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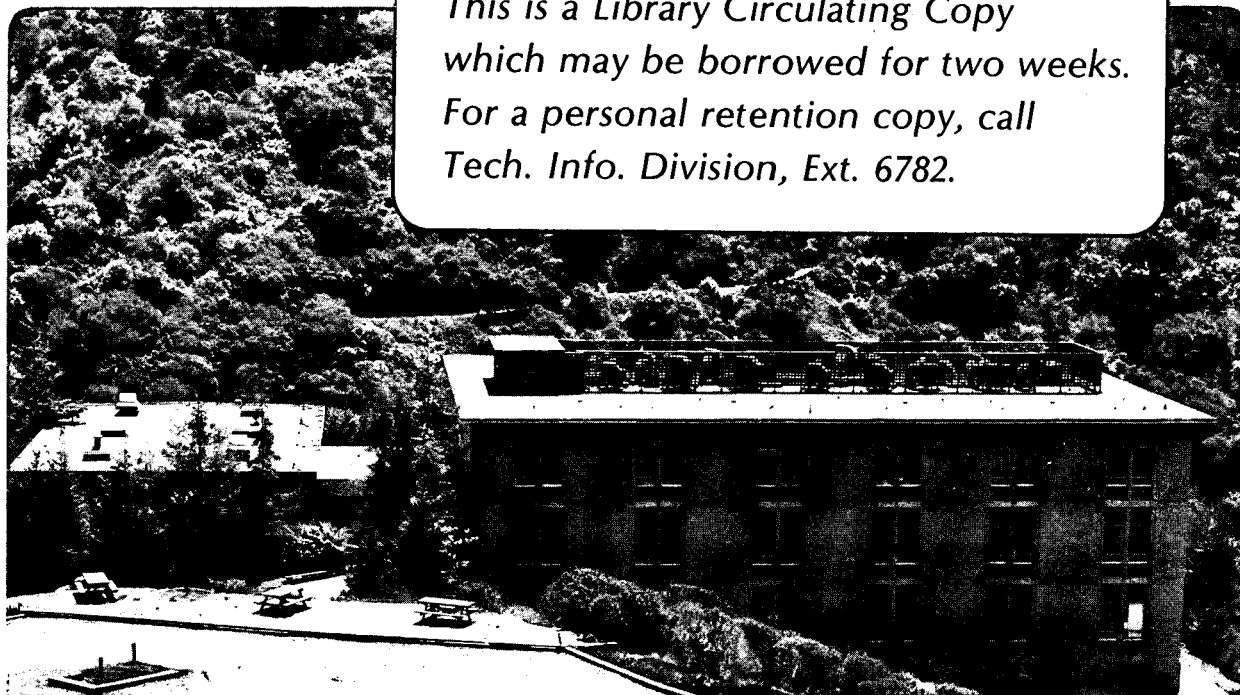
OXIDATIVE ADDITION OF SOLUBLE IRIDIUM AND RHODIUM COMPLEXES TO CARBON-HYDROGEN BONDS IN ALKANES

A.H. Janowicz, C.A. Kovac, R.A. Periana-Pillai, J.M. Buchanan, T.M. Gilbert, and R.G. Bergman

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OXIDATIVE ADDITION OF SOLUBLE IRIIDIUM AND RHODIUM COMPLEXES
TO CARBON-HYDROGEN BONDS IN ALKANES

By Andrew H. Janowicz, Caroline A. Kovac, Roy A. Periana-Pillai,
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Introduction

Alkanes are among the most unreactive organic molecules; yet they are ubiquitous in our environment. In addition to their presence in many natural organisms, alkanes are the primary constituents of petroleum and natural gas, and they are also a product of important large-scale chemical processes such as coal liquefaction and the Fischer-Tropsch reaction. Alkanes therefore present a challenge to chemical science—they are an important potential source of more highly functionalized organic molecules, and yet few reagents exist which are capable of carrying out such functionalization.

Alkanes are not completely unreactive. Certain free radicals have been known for many years which are capable of abstracting alkane hydrogen atoms, leading to alkyl radicals which then can be converted into other types of organic molecules(2). An example of such a process, which is carried out on a large scale in chemical industry, is free radical autoxidation. Examples also exist of organic reagents which react with alkanes by apparent non-radical mechanisms (examples are ozone, superacids and fluorine), although the mechanisms of these reactions are in some cases not well understood(3).

Why, then, is it important to find transition metal-based reagents which react with alkanes? In our view, there are two answers to this question. First, despite the fact that some organic reagents exist which react with alkanes, the number is still very small. A new class of reagents capable of carrying out such chemistry, therefore, would greatly improve our understanding of the factors which control reactivity of organic carbon-hydrogen bonds. It would also increase our general understanding of the mechanisms of organometallic reactions, a field which is in many ways still in its infancy. On the more practical side, a primary reason for seeking reactions of metals with alkanes lies in the area of selectivity. Organic reagents (even those which do not proceed via radical mechanisms) tend to react most rapidly with

C-H bonds which have either relatively low bond energies or relatively high acidities. Thus both organic cations and radicals react, for example, with tertiary C-H bonds more rapidly than with primary. Similarly, benzylic and allylic C-H bonds are more reactive than isolated C-H bonds toward a wide range of reagents. There is good reason to believe that significantly different selectivities (especially, enhanced primary/tertiary selectivities) might be achieved using transition metal-based reagents.

For these reasons, organometallic chemists have been attempting for several years(4) to find a simple example of the intermolecular insertion (or "oxidative addition") reaction illustrated in the equation at the bottom of Scheme 1. They have been tantalized by the fact that many intramolecular examples of this process (shown at the top of Scheme 1) are known(5), and frustrated by the fact that before the work outlined here was reported, all attempts to extend these intramolecular observations to the corresponding intermolecular reactions had failed. However, several multi-step reactions which may well be initiated by intermolecular oxidative addition are known(6). Two of the most interesting and clean-cut of these examples, reported recently at Gif-sur-Yvette and Yale University(7), are shown in Scheme 2.

This lecture summarizes our discovery(8) of a system which provides the first clear-cut example of the single-step intermolecular C-H oxidative addition reaction shown in Scheme 1, and discusses our preliminary studies of the nature of this reaction.

Generation and Oxidative Addition Reactions of $(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_3)\text{Ir}$.

In connection with a project aimed at examining the products of hydrogenolysis of metal alkyls, we had occasion to prepare dihydridoiridium complex 2 by the reaction shown in Scheme 3. Many dihydridometal complexes are known to undergo reductive elimination of H_2 upon irradiation(9). In

complexes related to 2 (e.g., Cp_2MoH_2 ; $\text{Cp} = \text{C}_5\text{H}_5$) the type of intermediates generated in such reactions have been shown to insert into at least some types of C-H bonds(10). We therefore decided to investigate the irradiation of 2. We were encouraged to find that in benzene only 3, the product of intermolecular C-H activation, was formed; no orthometallation product was observed. Benzene is well-known to be reactive toward C-H activation, presumably because of involvement of its π -electrons in the insertion transition state. Our next step, therefore, was to attempt this reaction using somewhat less inherently reactive compounds. Exploratory experiments of this type are relatively simple, because the presence of new metal hydride products can be detected by observing their characteristically high-field resonances in the ^1H NMR spectrum of the reaction mixture. Accordingly, we found that irradiation of 2 in acetonitrile gave H_2 and a new metal hydride product, and irradiation in tetrahydrofuran also gave new hydride products. We therefore proceeded immediately to alkanes. We were pleasantly surprised to find that irradiation of 2 in cyclohexane solvent gave a single new hydride in high yield, and a similar result was obtained in neopentane solvent.

These products are the hydridoalkyl complexes 4 and 5 shown in Scheme 4. The new complexes are extremely hydrophobic, and are therefore very difficult to obtain pure. However, they can be isolated and purified with some loss of material, and characterized fully by ^1H NMR, ^{13}C NMR and infrared techniques. Furthermore, they can be converted to the corresponding bromoalkyliridium derivatives (vide infra), which can be characterized using both spectroscopic and elemental analysis techniques. The hydrophobicity of these materials has so far prevented our obtaining X-ray quality crystals, but efforts in this direction are continuing.

Mechanism of the C-H Oxidative Addition Reaction

The conventional mechanism for the C-H insertion is shown in Scheme 5.

It first assumes that upon irradiation, an excited state of dihydride 2 is formed. This rapidly extrudes H_2 , leaving behind the reactive, coordinatively unsaturated fragment 6. Complex 6 then inserts into a C-H bond via transition state 7, leading to the hydridoalkyliridium complexes 4 and 5.

