

# Addition Reactions of Transition Metal Compounds

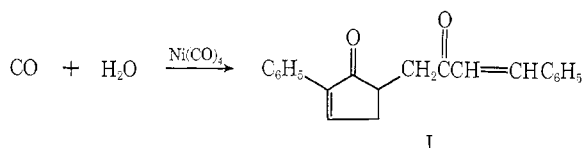
RICHARD F. HECK

*Hercules Research Center, Wilmington, Delaware**Received April 29, 1968*

Addition reactions of metal compounds to unsaturated molecules have been known for many years, but the very wide applicability of these reactions is just now beginning to be realized. These reactions are useful for preparing inorganic, organometallic, and organic compounds.

The synthesis of organic compounds by means of addition reactions of metal compounds is already common with main group metals, *e.g.*, the Grignard reaction, Reformatsky reaction, lithium alkyl additions, etc. Many new synthetic organic reactions are now being discovered which employ addition reactions of transition metal compounds. The variety of organic compounds which can be obtained by combining various unsaturated molecules with each other or with other groups in specific linear or cyclic ways is almost unlimited. Even though ways to effect every possible combination specifically will surely not be found, enough is now known to make it certain that these reactions will be of considerable importance in organic synthesis in the near future.

A remarkable example of the formation of a very complex molecule from "small molecules" in a series of addition reactions is the reaction of allyl chloride, phenylacetylene, water, and nickel carbonyl in acetone solution. This reaction produced compound I in 64% yield by what appears to be a series of five addition reactions, all of which must occur reasonably specifically and in high yield.<sup>1</sup> The steps involved in this transformation will be considered later.



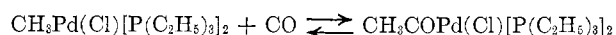
## Addition Mechanisms

Investigation of the mechanisms of the addition reactions of transition metal complexes with unsaturated compounds is still at an early stage. In general the reactions are very fast, and intermediate compounds are extremely reactive. Often the compounds are very easily oxidized by oxygen and are thermally unstable as well, making study of the reactions difficult.

Three modes of addition are commonly observed: 1,1-, 1,2-, and 1,4-additions. The addition of carbon monoxide is typical of the 1,1-type addition in which both parts of the metallic reagent are added to the carbon atom of the carbon monoxide. Thus, addition

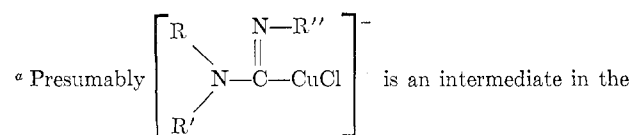
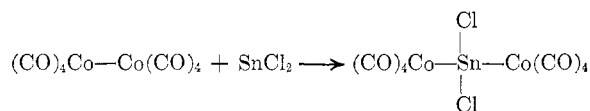
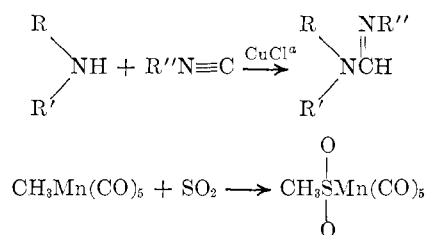
(1) G. P. Chiusoli, G. Bottaccio, and C. Venturello, *Tetrahedron Letters*, 2875 (1965).

of the methylpalladium group to carbon monoxide<sup>2</sup> results in the formation of an acylpalladium compound.



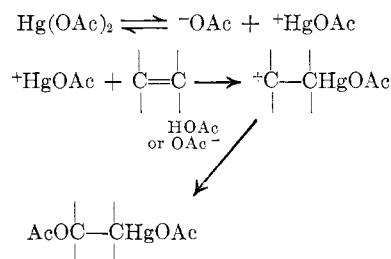
Isoocyanides,<sup>3</sup> sulfur dioxide,<sup>4</sup> and stannous chloride<sup>5</sup> react similarly (Chart I). These reactions are characterized by an increase of two in the coordination number of the atom attacked.

Chart I



reaction.

The 1,2-addition reactions are more complicated because they may occur by ionic, radical, or covalent mechanisms. Ionic additions are encountered most frequently with compounds of the main group elements, *e.g.*, cyanohydrin synthesis with potassium cyanide, Michael additions, alkali metal alkyl additions, etc. Additions of mercuric compounds to olefins are generally of this type.<sup>6</sup> The ionic additions generally



(2) G. Booth and J. Chatt, *J. Chem. Soc.*, A, 634 (1966).

(3) T. Saegusa, Y. Ito, S. Kobayash, K. Hirota, and H. Yoshioka, *Tetrahedron Letters*, 6121 (1966).

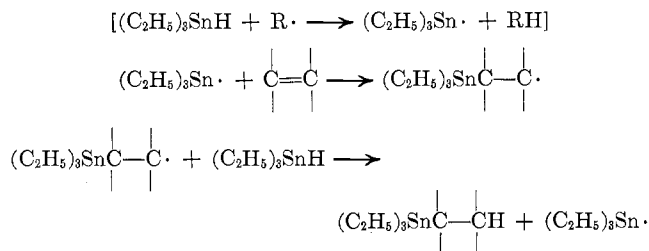
(4) F. A. Hartman and A. Wojcicki, *J. Am. Chem. Soc.*, **88**, 844 (1966).

