusoli, *Chim. Ind. (Milan)*, **51**, 1252 (1969).

(211) F. Guerrieri and G. P. Chiusoli, Italian Patent Appl. 28,260 A/70.

(212) I. T. Harrison, E. Kimura, E. Böhme, and J. H. Fried, *Tetrahedron Lett.*, 1589 (1969).

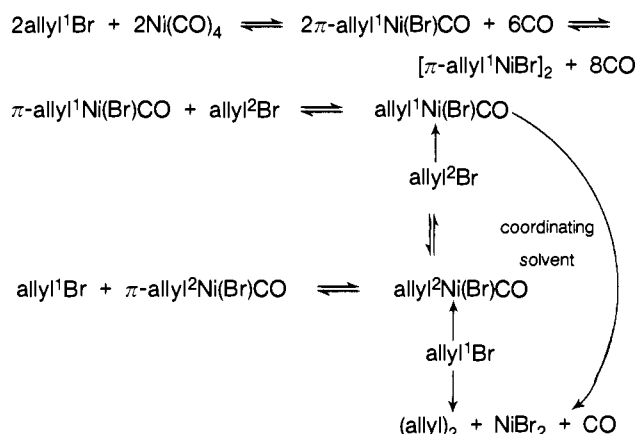


The mechanism of these allyl coupling reactions has been discussed, and the reactions of π -allylnickel bromides with allyl halides have been investigated.²⁰⁶ The equilibrium reaction (eq 17) was shown to take place since treatment of π -allylnickel bromide with methallyl bromide in tetraglyme led to a 95% yield of biallyl (35%), allylmethallyl (25%), and bimethallyl (40%). Allyl bromide was also detected when π -allylnickel bromide and methallyl bromide were mixed in dimethylformamide. Reaction of allylic halides and nickel carbonyl has also been shown to be reversible; a rapid coupling to bimethallyl occurs when carbon monoxide is bubbled into a solution of π -methallyl bromide (eq 18). Although an equi-

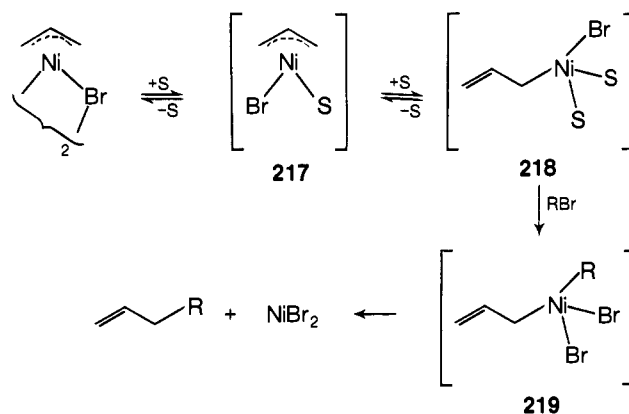


librium between π -allylnickel(0) and π -allylnickel halide complexes has been demonstrated,²¹³ evidence is available against the intermediacy of nickel(0) complexes in allylic coupling reactions. Bis(2-cyclooctenyl) was obtained in >99% selectivity from reaction of 2-cyclooctenyl bromide with nickel carbonyl in dimethylformamide, whereas a 1:1 mixture of this product and di(2-cyclooctenyl) ketone was obtained from reaction of bis(π -cyclooctenyl)nickel(0) with either carbon monoxide or with nickel carbonyl and/or nickel bromide. On the basis of these results it has been suggested that π -allylnickel halides are important in the coupling reactions (Scheme XXI); it was not determined whether the complexes involving carbon monoxide were in the σ - or π -allyl form.

SCHEME XXI



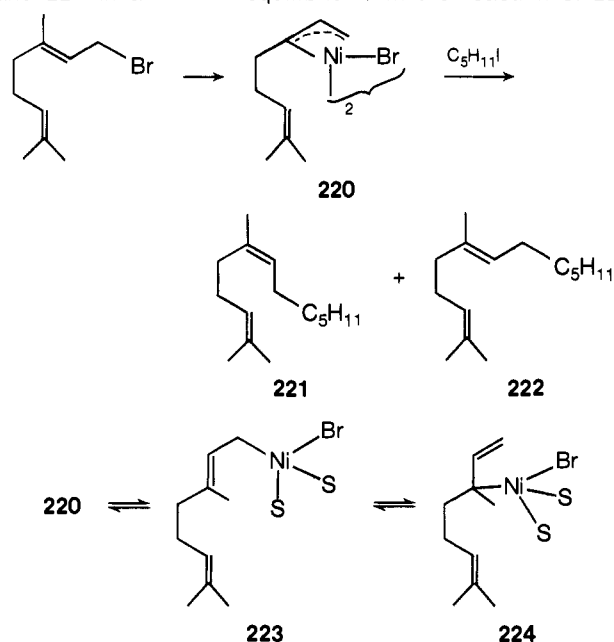
Although no direct evidence has been obtained, a number of intermediates have been suggested to be important in reaction of π -allylnickel halides with organic halides. An oxidative-addition of the halide to a σ complex (218) produced by coordination of solvent to the nickel in the π -allylnickel halide is a strong possibility since complexes of structure 217 have been formed in the presence of ligands such as triphenylphosphine and other strong ligands. Further reaction of 219 could then occur by radical-type coupling to yield the observed products.²⁰⁸



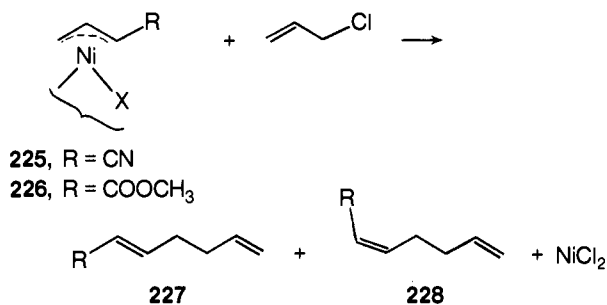
Questions of stereochemistry and selectivity have been considered in these reactions. Conversion of *trans*-geranyl bromide into its π -allylnickel bromide complex (220)

(213) E. J. Corey, L. S. Hegedus, and M. F. Semmelhack, *J. Amer. Chem. Soc.*, 90, 2417 (1968).

and reaction with cyclohexyl iodide in dimethylformamide lead to a mixture of cis and trans isomers **221** and **222**.²⁰⁸ This loss of stereochemical identity has been explained in terms of intervention of the σ complexes **223** and **224** in a $\pi \rightarrow \sigma$ equilibrium. In the reaction of **225**



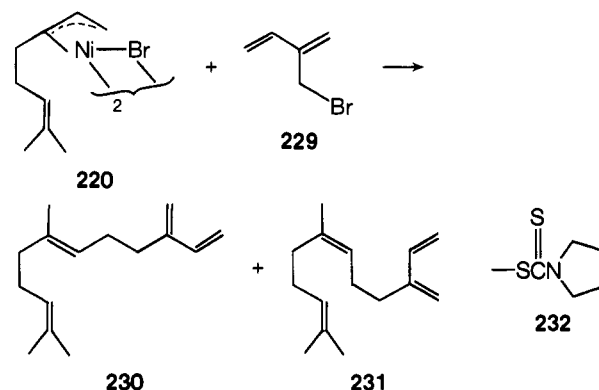
with allyl chloride, greater than 90% of the cis isomer **228** is formed in solvents of low polarity and low coordi-



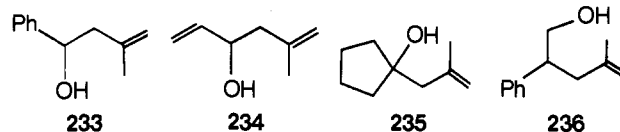
nating power while between 70 and 95% of **227** is formed from reaction of **226** in more polar solvents and in the presence of ligands such as quinoline or 2,6-lutidine.²¹⁴ Although the question of stereoselectivity in these reactions is complex, some generalizations have been made. Solvents of low polarity and low coordinating power lead to either trans or cis products depending upon the structure of the allylic group while solvents of higher polarity and coordinating ability favor formation of trans products. This latter observation has been suggested to be attributable to thermodynamic control or steric effects in the reactions.²¹⁴ It is apparent that stereoselectivity can be influenced by substituents and the appropriate choice of ligands and solvents.

With unsymmetrical π -allylnickel halides there is also the possibility of reaction at different sites. High selectivity is found for reaction at the less substituted carbon atom as indicated by reaction of **220** described above. Another problem which can also arise is self-coupling of the allyl groups of the nickel complex rather than cross-coupling reactions. Although more studies are required into this problem, it has been observed that electron-withdrawing groups in the coordinated allyl group favor the cross-coupling reaction.²¹⁴ It has also been shown that a different leaving group can be used with advan-

tage. Reaction of π -geranylnickel bromide (**220**) with **229** leads to only a 20% yield of β -farnesenes; **230** and **231**, with a cis:trans ratio of 55:45; the main products consist of the coupling products 3,6-dimethylene-1,7-octadiene and three C_{20} isomers from coupling of the π -geranyl group. A change in the leaving group from bromide to pyrrolidinedithiocarbamate (**232**), however gave the β -farnesenes in a yield of 46%.²¹⁵



Although longer reaction times are generally required, π -allylnickel halides also undergo reaction with other functional groups. With π -methallylnickel bromide at 50° for 24 hr, reaction with benzaldehyde, acrolein, cyclopentanone, and styrene oxide gives **233–236** in 85, 80, 50, and 60% yields, respectively.²⁰⁸ Alkylation of quinones by π -allylnickel bromide complexes has been shown to depend upon the substituent on the quinone (Table XIII).²¹⁶



The reactions involve addition of the π -allylnickel complex to the quinone in tetrahydrofuran under argon at -50°. After stirring for 2 hr at this temperature, the mixture is allowed to reach room temperature and the products are extracted after a further 4 hr of stirring. Allyl-substituted quinones were obtained in all cases except for *p*-benzoquinone which reacted to form hydroquinones. In quinones with a methyl group adjacent to an unsubstituted position, attack at both positions occurs, but with a twofold excess of quinone compared to the nickel reagent, only reaction at the unsubstituted position is found. Only monoalkylated products are found with the reactions although it is nonspecific with substituted quinones. A suggested mechanism is 1,4 addition of the π -allylnickel bromide to the quinone followed by hydrolysis or decomposition to yield the observed products (Scheme XXII). Although reduction to form hydroquinones occurs as a major side reaction, this can be readily reoxidized to the starting quinone and used for further reaction. Plastoquinone-1 (**239**) and coenzyme Q₁ (**240**) have been prepared in 61 and 40% yields, respectively, and it is apparent that this method can be extended to the alkylation of quinones with a variety of π -allylnickel halides.

The value of alkylations by π -allylnickel halides can now be seen in their versatility of reaction in the presence of functional groups which would interfere with reagents such as alkyllithium or alkyllithium derivatives. Even the presence of acidic hydrogens does not in-

(215) M. F. Semmelhack, Ph.D. Thesis, Harvard University, 1967.

(216) L. S. Hegedus, E. L. Waterman, and J. Catlin, *J. Amer. Chem. Soc.*, **94**, 7155 (1972).

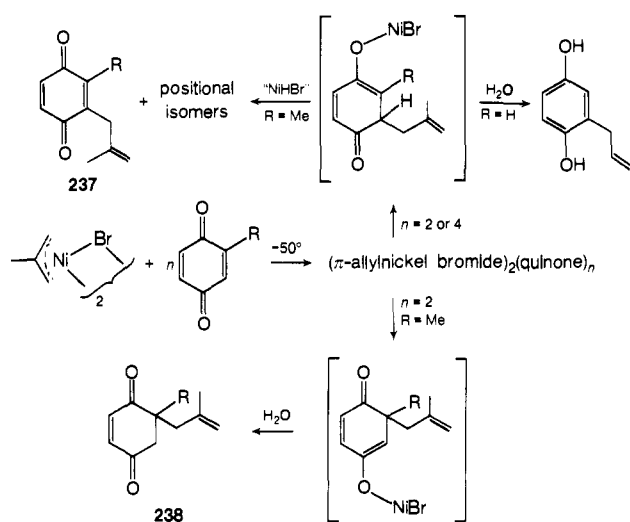
(214) G. P. Chiusoli, XXIIIrd International Congress of Pure and Applied Chemistry, Boston, 1971, Vol. 6.

