

PHYSICAL ORGANIC STUDIES OF ORGANOMETALLIC REACTIONS

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Abstract - The mechanisms of reactions of organotransition metal complexes have only begun to be understood in detail during the last ten years. The complementary interaction of techniques and concepts developed earlier in studies of organic reaction mechanisms, with those commonly used in inorganic chemistry, has played a crucial role in helping to elucidate organometallic reaction mechanisms. A few systems in which this interaction has proved especially fruitful are discussed in this article.

INTRODUCTION

The development of our understanding of reaction mechanisms in organotransition metal chemistry has benefited greatly from interaction of this field with physical organic chemistry--and physical organic chemists--during the past 15 years. The pioneering work of investigators such as Collman, Halpern, Whitesides, Kochi and others demonstrates the important information which can be obtained by combining the techniques and insights of physical organic chemistry with those developed in the inorganic and synthetic organometallic areas.¹

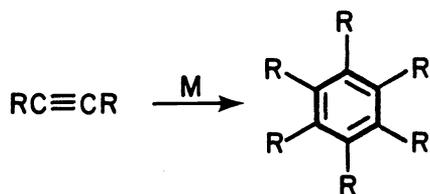
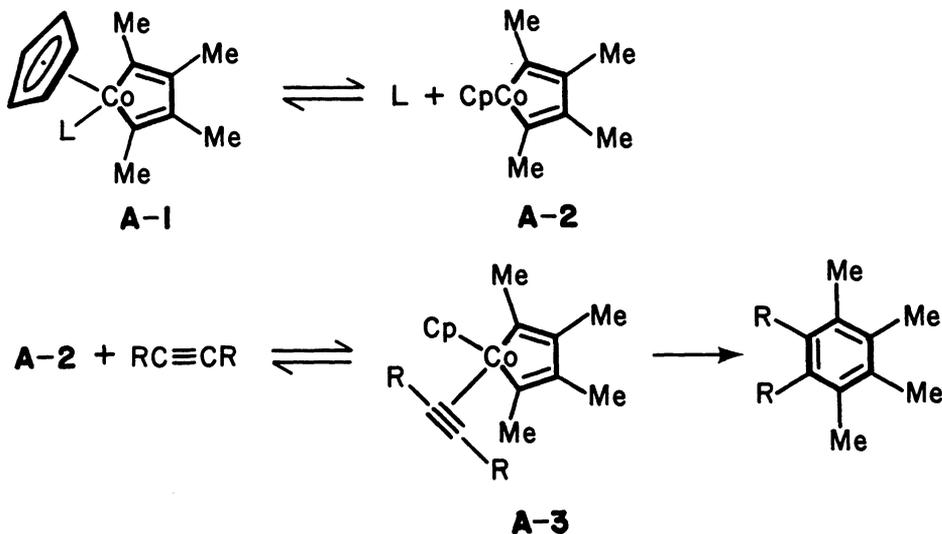
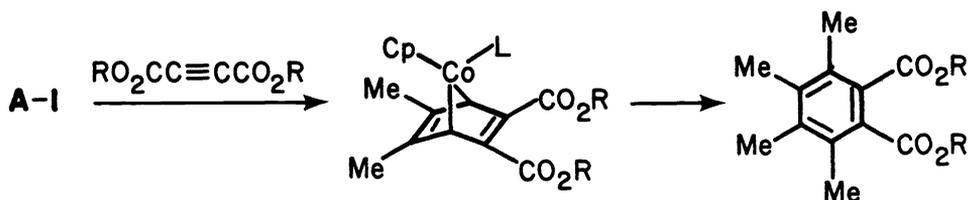
We have been attempting to continue this recent tradition, and apply the types of thinking and techniques developed in physical organic chemistry to organometallic reaction mechanism problems. This paper summarizes a number of recent studies we have carried out in which we feel the "physical organic" component, either in the techniques used or concepts uncovered, is particularly strong.