Although this mechanism is certainly reasonable, we felt the need to provide supporting evidence for it, especially in view of the fact that in certain other oxidative addition reactions more complicated mechanisms involving free radicals have been established(11). Many radical mechanisms proceed through a step in which the radical R^\bullet has independent existence. Thus the individual R and H groups located in each molecule of product 4 or 5 may not necessarily have been bound together in the starting hydrocarbon molecule. In order to obtain information about this, we carried out the crossover experiment summarized in Scheme 6. We first irradiated 2 in a 1:1 mixture of neopentane and cyclohexane. This established that the two hydrocarbons have similar reactivity toward 6, although the C-H bond in neopentane is slightly more reactive. Next, irradiation of 2 in a 1:1 mixture of neopentane and cyclohexane- d_{12} was carried out. As shown in Scheme 6, the products of this reaction were the hydridoneopentyl- and the deuterio-(perdeuterocyclohexyl)iridium complexes A and B, with very small amounts of contamination from the crossed products C and D. Therefore, the R and H groups remain associated with one another during the process which converts hydrocarbon to hydridoalkyliridium complex.

While this experiment rules out reactions involving radicals having a free existence and finite lifetime, it is more difficult to rule out processes proceeding predominantly through caged radical pairs. Our best evidence against such a postulate comes from relative reactivity studies. Hydrogen abstraction reactions of radicals favor C-H bonds with low bond

energies; very strong bonds are nearly always inert. In view of this, cyclopropane may be used as a very diagnostic substrate, since its C-H bond energy is 106 kcal/mole, even stronger than that of methane. Despite this, as shown in Scheme 7, irradiation of 2 in liquid cyclopropane at -35° C. leads only to the C-H insertion product 8. Thus addition to the C-H bond is favored even over insertion into the relatively weak C-C bond, which would lead to an iridacyclobutane complex. In view of this result, even a radical-cage mechanism seems extremely unlikely for these reactions.

Reductive Elimination and Functionalization Reactions of the Hydridoalkyliridium Complexes

Hydridoalkyl complexes 4 and 5 are quite stable thermally, reductive elimination occurring only at temperatures near 110° (Scheme 8). Treatment of 4 and 5 with Lewis acids or oxidizing agents (e.g., Br_2 , HBF_4 , ZnBr_2 , H_2O_2 and even alumina; cf. Scheme 8) in benzene at room temperature induces reductive elimination of hydrocarbon and leads to the hydridophenyl complex 9.

A primary goal of this work has been the conversion of the hydridoalkyliridium complexes to functionalized organic molecules. Unfortunately, as indicated above many of the reagents one might use to carry out such functionalization promote only reductive elimination, simply regenerating the starting hydrocarbon. We therefore decided to approach this problem by conversion of the hydrides to the corresponding bromoalkyliridium complexes. This can be done smoothly at room temperature by treating them with bromoform, as shown in Scheme 8. As indicated earlier, the bromine-containing products are somewhat easier to handle than their hydride precursors, and they do not easily undergo reductive elimination. As a result, functionalization of these materials has been more successful. The most convenient method we have found so far is summarized in Scheme 9.

Treatment of bromoalkyliridium complex 10 or 11 with mercuric chloride leads to the corresponding alkylmercurial 12 and bromochloroiridium complex 13. Conversion of 12 to organic halides can then be carried out using I_2 or Br_2 at room temperature. Thus overall conversion of an alkane to alkyl halide can be effected in good yield under mild conditions, in a non-radical process which completely avoids free radical intermediates.

Selectivity Studies

With information about mechanism and functionalization in hand, we turned our attention to the selectivity of the reactive intermediate $Cp'(PMe_3)Ir$ (6, $Cp' = C_5Me_5$; cf. Scheme 5). Irradiation of $Cp'(PMe_3)IrH_2$ (2) in the presence of solvents having different types of C-H bonds allowed the reactive intermediate $Cp'(PMe_3)Ir$ to compete for those bonds. At low conversion the ratio of the products formed in such an experiment is then directly equal to the ratio of rate constants for insertion into each type of C-H bond. Two types of selectivity experiments were carried out: those involving competition of the intermediate for C-H bonds in different molecules ("intermolecular selectivity") and competition for different types of C-H bonds located in the same molecule ("intramolecular selectivity").

Intermolecular selectivities can be established most readily, because each of the individual oxidative addition products can be independently generated. Each selectivity experiment was carried out using mixtures of two liquid hydrocarbons as solvent. First the dihydride 2 was irradiated in each pure solvent, and the NMR spectrum of the product recorded (due to the difficulty of isolating these materials, isolation was not attempted except in the case of cyclohexane and neopentane, as described earlier). Then the irradiation was carried out in a mixture (usually 1:1) of the two solvents, and the ratio of products measured, usually by repetitive integration of the hydride resonances in the high-field region of the spectrum. The rate ratio

was calculated by correcting the product ratio for the number of hydrogens available in each molecule. In this way, a neopentane/cyclohexane rate ratio of 1.4 and cyclopropane/cyclohexane ratio of 2.6 were obtained. Similarly, we were able to determine the relative rates of attack by $\text{Cp}^*\text{Ir}(\text{PMe}_3)$ on one C-H bond in each of the molecules in Scheme 10, with attack on cyclohexane set as 1.0. The results are quite interesting, and as far as we know unprecedented: reactivity seems to vary with ring size, smaller rings showing higher reactivity toward C-H insertion, and larger rings showing lower reactivity. The physical reason for this is not yet clear, but may be related partially to the greater steric accessibility of the C-H bonds in the smaller rings, where the two carbon atoms attached to the reacting carbon are somewhat more tightly "tied back" than they are in the larger systems. A competition experiment using a cyclohexane/benzene mixture demonstrated the aromatic C-H bonds to be 4.0 times more reactive than the cyclohexyl.

Intramolecular selectivities presented a more difficult problem. Here we were faced with determining both the identities and relative amounts of products which could not be generated independently. In general the hydridoalkyl complexes are so nonpolar, and so similar to one another in chromatographic properties (including instability in many cases), that preparative separation was not feasible. A possible solution to this problem became apparent during the intermolecular selectivity studies summarized above, and we discuss this here with reference to the chart shown in Scheme 11. The lowest line, labeled " $\text{P}(\text{CH}_3)_3$ ", illustrates the positions of the ^1H NMR metal hydride resonances observed on irradiation of **2** in the presence of a large number of hydrocarbons. Illustrated above this line are the hydride positions observed on irradiation of complexes related to **2**, but having phosphine ligands other than PMe_3 bound to the metal, which we have also synthesized and shown to undergo irradiatively induced C-H reactions with

alkanes.

The simplest cases are the ones discussed above with reference to intermolecular selectivities; i.e., hydrocarbons which have only one type of C-H bond, and therefore lead to only one new hydride. As can be seen by inspection of the $P(CH_3)_3$ results, the hydride resonances of the hydridoalkyl products formed from each of the cyclic hydrocarbons appear at very similar chemical shifts, ranging from δ -18.16 for the metal-bound hydride in the hydridocyclopropyl complex to -18.67 for the hydridocyclohexyl complex. The location of this narrow range differs substantially from the position of the hydride resonance observed for the hydridoneopentyl complex 5, which appears at -17.67. Insertion into the C-H bond of benzene gave a complex which exhibits a hydride resonance at even lower field (-17.04 ppm). It seems that for some fortunate (but not well understood) reason, the hydride chemical shift appears to be determined by the type of substitution at the carbon atom of the alkyl fragment directly attached to the metal. Thus products formed by insertion into secondary C-H bonds may be distinguished from products formed by insertion into primary C-H bonds and aryl C-H bonds by the characteristic chemical shifts of the metal-bound hydride resonances in the hydridoalkyl products.

Although a smaller number of data are available, the top of the chart in Scheme 11 shows that the relative positions of these chemical shifts also hold for the complexes which contain other phosphines. In these cases the scale is shifted to higher or lower field, depending upon the electron-donating or -withdrawing power of the phosphine.

These conclusions were reinforced by the results of our first intramolecular selectivity experiment, carried out on p-xylene and summarized in Scheme 12. Irradiation of dihydride 2 in p-xylene gave two products, as judged by the appearance of only two new doublets in the high-field region of

the NMR spectrum. One of these, assigned to benzylic complex 15, appeared at -17.56 ppm, very close to that observed for the neopentyl complex 5 (i.e., in the "primary hydride" region). The other, due to aryl complex 14, appeared at the lower field position of -16.68 (the "aryl hydride" region). The fact that the primary insertion product is benzylic, and the aryl insertion product has an orthoalkyl substituent, apparently does not greatly perturb the relative positions of these resonances.