TABLE XIII. Alkylation of Quinones with π -Allylnickel Bromide Complexes^a

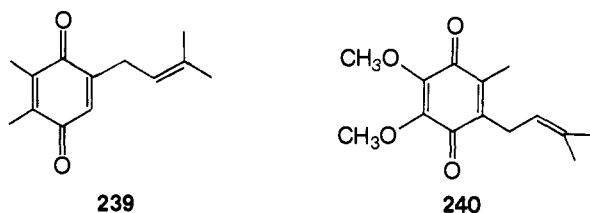
π -Allylnickel bromide (1)	Quinone	Quinone:Ni complex	Product	Yield, %
Allyl	<i>p</i> -Benzoquinone	2:1	Allylhydroquinone	58
2-Methallyl	<i>p</i> -Benzoquinone	2:1	(2-Methyl-2-propenyl)hydroquinone	86
1-Methallyl (crotyl)	<i>p</i> -Benzoquinone	2:1	(2-Butenyl)hydroquinone	83
1,1-Dimethylallyl	<i>p</i> -Benzoquinone	2:1	(3-Methyl-2-butenyl)hydroquinone	54
2-Methallyl	1,4-Naphthoquinone	2:1	2-(2-Methyl-2-propenyl)-1,4-naphthoquinone	39
2-Methallyl	2-Methylbenzoquinone	2:1	2-Methyl-?-(2-methyl-2-propenyl)-benzoquinone (237)	38
			5-Methyl-5-(2-methyl-2-propenyl)-cyclohex-2-ene-1,4-dione(238)	11
2-Methallyl	2-Methylbenzoquinone	4:1	237	45
			238	~0
2-Methallyl	2,3-Dimethylbenzoquinone	2:1	2,3-Dimethyl-5-(2-methyl-2-propenyl)-benzoquinone	82
1,1-Dimethylallyl	2,3-Dimethylbenzoquinone	2:1	Plastoquinone-1 (239)	61
1,1-Dimethylallyl	2,3-Dimethoxy-5-methylbenzoquinone	4:1	Coenzyme Q ₁ (240)	30
2-Methallyl	Duroquinone	2:1	Duroquinone	~100

^a Reaction conditions not optimized.

SCHEME XXII



terfere with the π -allylnickel reactions, and, since yields are generally good and the reagents relatively easy to handle, these reactions will become increasingly important in organic synthesis.

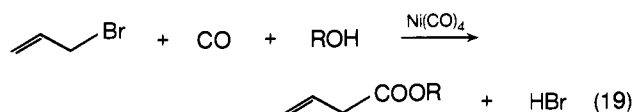


C. Nickel Carbonyl Catalyzed Reactions of Allyl Halides

Reviews have recently appeared^{214,217,218} of this important class of reactions, and a brief account is included

(217) G. P. Chiusoli and L. Cassar, *Angew. Chem., Int. Ed. Engl.*, **6**, 124 (1967).(218) G. P. Chiusoli, *Bull. Soc. Chim. Fr.*, 1139 (1969).

now for completeness. The reactions involve formation of a π -allylnickel complex from nickel carbonyl and an allyl halide followed by reaction with carbon monoxide or with carbon monoxide and an acetylene. The simplest reaction is formation of an unsaturated ester by "carbonylation" (eq 19). This reaction is best carried out at room

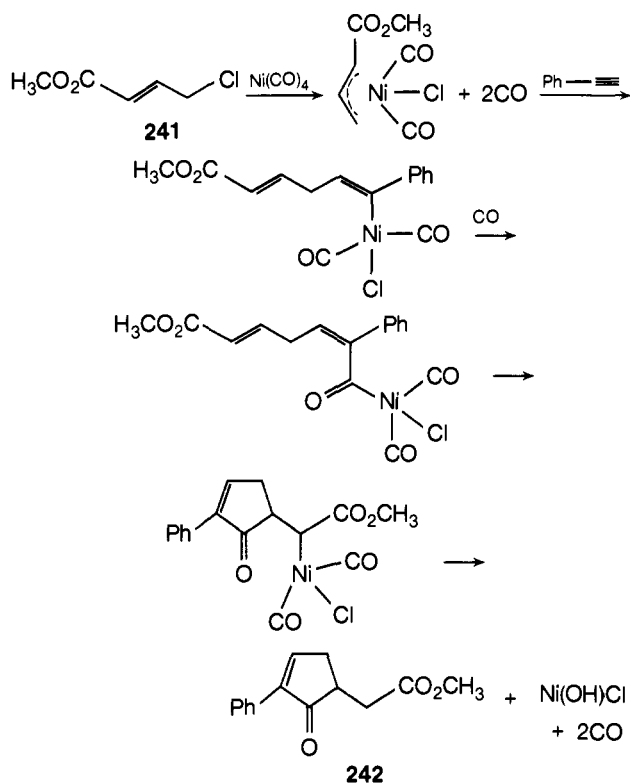


temperature and 2–3 atm of pressure and gives yields of about 50%; at higher temperatures dimerization of the allyl groups becomes increasingly favored. If acetylene is present together with carbon monoxide, "insertion" of both takes place and methyl *cis*-hexa-2,5-dienoate is formed (Scheme XXIII); this type of reaction proceeds with yields up to 80%.^{214,217} The progress of the reaction can be followed since the reaction mixture becomes red and changes to green toward the end of the reaction. In the presence of an inert solvent (ethers or hydrocarbon), an acyl halide is formed, and all these reactions are best carried out in dilute solution with an excess of nickel carbonyl.

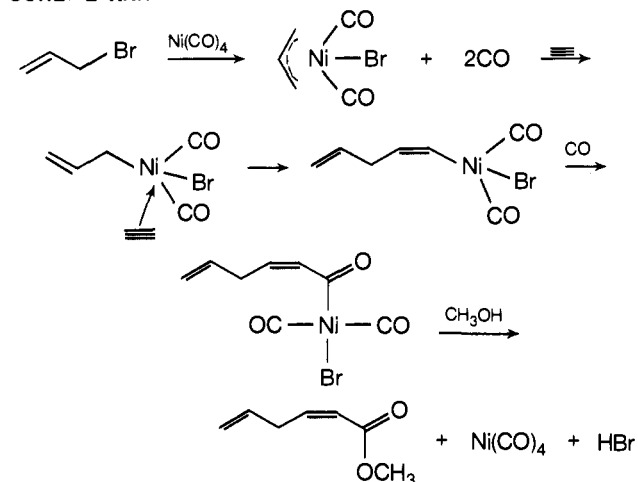
In Scheme XXIII, the mechanism involves an oxidative addition of allyl chloride to nickel carbonyl with formation of the π -allylnickel complex. Stepwise insertion is then suggested to follow conversion of the π -allyl form into a σ -allyl derivative. The termination step involves a nucleophile and results in formation of a zerovalent nickel species which can be used for further reaction. In the reaction to form methyl *cis*-hexa-2,5-dienoate two molecules are inserted, but in other cases subsequent insertions, cyclizations, and different termination steps can occur.

A reaction involving cyclization is formation of methyl 3-phenylcyclopent-3-en-2-on-1-ylacetate (242) from 241, phenylacetylene, and carbon monoxide in aqueous acetone. In this case the termination step is affected by a proton, and a divalent nickel species is formed.²¹⁹

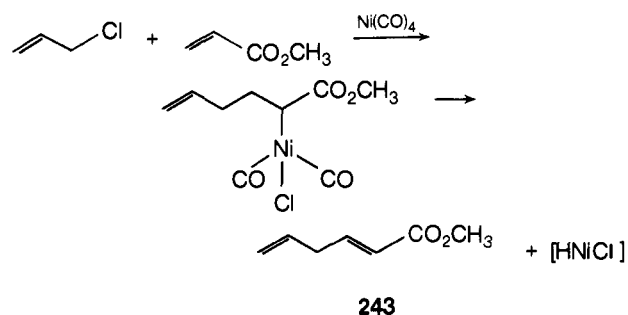
(219) G. P. Chiusoli and G. Bottaccio, *Chim. Ind. (Milan)*, **47**, 165 (1965); G. P. Chiusoli, G. Bottaccio, and C. Venturolo, *ibid.*, **48**, 107 (1966).



SCHEME XXIII



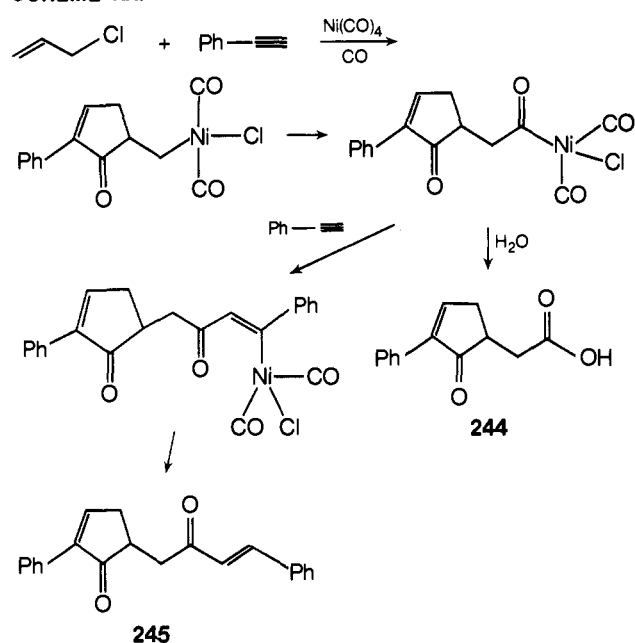
Hydrogen elimination can also provide the termination step illustrated by formation of methyl *trans*-hexa-2,5-dienoate (**243**) from methyl acrylate and allyl chloride; this results in a stoichiometric reaction.²²⁰



It is evident that these reactions can provide a powerful technique in organic synthesis as long as predictions can be made regarding the stage at which termination

(220) M. Dubini, F. Montino, and G. P. Chiusoli, *Chim. Ind. (Milan)*, **47**, 839 (1965); M. Dubini and F. Montino, *J. Organometal. Chem.*, **6**, 188 (1966).

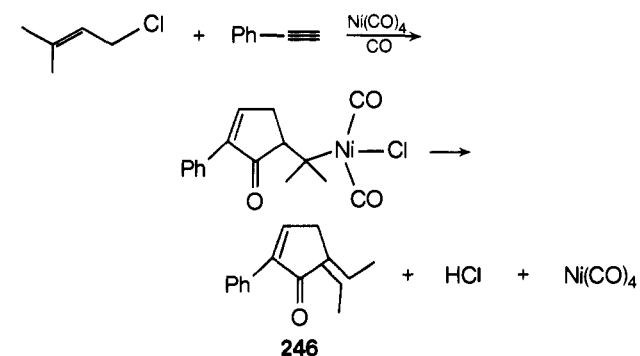
SCHEME XXIV



will occur in the processes. Large advances have been made in this area, and it has been shown that some control can be exerted by choice of the appropriate reactants.

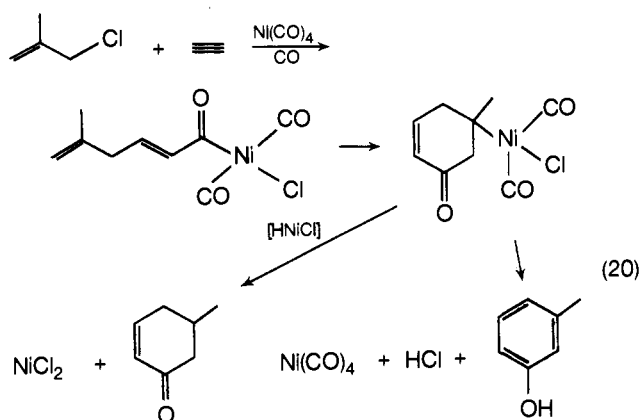
When allyl chloride is allowed to react with phenylacetylene and carbon monoxide, insertion is followed by cyclization and further insertion of a molecule of phenylacetylene and carbon monoxide. The final termination step is protolytic cleavage of a carbon-nickel bond yielding a bivalent nickel species and making the reaction stoichiometric in nickel (Scheme XXIV). Even when water is present, cyclization still occurs, and although some phenylcyclopentenylacetic acid (**244**, 24%) is formed, most of the reaction continues with further insertion of phenylacetylene to give **245** (64%). With *o*-hydroxyphenylacetylene, however, termination of the reaction occurs after the first addition of carbon monoxide.²¹⁴

Termination can also occur by elimination before further insertion, and **246** can be formed by reaction of phenylacetylene and 3-methylbut-2-enyl chloride. In this



case hydrogen elimination is favored by formation of a double bond conjugated with the carbonyl group.²¹⁴ In this case the hydrogen eliminated has been written as a proton, and the nickel would then be produced in the zerovalent state; a catalytic reaction would therefore be possible. Alternatively if the hydrogen is eliminated as a hydride, a stoichiometric process would result since the nickel would be in the bivalent state. In practice the former process has not been observed in the absence of the latter.

