

# Addition Reactions of Transition Metal Compounds

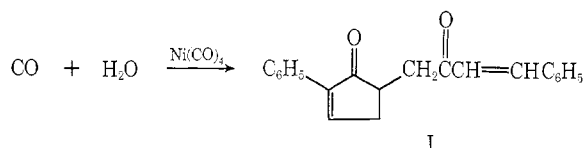
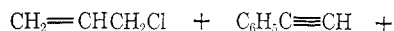
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Addition reactions of metal compounds to unsaturated molecules have been known for many years, but the very wide applicability of these reactions is just now beginning to be realized. These reactions are useful for preparing inorganic, organometallic,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



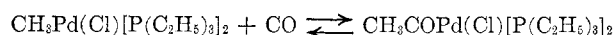
## Addition Mechanisms

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

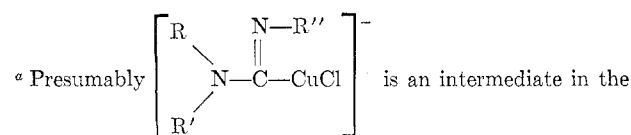
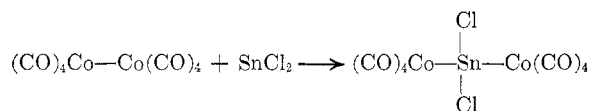
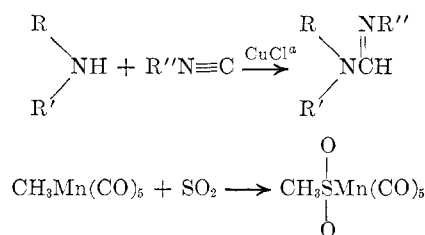
(1) G. P. Chiusoli, G. Bottaccio, and C. Venturello, *Tetrahedron Letters*, 2875 (1965).

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



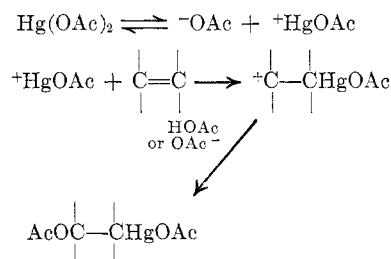
Isocyanides,<sup>3</sup> sulfur dioxide,<sup>4</sup> and stannous chloride<sup>5</sup> react similarly (Chart I). These reactions are characterized by an increase of two in the coordination number of the atom attacked.

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).

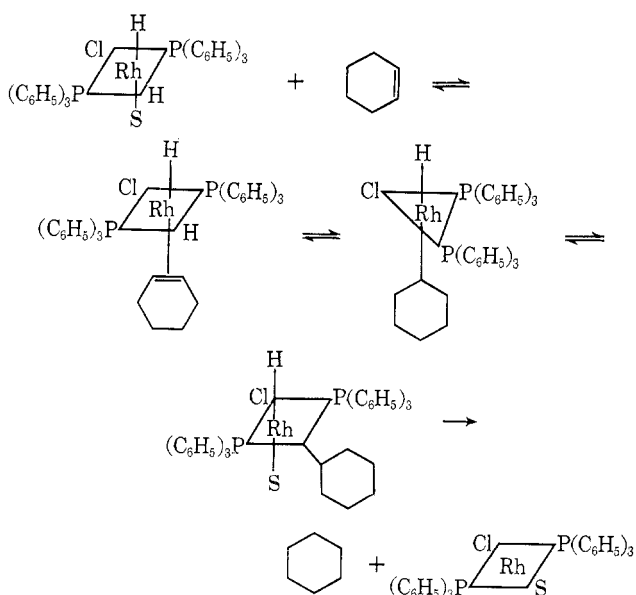
(4) F. A. Hartman and A. Wojcicki, *J. Am. Chem. Soc.*, **88**, 844 (1966).