(5) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **5**, 1405 (1966).

(6) J. Chatt, *Chem. Rev.*, **48**, 7 (1951).

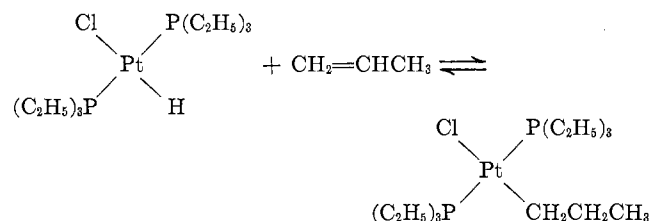
follow the Markovnikov rule of direction of addition.

The addition reactions of group IV compounds, particularly the hydrides, commonly proceed by a radical mechanism; a typical reaction follows.<sup>7</sup> The



direction of addition in these radical reactions may be predicted on the basis that the most stable new radical is produced in the first addition step.

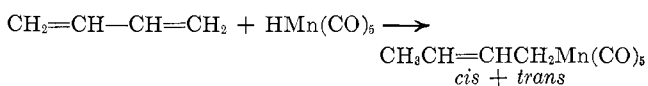
Covalent 1,2-additions occur most frequently in the addition reactions of transition metal compounds. The addition of hydrido-chlorobis(triethylphosphine)-platinum(II) to propylene is a good example.<sup>8</sup> Ex-



clusive anti-Markovnikov orientation was observed in this reaction.

The directions of addition observed in the covalent reactions appear to depend upon several factors which have not yet been investigated in detail. Steric effects often seem to be of primary importance, but electronic, solvent, temperature, and salt effects may also be dominant. Mechanisms of addition may also change with changes in reaction conditions so that prediction of directions of covalent addition with any certainty using present knowledge is generally not possible.

1,4-Additions may occur in reactions with conjugated unsaturated compounds. The addition of hydrido-pentacarbonylmanganese(I) to butadiene to produce the 2-butenylmanganese derivative is probably an example of a 1,4-covalent addition.<sup>9</sup> If both hydrogen and  $Mn(CO)_5$  were added simultaneously to the *cis* form of butadiene, a pure *cis* adduct would have been expected. It is not clear why some of the *trans* isomer was also produced in the reaction.



### Organic Syntheses with Transition Metal Compounds

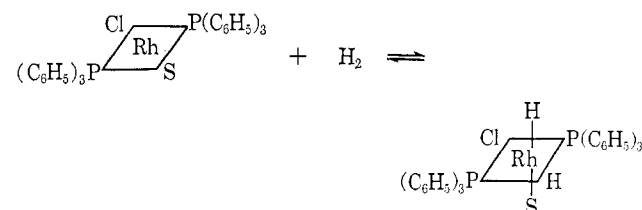
Many specific and general reactions leading to completely organic products have been found which em-

ploy transition metal compounds. Almost all of these reactions appear to involve addition reactions. Only a few examples can be given here, but from these it should be obvious that the addition reactions can be useful and that potential applications are very numerous. Both stoichiometric and catalytic reactions based upon the transition metal compound are common. Fortunately, catalytic reactions, which generally are the most useful, are observed more frequently with transition metal compounds than with the main group metal compounds. The reason for this is at least partly that the transition metals generally have a considerably lower affinity for oxygen relative to carbon and hydrogen than do the main group elements; therefore the catalyst is not usually lost by formation of relatively unreactive metal-oxygen compounds.

**Homogeneous Hydrogenation.** Hydrogenation is perhaps the simplest of the catalytic reactions involving addition reactions of transition metal compounds. The basic reactions involve an addition of a metal hydride to the unsaturated compound followed by hydrogenolysis of the metal-carbon (or metal-other element) bond so produced. In detail the reaction is more complicated.

The most thoroughly studied homogeneous hydrogenation catalyst is  $[(C_6H_5)_3P]_3RhCl$ . A combination of chemical and kinetic studies has given convincing evidence for a detailed mechanism of the reaction.<sup>10</sup> The complex is largely dissociated in solution, and presumably a solvent molecule replaces the triphenylphosphine group which leaves the metal in the dissociation step. The dissociation step, which is prob-

ably caused by steric repulsion between ligands, is apparently necessary for hydrogenation to occur since complexes with other (smaller) phosphine ligands which do not dissociate are not hydrogenation catalysts.<sup>11</sup> The dissociated complex then can react with hydrogen by what has been termed oxidative addition (an oxidation of Rh(I) to Rh(III) by hydrogen) to produce a dihydride which also may be solvated.



The coordinated solvent molecule is then replaced by the material being hydrogenated, cyclohexene, for example, presumably by a first-order dissociation mechanism. The metal hydride then adds to the coordinated olefin to form a five-coordinate rhodium(III) species which presumably solvates to the more

(7) W. P. Neumann and R. Sommer, *Ann.*, **675**, 10 (1964).