In acyclic hydrocarbons, the chemical shift patterns also appear to hold up. Thus, irradiation of dihydride 2 in liquid n-propane gives a mixture which exhibits two new hydride doublets in the NMR, one in the primary region at -17.81, and the other in the secondary region at -18.51 ppm (Scheme 13); integration and statistical correction gives a primary/secondary rate ratio of 1.5. The situation with higher acyclic hydrocarbons is more complicated. In the case of n-pentane, four new hydride doublets are detected. There is a unique lowest-field hydride signal; although this appears at -17.96, somewhat higher than that in propane, we assign it to the primary insertion product 16 (Scheme 14). The three other resonances appear at -18.50, -18.54 and -18.61 ppm, consistent with their assignment as secondary insertion products. We presume the formation of three complexes is due to the fact that insertion into the hydrogen at C-2 in pentane is capable of generating two diastereomers due to the fact that the iridium is a chiral center. Although we cannot assign the identity of each of these very similar complexes, summation of the secondary integrations and correcting for statistics gives a primary/secondary attack ratio of 2.7.

Heating this mixture of hydridoalkyl complexes to 110° in pentane causes disappearance of the resonances assigned to the secondary C-H insertion products, and a corresponding increase in the resonances due to the primary insertion product 16. We assume this occurs because this temperature is

sufficient to cause reversible reductive elimination and readdition, and thus the thermodynamically most stable product (i.e., the primary product 16) is formed. This is an extremely important result from a practical point of view, because it suggests that a combination of photolysis followed by thermal equilibration will allow exclusive primary functionalization of linear alkanes. Supporting evidence for the reductive elimination/readdition mechanism has been obtained by heating the mixture of hydridopentyliridium complexes with cyclohexane instead of n-pentane, as shown in Scheme 15. Under these conditions, the secondary products again disappear, but are converted into the cyclohexylhydrido-iridium complex instead of additional pentylhydrido-iridium complex.

Synthesis and Reactions of $(\eta^5\text{-C}_5\text{Me}_5)\text{IrH}_4$.

As part of this research, we have also investigated the possibility of replacing the phosphine ligand in 2 with additional hydride ligands, with the hope of utilizing such molecules in C-H activating hydrogen exchange processes. As shown in Scheme 16, one interesting material which has been prepared in the course of this work is $(\eta^5\text{-C}_5\text{Me}_5)\text{IrH}_4$ (18), a rare example of an iridium(V) complex; this material is obtained in good yield by hydride reduction of the trihydrido-iridium cation 17 prepared earlier by Maitlis and coworkers(12). X-ray quality crystals of this material have been obtained and a structure completed. Decomposition problems in the X-ray beam prevented us from obtaining data accurate enough to locate the hydrogen atoms, but the relationship of the metal and C_5Me_5 ring are shown in the ORTEP drawing illustrated in Scheme 17. Scheme 16 summarizes some of the chemistry of this complex. Perhaps most intriguing is that 18 undergoes exchange with D_2 at 60° , but is converted back to 2 in the presence of PMe_3 only at 100° . Thus the simplest mechanism for the exchange--reductive elimination of H_2 to give $(\text{C}_5\text{Me}_5)\text{IrH}_2$, followed by oxidative addition of D_2

to this intermediate--cannot be operating, and exchange must be proceeding by some other mechanism, whose nature we are currently attempting to elucidate.

Preliminary Results on C-H Oxidative Addition Using Rhodium Complexes

Recently we have prepared the rhodium complex 19 analogous to dihydride 2, and found that it, too, participates in C-H oxidative addition reactions (Scheme 18). Irradiation of 19 at room temperature leads only to an unidentified black substance. However, irradiation at -50° produces new hydrides, again by observation of their absorptions in the high-field region of the low-temperature ^1H NMR spectrum. Preliminary studies have indicated that the C-H insertion reactions of the proposed intermediate $\text{Cp}'\text{RhL}$ ($\text{Cp}' = \text{C}_5\text{Me}_5$; $\text{L} = \text{PMe}_3$) shown in Scheme 18 are successful(13). In all cases except benzene, warming the reaction solutions to -10° causes reductive elimination of hydrocarbon and deposition of the black decomposition product. However, conversion of the hydridoalkyl complexes to the corresponding halides can be carried out at low temperature, and these products appear to be more stable than the hydrides. Research aimed at isolating and purifying these materials, and comparing the selectivities of the rhodium and iridium systems, is currently under way.

Conclusions

In summary, we have uncovered an example of the intermolecular reaction shown in Scheme 1, in which a soluble metal complex undergoes oxidative addition into the C-H bonds of completely saturated hydrocarbons, leading to hydridoalkylmetal complexes. Our most extensive work has been done with iridium, but preliminary results indicate that the analogous rhodium complexes undergo similar C-H insertions, although the products are considerably less stable. We have found it possible to convert the insertion products into organic halides, indicating that overall conversion of alkanes into functionalized organic molecules is feasible. Selectivity studies have

shown that the reactive iridium complex favors insertion into aromatic, primary and small-ring C-H bonds.

This work has raised many intriguing questions about the nature of C-H oxidative addition. First, we do not as yet understand why the systems discussed here seem to favor intermolecular addition, whereas other metal complexes either favor intramolecular cyclometallation, or do not react with unactivated C-H bonds at all. We also do not yet understand the physical basis for the selectivities we have observed. Finally, our results raise questions about the supposed requirement for a very electron-rich metal center in order to induce C-H activation. We have found that replacing PMe_3 with the more electron-withdrawing phosphine P(OMe)_3 gives a system which also effects oxidative addition. Independent work in Graham's laboratory, illustrated in Scheme 19, demonstrates that even a CO ligand is not electron-withdrawing enough to prevent C-H insertion(14). We intend to seek answers to these questions in further research on this unique system.

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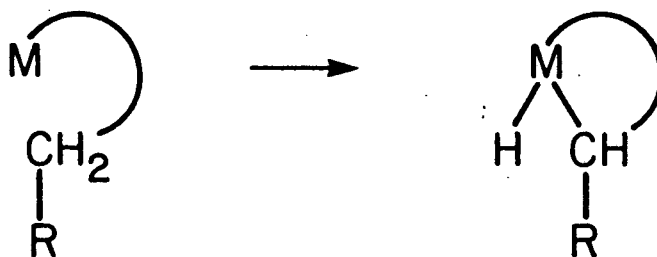
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Scheme I

Homogeneous Saturated C-H Bond Activation:

Intramolecular:



(Many examples)

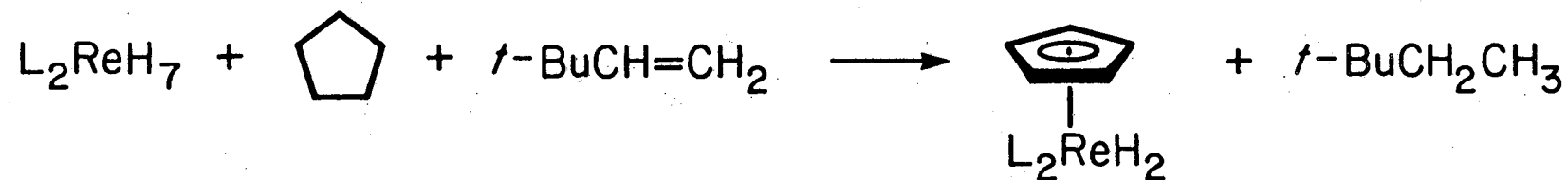
Intermolecular:



(Few examples; none where R-H is a completely saturated hydrocarbon)

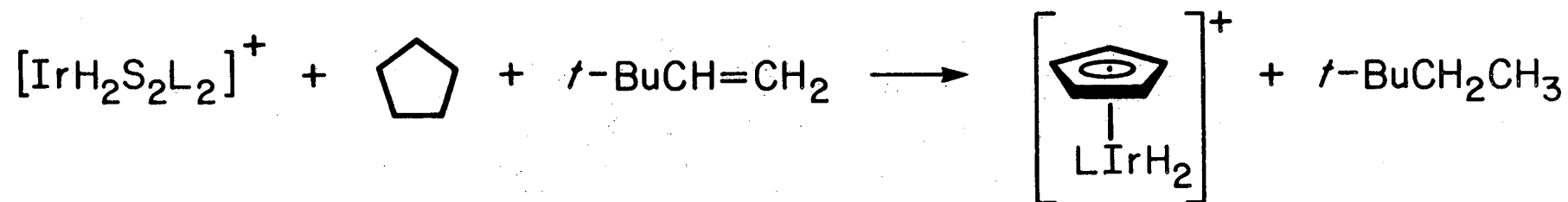
Scheme 2

Baudry, Ephritikine, Felkin, 1980:



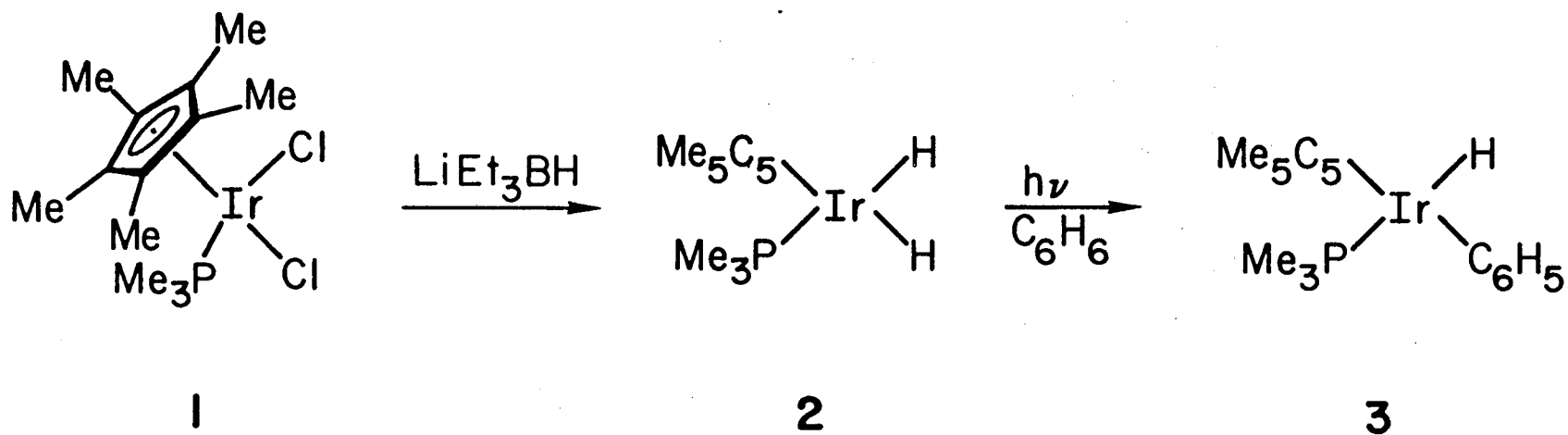
(L = PPh₃, PEt₂Ph)

Crabtree, Mihelcic, Quirk, 1979:

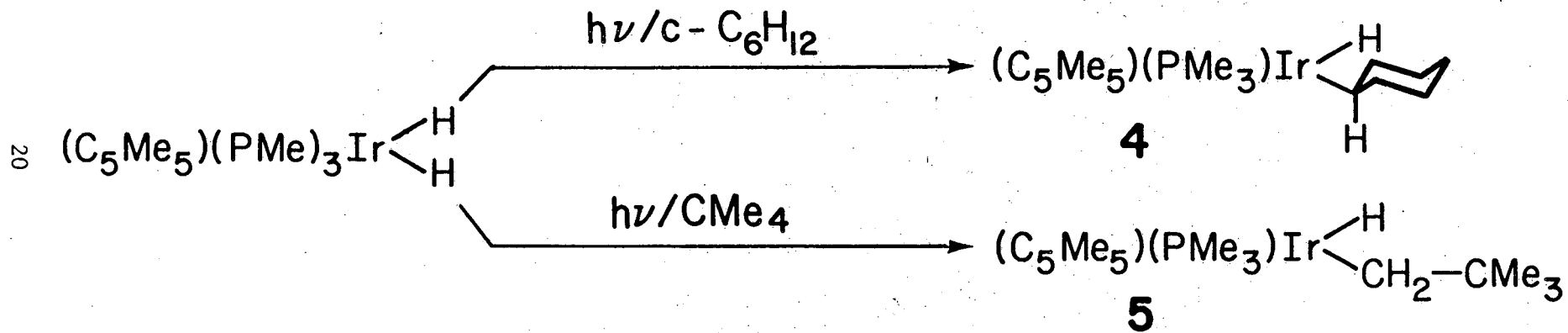


(L = PPh₃, S = H₂O or acetone)

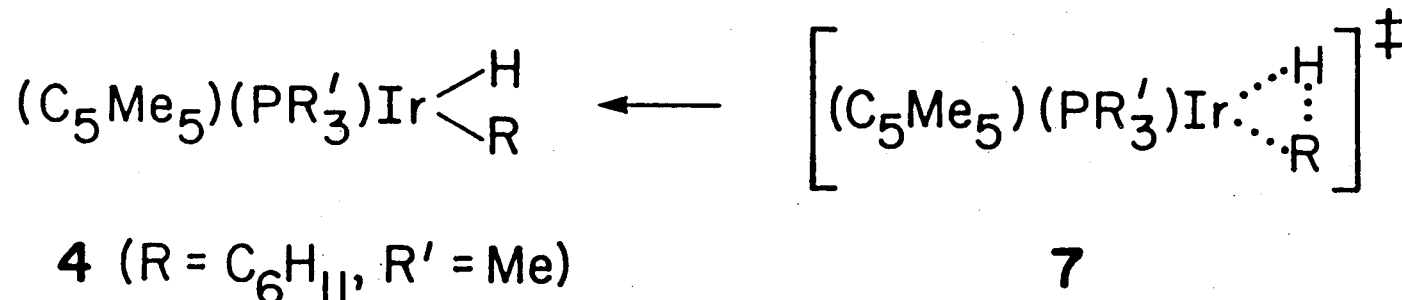
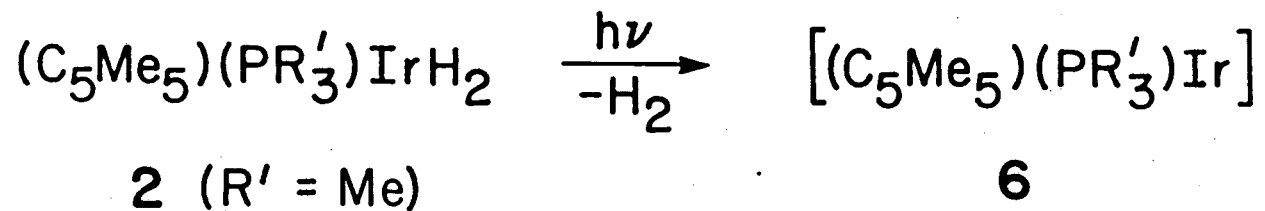
Scheme 3



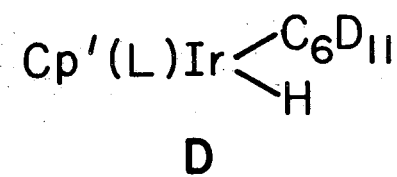
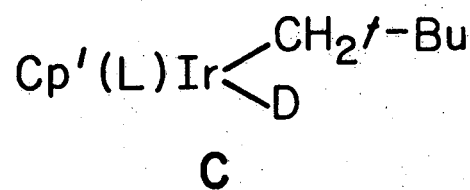
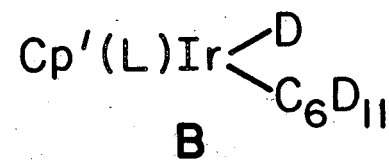
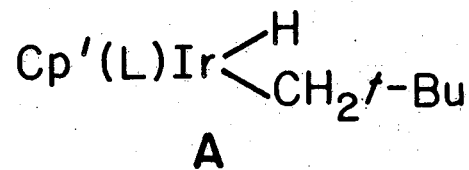
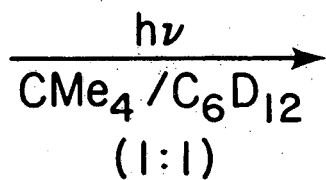
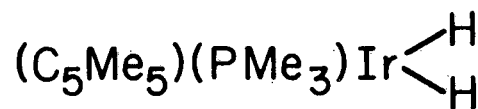
Scheme 4