I. ALKYNE TRIMERIZATION AND REACTIONS OF METALLACYCLOPENTADIENES

One of our first mechanistic investigations in organometallic chemistry grew out of studies of the catalytic conversion of alkynes to benzene derivatives. It has been known for some time that one class of such reactions proceeds through metallacyclopentadienes ["metalloles" in organic terminology]. However, in 1975 little was known about the detailed mechanism by which these complexes react with an additional alkyne, leading to a benzene derivative. This mechanism is still largely obscure, but we were able to make some progress on it in a collaboration which emphasizes the importance of organic/inorganic interaction in this field. Donald McAlister, a Caltech graduate student who carried out a joint thesis project with John Bercaw and me, uncovered two mechanisms for conversion of "phosphine-stabilized" metallacycle \bar{A}_2L (see Chart A) to benzenes.² In mechanism (a), alkyl-substituted alkynes such as 2-butyne must first enter the metal coordination sphere, and this requires prior dissociation of phosphine, which occurs at a reasonable rate only at temperatures near 70°C. Acetylene dicarboxylate, on the other hand, reacts in a direct bimolecular process at room temperature without prior dissociation of L, we propose by the Diels-Alder process shown as mechanism (b) in Chart A. Organic chemists will not be surprised that an "activated" alkyne such as acetylene dicarboxylate is required to make the direct Diels-Alder process (b) supercede path (a).

II. INSERTION OF ALKYNES INTO NICKEL CARBON BONDS

Another potentially important method for formation of new C-C bonds to alkynes involves the addition of metal alkyls across triple bonds. With

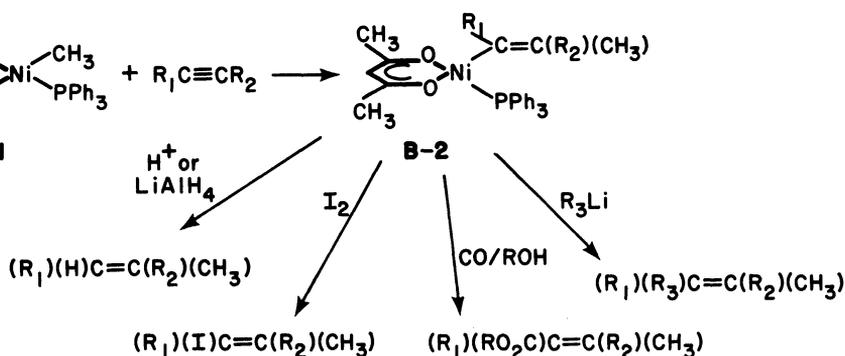
Chart AMechanism (a):Mechanism (b):

unsymmetrically substituted alkynes, the regiochemistry of these reactions is normally assumed to be such that the metal is transferred to the more electronegative carbon. The stereochemistry of the addition is thought to be cis, although there appear to be some exceptions to this rule.

As one example of this class of transformation, we have been studying³ the insertion of alkynes into the nickel-methyl bond of complex B-1 in Chart B. This is an unusually general reaction; a wide range of alkynes³ undergo this insertion (although with alkynes of small steric bulk, multiple addition occurs), and the reaction can be stopped at the vinylnickel complex (B-2) stage, or carried on to a number of different organic products without isolation of the intermediate vinyl complex (see Chart B).

The regiochemistry of the reaction is unusual on two counts. First, it seems to be controlled only by steric, rather than electronic effects. Second, it is the metal end of the nickel-carbon bond, rather than the CH₃ group, which behaves as the sterically least bulky side of the addend. For example, the complex reacts with PhC \equiv CH so as to put the nickel on the phenyl-substituted carbon, but addition to tBuC \equiv CH also puts Ni on the substituted carbon. In the case of p-Me-C₆H₄C \equiv CC₆H₅, both regioisomers are obtained in similar amount.