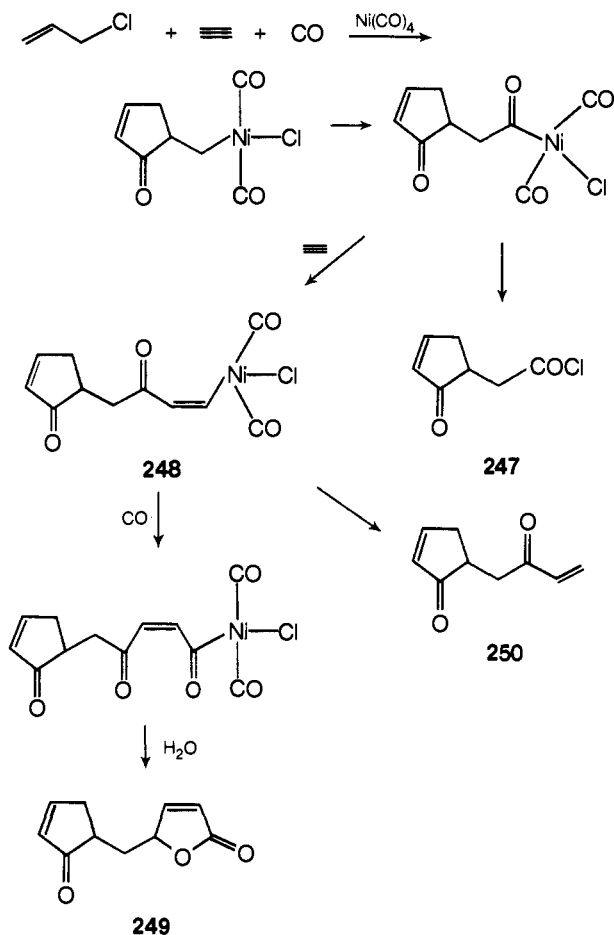
This can be illustrated by formation of *m*-cresol by a similar reaction (eq 20) in a reaction which is only par-



tially catalytic. While only 4–5% is obtained in aqueous or alcoholic solvents, a 40–50% yield is found in the presence of magnesium oxide as a hydrochloric acid acceptor and anhydrous acetone as solvent; methylcyclohexenone is also produced as a result of the nickel hydride produced in the reaction. In this case it is apparent that termination is favored over further insertion because of aromatization.²¹⁴

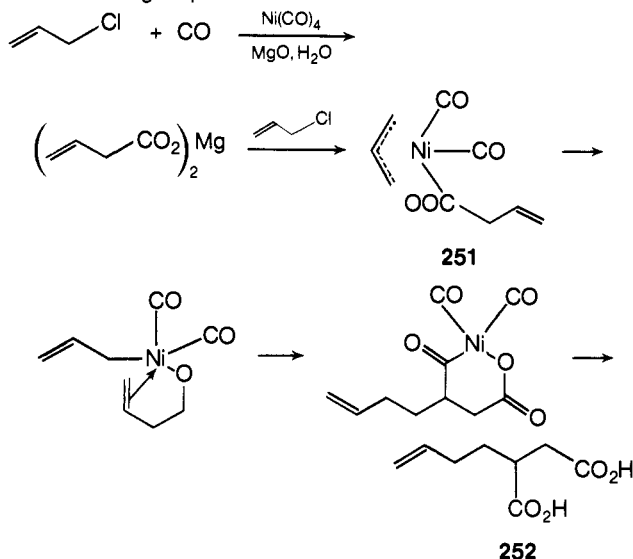
In inert solvents such as ketones, esters, or ethers, the main products obtained are derivatives by cyclization of

SCHEME XXV

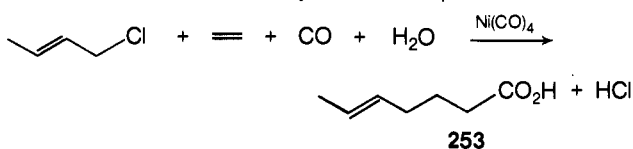


the intermediate acyl halides. The main product from reaction of allyl chloride, carbon monoxide, and acetylene in moist acetone is **249**²²¹ (Scheme XXV). In diethyl ether, benzene, or heptane, however, the reaction can be terminated at the acid chloride **247** which gives 2-oxocyclopent-3-enylacetic acid on reaction with water.²²² In ketones protolysis of **248** occurs to yield **250**. These reactions can be seen to be extremely solvent dependent, but a choice of conditions enables a variety of syntheses to be achieved. β,γ -Unsaturated lactones have been obtained by nickel carbonyl catalyzed reaction of acid halides with carbon monoxide and acetylene in ketonic solvents.²²³

Some competition also occurs between molecules for insertion, and a case has been reported of insertion of an olefinic double bond which is assisted by geometric factors. In the presence of nickel carbonyl and magnesium oxide as neutralizing agent, but-3-enylsuccinic acid (**252**) was also obtained in 60% yield on reaction of allyl chloride and carbon monoxide in water. But-3-enoic acid was considered to be an intermediate since **252** was also formed on treatment of allyl halides with sodium but-3-enoate under similar conditions. The reaction was suggested to involve **251** which in the σ -allyl form makes a coordination site available to the double bond of the but-3-enoic acid group.^{224, 225}



A 40% yield of **253** has been obtained by reaction of 1-chloro-2-butene with ethylene under pressure and car-



bon monoxide in aqueous acetone at 40–80°; pent-3-enoic acid and products resulting from coupling of the allyl group were also formed.²²⁶ Although yields with other olefins were extremely low (2–4%), reaction with 1,5-hexadiene was more effective. In this case on reaction with allyl chloride, **254** was formed together with a

(221) G. P. Chiusoli and G. Bottaccio, *Chim. Ind. (Milan)*, **47**, 165 (1965); L. Cassar and G. P. Chiusoli, *Tetrahedron Lett.*, 3295 (1965).

(222) L. Cassar, G. P. Chiusoli, and M. Foa, *Tetrahedron Lett.*, 285 (1967).

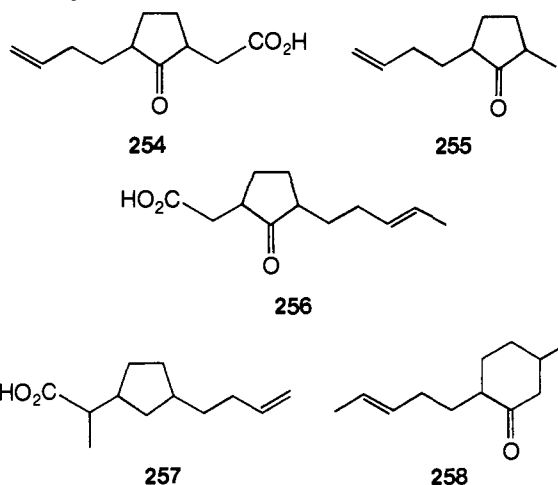
(223) L. Cassar, G. P. Chiusoli, and M. Foa, *Chim. Ind. (Milan)*, **50**, 515 (1968).

(224) G. P. Chiusoli and S. Merzoni, *Chem. Commun.*, 522 (1971).

(225) G. P. Chiusoli, G. Cometti, and S. Merzoni, *Organometal. Chem. Syn.*, **1**, 439 (1972).

(226) G. P. Chiusoli and G. Cometti, *Chem. Commun.*, 1015 (1972).

small amount of **255**. The reaction was favored by addition of KPF_6 , SnCl_2 , or KF , and yields of between 10 and 40% were obtained. Reaction with either the unsubstituted or substituted end can take place with substituted allyl compounds, and, with 1-chloro-2-butene and 1,5-hexadiene in the presence of stannous chloride in aqueous acetone at 45° , a mixture of products **256**, **257**, and **258** was obtained in the ratio of 72:27:1. 1,4-Pentadiene, 1,6-heptadiene, and 1,7-octadiene react as simple olefins under similar conditions, indicating the importance of the positional relationship of the two double bonds in 1,5-hexadiene.

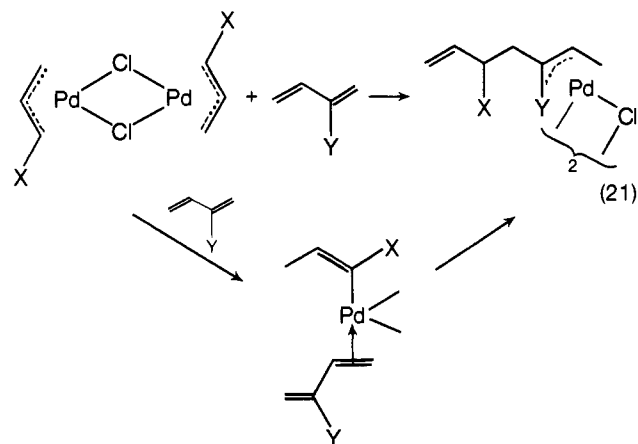


While the reactions are stereoselective, it has been possible to work out procedures for obtaining *cis* and *trans* stereoisomers. Insertion of an acetylene between two coordinated ligands gives rise to a *cis* double bond. In the synthesis of *trans*-hexa-2,5-dienoate from allyl chloride and methyl propiolate, a *trans* double bond results from acid attack on the nickel complex.²¹⁴ Further studies will indicate how the stereochemistry of the double bond derived from coordinated allyl groups depends upon substituents, ligands, and solvents.

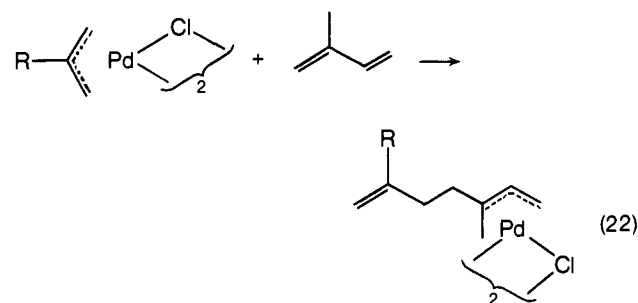
A catalytic nickel species for formation of *cis*-methyl-2,5-dienoate, in yields between 70 and 80%, from allyl chloride, acetylene, and carbon monoxide in methanol has been made *in situ* by reduction of nickel chloride with a manganese-iron alloy in the presence of thioarea.²²⁷

D. Insertion Reactions

π -Allylic palladium complexes react with 1,3-dienes to yield new π -allylpalladium complexes with addition of the allyl fragment to the diene molecule. These reactions can be regarded as insertion of the diene between the π -allyl group and the palladium atom, and addition takes place at the most substituted carbon of the π -allyl group (eq 21). Electron-withdrawing groups in the π -allyl group favor the reaction which is suggested to be due to increasing ease of coordination to the palladium atom. The reaction is retarded by alkyl substituents on the diene due to steric effects.²²⁸⁻²³¹ Isoprene gave 1,1-disubsti-



tuted allyl complexes rather than 1,2-disubstituted complexes (eq 22), and the reactivity order was allyl > 2-methylallyl > 1-methylallyl > cinnamyl and butadiene > isoprene > chloroprene > 2,3-dimethylbutadiene.²³²



A mechanism has been proposed in which the diene, acting as a monodentate ligand, coordinates to the palladium through the least substituted double bond and yields a σ -allyl derivative. An electrocyclic reaction then occurs in a *cis*-planar orientation to give the insertion product. It was not possible to ascertain if this insertion process is concerted or whether a two-step mechanism is operating, but the insertion step and not initial coordination of the 1,3-diene is rate-determining.^{233,234} Further addition of butadiene takes place to the π -allylic group at 50° .^{211,212}

Reaction of π -allylpalladium complexes with 2-chlorobutadiene has also been studied, and multiple insertion products containing up to 40 carbon atoms have been obtained under mild conditions.²³⁵ Reaction of bis(benzonitrile)palladium dichloride with 2-chlorobutadiene in benzene solution at room temperature gave a yellow crystalline material **259**, assumed to arise by formation of a π -allyl complex followed by rapid insertion of a second molecule of diene. The presence of a chlorine substituent in the reactant π -allyl complex was observed to enhance the rate of insertion reaction and also to facilitate further insertion steps. It was also suggested that the σ -allylic intermediate involved in the *syn* \rightleftharpoons *anti* exchange in the π -allyl isomerization is also important in the insertion processes. Nmr studies indicated that the first and subsequent insertion steps proceeded differently since the σ bond in the initially formed σ -allylic derivative is to the unsubstituted carbon atom, whereas, in subsequent steps, the σ bond is to the carbon atom having an alkenyl group capable of coordination in the molecule.

(227) G. P. Chiusoli, M. Dubini, M. Ferraris, F. Guerrieri, S. Merzoni, and G. Mondelli, *J. Chem. Soc. C*, 2889 (1968); F. Guerrieri, *Chem. Commun.*, 983 (1968).

(228) D. Medema and R. Van Helden, *Recl. Trav. Chim. Pays-Bas*, 90, 304 (1971).

(229) D. Medema, R. Van Helden, and C. F. Kohll, *Inorg. Chim. Acta*, 3, 255 (1969).

(230) R. Van Helden, C. F. Kohll, D. Medema, G. Verberg, and T. Jonkhoff, *Recl. Trav. Chim. Pays-Bas*, 87, 961 (1968).