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

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



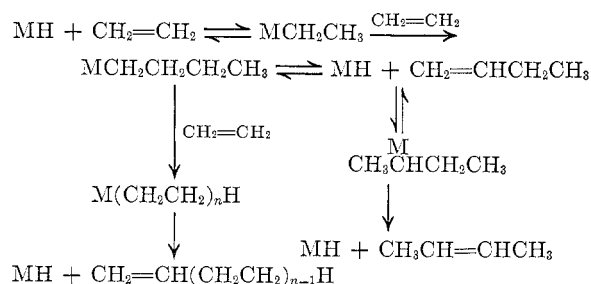
stable six-coordinate species. Finally, the second hydride group reacts with the alkyl group, by what could be termed a reductive elimination, giving hydrogenated olefin and the catalyst back again.



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.

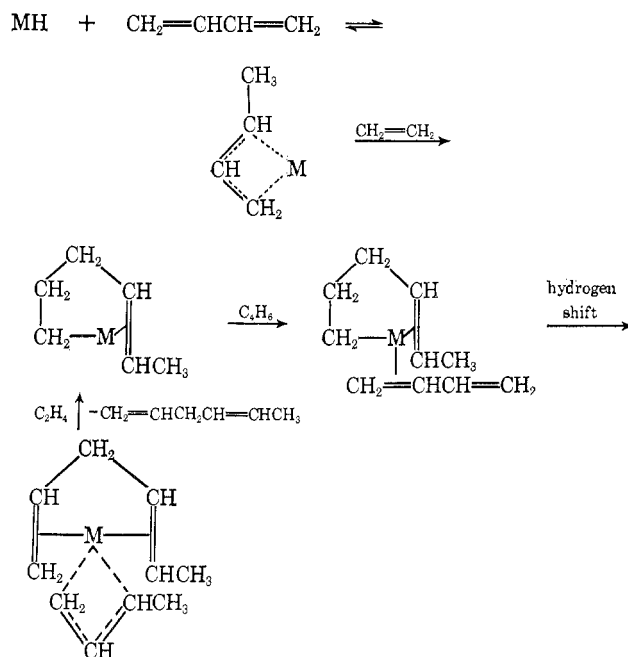
**Olefin Dimerizations, Polymerizations, and Dienylations.** Olefin dimerization or polymerization is related to hydrogenation because the first steps of the reactions are probably the same. The catalysts are generally metal hydrides, and the first step is usually addition of the hydride to the olefin. 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).

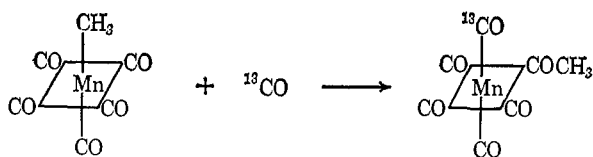
(13) R. Cramer, *ibid.*, **87**, 4717 (1967); *Accounts Chem. Res.*, **1**, 186 (1968).

(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).

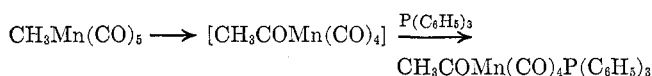
(17) K. Noack and F. Calderazzo, *J. Organometal Chem. (Amsterdam)*, **10**, 101 (1967).

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

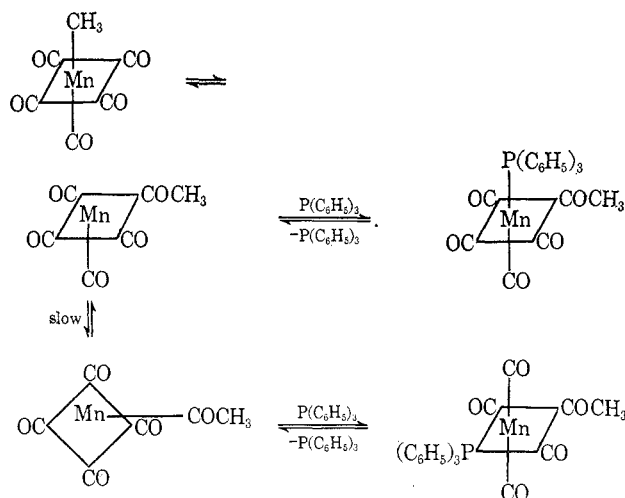
(19) C. S. Kraihanzel and P. K. Maples, *J. Am. Chem. Soc.*, **87**, 5267 (1965).