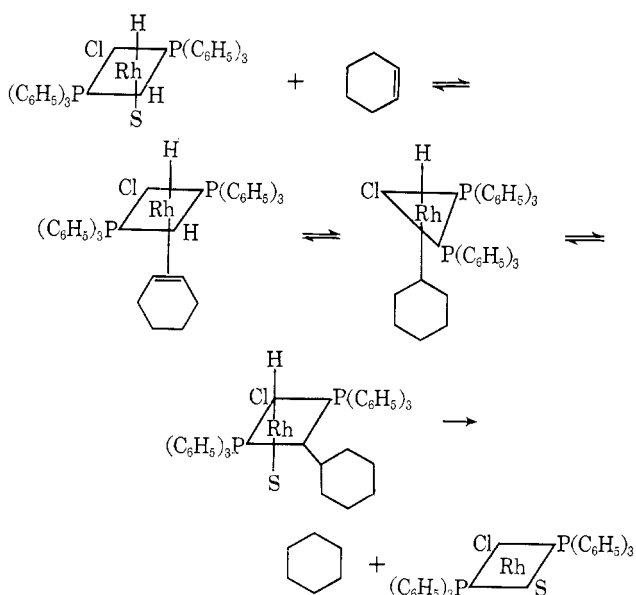
(8) J. Chatt, R. S. Coffey, A. Gough, and D. T. Thompson, *J. Chem. Soc., A*, 190 (1968).

(9) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *J. Am. Chem. Soc.*, **83**, 1601 (1961).

(10) F. H. Jardine, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc., A*, 1711(1966); 1574 (1967).

(11) S. Montelatic, A. van der Ent, J. A. Osborn, and G. Wilkinson, *ibid.*, 1054 (1968).

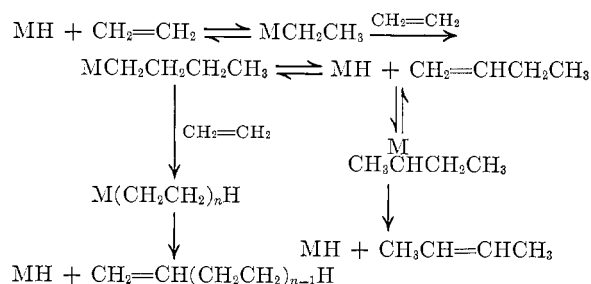
stable six-coordinate species. Finally, the second hydride group reacts with the alkyl group, by what could be termed a reductive elimination, giving hydrogenated olefin and the catalyst back again.



Coordinationally unsaturated species seem to be required in most transition metal compound additions, although this point has been proven in only a very few cases. The importance of unsaturated species in addition reactions is probably greater than it first appears in mechanisms such as the above because solvent has been used to complete the coordination spheres of some of the intermediate species. The solvent-saturated intermediates are probably the more stable forms of the intermediates, but it is also likely that replacements of coordinated solvent by the unsaturated molecules occur by dissociative mechanisms and that coordinationally unsaturated species are the true reactive intermediates. As in the above example; the vacant position is thought to be necessary in order for the unsaturated molecule to coordinate with the metal, a step which it is argued is necessary in order to "activate" the olefin. This point has been a subject of controversy because convincing evidence that complexing is a necessary feature of the addition has been obtained in only a very few examples.

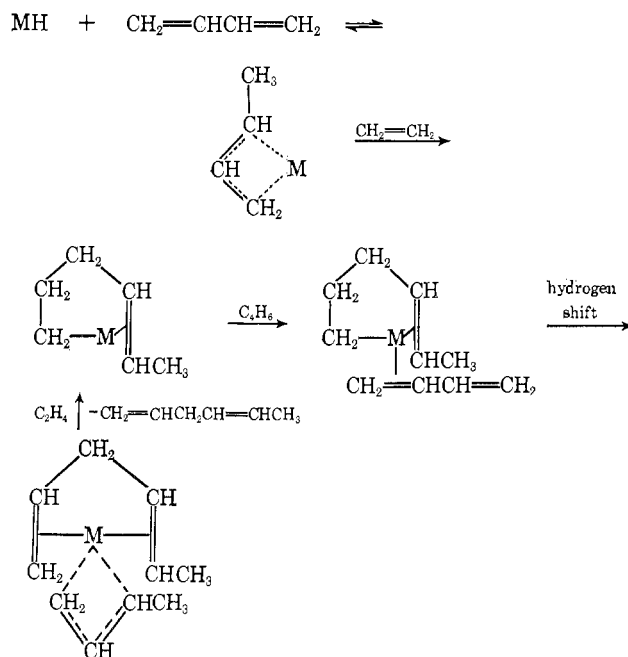
**Olefin Dimerizations, Polymerizations, and Dienylations.** Olefin dimerization or polymerization is related to hydrogenation because the first steps of the reactions are probably the same. The catalysts are generally metal hydrides, and the first step is usually addition of the hydride to the olefin. The metal alkyl so formed produces dimers or polymers by undergoing further additions to the olefin. Dimers are produced when metal hydride elimination occurs in preference to metal alkyl addition to the olefin. Of course, the dimers can re-react with metal hydride or metal alkyl and eventually produce higher polymers. Quite often dimers are the major products because they are less reactive than the monomer. Sometimes double-

bond migration in the dimer occurs rapidly relative to subsequent additions; the isomerized dimers are generally much less reactive than the original ones.