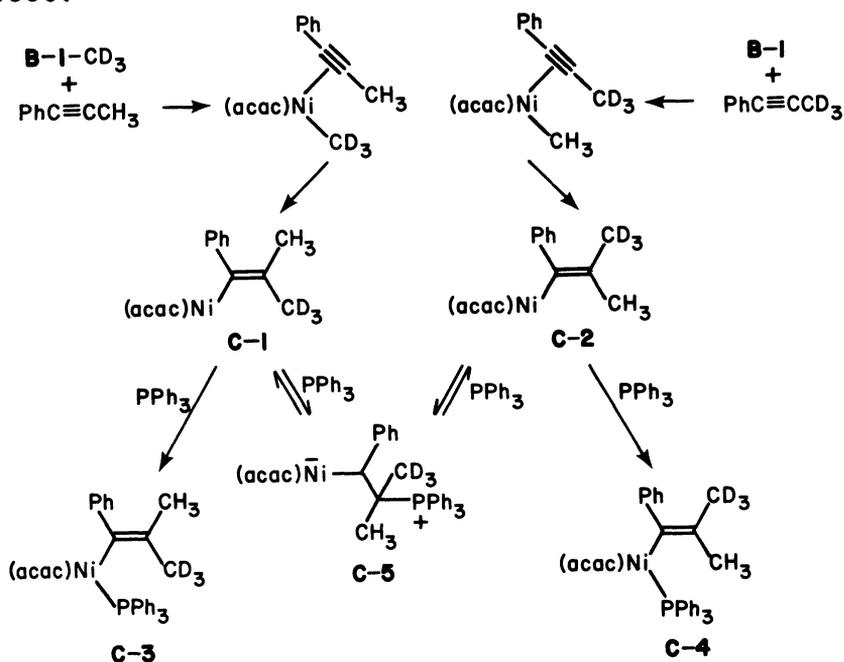
Chart B



The stereochemistry of the reaction also has unusual characteristics. Addition of B-1 to $\text{PhC}\equiv\text{CPh}$ gives only the vinyl complex formed⁴ on trans addition (Z-B-2 , $\text{R}_1=\text{R}_2=\text{Ph}$). In order to be sure of this result, the structure of this complex was determined by X-ray diffraction. Heating Z-B-2 converts it to an equilibrium mixture of it and its isomer E-B-2 ; thus Z-B-2 is the kinetic product of the addition. In other additions, the stereochemistry is dramatically dependent upon alkyne structure; sometimes one observes predominantly cis-, and sometimes predominantly trans- addition to form kinetic products. Perhaps the most informative example is the addition of $(\text{acac})\text{Ni}(\text{PPh}_3)\text{CD}_3$ (B-1-CD_3) to $\text{PhC}\equiv\text{CCH}_3$ (and its label-inverse experiment), illustrated in Chart C. Here addition is predominantly cis, there is only a small isotope effect, and the equilibrium ratio of products is (as one would expect) 1:1.

In order to satisfactorily account for these results, as well as for kinetic data and other information obtained on this system, we postulate the mechanism summarized in Chart C. We believe the initial insertion proceeds with cis stereochemistry. However, this gives a coordinatively unsaturated vinyl complex C-1 , which can undergo rapid cis-trans isomerization (leading to C-2) in competition with trapping by phosphine to give isolable product C-3 . We have found that varying the phosphine concentration produces little

Chart C



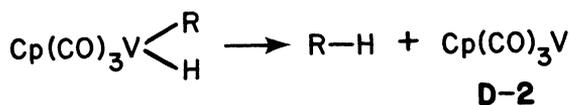
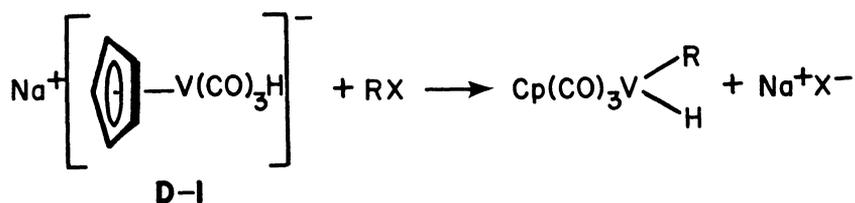
change in the stereochemistry of the final product. We therefore suggest that the rate of the $C_{-1} \rightleftharpoons C_{-2}$ isomerization is first order in $[PPh_3]$ (as is the phosphine-trapping step), perhaps because it requires addition of phosphine to the end of the double bond, forming an intermediate such as C_{-5} .