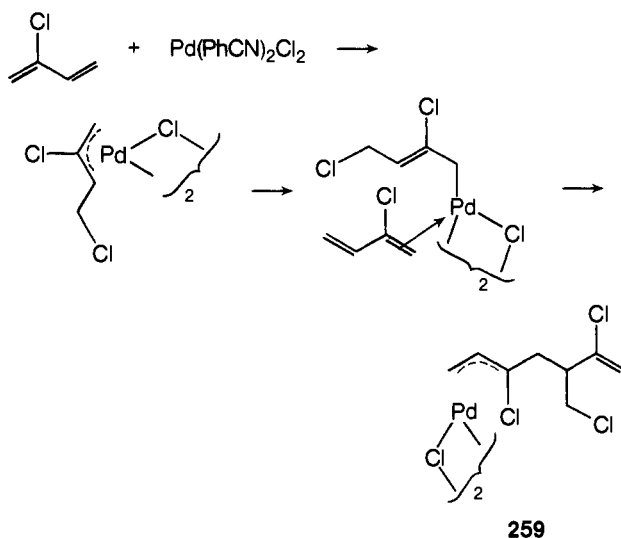
(231) D. Medema and R. Van Helden, *Amer. Chem. Soc., Div. Petrol. Chem. Prepr.*, 14, B92 (1969).

(232) Y. Takahashi, S. Sakai, and Y. Ishii, *J. Organometal. Chem.*, 16, 177 (1969).

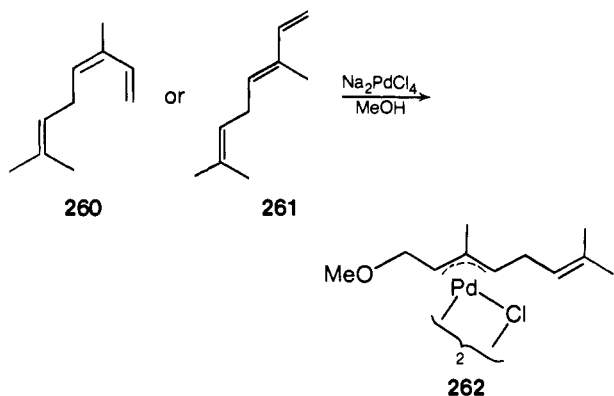
(233) R. P. Hughes and J. Powell, *J. Amer. Chem. Soc.*, 94, 7723 (1972).

(234) R. P. Hughes and J. Powell, *Chem. Commun.*, 275 (1971).

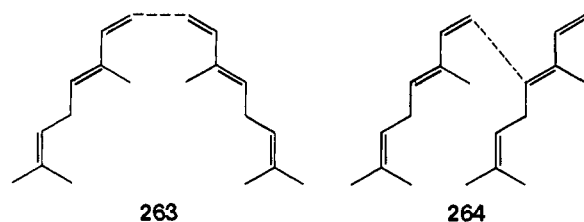
(235) D. J. S. Guthrie and S. M. Nelson, *Coord. Chem. Rev.*, 8, 139 (1972).



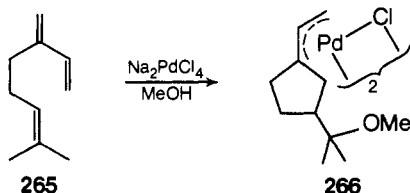
Treatment of *cis*- or *trans*-ocimene (260 and 261) with disodium tetrachloropalladate gave a π -allylpalladium complex of geranyl methyl ether (262). Dimerization of



cis-ocimene to a palladium(II) complex of a C_{20} terpene occurred in acetate solution accompanied by limonene and *trans*-ocimene. This dimerization was shown to take place via a head-to-head process (263) rather than head-to-tail (264). Similarly, myrcene (265) gave a palladium(II) complex of a C_{20} dimer, again by head-to-head dimerization; in methanol, cyclization to 266 occurred.²³⁶



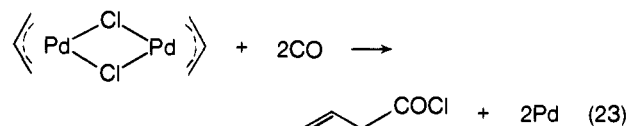
Similarly, myrcene (265) gave a palladium(II) complex of a C_{20} dimer, again by head-to-head dimerization; in methanol, cyclization to 266 occurred.²³⁶



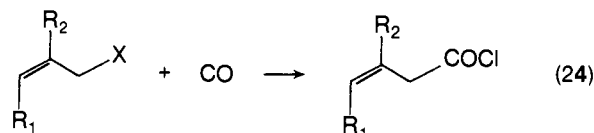
Reaction of disodium tetrachloropalladate with linalyl acetate, nerolidyl acetate, limonene, and α - and β -pinene has also been studied.²³⁷ Dimerization of nerolidyl acetate, 1-vinylcyclohexyl acetate, and myrcene occurs with tetrakis(triphenylphosphine)palladium.²³⁸

(236) K. Dunne and F. J. McQuillin, *J. Chem. Soc. C*, 2196 (1970).
 (237) K. Dunne and F. J. McQuillin, *J. Chem. Soc. C*, 2200 (1970).

Reaction of π -allylpalladium chloride with carbon monoxide yields vinylacetyl chloride (eq 23).^{229,239} Carbonylation



tion of allyl chloride can also be achieved in dimethoxyethane with bis- π -allylpalladium chloride as catalyst to give 90% conversion to vinylacetyl chloride. Other palladium compounds can also be used as catalysts with reaction rate increasing in the order $\text{Pd} < \text{PdCl}_2 < (\text{C}_6\text{H}_5\text{CN})_2\text{PdCl}_2 < (\pi\text{-C}_3\text{H}_5\text{PdCl})_2$; π -allylrhodium complexes have also been employed. The reactions have been shown to be general for a series of allylic compounds (eq 24).^{229,240} Carbon monoxide always enters at



$\text{R}_1 = \text{Cl, alkyl, H; R}_2 = \text{alkyl, H}$
 $\text{X} = \text{halogen, OH, OR, OCOR}$

the least substituted carbon atom in the allyl fragment; *trans*-pent-3-enoyl chloride is obtained from either crotyl chloride or methylvinylcarbonyl chloride at about the same rate with 70% conversion at 90° in 6 hr. For allylic chlorides the rates decreased in the order allyl > crotyl \approx methylvinylcarbonyl \gg cyclooctenyl \approx methallyl > 1-chloroallyl \approx 4-chlorocrotyl. π -Allylpalladium halides also react with both butadiene and carbon monoxide; 3,7-octadienoyl chloride was obtained from reaction of allyl chloride, butadiene, and carbon monoxide catalyzed by bis- π -allylpalladium chloride.²²⁹ In methanol solution the acid chlorides react further to yield esters.^{241,242}

The rate of carbonylation of allyl chloride to butenoyl chloride catalyzed by π -allylpalladium chloride in the presence of a donor ligand such as triphenylphosphine has been shown to be a maximum when $\text{PPh}_3:\text{Pd} = 0.5$.^{229,230,243}

Carbonylation of allylic ethers and anhydrides catalyzed by palladium chloride in ethanol has been shown to yield esters. With 1,4-diethoxy-2-butene, although hexenedioate was the major product, smaller amounts of 5-ethoxy-3-pentenoate, 2-ethoxymethyl-3-butenolate, 3-pentenoate, and pentadienoate were also obtained.²⁴⁴ Insertion of sulfur dioxide into bis- π -allylpalladium has been reported.²⁴⁵

Similar carbonylation reactions have been reported between 1,3-dienes and carbon monoxide catalyzed by palladium salts. With butadiene and carbon monoxide in ethanol in the presence of a catalytic amount of palladium chloride, ethyl 3-pentenoate is formed with a 30% conversion at 100° for 24 hr (eq 25).²⁴⁶⁻²⁴⁹ 2-Cyclohexene-

(238) K. Dunne and F. J. McQuillin, *J. Chem. Soc. C*, 2203 (1970).

(239) J. Tsuji, *Accounts Chem. Res.*, 2, 144 (1969); *Advan. Org. Chem.*, 6, 109 (1969).

(240) J. Tsuji, J. Kiji, S. Imamura, and M. Morikawa, *J. Amer. Chem. Soc.*, 86, 4350 (1964).

(241) R. Long and G. H. Whitfield, *J. Chem. Soc.*, 1852 (1964).

(242) J. Tsuji, J. Kiji, and M. Morikawa, *Tetrahedron Lett.*, 1811 (1963).

(243) H. C. Volger, K. Vrieze, J. W. F. M. Lemmers, A. P. Praat, and P. W. N. M. van Leeuwen, *Inorg. Chim. Acta*, 4, 435 (1970).

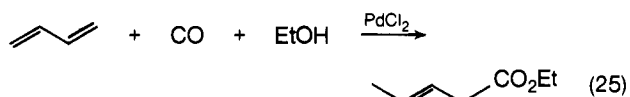
(244) S. Imamura and J. Tsuji, *Tetrahedron*, 25, 4187 (1969).

(245) S. O'Brien, *J. Chem. Soc. A*, 9 (1970).

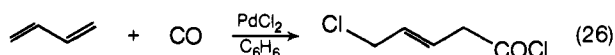
(246) J. Tsuji, J. Kiji, and S. Hosaka, *Tetrahedron Lett.*, 605 (1964).

(247) S. Hosaka and J. Tsuji, *Tetrahedron*, 27, 3821 (1971).

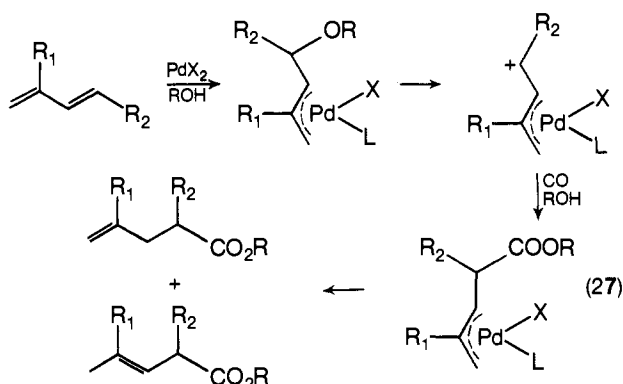
(248) S. Brewis and P. R. Hughes, *Chem. Commun.*, 157 (1965).



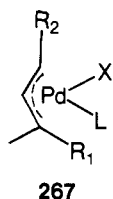
carboxylate and 4-cyclooctenecarboxylate were obtained from 1,3-cyclohexadiene and 1,3-cyclooctadiene in 80 and 58% yields, respectively.²⁵⁰ With unsymmetrical dienes, although carbon monoxide might have been expected to attack two positions, 4-methyl-3-pentenoate, 2-methyl-3-pentenoate, and 4-chloro-3-pentenoate were obtained in major amounts from isoprene, piperylene, and chloroprene, respectively.^{247,248,251} In aprotic solvents such as benzene, acid chlorides are formed (eq 26).²⁵² A number of mechanistic pathways for these



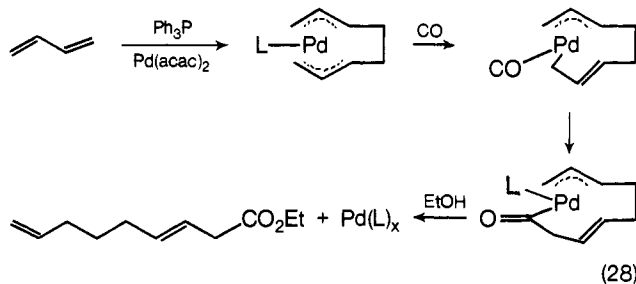
reactions are possible involving π -allylpalladium intermediates, one of which involves a carbonium ion (eq 27),



but a process involving the complex **267** must also be considered.



A different reaction is observed when butadiene is allowed to react with carbon monoxide catalyzed by a complex, prepared in ethanol from palladium acetylacetonate and triphenylphosphine; ethyl nona-3,8-dienoate is formed together with ethoxyoctadienes in the ratio 24:1. Formation of a bis- π -allyl intermediate was suggested followed by insertion of carbon monoxide (eq 28).^{253,254}



(249) K. Bittler, N. v. Kutepour, D. Neubauer, and H. Reis, *Angew. Chem., Int. Ed. Engl.*, **7**, 329 (1968).

(250) J. Tsuji, S. Hosaka, J. Kiji, and T. Susuki, *Bull. Chem. Soc. Jap.*, **39**, 141 (1966).

(251) C. Bordenca and W. E. Marsico, *Tetrahedron Lett.*, 1541 (1967).

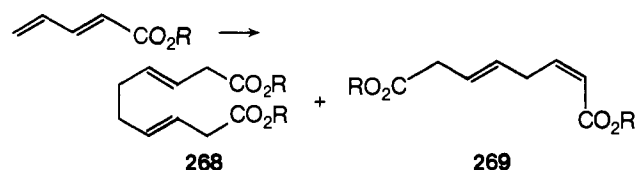
(252) J. Tsuji and S. Hosaka, *J. Amer. Chem. Soc.*, **87**, 4075 (1965).

(253) W. E. Billups, W. E. Walker, and T. C. Shields, *Chem. Commun.*, 1067 (1971).