Olefin dimerization has been studied in detail by Alderson, *et al.*,<sup>12</sup> and a complete mechanistic study of the rhodium-catalyzed ethylene dimerization has been carried out by Cramer.<sup>13</sup>

Transition metal catalyzed additions of olefins to conjugated dienes occur by mechanisms closely related to the above. The reactive intermediates are  $\pi$ -allyl-metal species formed from the diene and metal hydride, and these selectively react with the olefin. The  $\pi$ -hexenylmetal derivative formed then reacts with another molecule of the conjugated diene, a hydrogen shift occurs, and the  $\pi$ -complexed nonconjugated diene formed is replaced by more olefin; thus a catalytic cycle results.



This reaction, catalyzed by rhodium trichloride, has been studied in detail by Cramer<sup>14</sup> and the reader is referred to the excellent review on the subject by Cramer in this journal.<sup>13</sup>

The stereochemistry of the diene produced depends

(12) T. Alderson, E. L. Jenner, and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **87**, 5638 (1965).

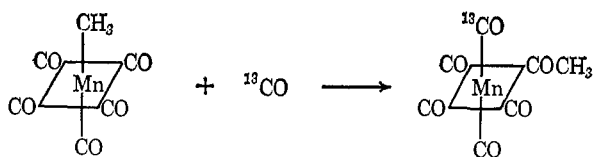
(13) R. Cramer, *ibid.*, **87**, 4717 (1967); *Accounts Chem. Res.*, **1**, 186 (1968).

(14) R. Cramer, *J. Am. Chem. Soc.*, **89**, 1633 (1967).

upon the structures of the intermediate complexes. The rhodium-catalyzed reaction appears to give a mixture of *cis* and *trans* isomers while other catalysts such as iron acetylacetonate-triethylaluminum produce only the *cis* isomer.<sup>15</sup> Isomerization of the diene may also occur after it is formed. Evidence has been obtained supporting a very similar mechanism to explain the cobalt chloride-sodium borohydride catalyzed dimerization of butadiene to 3-methyl-4,6-heptatriene.<sup>16</sup>

**Carbonylation Reactions.** Transition metal hydrides, alkoxides, amides, halides, and alkyls are all believed to be capable of adding to carbon monoxide under some conditions. The additions of metal-carbon compounds to carbon monoxide have received the most attention and appear to be the most useful in terms of organic syntheses.

The mechanism of the carbonylation reaction has been the subject of several investigations. The example studied in the most detail is the addition of pentacarbonylmethylmanganese(I) (or its triphenylphosphine substitution product). The reaction occurs at room temperature with only 1 atm of carbon monoxide to produce pentacarbonylacetylmanganese(I). By use of <sup>13</sup>C-labeled carbon monoxide and analyses by infrared techniques it has been shown that a previously coordinated carbon monoxide group ends up as the carbonyl of the acyl group while the entering, radioactive carbon monoxide is added at a position *cis* to the acyl group.<sup>17</sup>



Pentacarbonylmethylmanganese reacts with coordinating molecules other than carbon monoxide in an analogous way. The reaction with triphenylphosphine has given more information about the addition step. The reaction which produces *cis*-tetracarbonyltriphenylphosphineacetylmanganese(I) initially<sup>18</sup> was found to be first order in the manganese compound and zero order in the triphenylphosphine.<sup>19</sup> The kinetic data therefore indicate that the rate-determining step of the reaction is the formation of a tetracarbonylacetylmanganese(I) intermediate which then reacts rapidly with the phosphine.<sup>20,21</sup>

(15) G. Hata and D. Aski, *J. Org. Chem.*, **32**, 3754 (1967).

(16) G. Natta, U. Giannini, P. Pino, and A. Cassata, *Chem. Ind. (Milan)*, **47**, 524 (1965); G. Allegra, F. LoGuidice, G. Natta, U. Giannini, and G. Fagherazzi, *Chem. Commun.*, 1263 (1967).

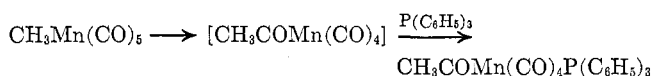
(17) K. Noack and F. Calderazzo, *J. Organometal Chem. (Amsterdam)*, **10**, 101 (1967).

(18) K. Noack, M. Ruch, and F. Calderazzo, *Inorg. Chem.*, **7**, 345 (1968).