III. REACTION OF η^5 -CYCLOPENTADIENYL (TRICARBONYLHYDRIDOVANADATE) WITH ALKYL HALIDES

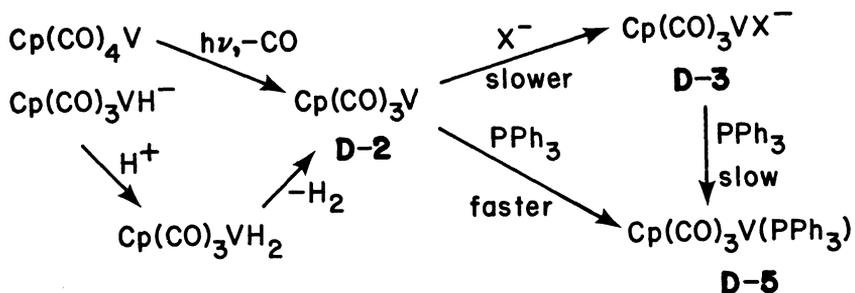
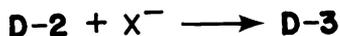
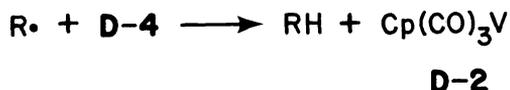
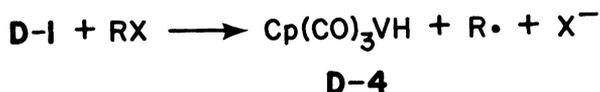
A study in the metal carbonyl anion area, although rather different from the metallacycle work discussed above, also benefited from the insights of physical organic chemistry. After finding that Fischer's vanadium dianion $[CpV(CO)_3]^{-2}$ could be protonated to give the hydride D_{-1} (Chart D), we learned that this material would replace halogen with hydrogen in a wide range of organic halides.⁵ Two conventional organometallic mechanisms for this process are shown in Chart D; these are based on known alkylation processes⁶ in related anions such as $CpFe(CO)_2^-$ and $CpMo(CO)_3^-$.

Chart D

Mechanism (a):



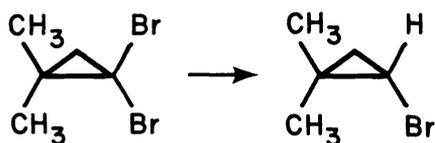
Mechanism (b):



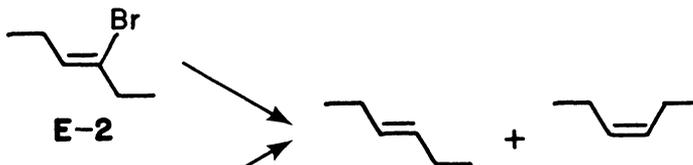
These mechanisms have in common the intermediacy of the 16-electron transient complex $\text{Cp}(\text{CO})_3\text{V}(\text{D}-2)$. By excluding $\text{D}-2$ as an intermediate, we were first able to show that neither of these mechanisms was operative. This was done by determining the kinetically controlled products formed on reaction of $\text{D}-2$ with halide and phosphine ligands. In the absence of phosphine, the anionic halide complex $\text{D}-3$ is the organometallic product of the reduction. When phosphine is present, neutral complex $\text{D}-5$ is the product isolated on completion. However, monitoring the reaction by IR shows that even in the presence of a large excess of phosphine, the halide complex $\text{D}-3$ is the kinetic product of the reduction; this is converted to $\text{D}-5$ only in a subsequent (slower) substitution reaction. The only way $\text{D}-2$ could be an intermediate in the reduction, therefore, is if X^- traps it faster than L (i.e., if $\text{D}-3$ is the kinetic product of the trapping reaction, and $\text{D}-5$ the thermodynamic product). The experiments summarized at the bottom of Chart D demonstrate this is not the case. $\text{Co}(\text{CO})_3\text{V}$, generated independently (in the presence of both X^- and L) by protonation of $\text{D}-1$ or irradiation of $\text{Cp}(\text{CO})_4\text{V}$, gives $\text{D}-5$ as kinetic product ($\text{D}-3$ is stable to these reaction conditions). Thus free $\text{Cp}(\text{CO})_3\text{V}$ is excluded as an intermediate in the reduction reaction.