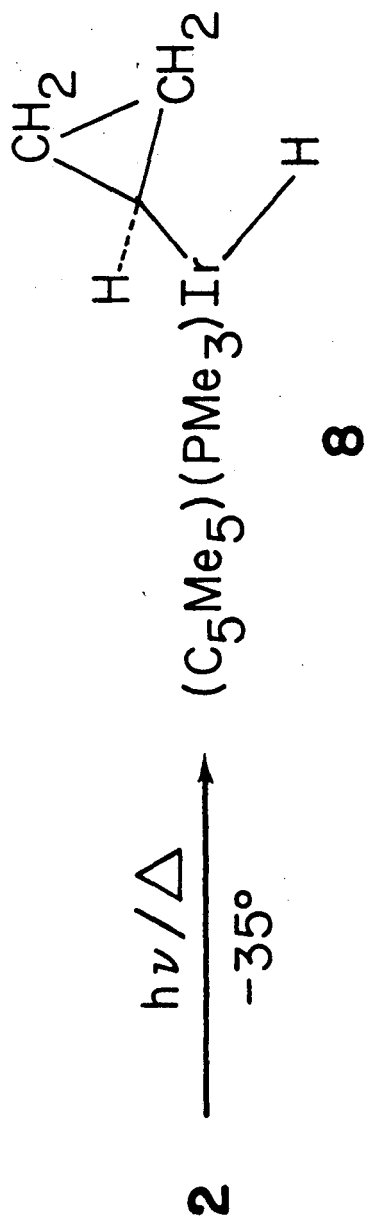
Scheme 5



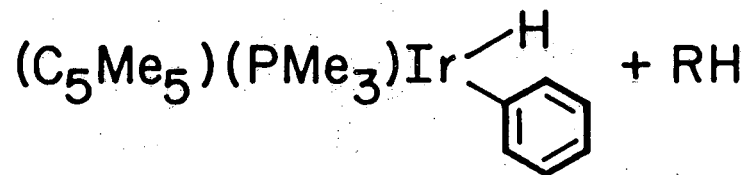
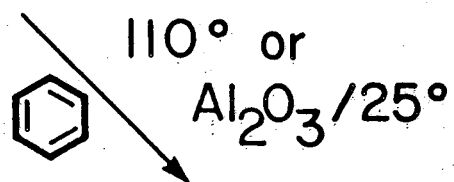
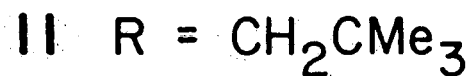
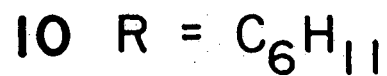
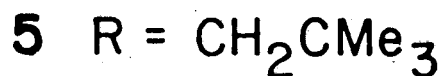
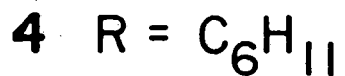
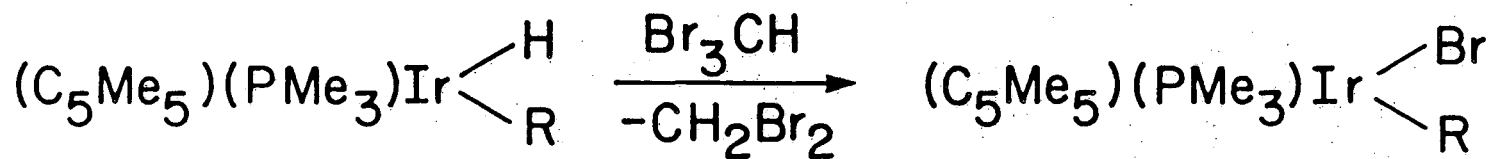
Scheme 6