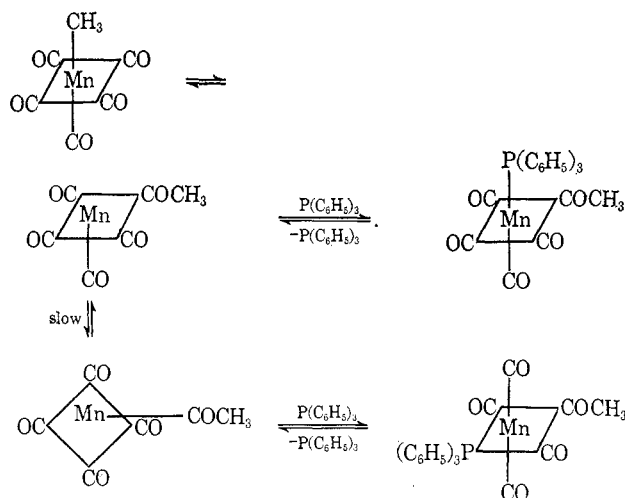
(19) C. S. Kraihanzel and P. K. Maples, *J. Am. Chem. Soc.*, **87**, 5267 (1965).

(20) R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 5043 (1964).

(21) F. Calderazzo and F. A. Cotton, *Chem. Ind. (Milan)*, **46**, 1165 (1964).



Whether the intermediate is truly a five-coordinate or a six-coordinate, solvated complex is not clear at this time. The fact that triphenylphosphine does not displace carbon monoxide directly when it reacts with pentacarbonylmethylmanganese(I) suggests that it probably would not directly displace solvent from a solvated six-coordinate intermediate; it follows that a true five-coordinate intermediate is probably involved. The fact that the *cis* isomer is formed initially in the reaction of pentacarbonylmethylmanganese(I) with triphenylphosphine<sup>21</sup> suggests that the five-coordinate intermediate holds its configuration at least long enough to react with triphenylphosphine. Since a slower isomerization of the *cis* to the *trans* isomer also occurs, the intermediate probably slowly changes its configuration. Presumably a square pyramid is formed initially which can either react with triphenylphosphine or isomerize.



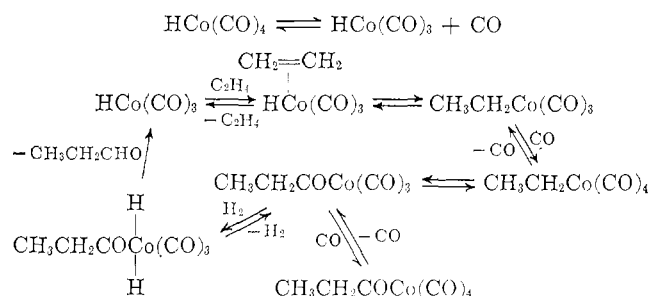
Another point of mechanistic interest in connection with the additions to coordinated carbon monoxide is whether the alkyl group is migrating by a 1,2-shift or if a coordinated carbonyl group is moving to produce the acylmetal derivative. An attempt to distinguish between these possibilities was made by thermally decarbonylating tetracarbonyltriphenylphosphineacetylmanganese(I), but equilibration of isomers occurred and no conclusion could be reached.<sup>19,20</sup> More recent work with <sup>13</sup>C-labeled carbon monoxide, using infrared techniques to identify isomers, has quite clearly shown that carbonyl migration does not occur to any appreciable extent. The data were consistent with the 1,2-shift mechanism where methyl in pentacarbonylmethylmanganese(I) moves from manganese to carbon.<sup>22</sup>

The carbonylation reaction is useful in organic synthesis because the acylmetal compounds are generally very reactive and can be converted into various organic compounds. Hydrogenation converts them to alde-

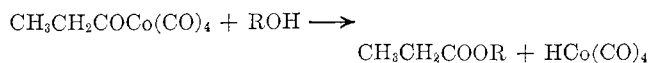
(22) K. Noack and F. Calderazzo, *J. Organometal Chem. (Amsterdam)*, **10**, 101 (1967).

hydrides and metal hydrides. Combining the reduction reaction with a metal hydride addition to an olefin followed by carbonylation produces the catalytic cycle believed operating in the hydroformylation reaction.<sup>23</sup> The metal hydride catalyst is cobalt hydrotetracarbonyl.

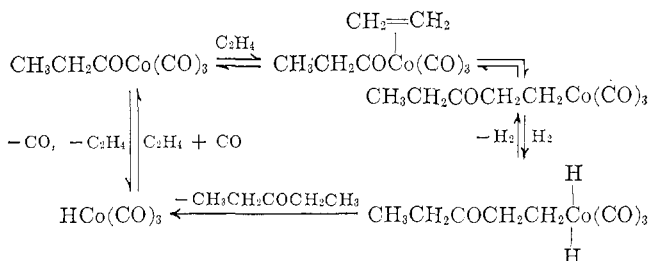
The inhibitory effects of carbon monoxide on the hydride-olefin addition and the hydrogen reduction of the acylcobalt intermediate suggest that coordinately unsaturated species are involved in both steps. Presumably, in the former reaction, the coordinately unsaturated complex is required so that an olefin  $\pi$ -complex can be formed. In the latter reaction the coordinately unsaturated complex is believed to be necessary in order to allow an oxidative addition of hydrogen to occur. A 1,2-shift of hydride from cobalt to acyl carbon then would produce aldehyde and the hydrocarbonyl.