(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.



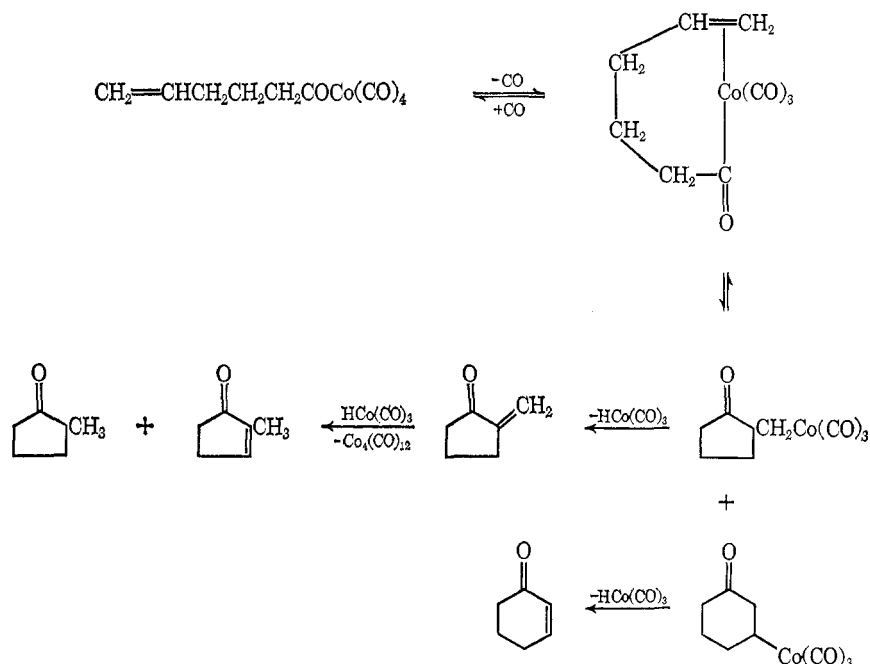
Another point of mechanistic interest in connection with the additions to coordinated carbon monoxide is whether the alkyl group is migrating by a 1,2-shift or if a coordinated carbonyl group is moving to produce the acylmetal derivative. An attempt to distinguish between these possibilities was made 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).



Chart II

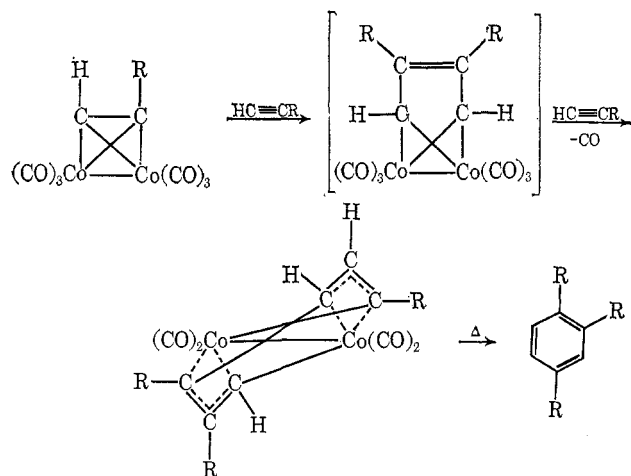


is the trimerization of acetylene catalyzed by cobalt octacarbonyl.<sup>29,30</sup> Two of the intermediate complexes have been isolated. The first complex formed is the well-known acetylenedicobalt hexacarbonyl containing a bridging acetylene group. Very likely a two-acetylene-containing complex is 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 Co(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. Krücker, C. Hoogzand, and W. Hübel, *Chem. Ber.*, **94**, 2817 (1961).

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

(31) U. Krücker, 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).