Chart E

Reduction reactions involving organic halides and $\text{Cp}(\text{CO})_3\text{VH}^-$:



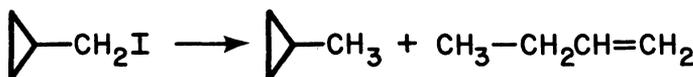
E-1



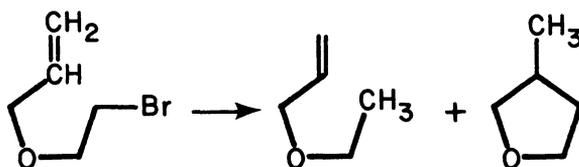
E-2



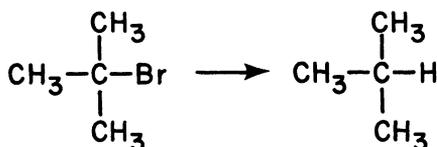
E-3



E-4



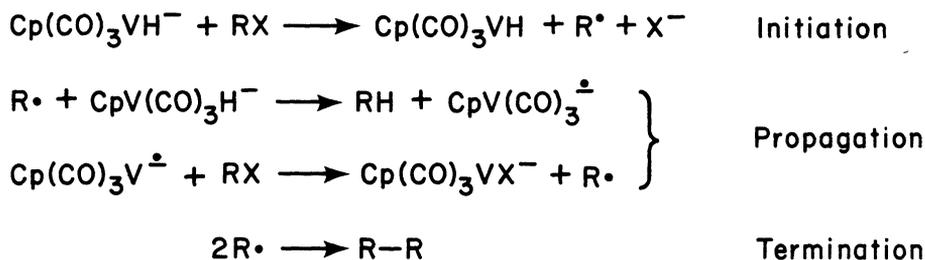
E-5



E-6

Despite our ability to rule out D_{-2} as an intermediate, other physical organic studies demonstrated that free organic radicals were involved in the $Cp(CO)_3VH^-$ reduction reactions. As shown in Chart E, tertiary, cyclopropyl and vinyl halides are easily reduced, carbon stereochemistry is scrambled, and typical radical rearrangements, if they are rapid enough, occur. In fact, the observed products and relative rate studies are very similar to those seen in halide reductions using R_3SnH , a reaction known to proceed by a free radical chain mechanism. We therefore propose that the majority of these reductions proceed by the chain mechanism shown in Chart F (for some exceptions, see our paper describing the full details of this study).^{5b} Based on an estimated rate for cyclization of the radical formed from unsaturated halide E_{-5} , we calculate that the rate constant for transfer of hydrogen atoms from $Cp(CO)_3VH^-$ to primary alkyl radicals is $\sim 2.0 \times 10^7 \text{ sec}^{-1}$, some ten times faster than the very good H atom donor Bu_3SnH .