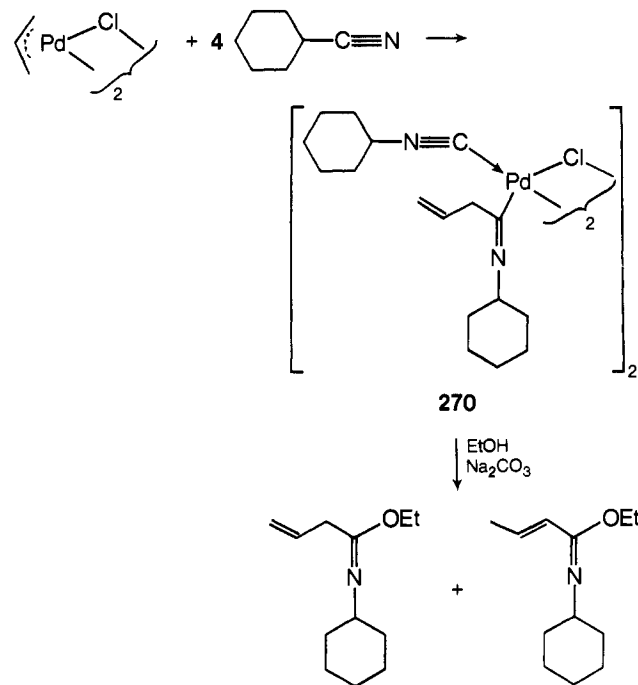
(254) J. Tsuji, Y. Mori, and M. Hara, *Tetrahedron*, **28**, 3721 (1972).

Insertion reactions of acetylene and carbon monoxide with allyl derivatives catalyzed by nickel catalysts are mentioned elsewhere, but some are relevant to the present discussion. Halo(carbonyl)(phosphine) π -allylnickel complexes have been prepared and π -allylnickel halides react with acetylene and carbon monoxide to yield methyl *cis*-hexa-2,5-dienoate in 47% yield.^{255,256}

1,4-Diallyl-*cis,cis*-1,3-butadiene has been prepared by reaction of acetylene and allyl bromide with π -allylnickel bromide in benzene, toluene, or acetonitrile although the yield was low since the product readily polymerizes.²⁵⁷ In the presence of iodotricarbonylnickel anions, prepared *in situ* from nickel tetracarbonyl and inorganic iodides, vinyl acrylate undergoes reaction with acetylene and carbon monoxide to form a mixture of **268** and **269**, although no yield was recorded.²⁵⁸



Reaction of cyclohexyl isocyanide with π -allylpalladium chloride in benzene at room temperature gave **270** which on ethanolysis gave a mixture of *n*-cyclohexyl-3-butenimide and ethyl *n*-cyclohexyl-2-butenimide.²⁵⁹ Inser-



tion of norbornene into nickel-allyl²⁶⁰ and palladium-allyl²⁶¹ derivatives has been reported; *cis*-*exo* addition is observed. 1-Ferrocenylmethyl- π -allylpalladium chloride derivatives²⁶² and a complex from hexafluoro-2-butyne and π -allylpalladium²⁶³ have been prepared. A facile

(255) F. Guerrieri and G. P. Chiusoli, *J. Organometal. Chem.*, **15**, 209 (1968).

(256) F. Guerrieri and G. P. Chiusoli, *Chem. Commun.*, 781 (1967).

(257) F. Guerrieri and G. P. Chiusoli, *J. Organometal. Chem.*, **19**, 445 (1969).

(258) M. Foa and L. Cassar, *Gazz. Chim. Ital.*, **102**, 85 (1972).

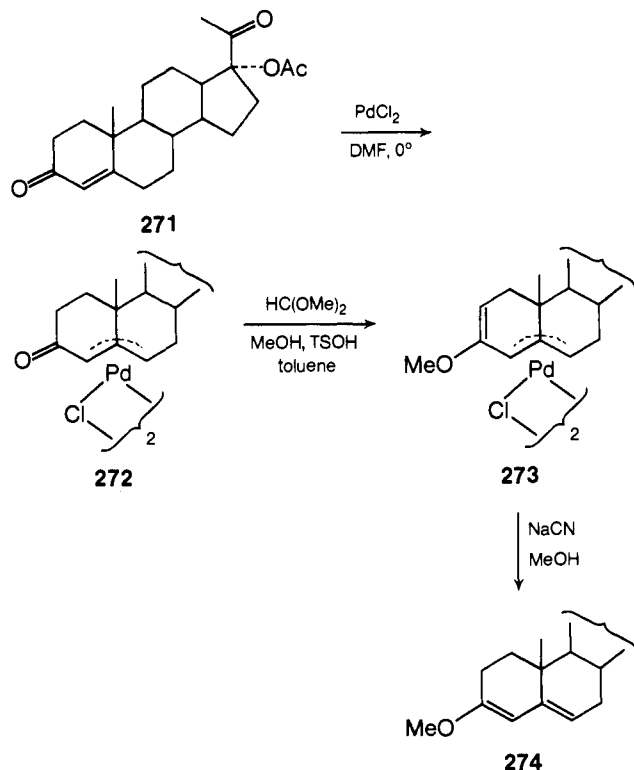
(259) T. Kajimoto, H. Takahashi, and J. Tsuji, *J. Organometal. Chem.*, **23**, 275 (1970).

(260) M. C. Gallazzi, T. L. Hanlon, G. Vitulli and L. Porri, *J. Organometal. Chem.*, **33**, C45 (1971).

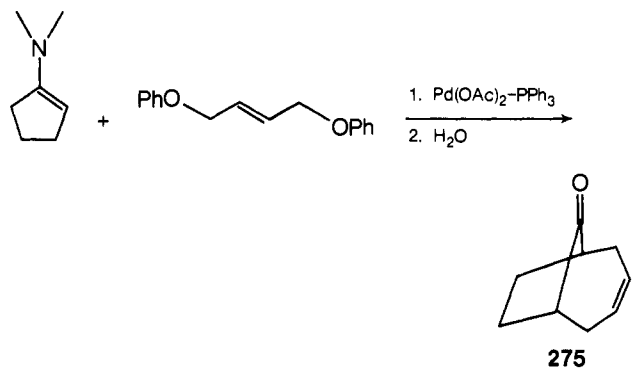
(261) R. P. Hughes and J. Powell, *J. Organometal. Chem.*, **30**, C45 (1971); M. Zocchi, G. Tieghi, and A. Albinati, *ibid.*, **33**, C47 (1971).

(262) A. Kasahara and T. Izumi, *Bull. Soc. Chem. Jap.*, **45**, 1256 (1972).

dehydrogenation reaction to form dienones has been observed on warming the π -allylpalladium complex produced from reaction of 3-oxo- $\Delta^{4,5}$ steroids with Na_2PdCl_4 , $(\text{PhCN})_2$ or $\text{C}_2\text{H}_4\text{Cl}_2$.²⁶⁴ Formation of **272** was found on heating **271** with palladium chloride in dimethylformamide; treatment of **272** with methyl orthoformate led to **273** which yielded **274** on reaction with sodium cyanide in methanol.²¹²



Reaction of 1-piperidinocyclohexene with allyl phenoxide in the presence of palladium acetate and triphenylphosphine in benzene gave, after hydrolysis, 2-allylcyclohexanone and 2,6-diallylcyclohexanone in 70 and 13% yields, respectively.²⁶⁵ This procedure was adapted to a synthesis of bicyclic derivatives, and a 28% yield of bicyclo[4.2.1]non-3-en-9-one (**275**) was found on reaction of

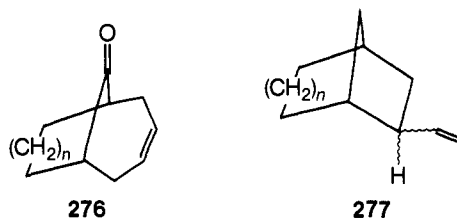


1-piperidinocyclopentene with 1,4-diphenoxy-*trans*-2-butene. With enamines of cyclohexanone, cycloheptanone, and cyclooctanone, mixtures of the bicyclic derivatives **276** and **277** were formed. These reactions were suggested to involve nucleophilic attack on the intermediate π -allylpalladium complexes.

(263) T. G. Appleton, H. C. Clark, R. C. Poller, and R. J. Puddephatt, *J. Organometal. Chem.*, **39**, C13 (1972).

(264) R. W. Howsam and F. J. McQuillin, *Tetrahedron Lett.*, 3667 (1968).

(265) H. Onoue, I. Moritani, and S. I. Murahashi, *Tetrahedron Lett.*, 121 (1973).

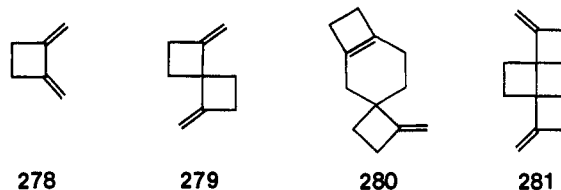


VI. Reactions of Allene

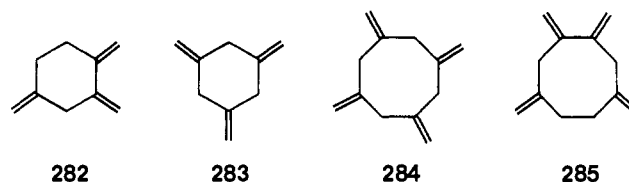
The organometallic chemistry of allene, virtually nonexistent 15 years ago, has rapidly become of interest to the polymer and organic chemist. It was not until 1964 that definite metal compounds of allene were prepared and characterized,²⁶⁶ although the polymerization of allenes using metal catalyst initiators was reported in 1956.²⁶⁷ A high molecular weight polymer was obtained when allene was allowed to react with dicobalt octacarbonyl at room temperature to afford an organocobalt complex which catalyzed allene polymerization. More recently there has been interest in the precise nature of bonding in allene-metal complexes and the variety of organic products that can be derived from allene. It is not the intention to review all documented allene complexes or all reported metal catalyzed polymerizations, but to focus more on the synthetic organic work cited.

A. Oligomerization

Thermal dimers, trimers, and tetramers of allene (**278–281**) have been reported as far back as 1913.²⁶⁸



However, entirely different products were obtained when allene and bis(triphenylphosphine)nickel dicarbonyl in tetrahydrofuran were allowed to react at 105–110° for 5–6 hr in an autoclave.²⁶⁹ A 41% yield was obtained of two trimers and a tetramer, **282–284**; tris(triphenyl phos-



phite)nickel carbonyl, (triphenyl phosphite)nickel tricarbonyl, and bis(triphenylphosphine)nickel dicarbonyl were also effective for reaction. (The structure of the tetramer **284** has now been reassigned **285**.²⁷⁰) On reaction with the polymeric catalytic species $[\text{Ph}_2\text{PC}_6\text{H}_4\text{PPh}_2\text{Ni}(\text{CO})_2]$ in the vapor phase at 200°, allene was converted in 61% yield into a mixture of dimers, 1,3-dimethylenecyclobutane (60%) and 1,2-dimethylenecyclobutane (13%), and trimers (27%)²⁷¹ (1,2-dimethylenecyclobutane is the pre-

(266) R. G. Schultz, *Tetrahedron Lett.*, 301 (1964); H. S. Lupin and B. L. Shaw, *ibid.*, 833 (1964).

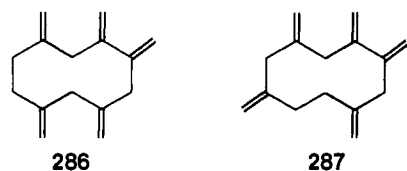
(267) H. Greenfield, I. Wender, and J. H. Wotiz, *J. Org. Chem.*, **21**, 875 (1956).

(268) S. V. Lebedev and B. K. Merezkovskii, *J. Russ. Phy. Chem. Soc.*, **45**, 1249 (1913).

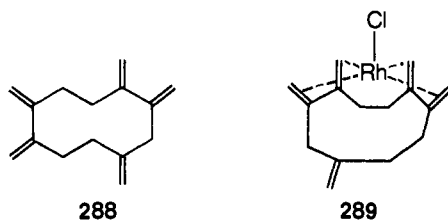
(269) R. E. Benson and R. V. Lindsey Jr., *J. Amer. Chem. Soc.*, **81**, 4247 (1959).

(270) S. Otsuka, A. Nakamura, T. Yamagata, and K. Tani, *J. Amer. Chem. Soc.*, **94**, 1037 (1972).

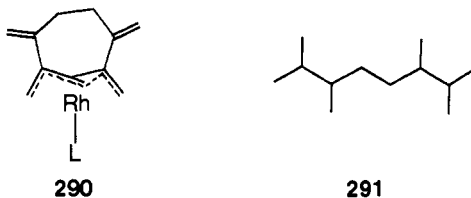
dominant thermal dimer isomer). With the catalyst bis(triphenylphosphine)nickel dicarbonyl under the same conditions the product was trimeric, but these reactions were highly exothermic and difficult to control. Reaction with $[\text{Ph}_2\text{PC}_6\text{H}_4\text{PPh}_2\text{Ni}(\text{CO})_2]$ was also performed in the liquid phase to yield a tetramer, a pentamer, and higher oligomers, but no dimers were formed. While the tetramer (**285**) was identical with that obtained with bis(triphenylphosphine)nickel dicarbonyl in the liquid phase, the pentamer was not definitely characterized but considered to be either **286** or **287**. When bis(1,5-cyclooctadiene)nickel in the absence of air at 40–70° was treated with allene in either polar or nonpolar solvents, the pentamer **286** was formed in 50–55% yield together with a small amount of liquid polymer.²⁷² It had previously been reported²⁷³ by the same author that bis(1,5-cyclooctadiene)nickel was effective as a polymerization catalyst for allene, forming firstly a red-brown allene-nickel complex which was active for polymerization above 10°.