Scheme 7

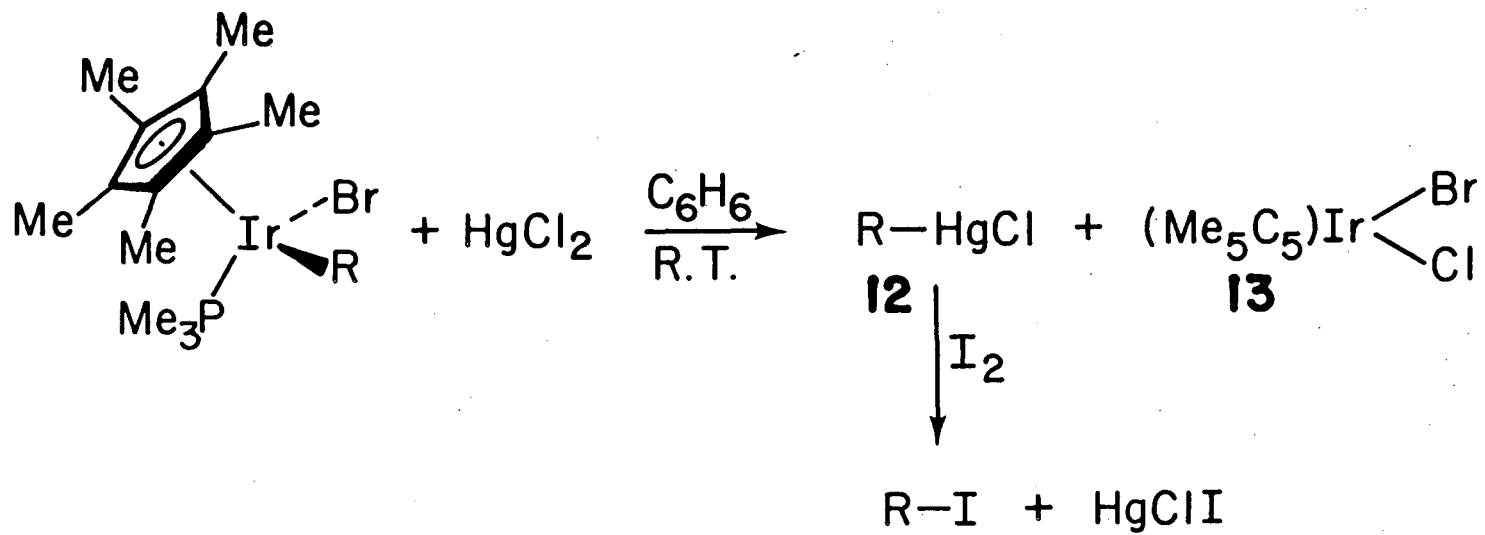


Scheme 8

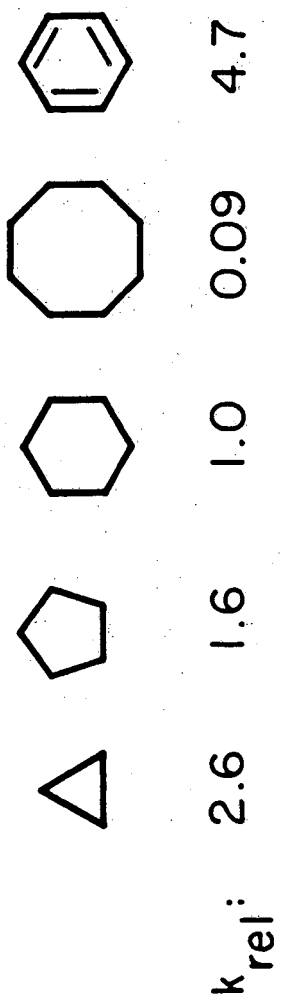


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Scheme 9

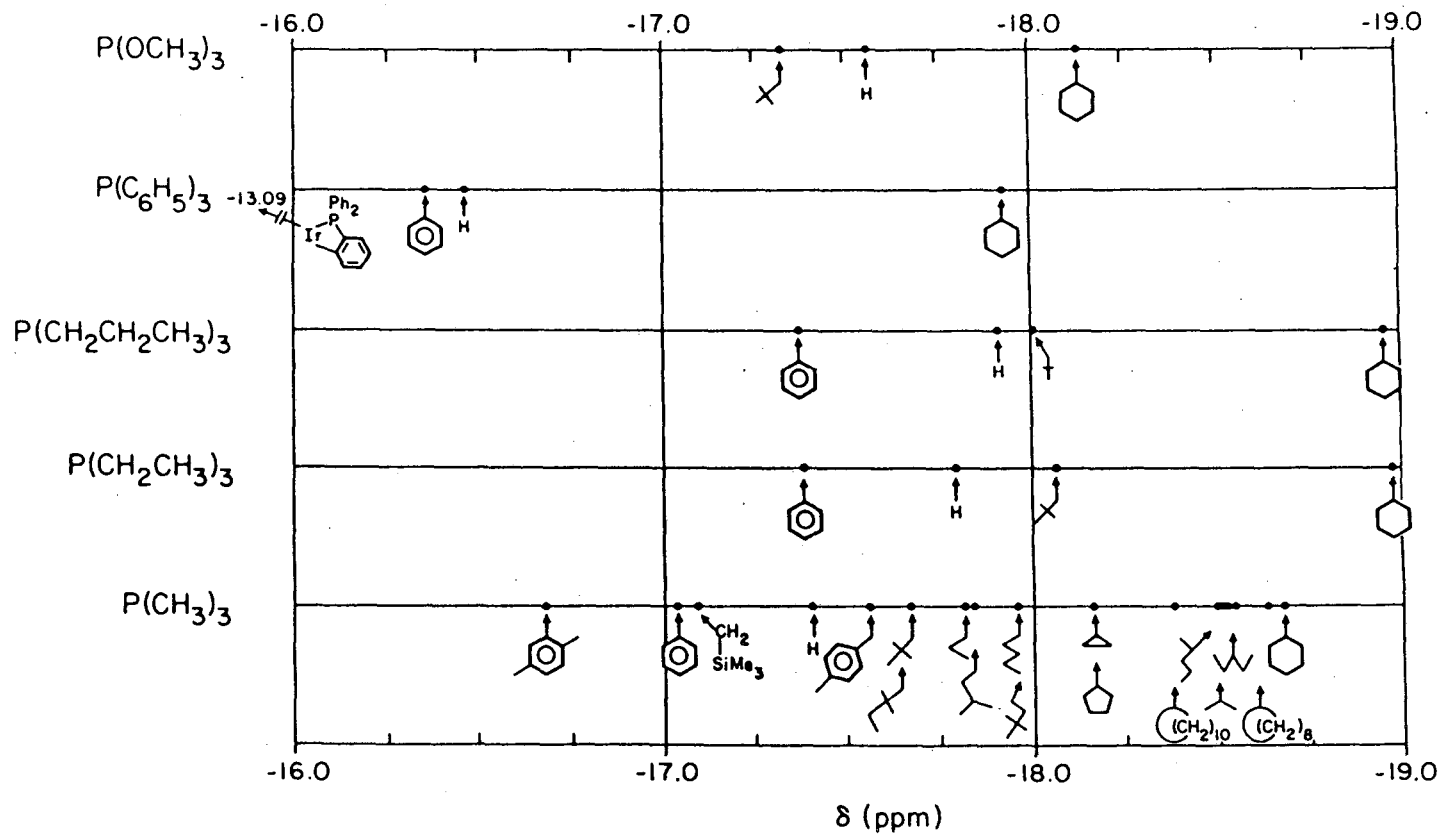


Scheme 10

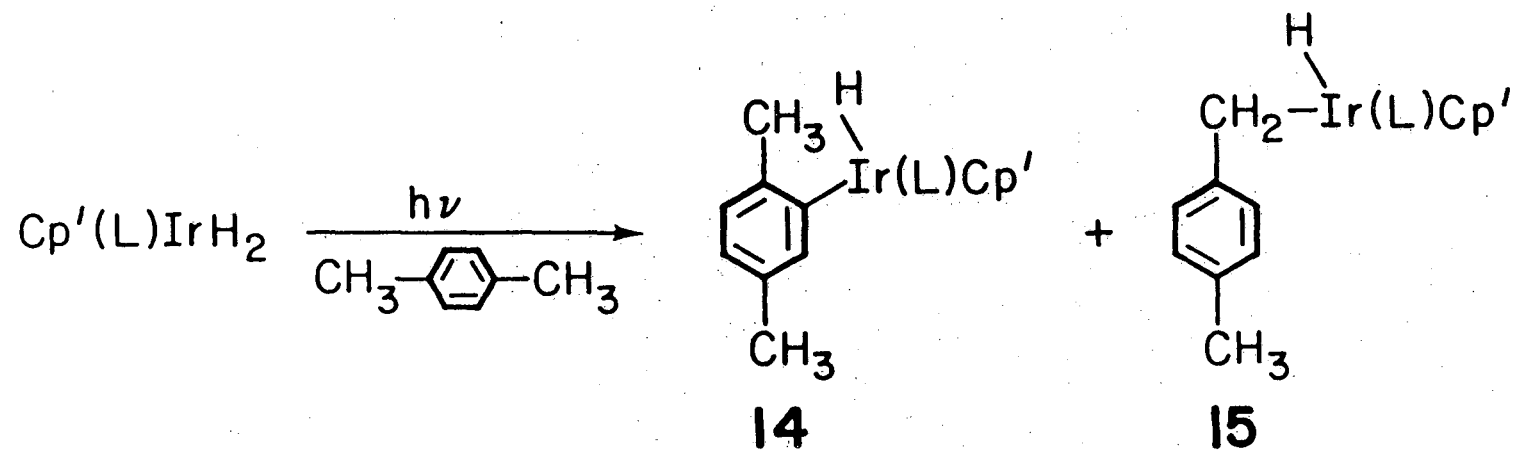


Scheme II

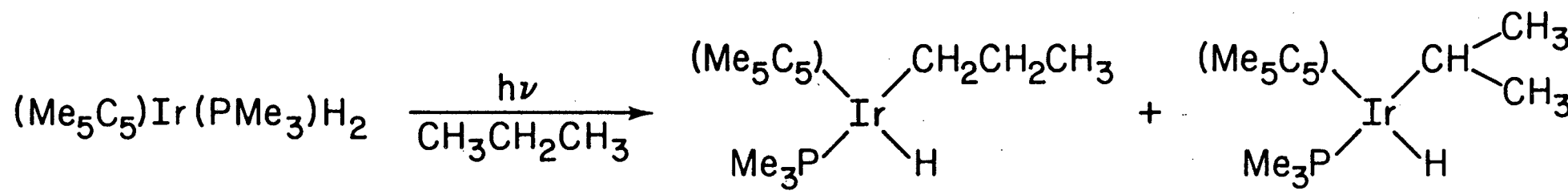
$^1\text{H-NMR}$ HYDRIDE CHEMICAL SHIFTS FOR $(\eta^5\text{-C}_5\text{Me}_5)(\text{L})\text{Ir} \begin{matrix} \text{R} \\ \diagup \\ \text{H} \end{matrix}$ IN C_6D_6