Chart F



IV. CARBON-CARBON BOND-FORMING REACTIONS IN BINUCLEAR COBALT COMPLEXES

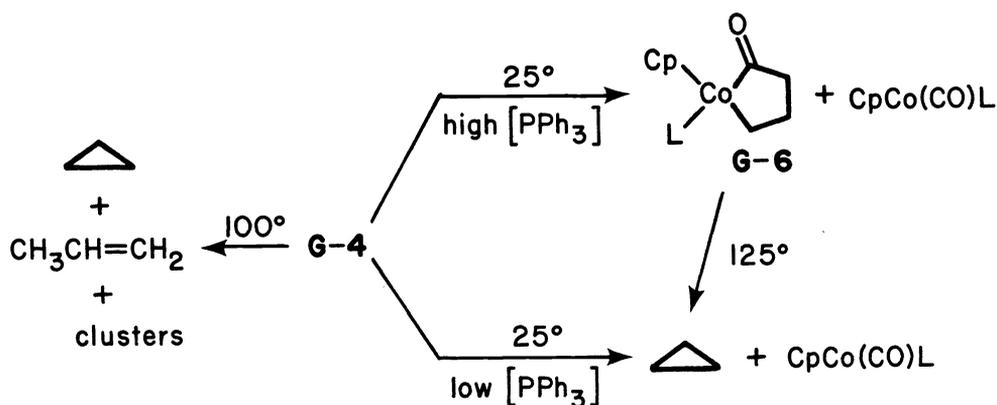
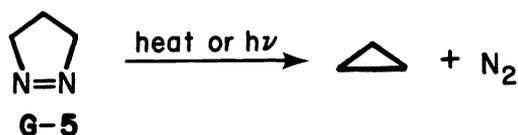
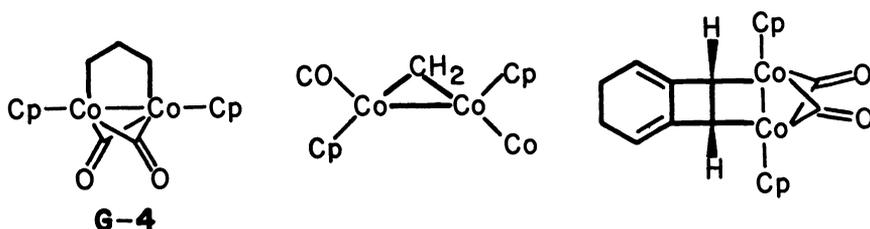
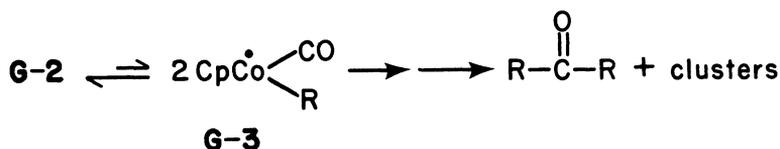
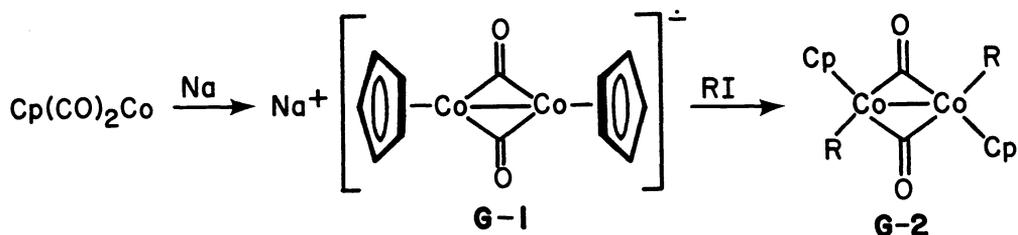
Our interest in metal carbonyl anions led us to examine the chemical reduction of $(\eta^5C_5H_5)Co(CO)_2$ as a potential source of low-valent anions in the cobalt series. Isolated in this reaction, and characterized by X-ray diffraction,⁷ were salts of the unusual binuclear radical anion G_{-1} . Treatment of these salts with primary alkyl halides gives the dialkyl species G_{-2} . We were intrigued to find that this molecule decomposed at 35° , in the presence or absence of CO, to give acetone in high yield.⁸

Because the number of binuclear species which are known to lead to the formation of C-C bonds is still very small, we have studied the mechanism of this reaction extensively. The details of this work are summarized in a recent review article,⁹ and so they will not be repeated here. Perhaps the most significant thing about this system is the fact that the dimers G_{-2} are in rapid equilibrium with "radical-like" paramagnetic Co(II) monomers of composition $CpCo(CO)R$ (G_{-3}) and these monomers play a critical role in product formation. The most important technique employed in studying these reactions involved isotope crossover experiments, a classic method used in organic mechanisms studies for distinguishing inter- from intramolecular processes. In the case of dimethyl derivative G_{-2} ($R=CH_3$), we found that mixtures of d_0 - G_{-2} and d_6 - G_{-2} (labeled methyl groups) gave large amounts of d_3 -acetone, and this provided the first clue that an intermolecular mechanism was operating.

Our major effort in this area is now concentrated on the study of binuclear metallacycles; i.e., those containing two cobalt atoms, which we have found can be prepared by reactions analogous to those shown in Chart G, but involving dihalides rather than monohalides.¹⁰ This method appears to be quite general, and so far the binuclear metallacycles shown in the middle of Chart G are among those we have prepared and characterized.

Consciously, we took this direction because of the rich chemistry of mono-nuclear metallacycles uncovered by several groups;¹¹ it seemed to us that binuclear metallacycles would have an equally rich, although probably qualitatively different, set of chemical properties. To an organic chemist, however, these molecules are heterocycles, except that metal atoms (and their associated ligands) take the place of more common main-group heteroatoms.