Addition of 1,2-bis(diphenylphosphine)ethane to complex **289**, formed by introduction of allene into a benzene suspension of $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ at room temperature, gave cyclic pentamer **288**.²⁷⁴ Complexes of the lower oligomers of allene were not formed, although the geometries of a cyclic allene dimer, the 1,2,4-trimethylenecyclohexane trimer, and the 1,2,5,6-tetramethylene tetramer are all adequate for π -diene coordination (cf. **289**). A linear al-



lene tetramer complex has subsequently been isolated;²⁷⁵ when allene was bubbled through a suspension of $(\text{DBM})\text{Rh}(\text{C}_2\text{H}_4)_2$ or bis(ethylene)rhodium acetylacetonate in pentane at room temperature (DBM = diphenylpropane-1,3-dionato), yellow crystals of the bis- π -allyl species **290** were formed on cooling. X-Ray studies confirmed the structure to be **290** and on hydrogenation in ethanol at room temperature the complex afforded **291**.



An allene monomer complex has been isolated;²⁷⁴ stoichiometric addition of allene with tris(triphenylphosphine)-

(271) F. W. Hoover and R. V. Lindsey Jr., *J. Org. Chem.*, **34**, 3051 (1969).

(272) S. Otsuka, A. Nakamura, K. Tani, and S. Ueda, *Tetrahedron Lett.*, 297 (1969).

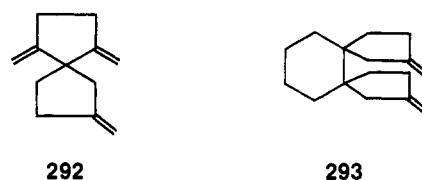
(273) S. Otsuka, K. Mori, and F. Imaizumi, *J. Amer. Chem. Soc.*, **87**, 3017 (1965).

(274) S. Otsuka, K. Tani, and A. Nakamura, *J. Chem. Soc. A*, 1404 (1969).

(275) G. Pantini, P. Racanelli, A. Immirzi, and L. Porri, *J. Organometal. Chem.*, **33**, C17 (1971).

rhodium chloride at room temperature gave the yellow, air-stable monomer complex $\text{RhCl}(\text{PPh}_3)_2\text{C}_3\text{H}_4$. X-Ray and nmr studies have appeared on analogous compounds suggesting that bonding is through one double bond.²⁷⁶ The phosphine in tris(triphenylphosphine)rhodium chloride hindered further ligation to **289**. However, the monomer complex was suitable for catalyzing oligomerization to the tetramer **292**; this same tetramer can be obtained using $\text{Rh}_2\text{Cl}_2(\text{C}_2\text{H}_4)_4$ as catalyst. From this, it can be inferred that the monomer complexes are precursors to **292**.

A variety of Rh(I) compounds, e.g., $(\text{CO})_4\text{Rh}_2\text{Cl}_2$ and $(\text{acac})\text{Rh}(\text{C}_2\text{H}_4)_2$, have been shown to catalyze oligomerization at 50° to polymeric oily mixtures.²⁷⁷ However, if triphenylphosphine is added, or a preformed phosphine complex used, allene tetramer and pentamer are formed in 42–60% yields respectively (the pentamer was not fully characterized). It appears that if forcing conditions are used (~ 16 hr, $\sim 80^\circ$, in a pressure tube) pentamer formation can be effected even with a phosphine present. Otsuka and coworkers also reported²⁷⁸ formation of the tetramer **292** and further commented that π -acceptor lig-



ands, e.g., carbon monoxide and isocyanides, caused polymerization rather than tetramerization when added to the effective catalytic system, $\text{Rh}_2\text{Cl}_2(\text{C}_2\text{H}_4)_4$ and triphenylphosphine. The lack of activity of the structurally related tris(triphenylphosphine)irridium chloride, which gave almost no reaction, and the polymer formation from tris(triphenylphosphine)cobalt chloride was noted. An allene hexamer **293** has been isolated²⁷⁹ by workers studying polymerization of allene by dicarbonylrhodium dichloride and 2 equiv of triphenylphosphine in an autoclave for 6 hr at 40°. Pentamer and tetramer were formed together with **293**, although the oligomers were formed in less than 3% yield; the polymer/oligomer ratio was suggested to be dependent on the triphenylphosphine content of the catalyst molecule.

The effect of addition of a ligand such as triphenylphosphine substantially altering the reaction pathway by the blocking of a coordination site is also demonstrated by the nickel-catalyzed oligomerization reactions of allene. A trimer-nickel(0) complex, $\text{Ni}(\text{C}_9\text{H}_{12})(\text{PPh}_3)$, was isolated as an orange-red crystalline complex from reaction of allene and bis(1,5-cyclooctadiene)nickel at -70° .²⁸⁰ Red needles of $\text{Ni}(\text{C}_9\text{H}_{12})$ were first isolated and found to be very unstable, and addition of triphenylphosphine at -30° afforded $\text{Ni}(\text{C}_9\text{H}_{12})(\text{PPh}_3)$; treatment of this with carbon disulfide afforded **282**. Cyclopentamerization is effected with bis(1,5-cyclooctadiene)nickel, but addition of phosphine and low temperatures reduced this catalytic reaction.²⁷⁰ The tetramer complex **297** has also been shown to be present in the reaction of bis(1,5-

(276) G. Pantini, P. Racanelli, A. Immirzi, G. Allegra, and L. Porri, *Chem. Commun.*, 361 (1969); T. Kashiwagi, N. Kasai, and M. Kukudo, *ibid.*, 317 (1969).

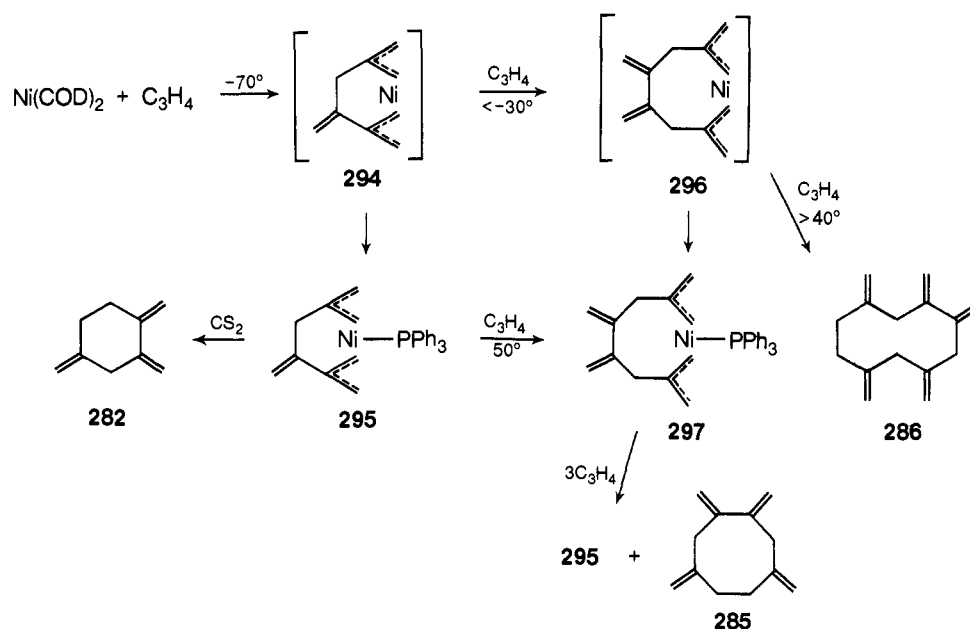
(277) F. N. Jones and R. V. Lindsey Jr., *J. Org. Chem.*, **33**, 3838 (1968).

(278) S. Otsuka, A. Nakamura, and H. Minamida, *Chem. Commun.*, 191 (1969).

(279) J. P. Scholten and H. J. V. D. Ploeg, *Tetrahedron Lett.*, 1685 (1970).

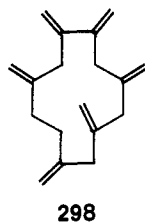
(280) S. Otsuka, A. Nakamura, S. Ueda, and K. Tani, *Chem. Commun.*, 863 (1971).

SCHEME XXVI



cyclooctadiene)nickel with allene. (Scheme XXVI), but this was not recrystallized because of its decomposition to an orange binuclear complex $\text{Ni}_2(\text{C}_{12}\text{H}_{16})(\text{PPh}_3)_3$. Formation of **296** and **297** from **294** and **295** implies that allene insertion occurs preferentially at the π -allyl group adjacent to the exo-methylene group. It follows that if **286** is to be formed from **296**, there can be only one possible structure for the pentamer. It was considered that a nickel(0) species, free from nonreacting ligands, acts as a template for a multistep reaction to yield the pentamer **286**. The effect of different phosphines was noted. With 1–4 mol of tertiary alkyl or aryl phosphine added, the major product was tetramer **285**. However with triaryl phosphite the trimer **282** is the predominant oligomer. At high phosphine:nickel ratios (>2:1) or higher catalyst concentration, pentamer formation is reduced relative to the lower oligomers; this selectivity was explained by competitive coordination of allene and ligand toward the complexes.

A Ni(0) species assigned $(\text{Ph}_3\text{P})_2\text{Ni}$ was prepared²⁸¹ and dissolved in various solvents, totally converted allene at 75° to a mixture of **282**, **283**, **285**, and **286**, and isomeric hexamers of which **298** was the major prod-



uct.²⁸⁴ Trimers and the tetramer were favored as the catalyst/allene ratio decreased; added triphenylphosphine also favored formation of the lower oligomers when $(\text{Ph}_3\text{P})_2\text{Ni}$ was considered to give the coordinatively satu-

(281) The structure was assigned on spectroscopic and chemical data, and the preparation of bis(triphenylphosphine)nickel is briefly described in the patent literature.²⁸² It is a 14-electron complex and as such must be considered inherently unstable on the basis of the 16–18 electron rule.²⁸³

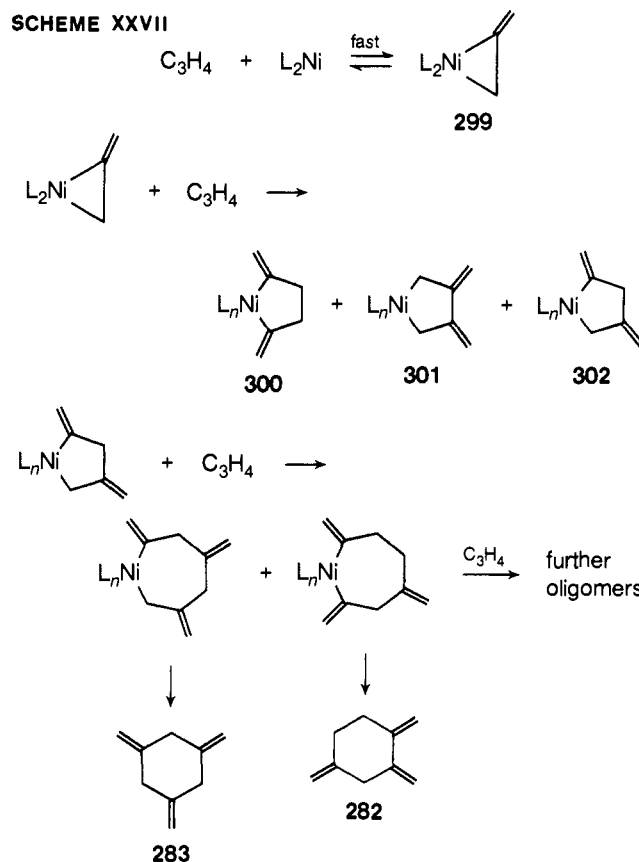
(282) G. Wilke, E. W. Muller, M. Kröner, P. Heimbach, and H. Breil, British Patent 935,716 (1963).

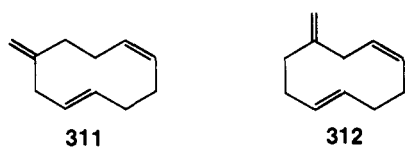
(283) C. A. Tolman, *Chem. Soc. Rev.*, 1, 337 (1972).