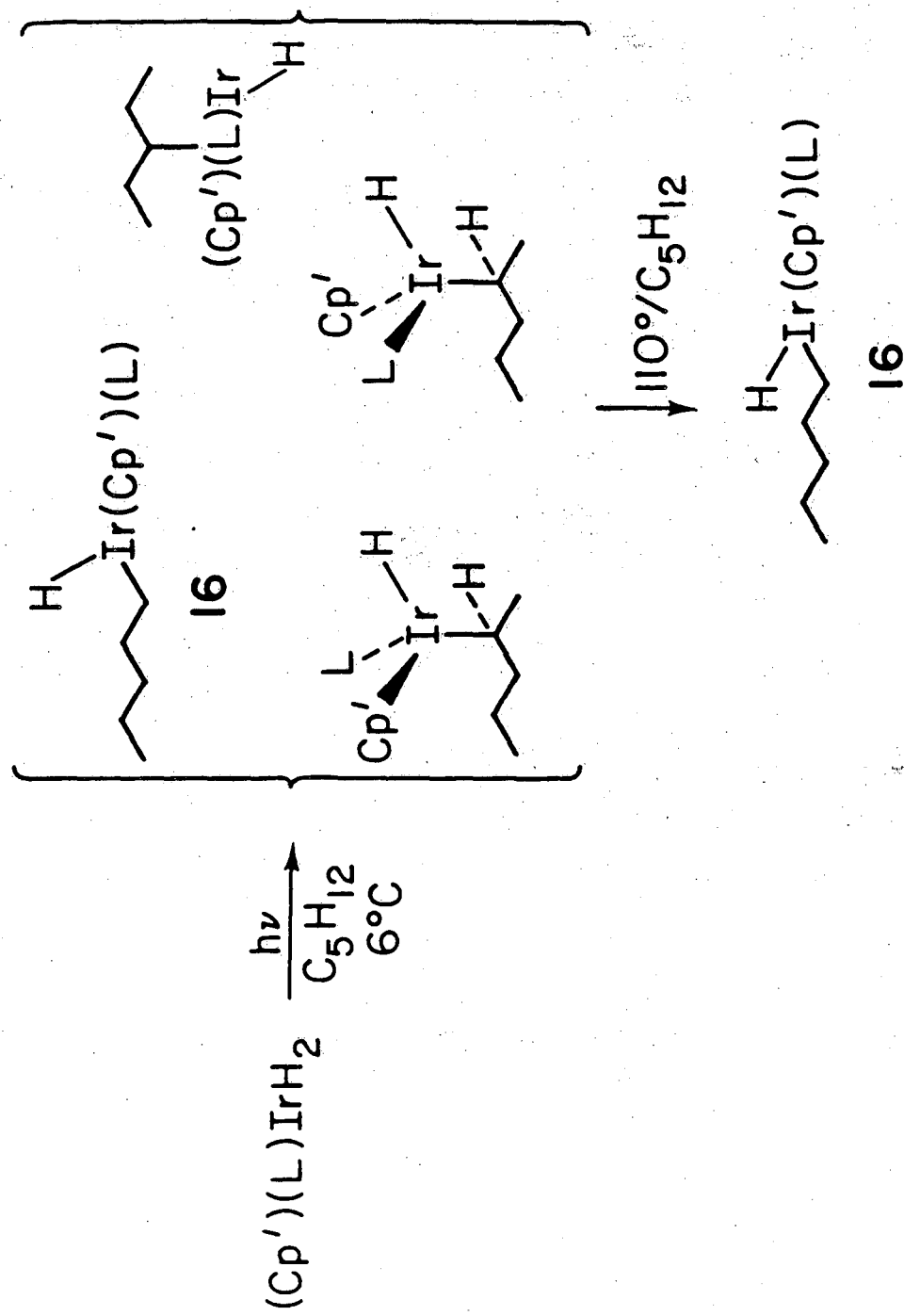
Scheme 12



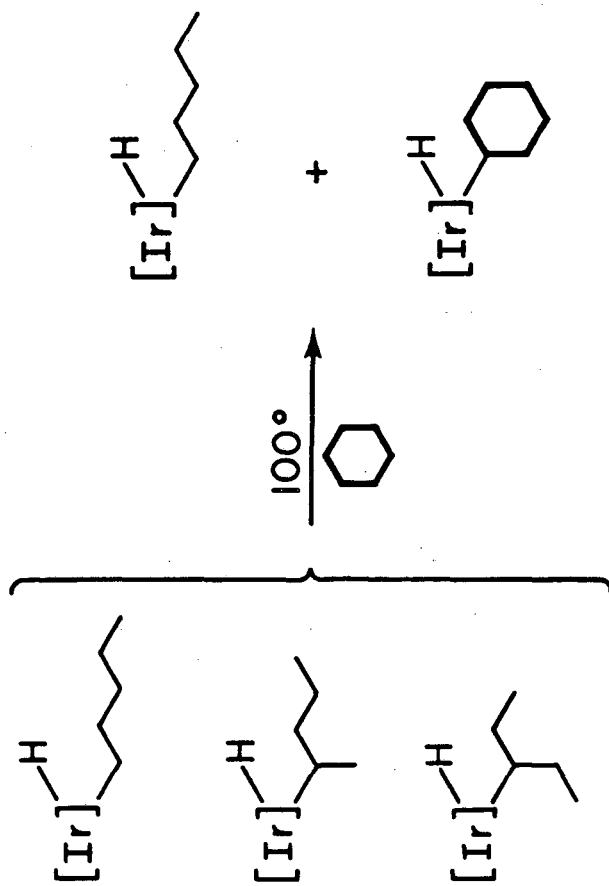
Scheme 13



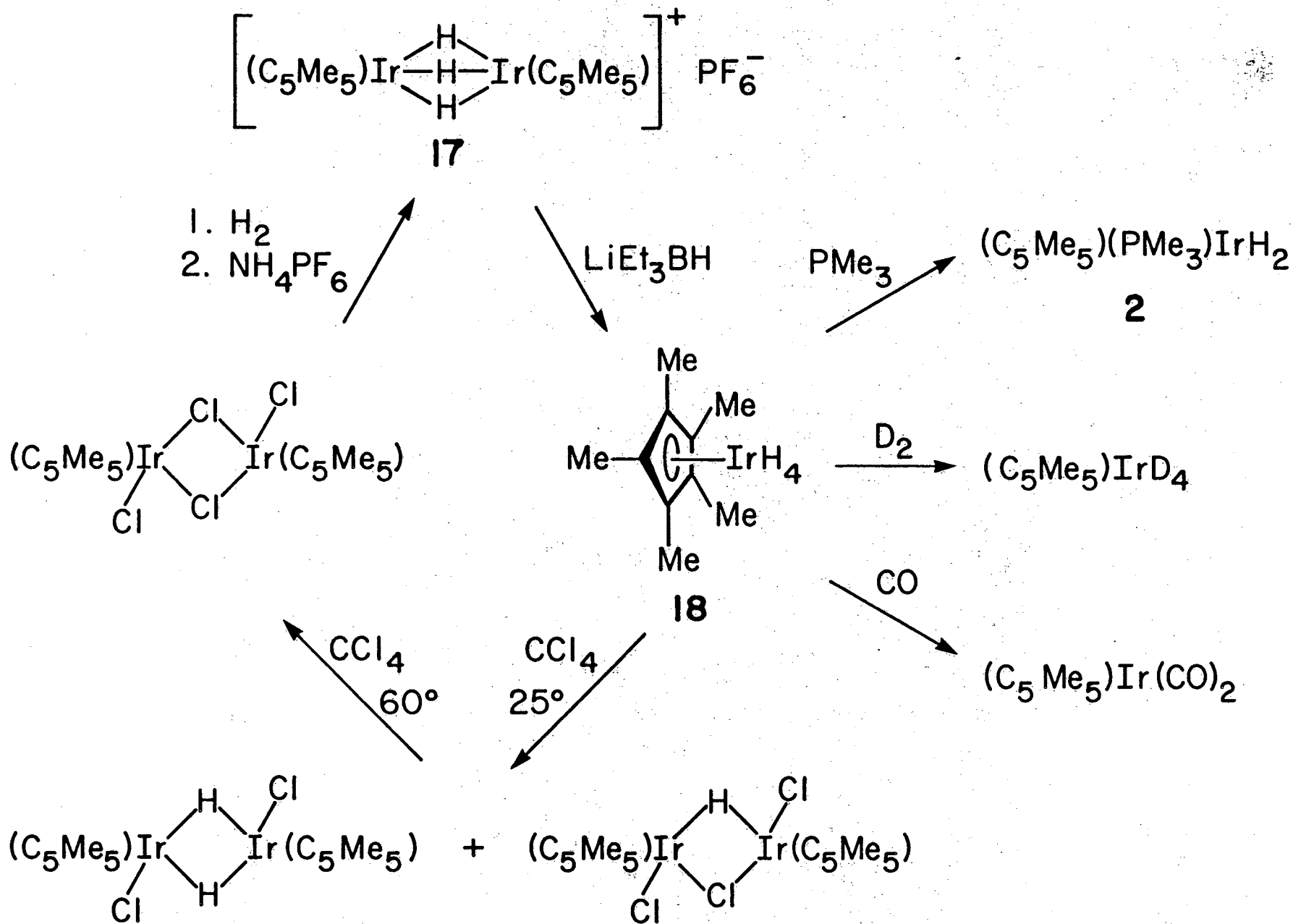
Scheme 14



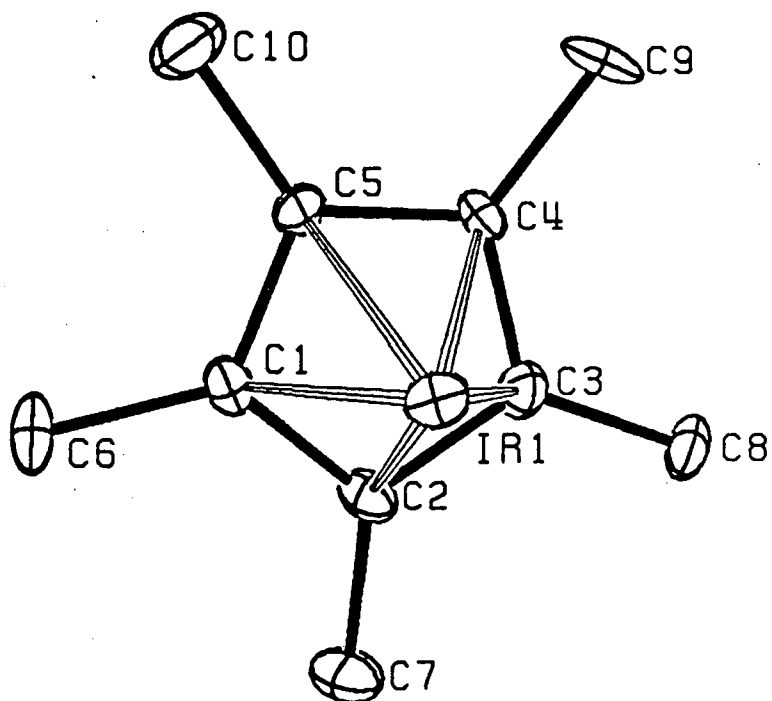
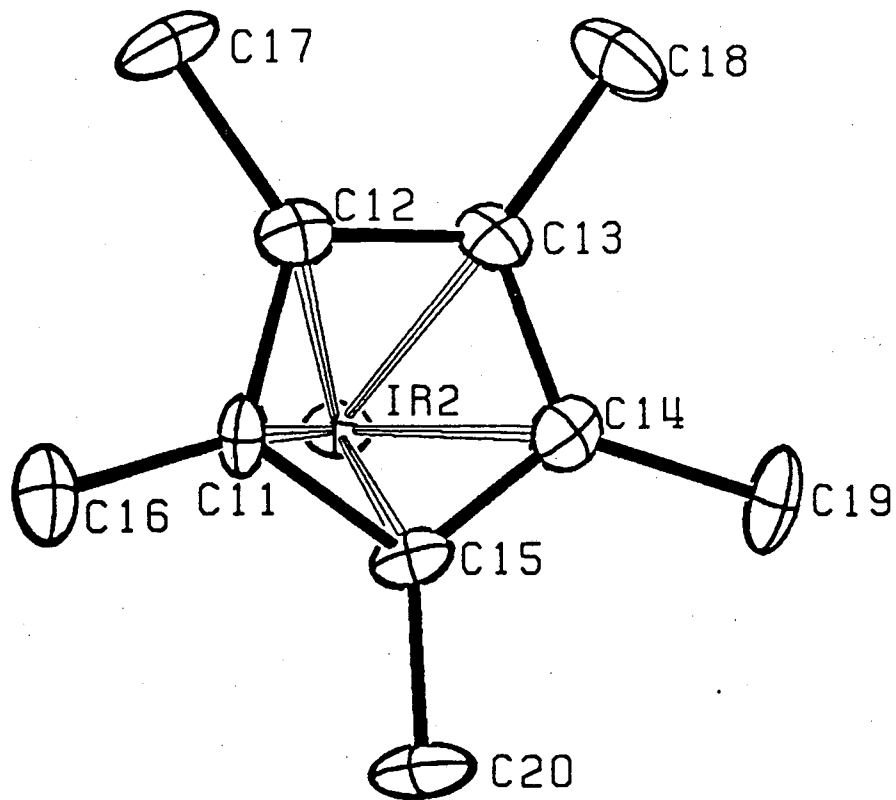
Scheme 15