Chart G



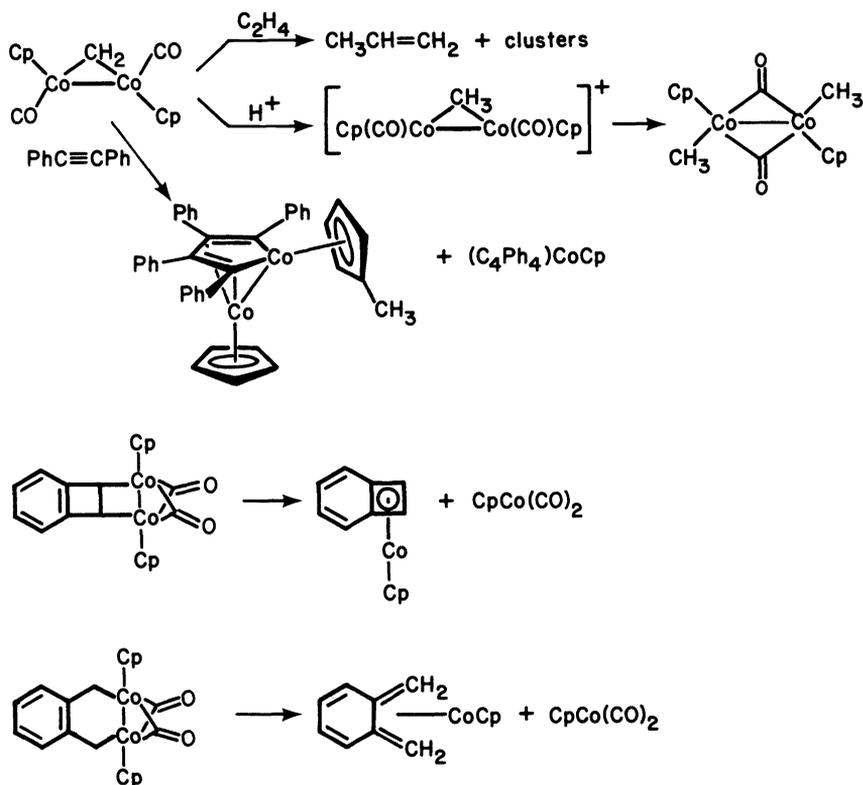
Complex G-4 is especially similar to pyrazoline derivatives G-5 , which give cyclopropanes on thermal and photochemical decomposition; we ourselves have carried out detailed studies on the mechanisms of pyrazoline decomposition.¹² Perhaps subconsciously we were aware of the analogy between these systems, and hoped complexes G-4 might lead to cyclopropane.

This possibility seemed rather remote, because we never observed ethane, the product of direct C-C bond formation, in the reactions of G-2 . We were therefore surprised to find¹⁰ that G-4 does in fact give cyclopropane and propene on thermal decomposition. Cyclopropane (and $\text{CpCo}(\text{CO})\text{I}_2$) is also formed cleanly on reaction of G-4 with I_2 . This is our first observation of overall direct C-C bond formation from a binuclear dialkyl. However, the actual product-forming intermediate may be mono- rather than binuclear. Some indication of this is provided by the chemistry observed on treatment of G-4 with PPh_3 . In the presence of excess phosphine, the dependence of the pseudo-

first-order rate constant for this reaction upon $[PPh_3]$ shows a saturation effect. Thus G_{-4} rearranges to an intermediate which is trapped by phosphine in a second step. The product distribution is also dependent upon phosphine; at low $[PPh_3]$, cyclopropane is formed, but at high $[PPh_3]$, the exclusive products are the mononuclear metallacyclopentanone G_{-6} and $CpCo(CO)PPh_3$. Furthermore, heating G_{-6} gives cyclopropane rather than cyclobutanone, presumably in a process involving initial dissociation of PPh_3 . The inter-relatedness of these reactions is evident; although we do not yet understand the mechanisms involved, it seems likely that cyclopropane is formed from a mononuclear cobaltacyclobutane, which can also undergo competitive CO insertion and reaction with PPh_3 to give G_{-6} .