A similar catalytic cycle is obtained when an olefin, carbon monoxide, and a hydroxylic compound are allowed to react in the absence of hydrogen with cobalt hydrocarbonyl. The intermediate acylcobalt complex now reacts with the hydroxylic compound producing an ester instead of an aldehyde and regenerating the catalyst, cobalt hydrocarbonyl.<sup>24</sup>



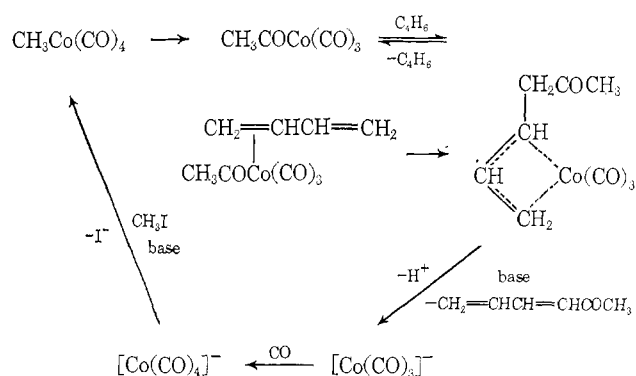
Another variation of the hydroformylation reaction occurs when the amount of hydrogen employed is limited and an inert solvent is used. Apparently the intermediate acylcobalt tricarbonyl preferentially reacts with olefin rather than hydrogen under these conditions. The resulting 3-keto-1-pentylcobalt derivative, however, does react readily with the small concentration of hydrogen present to produce dialkyl ketone. This reaction also is catalytic as long as the low concentration of hydrogen is maintained.<sup>25</sup>



(23) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961).

(24) R. Ercoli, G. Signorini, and E. Santambrogio, *Chem. Ind. (Milan)*, **42**, 587 (1960).

Acylmetal complexes generally react with conjugated dienes, and in some instances this addition reaction can be used to produce useful organic reactions. The acylcobalt carbonyls, for example, add to conjugated dienes, producing 1-acylmethyl- $\pi$ -allyl cobalt derivatives,<sup>26</sup> and these derivatives undergo elimination of the elements of  $\text{HC}(\text{CO})_3$  on treatment with base (hindered amines are best), forming 1-acyldienes.<sup>27</sup> The cobalt species eliminated reacts with carbon monoxide (and base) to form the stable cobalt tetracarbonyl anion. Since this anion reacts with alkyl halides to produce alkylcobalt tetracarbonyls, 1-acyldienes can be made catalytically with respect to the cobalt tetracarbonyl anion if all of the other reagents are present simultaneously.<sup>27</sup>



### Cyclization Reactions

The addition reactions discussed so far have produced only linear products. Cyclic products may also be formed. At least two basic mechanisms of reaction are observed which result in the formation of cyclic organic products. Either a series of linear additions occurs and then the adduct undergoes cyclization, or a heterocyclic compound is formed with the metal as the hetero atom and it undergoes further additions at either of the metal-carbon bonds present with the complex eventually forming a cyclic organic compound by eliminating the metal from the ring.

The decomposition of  $\delta$ -hexenoylcobalt tetracarbonyl<sup>28</sup> is an example of the cyclization of a linear metal complex. This complex decomposes on slight warming, presumably first forming a cyclic olefin  $\pi$  complex. Then the acylcobalt group adds internally to the coordinated double bond and the adduct loses cobalt hydrotricarbonyl, forming cyclic unsaturated ketones in a  $\beta$ -elimination reaction. The hydride produced then reduces part of the unsaturated ketones to saturated ketones. Both five- and six-membered ring products are formed, with the five being favored. (See Chart II.)

There are many examples of the metal heterocycle-forming reactions known, but little is known about the details of the reactions. Typical of this type of reaction