(284) R. J. De Pasquale, *J. Organometal. Chem.*, 32, 381 (1971).

rated tetra(triphenylphosphine)nickel. In excess, triphenylphosphine reduced the reaction rate, but not the allene conversion. It has again been suggested that triphenylphosphine competes with allene for coordination sites. The ratio of (C_9 – C_{18}) oligomers to waxes and polymer was unaffected by the added ligand and catalyst to allene ratio, and the inference was drawn that cyclooligomers were derived from different intermediates to the waxes and polymer. Also reported was an orange-red complex $(\text{Ph}_3\text{P})_2\text{NiC}_3\text{H}_4$ (**299**) capable of catalyzing allene oligomerizations. This allene monomer complex was prepared by reduction of bis(triphenylphosphine)nickel bromide in the presence of allene or by reaction of allene

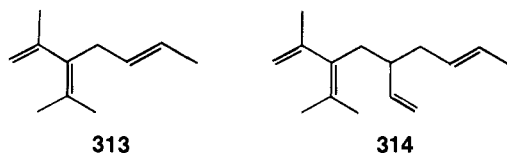
SCHEME XXVII



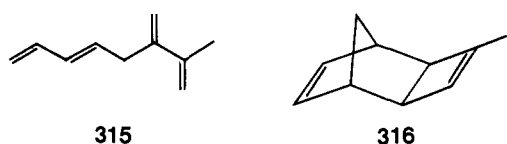


was increased up to 70% when the gaseous mixture was passed into the catalyst keeping the steady state concentration of allene low. Bis(methylene)-12-membered rings, from the 2:2 allene:butadiene reaction (1,2-, 1,3-, 1,4-bismethylene were shown to be formed), were also reported. Compounds analogous to **311** and **312** were obtained from reaction of 1,1-dimethylallene and methoxyallene with butadiene.

Tetramethylallene has been cooligomerized with butadiene using iron catalysts.²⁸⁹ The Ziegler-Natta system, ferric chloride and a Grignard reagent in ether, ferric acetylacetonate and triethylaluminum in benzene, and bis(cyclooctatetraene)iron have been shown to give 1:1 (C_{11}) and 1:2 (C_{15}) tetramethylallene:butadiene adducts. Five different C_{11} isomers were reported, principally **313**, and the predominant C_{15} isomer was found to be **314**. It is interesting to note that the addition involves a hydrogen transfer from the methyl group of tetramethylallene to butadiene and the carbon atom losing the hydrogen does not form a new carbon-carbon bond.

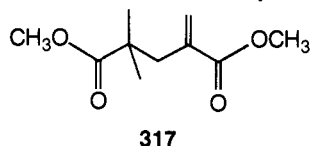


Allene, butadiene, and a catalytic amount of bis(triphenylphosphine)palladium-maleic anhydride were heated to 120° and gave a 39% yield of a 3:1 mixture of *cis*- and *trans*-**315**;²⁹⁰ 1,3,7-octatriene and 4-vinylcyclohexene were also formed. Bicyclo[2.2.1]hepta-2,5-diene was allowed to react under similar conditions, and a 25% yield of **316** was obtained.



C. Carbonylation

The reaction of allene, carbon monoxide, and methanol has been studied at 140° with a diruthenium nonacarbonyl catalyst and shown to give a 50% yield of methyl methacrylate; methacrylic acid was formed when water was substituted for methanol.²⁹¹ With methanol at 190°, dimethyl α,α -dimethyl- α -methylene-glutarate (**317**) was

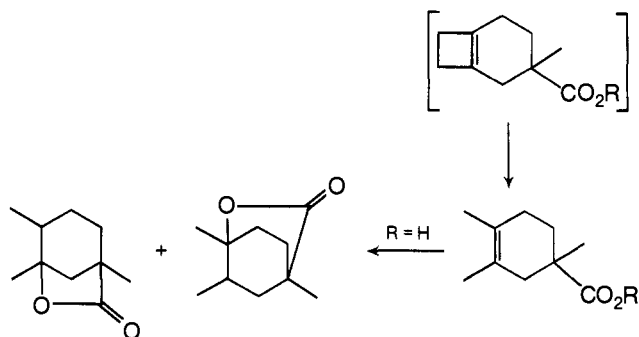
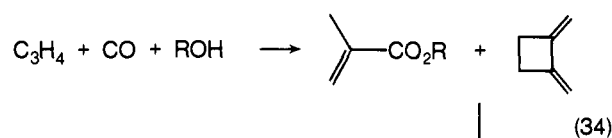


obtained in 23% yield, together with methyl methacrylate (18%), and considered to result from allene addition to methyl methacrylate. At 175–200°, the main products were lactones (20%) or the cyclic methyl ester (12%) depending on whether water or methanol was solvent (eq 34).

(289) A. Greco, A. Carbonaro, and G. Dall'Asta, *Tetrahedron Lett.*, 5009 (1969).

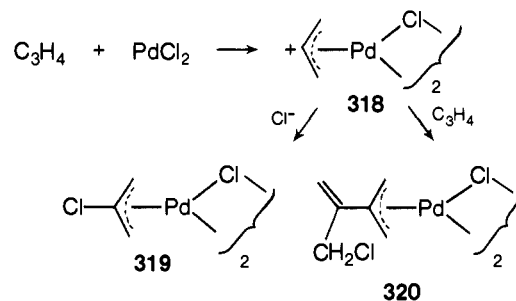
(290) D. R. Coulson, *J. Org. Chem.*, **37**, 1253 (1972).

(291) T. J. Kealy and R. E. Benson, *J. Org. Chem.*, **26**, 3126 (1961).



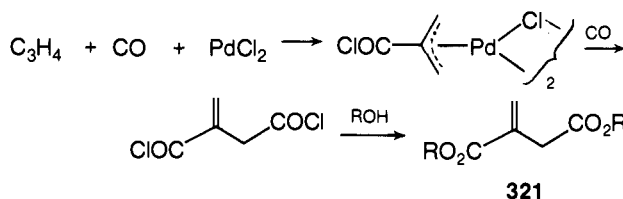
The carbonylation reaction of allene in methanol at 140° with carbon monoxide in the presence of nickel carbonyl and methacrylic acid or water gave methyl methacrylate in 62% yield.²⁹² Bis(triphenylphosphine)nickel bromide was not an effective catalyst; a stoichiometric process was observed with nickel carbonyl and hydrochloric acid to give a little methyl methacrylate and only trace amounts of products with nickel carbonyl alone. *trans*-2-Methyl-2-hexenoate and methyl 2-butyl-2-propenoate were formed in a 5:1 ratio in 15% yield from 1,2-hexadiene; in both reactions, the ester group was substituted on the central carbon of the allene group.

On reaction of allene with palladium chloride, **319** or **320** was obtained depending on the reaction condi-



tions.²⁹³ In benzene, formation of **319** can be considered to be insertion of the double bond of allene between the palladium-chlorine bond, whereas, in methanol, another molecule of allene reacts at the cationic center to give **320**. The positive species **318** was found to react with carbon monoxide and carboxylate anions to give π -allylic species which yield the products **321** and **322**, respectively. Stepwise addition of carbon monoxide to **320** gave three products **323**, **324**, and **325** (Scheme XXVIII).

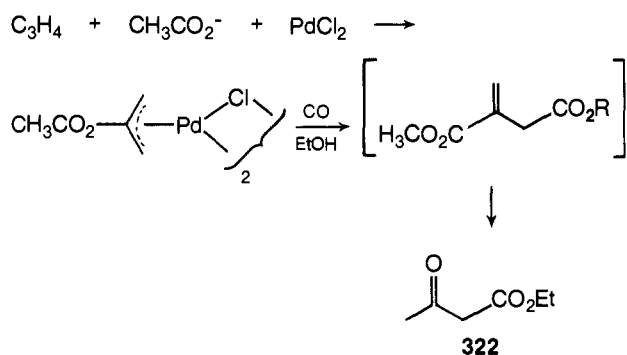
There has been considerable interest in the π -allyl derivatives of palladium and allene. Shultz reported²⁹⁴ the reaction of allene and bis(benzonitrile)palladium chloride



(292) S. Kunichika, Y. Sakakibara, and T. Okamoto, *Bull. Chem. Soc. Jap.*, **40**, 885 (1967).

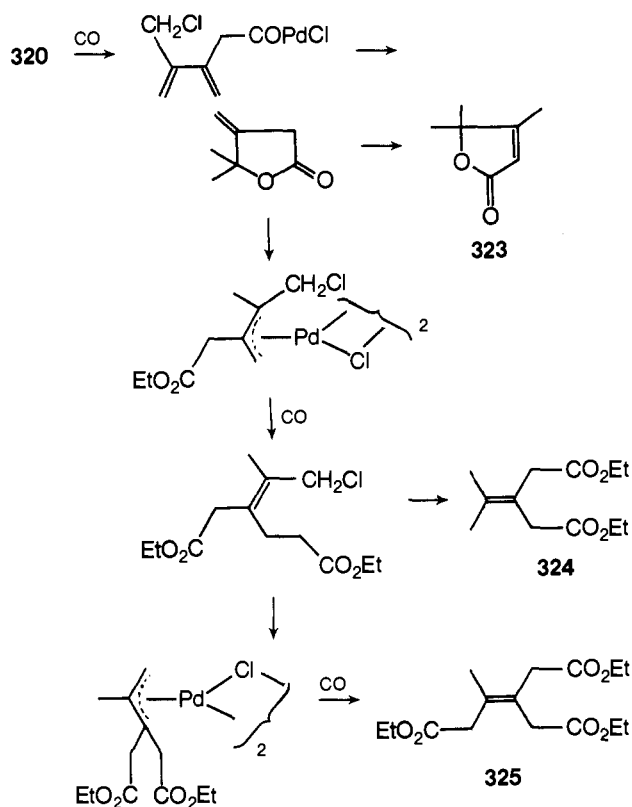
(293) T. Susuki and J. Tsuji, *Tetrahedron Lett.*, 3027 (1965); *Bull. Chem. Soc. Jap.*, **41**, 1954 (1968).

(294) R. G. Schultz, *Tetrahedron*, **20**, 2809 (1964).



to yield four products depending on the procedure (Scheme XXIX). When sodium chloropalladate was al-

SCHEME XXVIII

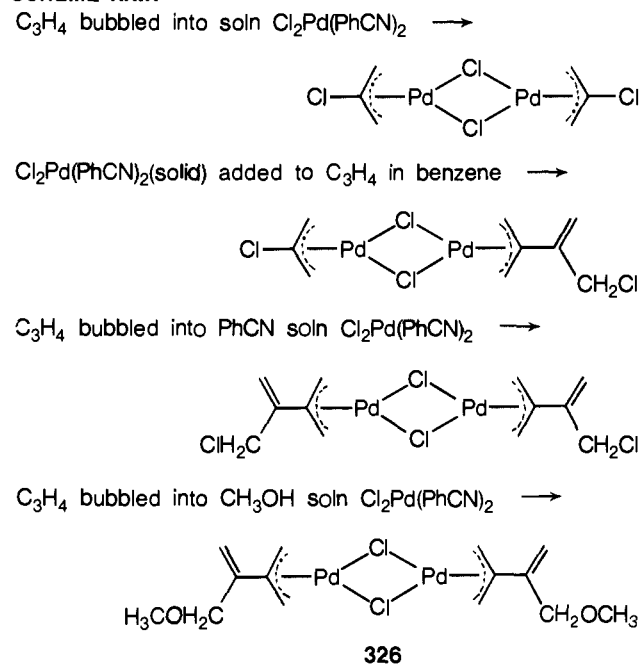


lowed to react with allene in methanol, no methoxy complex **326** was formed.²⁹⁵ The inference was that the benzonitrile group in the palladium complex plays some part in methanol incorporation. An analogous reaction with methylallene and 1,1-dimethylallene gave products which could not be crystallized, but methylallene reacted with bis(benzonitrile)palladium chloride in benzene to give **327**. The mechanism suggested was coordination of allene to palladium followed by migration of chlorine from palladium, or, alternatively, 2 mol of allene could become coordinated to palladium, followed by dimerization and chlorine migration from palladium to carbon; polar media favor dimer formation. Hughes and Powell have shown that reaction occurs between π -allylpalladium acetylacetonate and allene to give the insertion product **328** (eq 35).²⁹⁶ This complex is analogous to the reported 2,2-bis- π -allyl species formed from allene and diiron nonacarbonyl or triiron dodecacarbonyl to give complexes of the type $(\text{C}_6\text{H}_8)\text{Fe}_2(\text{CO})_6$.²⁹⁷⁻²⁹⁹ A trimeric allene bisallyl

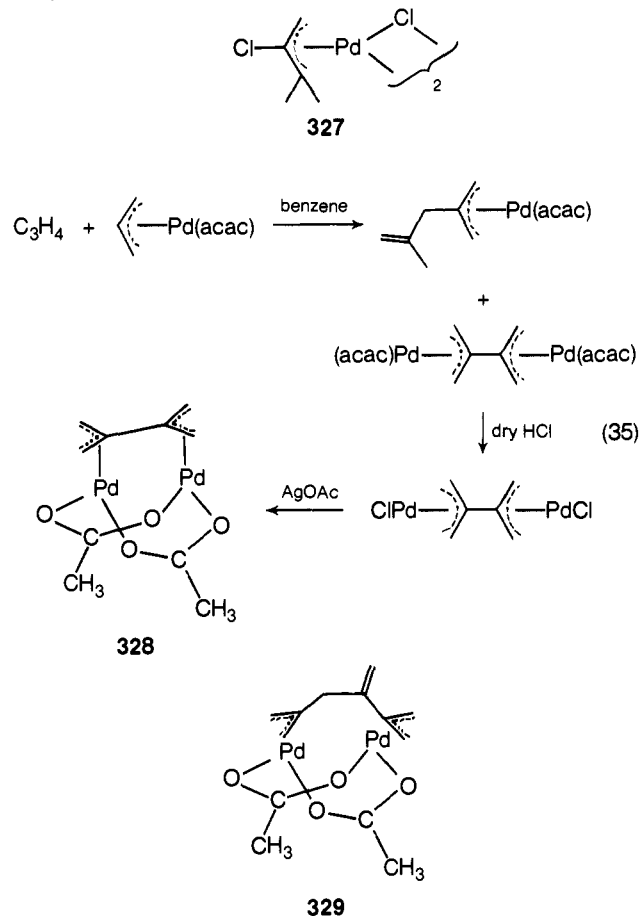
(295) M. S. Lupin, J. Powell, and B. L. Shaw, *J. Chem. Soc. A*, 1687 (1966).