We have carried out preliminary investigations on some of the other metallacycles prepared from radical anion G_{-1} . We do not yet know very much about the mechanisms of these processes but their overall course (shown in Chart H) is intriguing.^{10,13}

Chart H

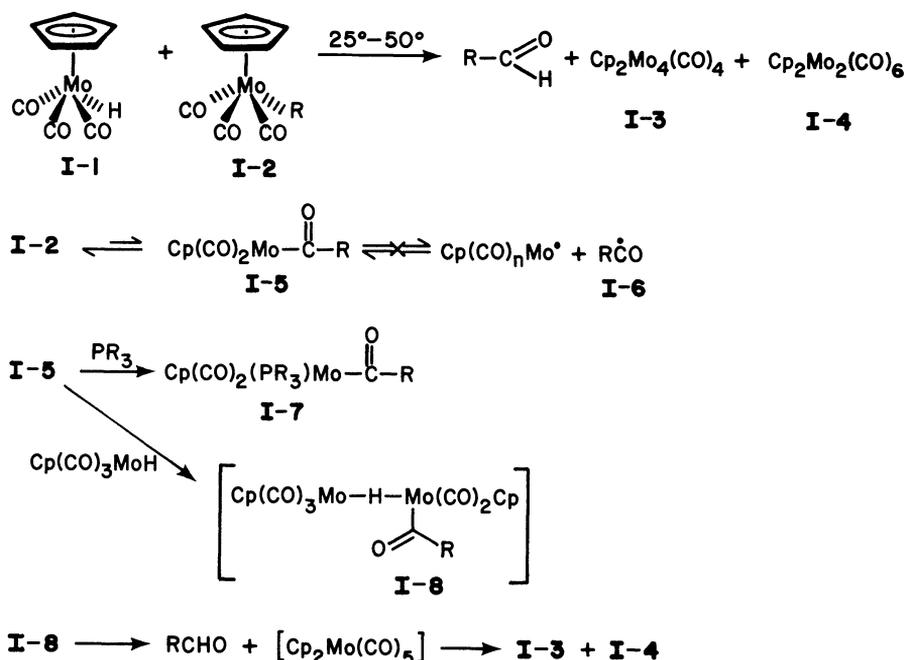


V. CARBON-HYDROGEN BOND FORMATION IN REACTIONS OF METAL HYDRIDES WITH METAL ALKYL

The last area I wish to discuss involves C-H bond forming reactions which take place upon interaction of metal hydrides and metal alkyls. In contrast to the binuclear cobalt alkyls discussed above, which fragment to give mononuclear product-forming complexes, these systems appear to lead to products via binuclear transition states.

Several examples of this type of reaction have been found recently.¹⁴ The system we uncovered is illustrated in Chart I. Molybdenum complexes I_{-1} and I_{-2} undergo a very clean reaction, leading to aldehyde and dimers I_{-3} and I_{-4} in quantitative yield. The kinetics of this reaction are second-order, and the relative rates of reaction of complexes I_{-2} , $R=Me, Et,$ and $PhCH_2$, are similar to those observed on phosphine-induced conversion of these complexes to acyl derivatives I_{-7} . Heating $MeCp(CO)_3MoCH_3$ and $Cp(CO)_3MoCD_3$ produces no interchange of methyl groups, and so reversible formation of free alkyl or

Chart I



acyl radicals (e.g., I-6) does not appear to take place in this system.

The mechanism most consistent with our data is illustrated in Chart I. Complex I-8 is the crucial intermediate in this scheme. Although it is not directly observable, we have at least been able to determine that the two molybdenum atoms are not released as mononuclear species and lose the "memory" of their origin during the transformation from starting materials to products. This was done by examining the reaction between $\text{Cp}(\text{CO})_3\text{MoCH}_3$ and $\text{MeCp}(\text{CO})_3\text{MoH}$. Only crossed Mo_2 dimers (those containing one Cp and one MeCp group) were formed in this reaction, even though we found it possible to resolve all six possible (singly and triply bonded) dimers by HPLC--again, a technique pioneered in organic chemistry, but finding increasing use in the organometallic area.

VI. CONCLUSION

In summary, I have tried to show how combining some of the important techniques and concepts of organic and inorganic chemistry has helped us to understand a number of organometallic reaction mechanisms. We expect to see this trend continue in the future, both in our own laboratory and in others.

VII. ACKNOWLEDGMENTS

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