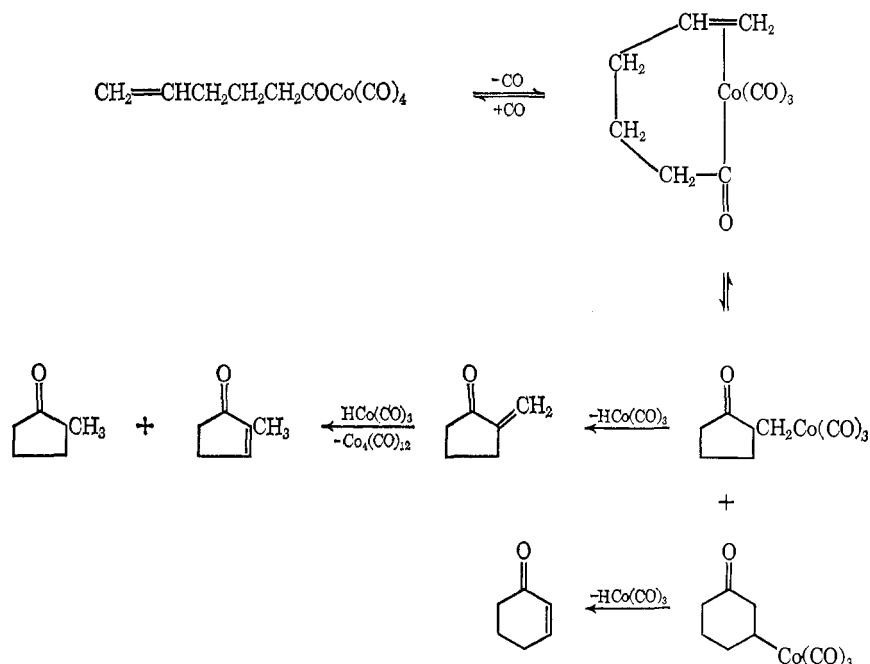
(25) J. H. Staib, W. R. F. Guyer, and O. C. Slotterbeck, U. S. Patent 2,864,864 (1958).

(26) R. F. Heck, *J. Am. Chem. Soc.*, **85**, 3381 (1963).

(27) R. F. Heck, *ibid.*, **85**, 3383 (1963).

(28) R. F. Heck, *ibid.*, **85**, 3116 (1963).

Chart II

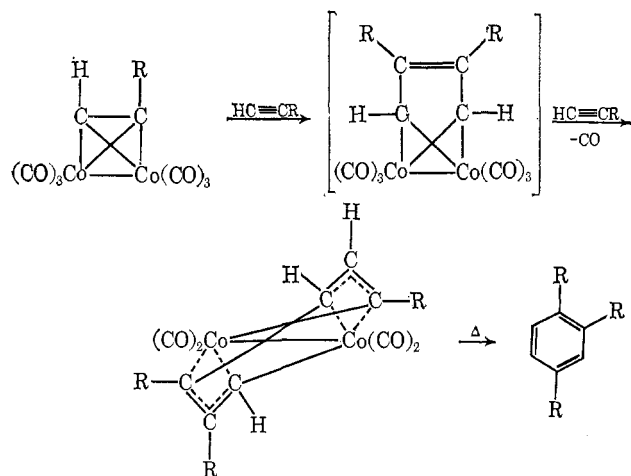


is the trimerization of acetylene catalyzed by cobalt octacarbonyl.<sup>29,30</sup> Two of the intermediate complexes have been isolated. The first complex formed is the well-known acetylenedicobalt hexacarbonyl containing a bridging acetylene group. Very likely a two-acetylene-containing complex is formed next, but it has not been identified. A heterocyclic, cobaltacyclopentene complex with the diene unit bridging the cobalt atoms seems a good possibility for the structure of the second complex. The third intermediate is a complex containing three acetylenes and two cobalt atoms. The structure of this complex as determined by X-ray analyses is unusual in that the ends of the six-carbon chain are bonded to different cobalt atoms and

the bonding is from  $\pi$ -allylic carbon atoms. The three carbons at the ends of the chain appear to be  $\pi$  bonded to the cobalt atoms, making the cobalt atoms formally  $\text{Co}(\text{III})$ . On further heating, the last complex produces the cyclic acetylene trimer. This reaction has been used to prepare 1,2,4-tri-*t*-butylbenzene,<sup>31</sup> hexaisopropylbenzene,<sup>32</sup> 1,3,5-triethynylbenzene,<sup>33</sup> and 1,2,3,4-tetra-*t*-butylbenzene.<sup>34</sup> Many related reactions have been carried out with nickel catalysts, for example, the trimerization of butadiene to cyclododecatriene. These reactions have been reviewed by Wilke.<sup>35</sup>

### Multiple, Cyclic, and Linear Addition Reactions

Obviously, from the foregoing examples, very complicated reactions involving multiple, cyclic, and linear addition reactions are possible. In the extreme case such reactions would lead to practically inseparable mixtures of high molecular weight compounds or polymers, but in favorable instances useful organic reactions occur because of the high specificity of the reactions. Useful syntheses involving more than three addition steps in the same reaction are relatively rare at the present time, but many more such reactions are likely to be discovered. The advantage of using these syntheses is that complicated organic molecules may be built up from simple molecules in a single reaction. It is not clear at this time how generally useful the multiple addition reactions will be since little is known about the factors influencing the orders or directions of



(29) U. Krüerke, C. Hoogzand, and W. Hübel, *Chem. Ber.*, **94**, 2817 (1961).

(30) O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 187 (1964).

(31) U. Krüerke, C. Hoogzand, and W. Hübel, *Chem. Ber.*, **94**, 2817 (1961).