(296) R. P. Hughes and J. Powell, *J. Organometal. Chem.*, **20**, P17 (1969).

SCHEME XXIX



complex of palladium, **329**, has also been reported from reaction of palladium acetate and allene.³⁰⁰ The same product was also formed from di- μ -acetate-2,2'-bis- π -allylpalladium.³⁰¹



(297) R. Ben-Shoshan and R. Pettit, *Chem. Commun.*, 247 (1968).

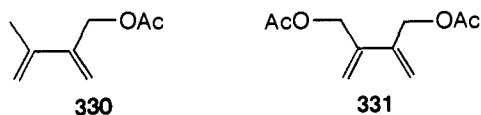
(298) A. Nakamura, P.-J. Kim, and N. Hagihara, *J. Organometal. Chem.*, **3**, 7 (1965).

(299) S. Otsuka, A. Nakamura, and K. Tani, *J. Chem. Soc. A*, 2248 (1968).

(300) T. Okamoto, Y. Sakakibara, and S. Kunichika, *Bull. Chem. Soc. Jap.*, **43**, 2658 (1970).

(301) T. Okamoto, *Chem. Commun.*, 1126 (1970).

Solutions of palladium(II) complexes of weak ligands (acetate, nitrate, chlorate) in glacial acetic acid catalyze the reaction of allene to acetic esters.³⁰² At 50° and 1 atm, allyl acetate, 2,3-dimethyl-1,3-butadiene, **330**, and **331** were formed in the ratio 7:19:100:14. Propene has

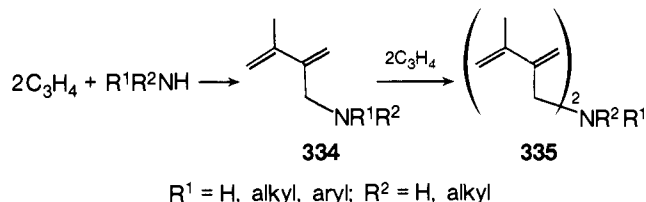


also been found as a product from the reduction of allene; **331** can be considered the oxidation product of 2 mol of allene. From this the palladium was considered to be acting as an oxidation-reduction catalyst through palladium(0) or a palladium hydride. The intermediate in the reaction is probably an acetate complex similar to **320** which being relatively unstable compared to the chloride-bridged complex could be the origin of a catalytic reaction. On addition of 1 mol of triphenylphosphine, head-to-head polymerization of allene occurred to give a polymer with molecular weight 1000–2000. In the presence of methylacetylene and allene, a catalytic reaction occurred to give **332** and **333** together with products of allene described above; a palladium acetylde appears to be implicated as an intermediate.³⁰³



D. Amines, Carbon Acids, and Carbonyl Derivatives

Catalytic formation of derivatives of 2,3-dimethyl-1,3-butadiene from allene and amines and carbon acids has been reported.³⁰⁴ A variety of compounds of palladium or rhodium [e.g., palladium chloride, rhodium trichloride, tetrakis(triphenylphosphine)palladium] were found to be effective catalysts for reaction with amines. The reaction could be carried out by bubbling allene into a solution of the amine and catalyst in hexamethylphosphoramide at 70–90° and also using lower boiling solvents in a sealed tube (100–140°). Reactions were reported for a variety of amines, and yields up to 80% were obtained; **334** or **335** was formed depending on conditions and reactant amine. Similar reactions with enamines were also studied.

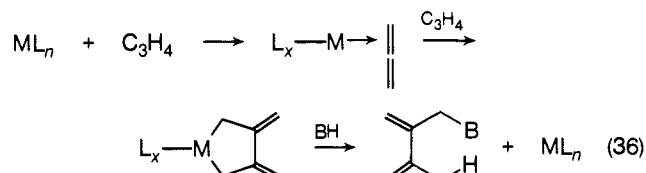


A palladium(0) species produced a faster overall reaction rate than the related palladium(II) derivatives, suggesting the former might be produced in the catalytic cycle. The activity of the latter could be attributed to their reduction to palladium(0) with alkylamines. Reactions with carbon acids were analogous, but rhodium(III) and palladium(II) complexes were ineffective. Deuterium-labelling experiments placed the active hydrogen of the nucleophile predominantly on the methyl group. Intermediates were not observed, but a mechanism was postulated (eq 36).

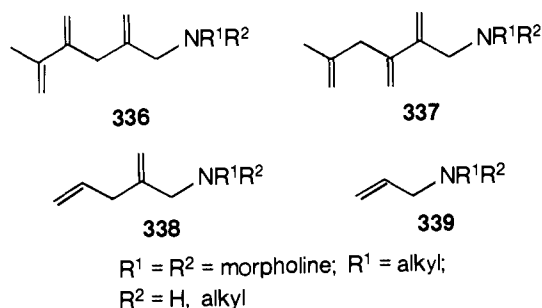
(302) G. D. Shier, *J. Organometal. Chem.*, **10**, P15 (1967).

(303) G. D. Shier, *Amer. Chem. Soc. Div. Petrol. Chem., Prepr.*, **14**, B123 (1969).

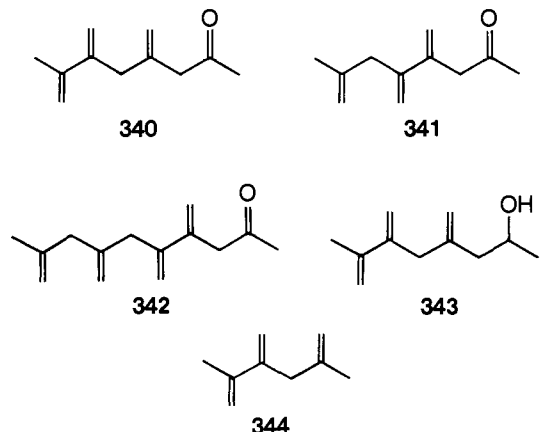
(304) D. R. Coulson, 163rd National Meeting of the American Chemical Society, Boston, Mass., April 9–14, 1972, Abstract PETR-52.



Further work has shown amines and a 3:1 excess of allene, when heated to 75–100° in the presence of the catalytic system nickel bromide and phenyldiisopropoxyphosphine in ethanol solvent, gave a mixture of alkylated amines in yields up to 100% containing predominantly the trimer adducts **336** and **337**.³⁰⁵ The dimer adducts **334** and **338** were also formed together with a trace of the monoadduct **339**. Omission of ethanol led to a reduced overall conversion of amine and an increase in formation of **338**. Under similar conditions the catalyst system, nickel acetylacetonate, sodium borohydride, and phenyldiisopropoxyphosphine in ethanol, gave almost exclusively trimer adducts.³⁰⁵



Reaction of allene and acetyl chloride at –30° in the presence of bis(1,5-cyclooctadiene)nickel in ether gave a mixture of **340–342**.³⁰⁵ A similar result was obtained with acetaldehyde, with **343** the major product; **344** was also isolated from these reactions together with the expected cyclooligomers. In both cases yields of the order 30% were obtained.



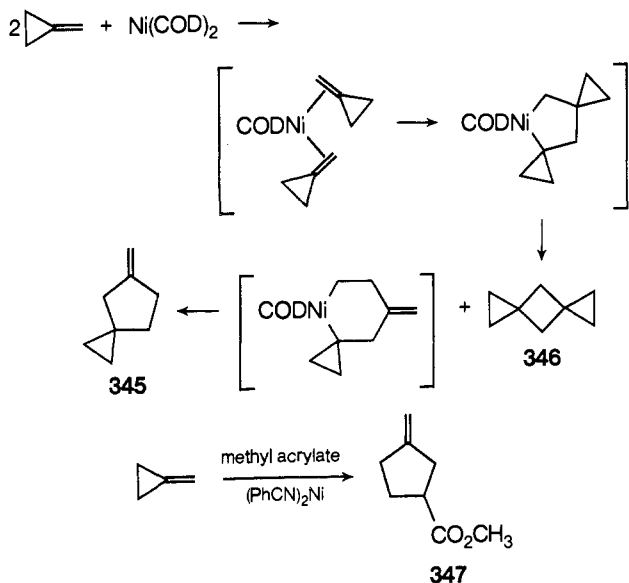
VII. Reactions of Methylene-cyclopropane

Oligomerization of methylenecyclopropane by bis(cyclooctadiene)nickel at –15° in hydrocarbon or ether solvent has been reported to yield a mixture of **345** and **346** (45%), six isomeric trimers (10%), and high molecular weight oligomers (45%).³⁰⁶ The cycloaddition of methylenecyclopropane across carbon-carbon double bonds with bis(acrylonitrile)nickel has also been reported.³⁰⁷ A 1:1 adduct (**347**) was formed in 82% yield, no reaction being observed without the nickel catalyst; methyl vinyl

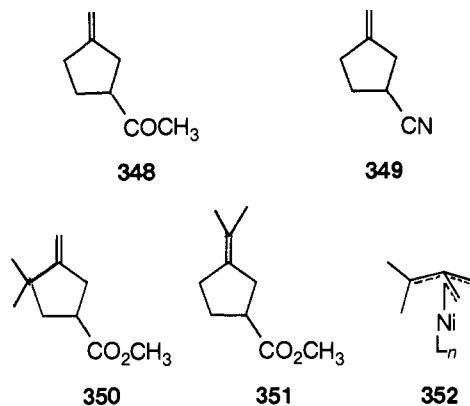
(305) R. Baker and A. H. Cook, unpublished work.

(306) P. Binger, *Angew. Chem., Int. Ed. Engl.*, **11**, 309 (1972).

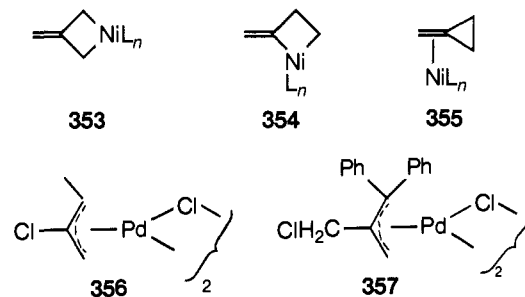
(307) R. Noyori, T. Odagi, and H. Takaya, *J. Amer. Chem. Soc.*, **92**, 5780 (1970).



ketone or acrylonitrile gave **348** and **349**. Reaction of 2,2-dimethylmethylenecyclopropane and isopropylidene-cyclopropane with methacrylate gave 60 and 61% conversions to **350** and **351**, respectively. These two results ruled out the possibility of a trimethylenemethane com-



plex (**352**) as an intermediate since identical products would have been expected from the two reactions. Possible intermediates were therefore proposed to be either **353**, **354**, or **355**. Methylenecyclopropane has been allowed to react in benzene with palladium chloride at room temperature, and yellow crystals of π -allylic species **356** were shown to be formed; 2,2-diphenylmethylenecyclopropane affords **357**.³⁰⁸ The direction of ring fusion to form π -allylic complexes is therefore effected by substitution of the cyclopropane ring. Methylenecyclopropane involves fusion of the C-1-C-2 bond; the diphenyl, on the other hand, gave the C-2-C-3 cleavage product.



Methylenecyclopropane, when allowed to react with iron tricarbonyl, has been shown to give butadienetetracarbonyliron,³⁰⁹ and with NiL_2 ($\text{L} = \text{P}(\text{OC}_6\text{H}_4\text{OC}_6\text{H}_5)_3$) the analogous nickel-butadiene species has been obtained.³¹⁰

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(308) R. Noyori and H. Takaya, *Chem. Commun.*, 525 (1969).

(309) R. Noyori, T. Nishimura, and H. Takaya, *Chem. Commun.*, 89 (1969).

(310) M. Englert, P. H. Jolly, and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, 10, 77 (1971).