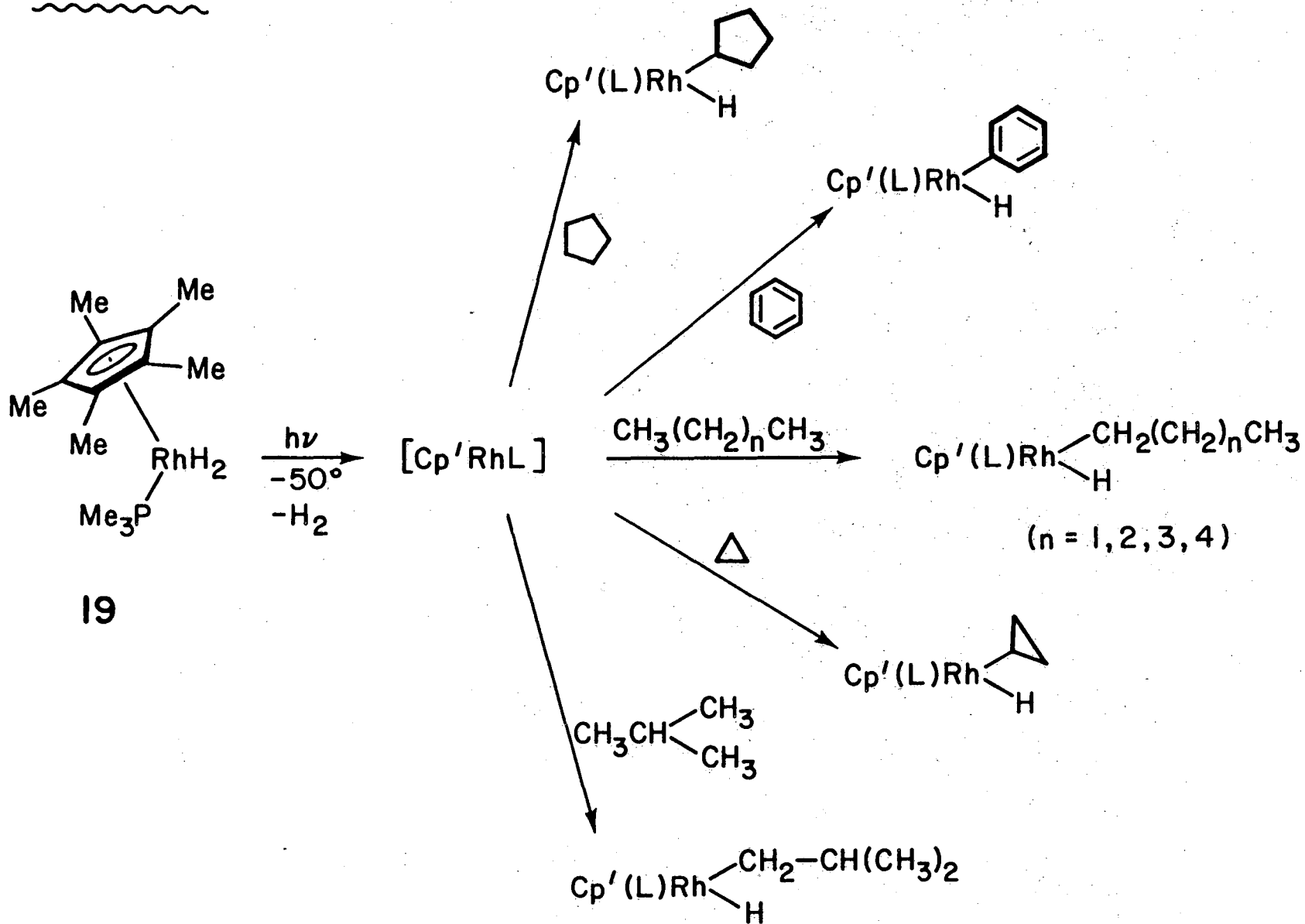
Scheme 16



Scheme 17

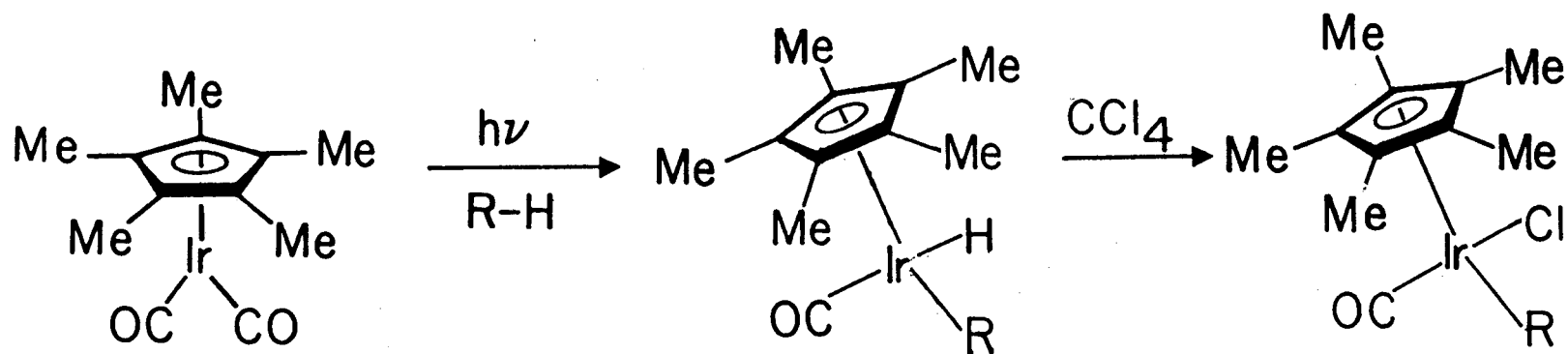


Scheme 18



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Scheme 19



J. K. Hoyano, W. A. G. Graham, 1982

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