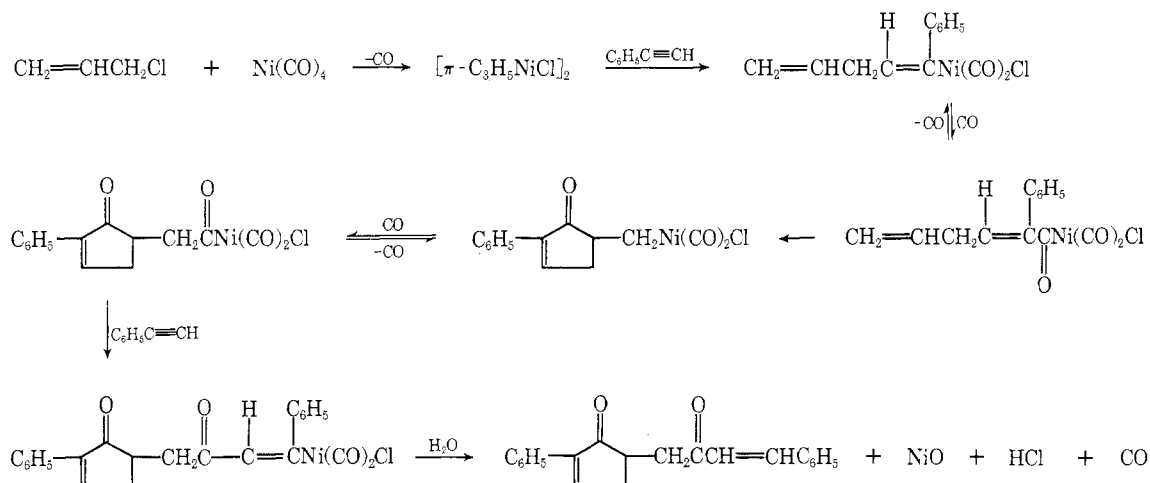
(32) E. M. Arnett and J. M. Bollinger, *J. Am. Chem. Soc.*, **86**, 4729 (1964).

(33) W. Hübel and R. Merenzi, *Chem. Ber.*, **96**, 930 (1963).

(34) C. Hoogzand and W. Hübel, *Tetrahedron Letters*, 637 (1961); E. M. Arnett, M. E. Strem, and R. A. Friedel, *ibid.*, 658 (1961).

(35) G. W. Wilke, *Angew. Chem.*, **75**, 10 (1963).

Chart III

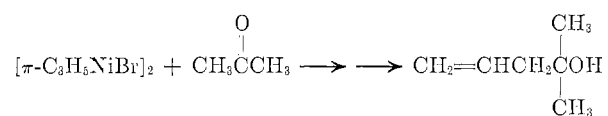


addition of the metal compounds to the unsaturated molecules. One example will be discussed to illustrate the remarkable selectivity of a series of five addition reactions occurring consecutively in a single operation.

The reaction of allyl chloride, phenylacetylene, carbon monoxide, and water with a nickel carbonyl catalyst in acetone solution has already been mentioned in the introductory section. The mechanism by which these reagents react by way of five addition reactions to produce one product in 64% yield can be closely approximated from what is known about nickel carbonyl reactions and the reactions of other group VIII metal complexes.

The initial reaction is quite surely the reaction of allyl chloride with the nickel carbonyl to produce the  $\pi$ -allylnickel chloride dimer (Chart III), since this reaction is known to occur in the absence of the other reagents. No doubt intermediates are involved in this step. The  $\pi$ -allylnickel derivative then adds to phenylacetylene, with nickel going on the carbon bearing the phenyl group. An addition to carbon monoxide must occur next to produce an acylnickel derivative. Actually, cyclic olefin  $\pi$  complexes are probably involved in these reactions, but they are written in open-chain form for simplicity in the absence of more data. An internal cyclization now occurs which is analogous to the 5-hexenylcobalt carbonyl cyclization mentioned above. Very probably the cyclic olefin  $\pi$  complex is involved here also. The five-membered-ring product is the major one, but six-membered-ring by-products were also observed. The  $\sigma$ -bonded nickel derivative formed in the cyclization reaction is apparently considerably more stable or much more reactive than the related cobalt

complex since the nickel compound undergoes further additions while the cobalt complex decomposed by eliminating a metal hydride group. The fourth addition step then is to carbon monoxide, again to produce another acylnickel derivative. The fifth addition is to phenylacetylene, again in the same direction as before, giving a vinylnickel derivative. As occurs with other vinylmetal derivatives, the vinylnickel complex is then cleaved by the water present. The fact that the vinylnickel complex hydrolyzes to put oxygen on nickel is surprising since the reverse happens with acylnickel compounds. Nickel does behave more like magnesium than other group VIII metals do, however, in some of its reactions. For example,  $\pi$ -allylnickel bromide dimer reacts with acetone as allylmagnesium bromide would, producing allyldimethylcarbinol.<sup>36</sup>



The few transition metal compound addition reactions described in this Account illustrate the utility of these reactions in organic synthesis. The study of the scope of these reactions has just begun, however, and when the factors determining the course of the reactions are better understood they will become very much more useful. Conceivably linear and cyclic combinations of almost any unsaturated molecules may eventually be made possible by addition reactions of the appropriate group VIII metal compounds.

(36) L. Cassar and G. P. Chiusoli, *Tetrahedron Letters*, 3295 (1965).